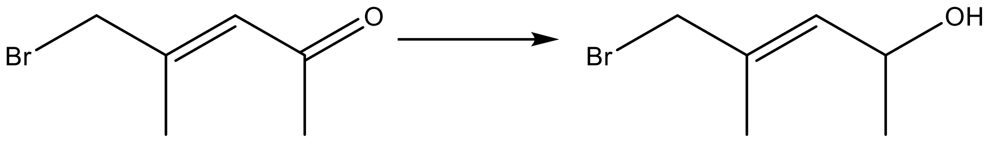
2021 YIJC Preliminary Examination H2 Chemistry Paper 3 with Mark Schemes

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]

16 σ and 2 π

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

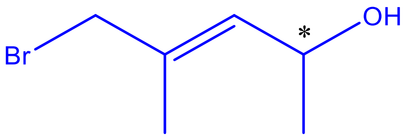
[2]

sp^2
1 σ bond – head on overlap of sp^2 hybridised orbitals of the 2 C atoms.
1 π bond – side on overlap of the unhybridised p orbitals of the 2 C atoms.

(ii) State the total possible number of stereoisomers that can be exhibited by **B**.

[1]

1 chiral carbon + 1 C=C that can exhibit cis trans isomerism = $\mathbf{2^2 = 4}$



(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]

The carbonyl carbon in ketone is electron deficient due to the difference in electronegativity between C and O. Hence it attracts the $:H^-$ nucleophile.

The C=C in alkenes are electron rich and will repel the negatively charged $:H^-$ nucleophile.

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

[2]

Test : 2,4 – DNPH, rtp
A: orange ppt formed
B : no orange ppt formed

Test : $KMnO_4$, H_2SO_4(aq), heat
A: purple $KMnO_4$ remains
B : purple $KMnO_4$ decolourises

Test : $K_2Cr_2O_7$, H_2SO_4(aq), heat
A: orange $K_2Cr_2O_7$ remains
B : orange $K_2Cr_2O_7$ turns green

Test : Na, rtp
A: no effervescence
B : effervescence observed, gas extinguish lighted splint with a pop sound

Test : anhydrous PCl_5 , $SOCl_2$, rtp
A: no white fumes
B : white fumes observed

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

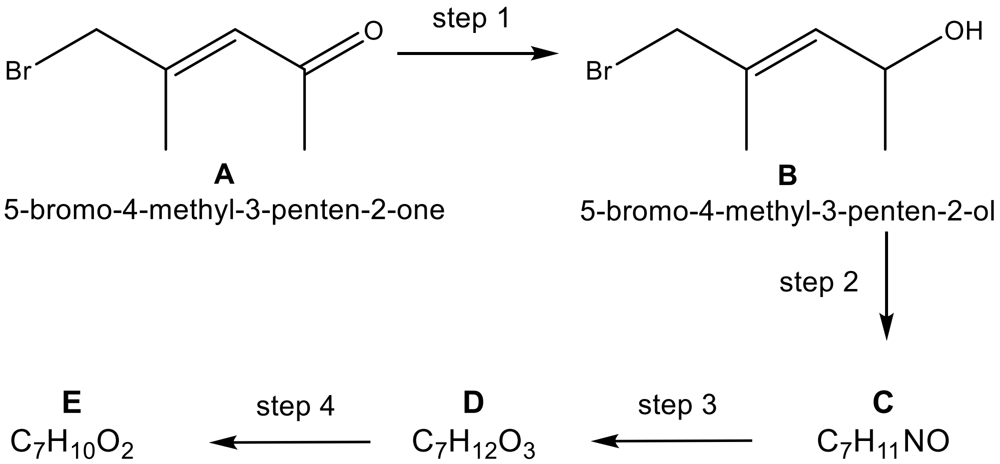


Fig. 1.2

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

[2]

Step 2: ethanolic KCN, heat

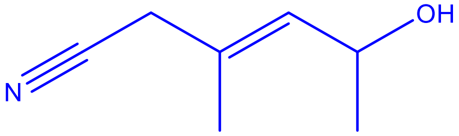
Step 3: H_2SO_4(aq), heat

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

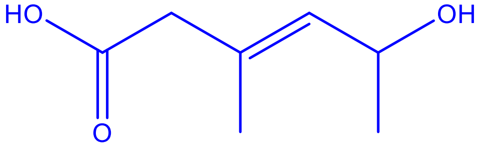
Draw the structures for compounds **C**, **D** and **E**.

[3]

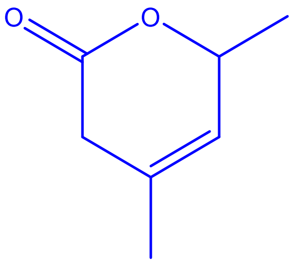
C:



D:



E:



(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.

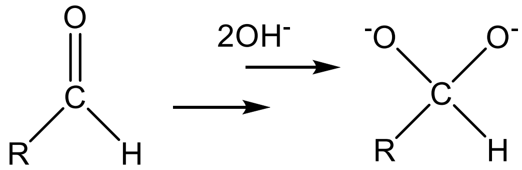
[2]

The chlorine atom has a **smaller valence orbital / less diffused/ smaller size / smaller radius/ smaller electron cloud size** than that of bromine.
Hence, the effectiveness of orbital overlap is **more effective** between C and Cl, making the **C–C*l* bond stronger** .
Hence more energy is required to break the C–C*l* bond and the reaction will be **slower**.

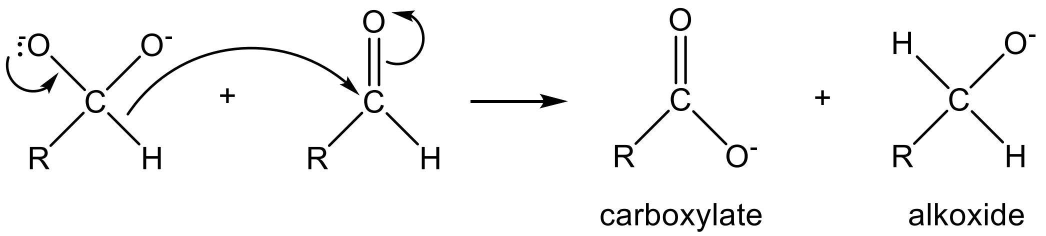
The Cannizzaro reaction is a base catalysed reaction, which involves the disproportionation of aldehydes to form a carboxylic acid and an alcohol.

$$2RCHO \rightarrow RCOOH + RCH_2OH$$

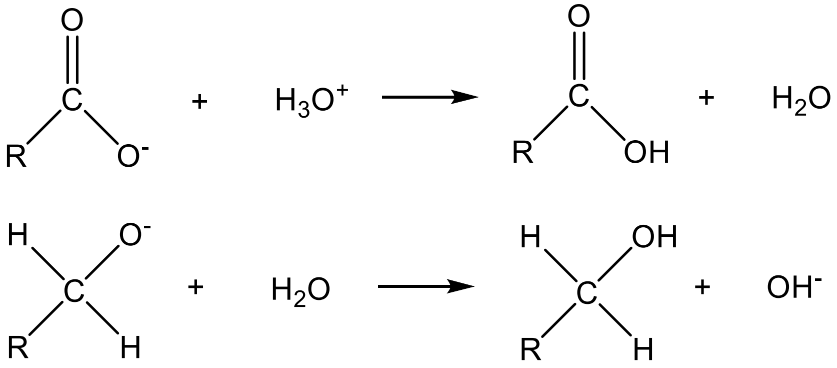
The mechanism of the Cannizzaro reaction involves 4 steps.
A nucleophilic attack on the carbonyl carbon of the aldehyde produces a dianion via a 2-step process.



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.

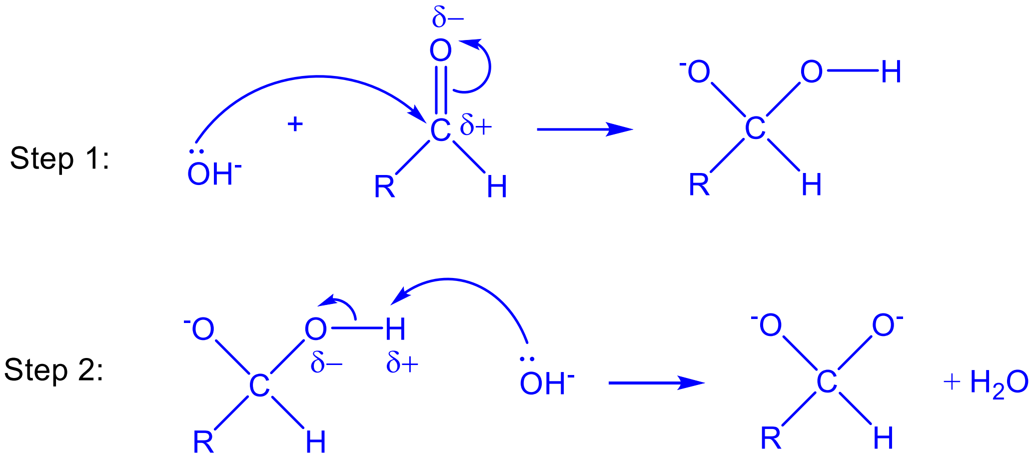


(c) **(i)** Define the term *disproportionation*, with reference to the Cannizzaro reaction. [2]

Disproportionation is a redox reaction where one species is oxidised and reduced simultaneously.
With reference to the Cannizzaro reaction, the aldehyde molecules undergo oxidation to form carboxylic acid and undergo reduction to form alcohol.
OR
The aldehyde molecules undergo **oxidation to form carboxylic acid** and undergo **reduction to form alcohol** simultaneously.

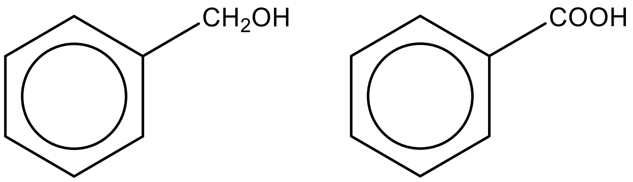
(ii) In step 1 of the mechanism, the OH^- ion acts as a nucleophile and attacks the carbonyl carbon to form an intermediate. In step 2, the second OH^- ion abstracts a proton from the hydroxyl group on the intermediate to form the dianion.

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 part of the 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]

$2HX(g) \rightarrow H_2(g) + X_2(g)$ (X = Cl, Br, I)

Down the group**, size of valence orbital of X increases. Overlap of orbitals** between H and X becomes **less effective**. This leads to the **H−X bond becoming weaker ,** as shown by the decreasing bond energy values**.**

Quote bond energy values

Bond	**Bond Energy / kJ mol^{-1}**
H–C*l*	**431**
H–Br	**366**
H–I	**299**

Less energy is required to break the covalent bond H−X for thermal decomposition. Hence**, thermal stability decreases.**

(ii) Describe the reactions, if any, of A*l*C*l*$_3$ and PC*l*$_5$ with water, stating the pH of the resulting solutions. Write equations where appropriate. [4]

$AlCl_3$ **hydrolyses partially/slightly** in water to form a slightly acidic solution of **pH 3**.

Hydration: $AlCl_3(aq) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^{-}(aq)$
Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^{+}(aq)$

PCl_5 **hydrolyses readily/completely** in water to form a strongly acidic solution of **pH 1-2**.
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

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.

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

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

F: Na_2O **G**: Al_2O_3 **H**: SO_3 (accept SO_2)

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

For **G**: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$

(accept ionic eqn: $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$)

For **H**: $SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

(accept $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$ if student used SO_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**.

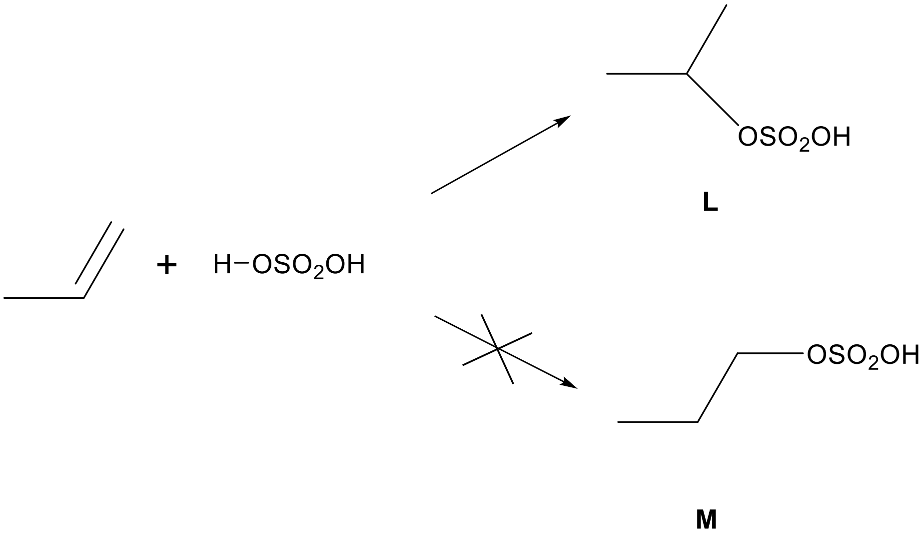
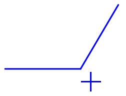
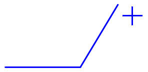


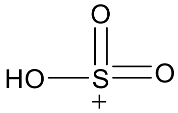
Fig. 2.1

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

Carbocation that form L	**Carbocation that form M**
	

In the **electrophilic addition** mechanism, the **carbocation** forming F is a **secondary carbocation** which has **1 more electron-donating alkyl group** whereas the carbocation forming G is a **primary carbocation**. Hence, the **positive charge on the secondary carbocation is dispersed more effectively**, and it is **more stable**.

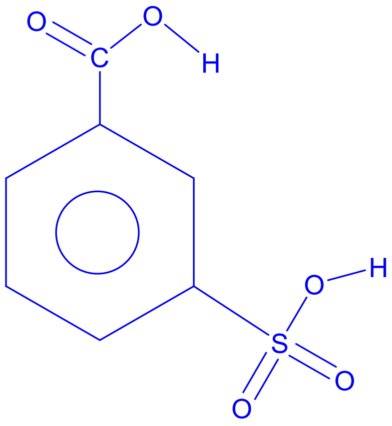
In sulfonation of benzoic acid, sulfonium ion, SO_3H^+, generated from sulphur trioxide and fuming sulfuric acid, reacts with benzoic acid via a substitution reaction to form mixtures of aromatic mono-substituted product.



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

sulfonium ion

(ii) 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]



-COOH group is 3-directing . Hence, incoming electrophile SO_3H^+ will substitute H atom at 3rd carbon **relative to the carbon bonded to –COOH group**.

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

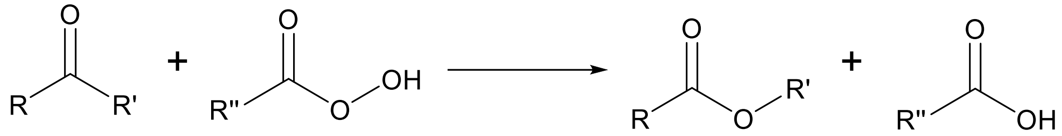


Fig. 2.3

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

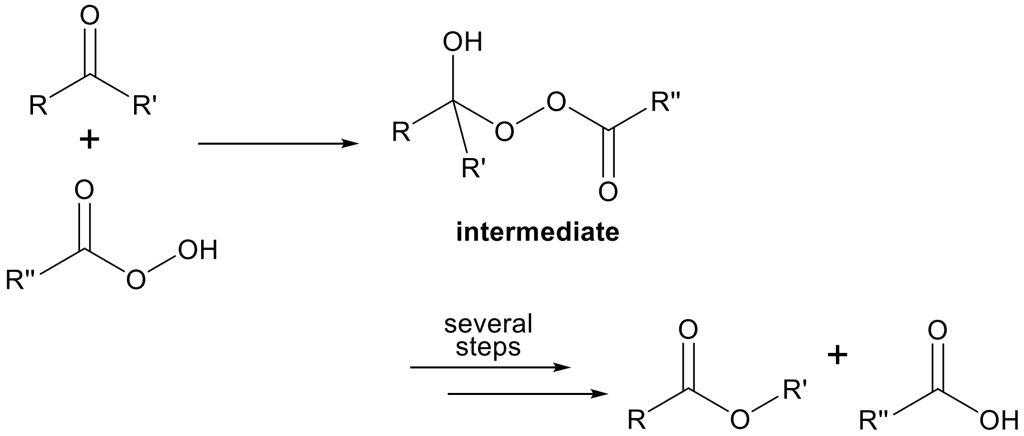


Fig. 2.4

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

For example:

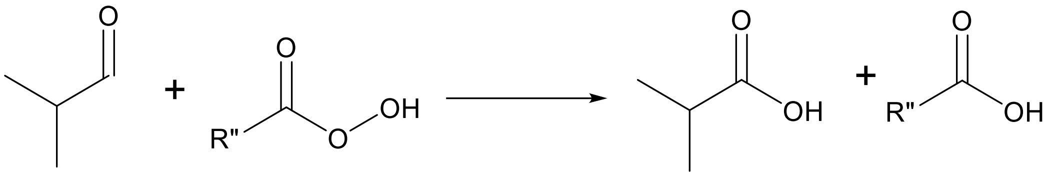
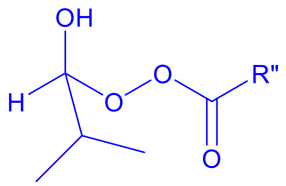


Fig. 2.5

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 structure of the organic products, **N1** and **N2**, for the reactions under the reagents and conditions shown in **Fig. 2.6**.

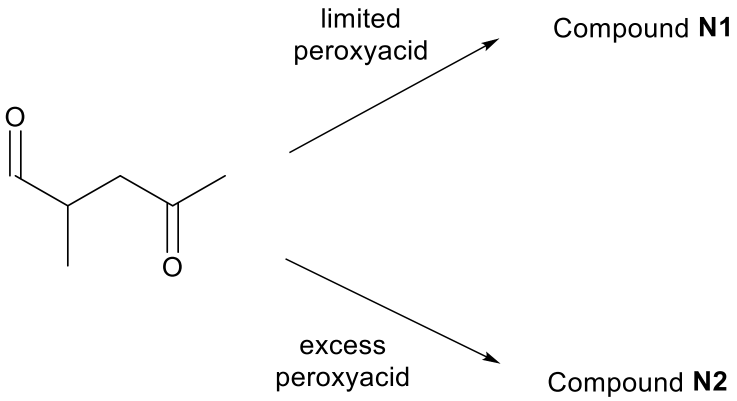
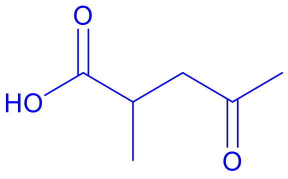


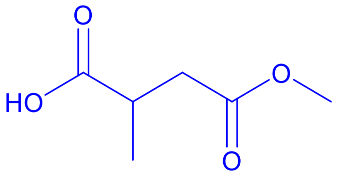
Fig. 2.6

[2]

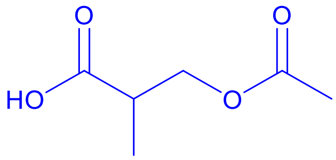
N1:



N2:



or



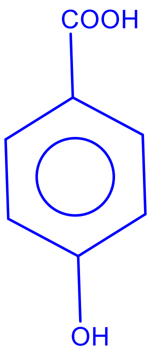
(d) Salsalate, $C_{14}H_{10}O_5$, is a medication that belongs to the nonsteroidal anti-inflammatory drug classes.

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]

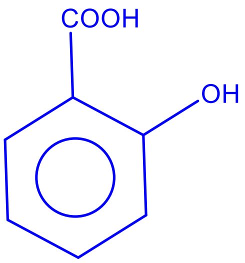
Carboxylic acid (based on reaction with Na_2CO_3)
and phenol (based on reaction with aqueous bromine)
(Do not accept arene)

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



(P1)

or



(P2)

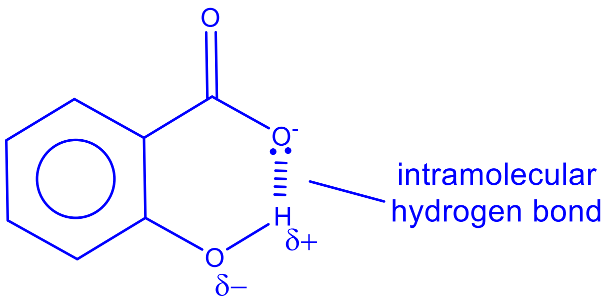
Note: -COOH must be in 2nd or 4th position relative to –OH, such that only 2 Br can be substituted.

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

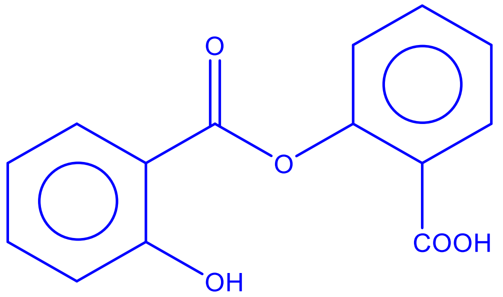
Use your answer in **(ii)** to suggest which structure, **P1** or **P2**, is the actual structure of **P**. Explain your answer. [2]

P2 (the 1,2-compound) (based on answer key) [could be P1 if student drew P1 as the 1,2-compound]

The –OH and $–COO^-$ groups are in close proximity such that the **carboxylate ion can be stabilised by the formation of intramolecular hydrogen bonding** .



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



Structure of salsalate

[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.

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

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

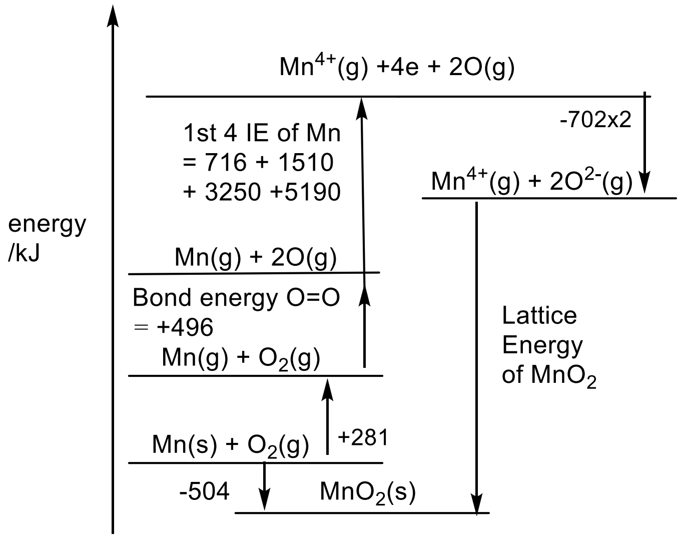
[1]

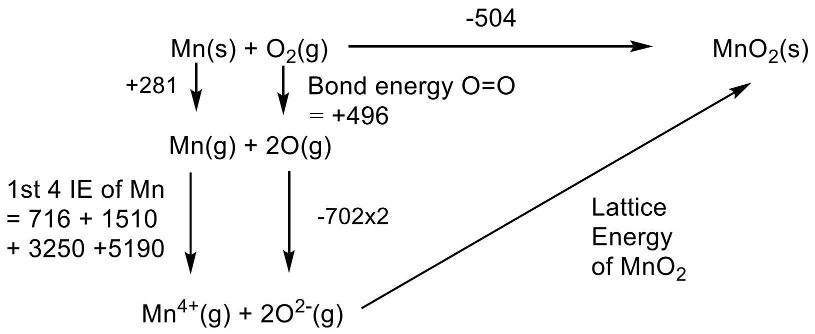
Mn^{4+} : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3$

(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.

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]





– 504 = 281 + 496 + (716+ 1510 + 3250 + 5190) + (– 702 x 2) + L.E.
L.E. = – 10543 kJ mol^{-1}
= – 10500 kJ mol^{-1} (3s.f.)

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

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]

No. of moles of H_2O_2 = (100/1000) x 0.1 = 0.0100 mol
No of moles of O_2 = 0.01 / 2 = 0.00500 mol
Volume of O_2 produced = 0.005 x 24 = 0.12 dm^3 or 120cm^3

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

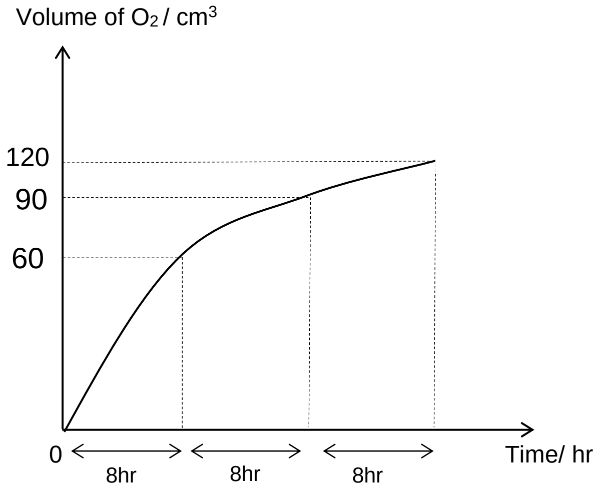
[1]

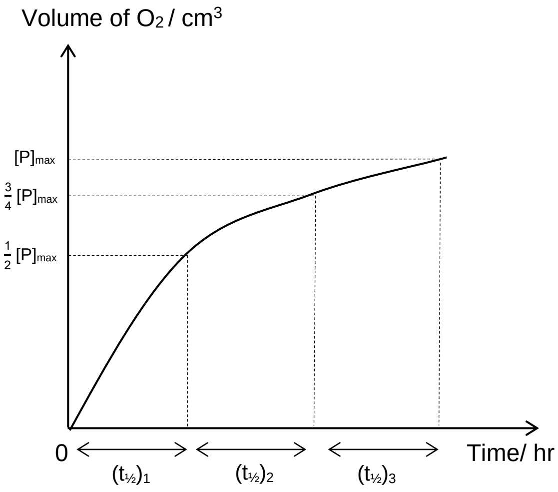
$$\underset{\text{(first half life)}}{0.1 \text{ mol} \rightarrow 0.05 \text{ mol}} \underset{\text{(second half life)}}{\rightarrow 0.025 \text{ mol}}$$

Two half lives = 16 hours
One half life = 8 hours

(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]

Half life = 8 hours

k = ln2 / half life
  = ln2 / 8hrs
  = 0.0866 hr^{-1}

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

The half equations for the cell are given.

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

(c) **(i)** Write the overall equation for when current flows.

[1]

$Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

(ii) Calculate the standard Gibbs free energy change, ΔG^o for this electrochemical reaction.

[2]

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$
$= +0.15 - (-1.28)$
$= +1.43V$

$\Delta G^\ominus = -nFE^\ominus_{cell}$
$\Delta G^\ominus = -(2 \times 96500 \times 1.43)$
$= -275990\ J\ mol^{-1} = -276000\ J\ mol^{-1}$ (3sf)

(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]

When Mg^{2+} ions are added, $Mg(OH)_2$ will be precipitated causing $[OH^-]$ to **decrease**.
As such the $ZnO(s) + H_2O(l) + 2e^- \rightleftharpoons Zn(s) + 2OH^-(aq)$ equilibrium shifts to the **right**.
$E^\ominus_{reduction}$(ZnO/Zn) to become **more positive/less negative** and $E^\ominus_{cell}$ **less positive**.

[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]

	$H_2O(g)$	+	$C(s)$	$\rightleftharpoons$	$H_2(g)$	+	$CO(g)$
Initial / atm	2.50		-		0		0
Change / atm	-1.66		-		+1.66		+1.66
Eqm / atm	0.84		-		1.66		1.66

Partial pressure of $H_2O(g)$ = 0.84 atm
Partial pressure of $CO(g)$ = 1.66 atm

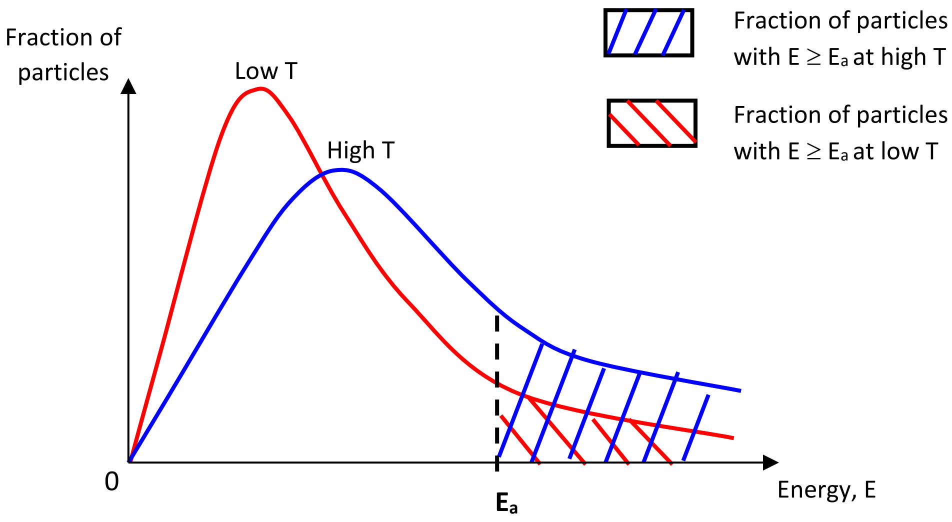
$K_p = 1.66 \times 1.66 / 0.84 = 3.28$ atm

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

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

By LCP, position of equilibrium will shift to the **left,** to favour the **backward exothermic** reaction, so as to **release heat** and **increase the temperature**.

(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]

Titanium objects are anodised to make it **more corrosion resistant/ durable/ decorative** .

Anodising **coats and increases the thickness of the titanium dioxide layer.**

(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]

Anode:
$2H_2O \rightarrow O_2 + 4H^+ + 4e$
$O_2 + Ti \rightarrow TiO_2$

(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]

The TiO_2 catalyst is in a solid state and it functions as a **heterogeneous catalyst** as it is in a different phase than CO(g) and O_2(g)

- CO(g) and O_2(g) are **adsorbed to the surface of the catalyst.**
- This adsorption **weakens the covalent bonds within the CO(g) and O_2(g) molecules**, thereby **reducing the activation energy** for the reaction.
- This adsorption also **increases the concentration of the CO_2(g) and O_2(g) molecules at the catalyst surface** and/or allows the reactant molecules to come into close contact with proper orientation/surface reaction for reaction.
- The CO_2 formed is subsequently **desorbed from the surface of the catalyst.**

(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]

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Overall equation: $2CH_3COO^- + 2H_2O \rightarrow CH_3CH_3 + 2CO_2 + H_2 + 2OH^-$
(accept: $2CH_3COOH \rightarrow CH_3CH_3 + 2CO_2 + H_2$)

(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]

$It = n_eF$
$(3.0)(30 \times 60) = n_e (9.65\times10^4)$
$n_e = 0.055959$ mol

amount of ethane = ½ (0.055959) = 0.027979 mol

mass of ethane = (0.027979) (30) = 0.83938 = 0.839g

(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.

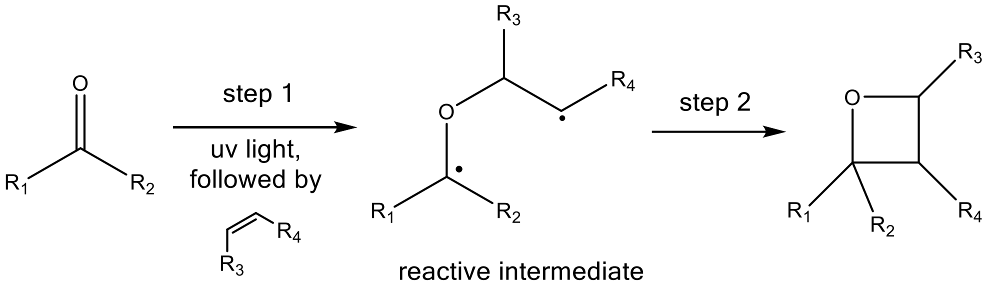
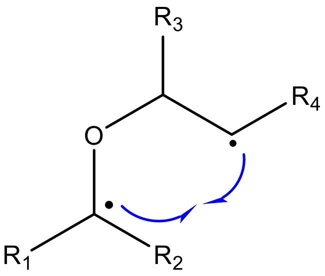


Fig. 4.1

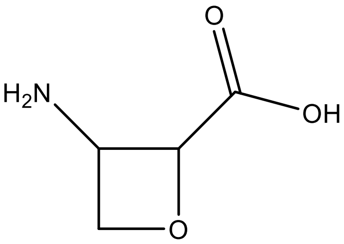
(i) State the shape of the carbonyl carbon before and after the reaction. [2]

	before	after
Shape	Trigonal planar	tetrahedral

(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.



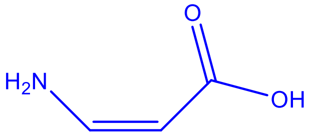
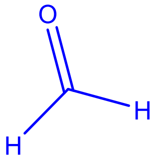
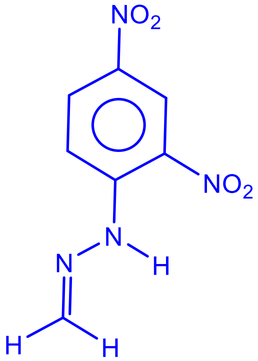
Q

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]

		
R	**S**	**T** (allow ecf for wrong carbonyl **S**)

[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]

Sum of 1st and 2nd IE of Mg = 736+1450 = 2186
Sum of 1st and 2nd IE of Ca = 590+1150 = 1740
The **ionisation energies of Ca is lower** than that of Mg.

OR
$Mg^{2+} + 2e \rightleftharpoons Mg$ $E^\ominus = -2.38V$ --- eqm (1)
$Ca^{2+} + 2e \rightleftharpoons Ca$ $E^\ominus = -2.90V$ --- eqm (2)
Ca has a **more negative $E^\ominus$ value** than Mg , indicating that the equilibrium (2) lies more to the left.

Ca has a greater tendency to lose electrons/ to be oxidised .

(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]

$Mg(OH)_2$ (s) → MgO(s) + H_2O(g)

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

[2]

Magnesium hydroxide has a **lower decomposition** temperature.

Mg^{2+} has a smaller ionic radius and hence, a **higher charge density** than Ca^{2+}.
As such, Mg^{2+} has a higher polarising power than Ca^{2+}.
The electron cloud on **OH^- is polarised/ distorted to a larger extent** , causing the **O-H bond in $Mg(OH)_2$ to be weaker** than that of $Cu(OH)_2$.
Less energy is needed to break the weaker O-H bond, hence, $Mg(OH)_2$ has a lower decomposition temperature.

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

It is the **enthalpy change/ energy change** when **one mole of substance is formed** from its **constituent elements, at their standard states,** under standard conditions of **298K and 1bar**.

(ii) Use data in Table 5.1 to calculate the $\Delta H^{\ominus}_{ppt}$ 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]

Precipitation equation: $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$

$\Delta H = -601.7 - [(-462.0) + 2(-230.0)] = +320.3$ kJ mol^{-1}

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

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

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

[1]

$\Delta G^{\ominus}_{ppt} = 2.303RT\log K_{sp}$
$= 2.303\ (8.31)\ (298)\ \log(7.1 \times 10^{-12})$
$= -63\ 600\ Jmol^{-1}$
$= -63.6\ kJmol^{-1}$

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

[2]

$\Delta G = \Delta H - T\Delta S$
$-63\ 600 = +320\ 300 - (298)\ \Delta S$
$\Delta S = +1.29 \times 10^3\ Jmol^{-1}\ K^{-1}$

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

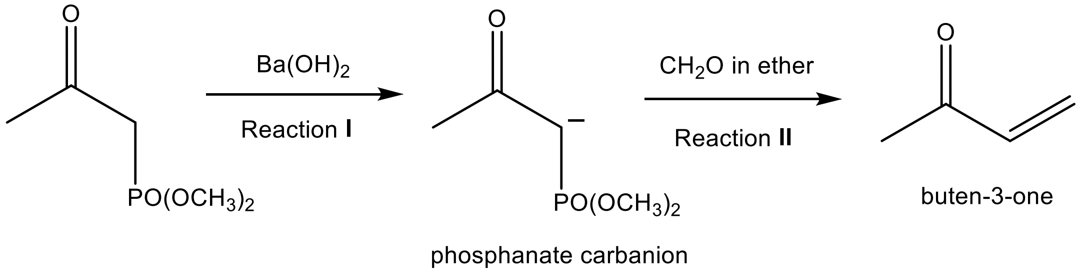


Fig. 5.2

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

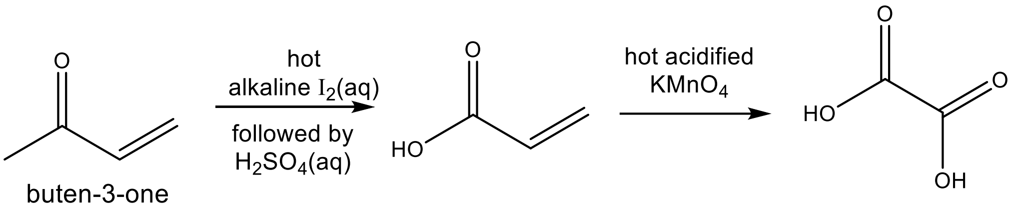
Reaction **I**: acid-base reaction

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

Suggest a reason for this stability. [1]

The **lone pair of electrons on C$^-$ is delocalised into the C=O bond** / the **carbanion is resonance-stabilised** / the **negative charge on C$^-$ is dispersed due to the electron-withdrawing C=O group**

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



W

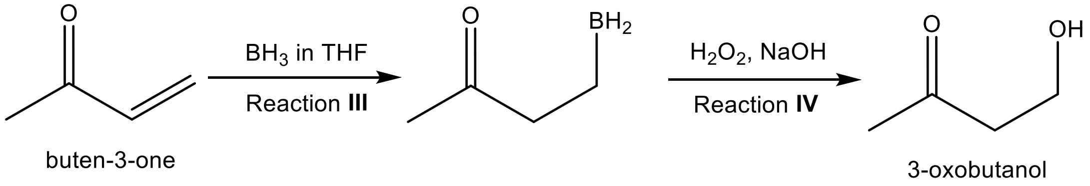
Explain why compound **W** could not be obtained from the synthesis and propose how the student could modify the synthesis to obtain **W**. [2]

$KMnO_4$ is a strong oxidising agent such that **W** (which is ethane-dioic acid) would be **further oxidised to CO_2 and H_2O**. OR **aqueous iodine may undergo electrophilic addition** with the alkene functional group in buten-3-one.

The student could **reverse the 2 steps** / carry out **oxidation with $KMnO_4$ first**.

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

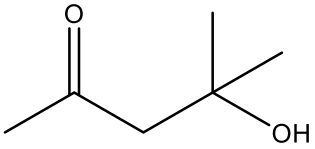
(d)



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

Reaction **III**: electrophilic addition

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

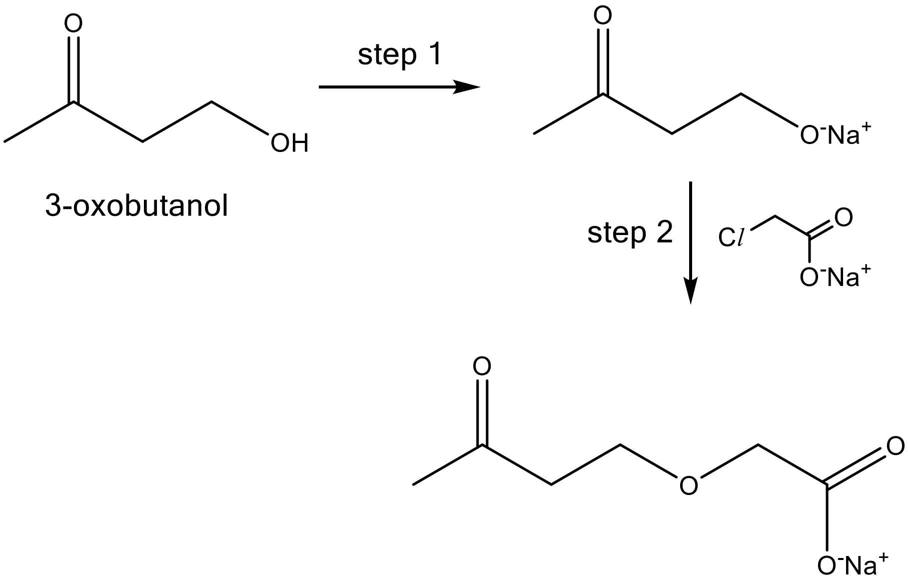


V

[2]

Test	V	3-oxobutanol
$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat	Orange solution remains.	Orange solution turns green.
$KMnO_4$(aq), H_2SO_4(aq), heat	Purple solution remains.	Purple solution decolourises.

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



X

Fig. 5.3

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

To generate a stronger R-O^- nucleophile.

(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]

There is **less steric hindrance at the carbon of the C- C*l* bond** as it is bonded to 2 small H atoms.

OR

The **carbon atom of the C=O bond is less electron deficient due to delocalisation** of lone pair of electrons on –O^-Na^+.

[Total: 20]