YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY 9729/03

Paper 3 Free Response **14 September 2023**

Candidates answer on the Question Paper. **2 hours**
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.

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** the questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A		
1	**/ 19**	
2	**/ 22**	
3	**/ 19**	
Section B		
4 or 5	**/ 20**	
Penalty	**units**	**significant figures**
Overall	**/ 80**	

This document consists of **XX** printed pages

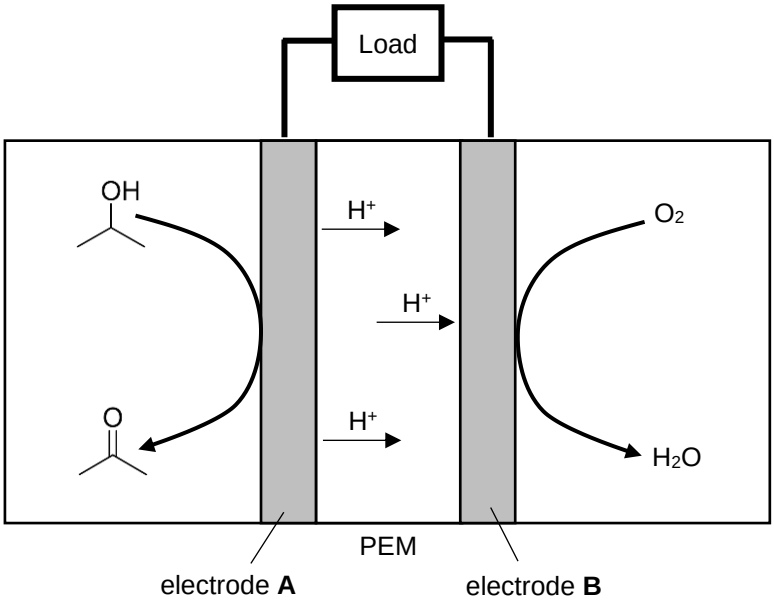
Section A

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

1 Alcohols are important organic compounds used in a wide variety of chemical reactions and frequently used as solvents.

(a) In a fuel cell, the direct oxidation of alcohols represents potentially the most efficient method of obtaining useful energy from a renewable fuel. For example, Direct Isopropanol Fuel Cell (DIFC) uses propan-2-ol in the fuel cell.

The diagram below shows a DIFC. The Proton Exchange Membrane (PEM) allows the transfer of protons between the half-cells.



The standard cell potential, $E^{\ominus}_{cell}$ of DIFC is +1.07V.

(i) By considering the given diagram, write the half-equations for the reactions occurring at electrodes A and B during discharge. Hence, write the overall equation for this reaction. [3]

Electrode A: $CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e$
Electrode B: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$

Overall: $2CH_3CH(OH)CH_3 + O_2 \rightarrow 2\ CH_3COCH_3 + 2H_2O$

(ii) In certain DIFC, air containing oxygen gas could be supplied to the H_2O/O_2 half-cell.

Explain how the $E^{\ominus}_{cell}$ would change, when pure oxygen, instead of air, is used for the O_2/H_2O half-cell. [2]

With high concentration of O_2, position of O_2/H_2O equilibrium shifts to the right, to remove O_2, resulting in a more positive $E(O_2/H_2O)$ value.

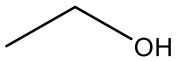
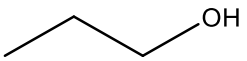
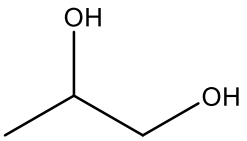
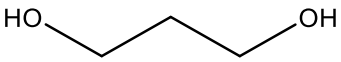
Hence, since $E_{cell} = E_{(electrode\ B)} - E_{(electrode\ A)}$, E_{cell} becomes more positive.

(iii) By considering the overall equation in **(i)**, calculate ΔG for the DIFC. [1]

$\Delta G = -nFE_{cell}$

$= -(4)(96500)(+1.07) = -413\ 020\ J\ mol^{-1} = -413 kJ\ mol^{-1}$

(b) The table below gives data on the boiling points of some alcohols.

alcohol	boiling point/ ^oC
 ethanol	78
 propan-1-ol	97
 propane-1,2-diol	188
 propane-1,3-diol	213

(i) In terms of structure and bonding, explain why the boiling point of ethanol is lower than the boiling point of propan-1-ol. [2]

Both ethanol and propan-1-ol have simple molecular structures, with (intermolecular hydrogen bonds) and instantaneous dipole-induced dipole (id-id) interaction.

Propan-1-ol has a larger electron cloud size or is more polarisable and forms stronger intermolecular id-id interaction. More energy is required to break the stronger id-id in propan-1-ol, giving rise to higher boiling point.

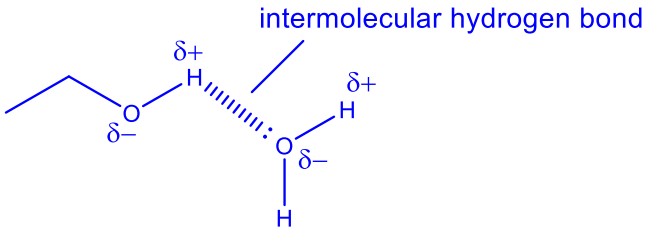
(ii) Suggest why propane-1,2-diol has a lower boiling point than propane-1,3-diol, despite both alcohols having same molecular mass. [1]

Due to the proximity of 2 -OH groups in propane-1,2-diol, it can form intramolecular hydrogen bonds.

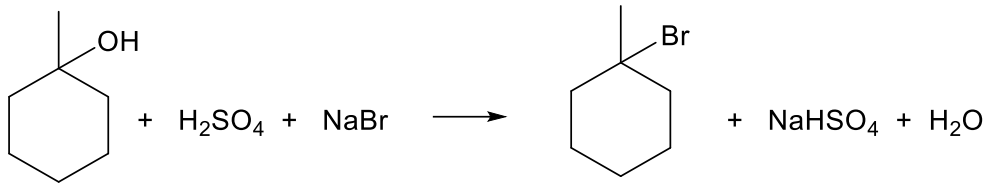
Less energy is required to break the less extensive intermolecular hydrogen bonds in propane-1,2-diol giving rise to a lower boiling point.

(c) Alcohols, such as ethanol, are soluble in water.

Draw a labelled diagram to show the significant force of attraction between a water molecule and an ethanol molecule. Include the name of the attraction in your diagram. [2]



(d) Alcohols can undergo substitution reactions in the presence of strong acids and sodium halides. For example, 1-methylcyclohexanol reacts with hot concentrated H_2SO_4 and NaBr to form 1-bromo-1-methylcyclohexane.

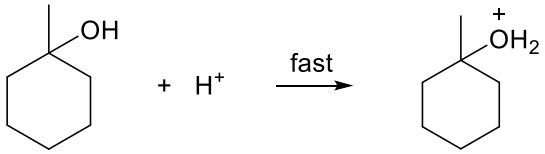


1-methylcyclohexanol 1-bromo-1-methylcyclohexane

When the reaction was investigated kinetically, it was found that its rate was independent of $[Br^-]$, but was first order with respect to $[H^+]$ and with respect to [1-methylcyclohexanol].

The mechanism for this reaction proceeds via 3 steps.

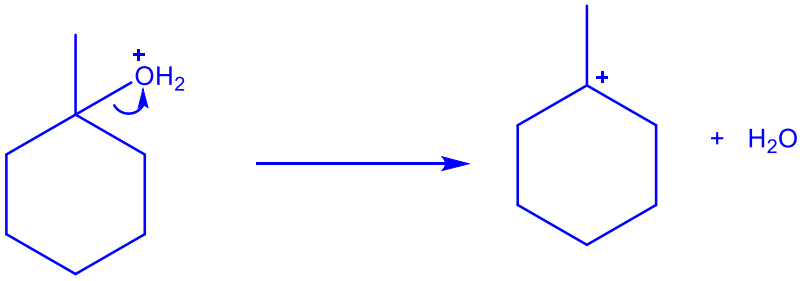
Step 1 is a fast step whereby the alcohol is protonated as shown below.

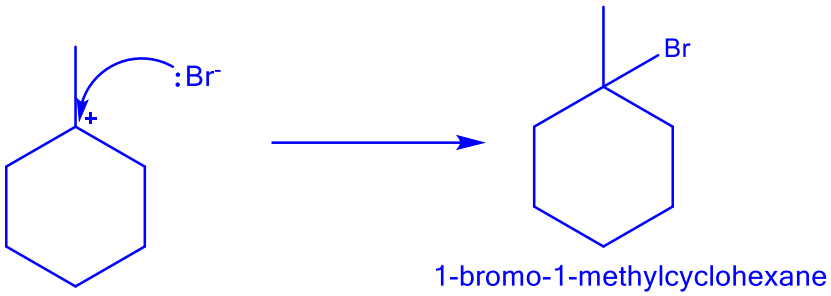


In step 2, a reactive carbocation is formed.
In step 3, the product 1-bromo-1-methylcyclohexane is formed.

Give equations for step 2 and 3 of this mechanism. Identify which of the steps is the rate-determining step.

Show relevant lone pairs of electrons, charges and use curly arrows to indicate movement of electron pairs. [3]

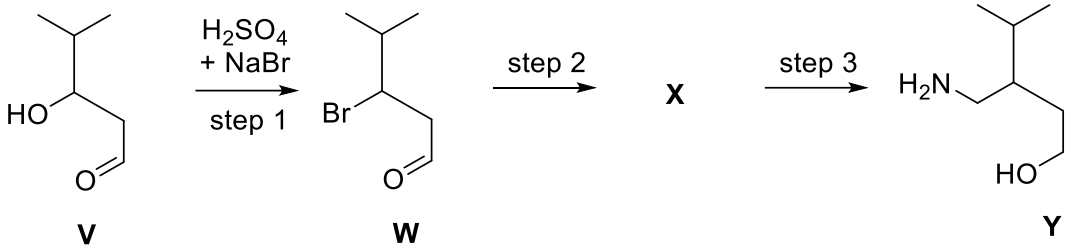




1-bromo-1-methylcyclohexane

Step 2 is the rate-determining step.

(e) The substitution reaction can be used as the first step in the following synthesis of compound **Y** from compound **V**, 3-hydroxy-4-methylpentanal.

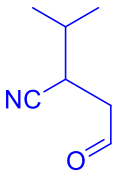


V **W** **Y**

(i) Give the reagents and conditions for step 2 and 3 and draw the structure of **X**. [3]

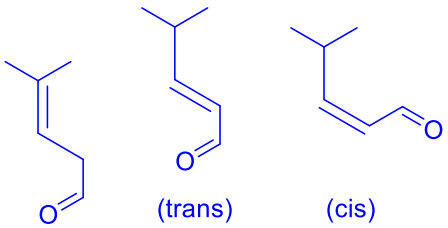
Step 1: ethanolic NaCN, heat

Step 2: $LiAlH_4$ in dry ether, room temp. or H_2, Ni, heat or H_2, Pt, room temp.



X:

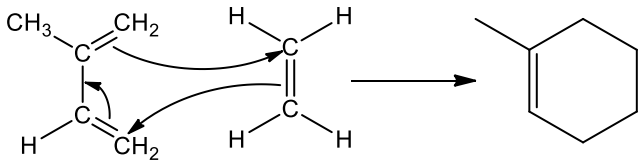
(ii) **W** can be eliminated to give a mixture of three isomeric products with the molecular formula $C_6H_{10}O$. Draw the structures of the products formed. [2]



(trans) (cis)

[Total: 19]

2 **(a)** Limonene can be obtained via a series of organic reactions involving the *Diels–Alder* reaction. The *Diels–Alder* reaction is a cycloaddition mechanism involving a diene and a dienophile as shown below:

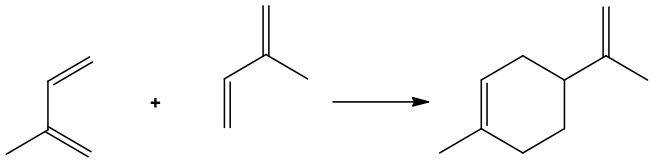


diene dienophile

The dienophile acts as the electrophile in the *Diels–Alder* reaction.

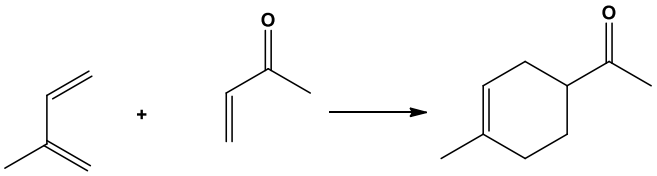
Isoprene, a diene, can be used to synthesise Limonene and **A** using the cycloaddition mechanism.

Reaction **I**:



Isoprene Limonene

Reaction **II**:



Isoprene **A**

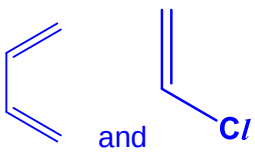
(i) With reference to the cycloaddition mechanism, explain qualitatively why the rate of reaction **II** is faster than that for reaction **I**. [1]

For reaction II: The electron withdrawing C=O group on the dienophile causes it to be more electron-deficient / decreases electron density of alkenes, thus making the dienophile a stronger electrophile. Hence, rxn is faster.

(ii) **D** may also be synthesised from the *Diels–Alder* reaction.

D

Suggest the structural formula of reactants **B** and **C** from which **D** may be synthesized. [2]

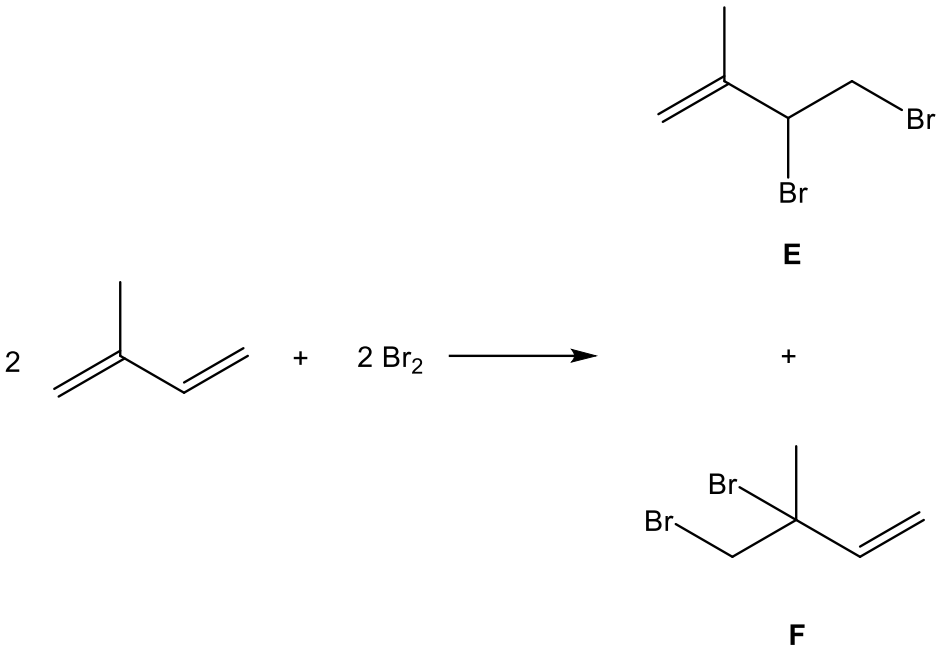


(iii) Compound **D** has a chiral carbon but no effect on the plane of polarised light. Explain your reasoning.

[1]

Racemic mixture/an equal amount of the two enantiomers is formed.

(b) When isoprene, $CH_2=C(CH_3)CH=CH_2$, is reacted with bromine, the following products may be formed in various proportions.



To determine the rate equation for the reaction between isoprene and bromine, a student conducted a series of experiments and obtained the following data:

expt	concentration / mol dm^{-3}		initial rate / mol dm^{-3} s^{-1}
	isoprene	Br_2	
1	0.04	0.064	0.88×10^{-3}
2	0.08	0.064	1.76×10^{-3}
3	0.08	0.128	3.52×10^{-3}

(i) Using data from the table above, determine the order of reaction with respect to Br_2 and isoprene, showing your working clearly. [2]

Using expt 2 and 3,

Keeping [isoprene] constant, when [Br_2] doubled, initial rate doubled.
Order of reaction with respect to Br_2 is one.

Using expt 1 and 2,

Keeping [Br_2] constant, when [isoprene] doubled, initial rate doubled.
Order of reaction with respect to isoprene is one.

(ii) Hence, construct the rate equation for the reaction. [1]

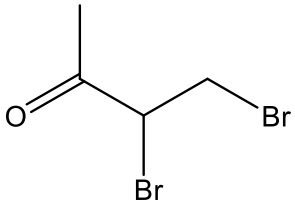
Rate = k[isoprene][Br_2]

(iii) State and explain whether **E** or **F** will be formed in greater proportion. [3]

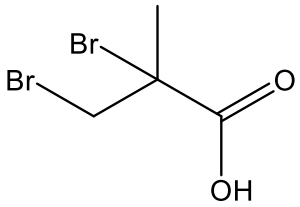
F will be formed in greater proportion as a tertiary carbocation is formed as the reactive intermediate while a secondary carbocation is the reactive intermediate to

form E. The additional electron donating alkyl group is able to disperse the positive charge to a greater extent stabilising the carbocation formed.

(iv) Both compound **E** and **F** can be oxidised to form compounds **E'** and **F'** respectively.



E'



F'

Suggest, with appropriate observations, how pure compound **E'** could be distinguished from pure compound **F'** by a simple chemical test. [2]

Test	Observation
aq I_2, aqueous NaOH, heat	**E:** yellow precipitate **F:** no yellow precipitate
2,4-DNPH	**E:** orange precipitate **F:** no orange precipitate
Na, rt	**E:** no effervescence **F:** effervescence. Gas formed pops with a lighted splint.
Na_2CO_3(aq) or $NaHCO_3$(aq), rt	**E:** no effervescence **F:** effervescence. Gas formed produces white ppt in limewater.
Anhydrous PCl_5 or $SOCl_2$, rt	**E:** no white fumes **F:** white fumes.

(c) Hydrogen iodide, HI, is a colourless gas at room temperature.

(i) HI can be formed from the reaction of I_2(s) with hydrazine, N_2H_4(g).

$$2I_2(s) + N_2H_4(g) \rightarrow 4HI(g) + N_2(g)$$

A sample containing 0.0100 mol of N_2H_4 is placed with excess I_2 in a reaction chamber connected to a gas syringe at 10 kPa.

The reactants are heated at 300 K until no further change is observed.

Calculate the total volume of gases present at the end of the reaction.

[2]

Amount of product formed = 0.0100 x 5 = 0.0500

Volume of gas present at the end of reaction
= [(0.0500)(8.31)(300)] / 10000
= 0.012465
= 0.0125m^3

Solutions of HI are strong acids commonly used in the manufacture of disinfectants.

Unlike HI, hydrazoic acid, HN_3 is a weak acid with a K_a value of 1.9×10^{-5} mol dm^{-3} at 298 K.

(ii) Calculate the pH of 0.0300 mol dm^{-3} HN_3(aq) at 298 K. Show your working. [2]

$[H_3O^+] = \sqrt{1.9 \times 10^{-5} \times 0.03} = 7.5498 \times 10^{-4}$ mol dm^{-3}

$pH = -\log(7.5498 \times 10^{-4}) = 3.12$

A buffer solution can be made from sodium azide, NaN_3 and hydrazoic acid.

(iii) Explain what is meant by the term *buffer.* [1]

A buffer solution is a solution in which its pH does not change significantly on the addition of a small amount acid or base.

100 cm^3 of 1.48 mol dm^{-3} sodium azide is added to 100 cm^3 of 1.00 mol dm^{-3} hydrazoic acid to produce a buffer solution, **T**, with pH value of 4.89.

(iv) Write an equation to show how **T** behaves as a buffer when small amounts of H_3O^+(aq) is added to portions of **T**. [1]

When small amount of H_3O^+ is added,

$$N_3^- + H_3O^+ \rightarrow HN_3 + H_2O$$

(v) When sodium hydroxide is added to solution **T**, it will be removed by HN_3 as shown in the following equation.

$$HN_3 + OH^- \rightarrow N_3^- + H_2O$$

Calculate the pH of solution **T** when 0.00500 mol of solid sodium hydroxide is used.

You may assume no change in volume when solid sodium hydroxide is added. [3]

Amount of HN_3 used = 0.100 x 1.00 = 0.1 mol
Amount of NaN_3 used = 0.100 x 1.48 = 0.148 mol

Amount of HN_3 after reaction = 0.100 – 0.005 = 0.095 mol
Amount of NaN_3 after reaction = 0.148 + 0.005 = 0.153 mol

pH = -lg(1.9 x 10-5) + lg(0.153/0.200 / 0.095/0.200) = 4.92

(vi) Calculate the pH when 0.00500 mol of solid sodium hydroxide is added to 200 cm^3 of water. [1]

Concentration of OH^- = 0.00500/ 0.200 = 0.025 mol dm^{-3}

pOH = -lg(0.025) = 1.602

pH = 14-1.602 = 12.4

[Total: 22]

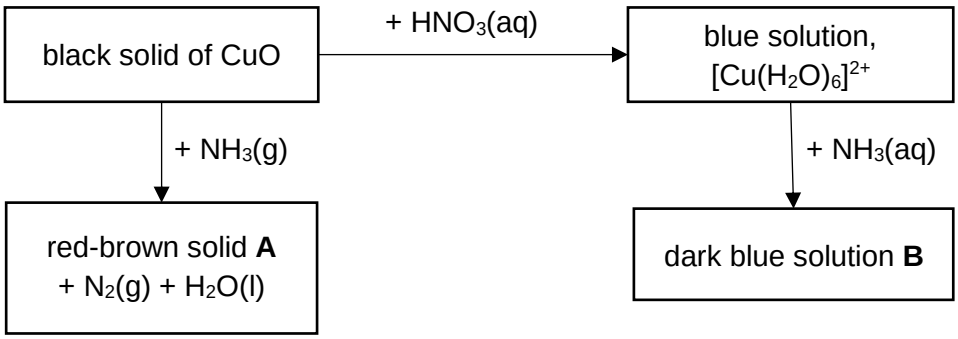
3 (a) (i) State the full electronic configurations for Cu and Ni. [1]

$_{29}Cu$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
$_{28}Ni$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

(ii) Suggest why the ionic radii of Cu and Ni are similar. [2]

Cu has more protons and a higher nuclear charge than Ni.
Cu has a greater shielding effect because the additional electron are added to the inner 3d subshell.
The increase in shielding effect cancels out the effect of the increase in nuclear charge.
Hence, effective nuclear charge and attraction for valence electrons remains fairly constant.
Hence Cu and Ni have similar ionic radii.

(b) The reactions involving copper(II) oxide, CuO, is shown in the following reaction scheme.



A is a good conductor of electricity.

(i) Identify the copper-containing species in **A** and **B**. [2]

A: Cu
B: $[Cu(NH_3)_4]^{2+}$ or $[Cu(NH_3)_4(H_2O)_2]^{2+}$

(ii) Write equations to show the formation of **A** and **B**. [2]

$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 6H_2O$
Or $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

(c) Glycinate, an anion of glycine, can act as a ligand and form 2 dative bonds to a transition metal ion. It can be formed by adding glycine in a basic solution.

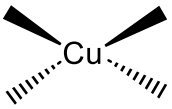
NH_2CH_2COOH
glycine

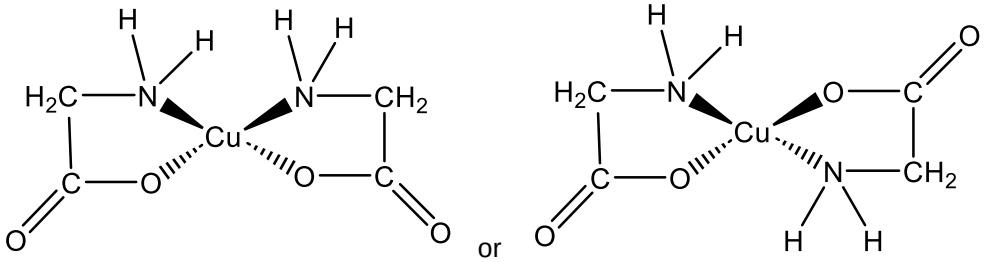
(i) Draw the structure of glycinate. [1]

$NH_2CH_2COO^-$

(ii) Two molecules of glycine in basic solution bond to one copper(II) ion to form a square planar complex. The formula of this complex may be written as

$Cu(CH_2(NH_2)CO_2)_2$. Copy the diagram below and complete the structure of the complex formed. [1]

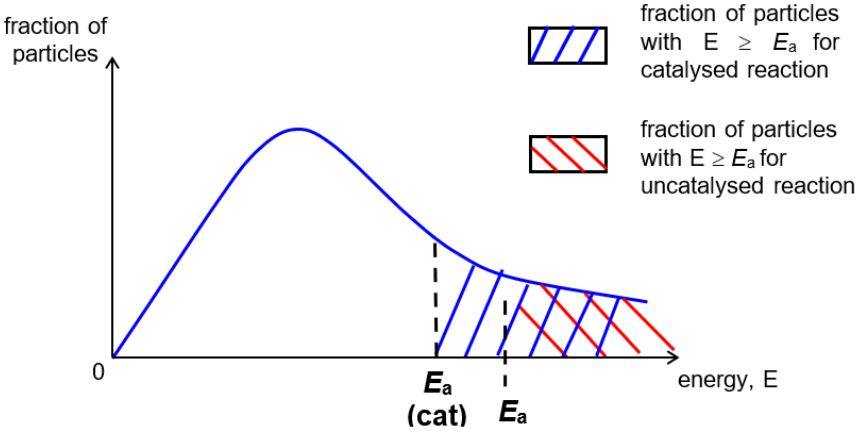




(d) Citral is a main component of citrus fruit peel oil. It has a strong lemon odour and can be used as an anti-tumor agent.

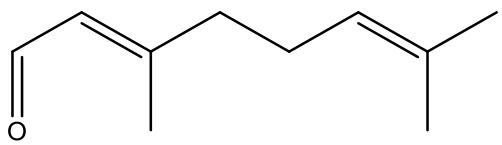
Citral is reduced by an excess of hydrogen gas in the presence of a platinum catalyst.

Explain, with the aid of a labelled Boltzmann distribution diagram, how the rate and rate constant is increased by a catalyst. [3]



- Catalyst provides an alternative reaction pathway which lowers the activation energy of reaction.
- Thus, the fraction of particles with energy equal to or greater than the activation energy of the catalysed reaction $E_{a(cat)}$ increases or deduce from legend.
- This results in an increase in frequency of effective collisions,
- This results in a larger rate constant, k hence the reaction rate increases.

(e) The structure of citral, $C_{10}H_{16}O$, is as shown.



citral

Ozone can be used to convert a C=C bond into two C=O bonds. Under certain conditions, ketones and/or carboxylic acids are formed, as shown in Fig 3.1.

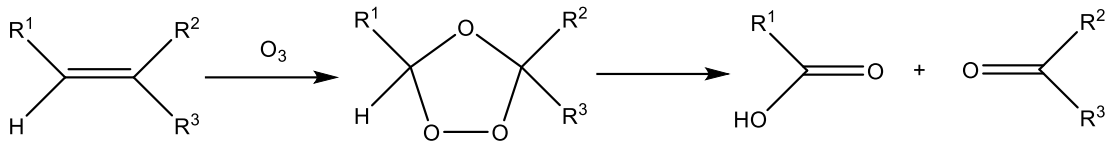


Fig. 3.1

(ii) Suggest the type of reaction when ozone is used in Fig. 3.1. [1]

Oxidation

Citral reacts with an excess of ozone under similar conditions to form compounds **F**, C_3H_6O; **G**, $C_5H_8O_3$ and **H**, $C_2H_2O_3$.

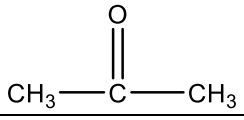
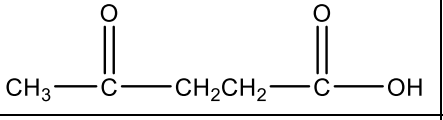
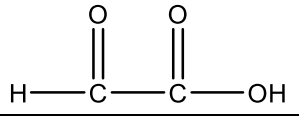
Compounds **F**, **G** and **H** give orange precipitate with 2,4-dinitrophenylhydrazine.

Compounds **F** and **G** give yellow precipitate when reacted with alkaline aqueous iodine.

Compounds **G** and **H** liberate CO_2 from Na_2CO_3(aq).

(iii) Suggest possible structures for **F**, **G** and **H**. For each reaction, state the type of reaction described. [6]

Information	**Type of Reaction**
Compounds **F**, **G** and **H** give orange precipitate with 2,4-dinitrophenylhydrazine.	condensation
Compounds **F** and **G** give a yellow precipitate when reacted with alkaline aqueous iodine.	oxidation
Compounds **G** and **H** liberate CO_2 from Na_2CO_3(aq).	acid carbonate or acid base reaction

		
F	**G**	**H**

[Total: 19]

Section B

Answer **one** question in this section.

4 (a) In the Contact Process for the manufacture of sulfuric acid, the following reversible reaction occurs:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -197\ kJ\ mol^{-1}$$

Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst V_2O_5 in a fixed volume vessel at 430 °C. When equilibrium is established, the percentage conversion of SO_2 into SO_3 is found to be 39.1%.

(i) Calculate the value of K_p at 430 °C, stating its units. [2]

Change in partial pressure for SO_2 = 0.391 x 2 = 0.782 atm

	$2SO_2\,(g)$	+ $O_2\,(g)$	⇌ $2SO_3\,(g)$
Initial Partial Press /atm	2	1	0
Change in Press /atm	-0.782	-0.391	+0.782
Final Partial Press /atm	1.218	0.609	0.782

$$\therefore K_p = \frac{(0.782)^2}{(1.218)^2(0.609)} = 0.6769 = 0.677 \text{ atm}$$

(ii) How would the percentage conversion of SO_2 into SO_3 be affected when the temperature is raised to 500 °C? Explain your answer. [2]

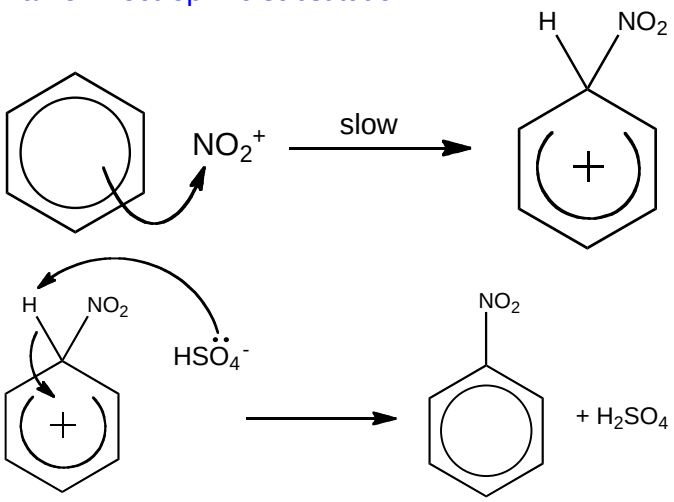
% conversion to SO_3 will decrease. By Le Chatelier's Principle, equilibrium will shift backwards/to the left with increased temperature/ which is endothermic to absorb the excess heat since the forward reaction is exothermic.

(b) Concentrated sulfuric acid is used as a catalyst in the nitration of benzene to produce nitrobenzene. The concentrated HNO_3 and H_2SO_4 react to generate NO_2^+.

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$$

State the name of this mechanism and outline the mechanism of this reaction, showing curly arrow, charges, dipoles, and any relevant lone pairs. [4]

Name: Electrophilic substitution



(c) Alkaloids are a class of basic, naturally occurring organic compounds that contain at least one nitrogen atom. One example is swainsonine found in plants. It has potential antitumor and antiviral activities and has been found to inhibit the growth and proliferation of certain tumor cells.

Fig. 4.1 shows a possible reaction sequence in the synthesis of swainsonine.

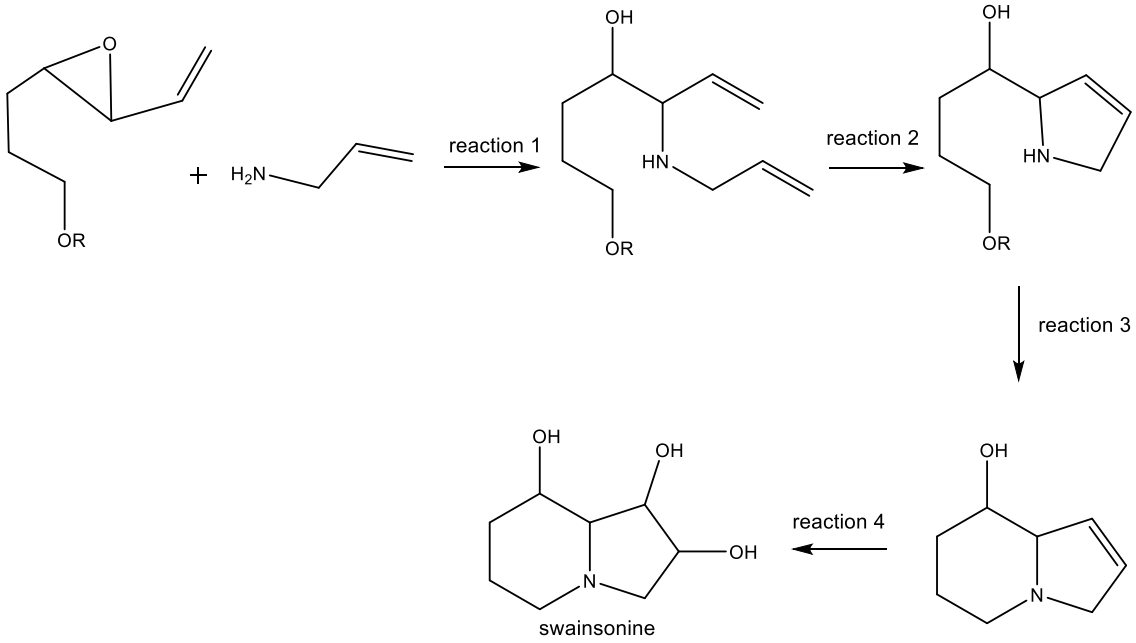


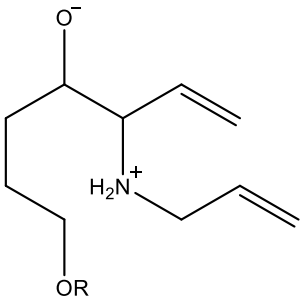
Fig. 4.1

(i) Suggest the type of reaction, reagents and conditions for reaction 4. [2]

Oxidation,
NaOH(aq), $KMnO_4$, cold

(ii) In reaction 1, the primary amine reacts the epoxide (cyclic 3-membered ether ring) via nucleophilic substitution.

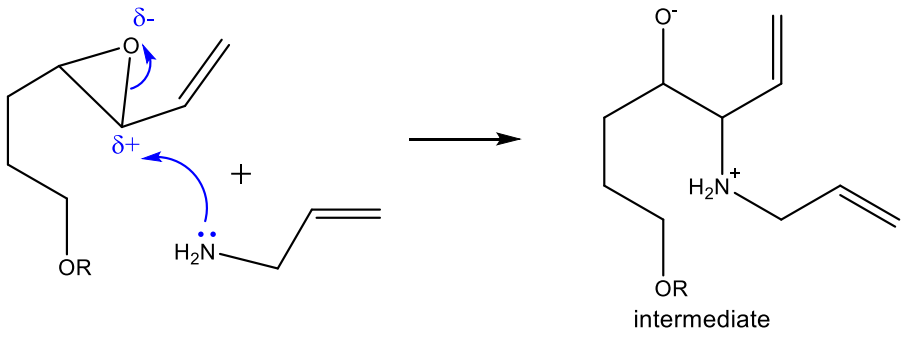
The intermediate formed is



Suggest the mechanism for the formation of the intermediate.

Show relevant lone pairs of electrons, charges and use curly arrows to indicate movement of electron pairs.

[2]



(d) The solubility product, K_{sp} for silver sulfate, at 298 K, is 1.4×10^{-5} mol^3 dm^{-9}.

(i) Write an expression for K_{sp} for Ag_2SO_4. [1]

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$

(ii) 10 cm^3 sample of saturated solution of Ag_2SO_4 is evaporated to dryness. Calculate the amount of solid produced.

[2]

Let the solubility be s mol dm^{-3}.
$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
$1.4 \times 10^{-5} = (2s)^2 (s)$
$4s^3 = 1.4 \times 10^{-5}$
$s = 1.5183 \times 10^{-2}$

In 10cm^3 sample, amount = $0.010 \times 1.5183 \times 10^{-2} = 1.5183 \times 10^{-4}$ mol

(e) A solution of concentrated NaC*l* is electrolysed, using platinum electrodes.

Write relevant half-equations for the reactions occurring during the electrolysis of concentrated NaC*l*.

[2]

Anode: $2Cl^- \rightarrow Cl_2 + 2e$
Cathode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

(f) Bromine and fluorine react together to give bromine trifluoride.

$$Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$$

$\Delta G^{\ominus} = -241$ kJ mol^{-1}
$\Delta H^{\ominus} = -301$ kJ mol^{-1}

Calculate, in J mol^{-1} K^{-1}, the standard entropy change of this reaction, and explain the significance of its sign.

[3]

$\Delta G = \Delta H - T\Delta S$
$\Delta S = \Delta H - \Delta G / T$
$= (-301 \times 1000) - (-241 \times 1000) / 298$
$= -201.34$ J mol^{-1} K^{-1}
$= -201$ J mol^{-1} K^{-1}

ΔS is negative because there is a decrease in number of moles of gaseous molecules. Disorderliness decreases as there is less ways to distribute particles and energy when liquid product forms.

[Total: 20]

5 Pyrotechnics refer to the devices capable of generating combustion reactions through a mixture of fuels and oxidants, designed to produce a combination of heat, light, sound and gases. It encompasses the designing of safety matches and fireworks.

(a) A classic example of pyrotechnic is gunpowder, which has been developed as a propellant in missiles and firecrackers.

Traditionally, gunpowder contains 10% of sulfur, 15% of carbon and 75% potassium nitrate by weight. The reaction of the ignition of gunpowder is:

$$10KNO_3(s) + 8C(s) + 3S(s) \rightarrow 2K_2CO_3(s) + 3K_2SO_4(s) + 6CO_2(g) + 5N_2(g)$$

Assuming complete ignition, calculate the total volume of gases that would be produced from 1kg of gunpowder under room temperature and pressure. [4]

In 1kg of of gunpowder,
10% of sulfur by weight → 100g of sulfur present:
no of moles of S = $\frac{100}{32.1}$ = 3.1152 mol
15% of carbon by weight → 150g of carbon present:
no of moles of C = $\frac{150}{12.0}$ = 12.5 mol
75% of KNO_3 by weight → 750g of KNO_3 present:
no of moles of KNO_3 = $\frac{750}{101.1}$ = 7.4183 mol

From the equation, the mole ratio is KNO_3 : C : S = 10 : 8 : 3
From the calculations, the mole ratio is KNO_3 : C : S = 7.4183 : 8.3333 : 3.1152 → KNO_3 is the limiting reactant.

No of moles of N_2 produced = $\frac{7.418397}{10} \times 5$ = 3.7091 mol
No of moles of CO_2 produced = $\frac{7.418397}{10} \times 6$ = 4.4510 mol
Vol of N_2 at r.t.p = 3.7091 mol x 24 dm^3 mol^{-1} = 89.020 dm^3
Vol of CO_2 at r.t.p = 4.4510 mol x 24 dm^3 mol^{-1} = 106.824 dm^3

Total volume of gases = 89.020 + 106.824 = 195.844 = <u>196 dm^3</u> (3.s.f.)

(b) Another common application of pyrotechnics is fireworks. When fireworks are propelled towards the sky, it produces whistling sounds. This is due to the mixing of various compounds including potassium perchlorate and aromatic compounds such as sodium benzoate and gallic acid, upon ignition with oxidizers that can release oxygen.

The equation for the production of whistling sound effect with sodium benzoate is given below.

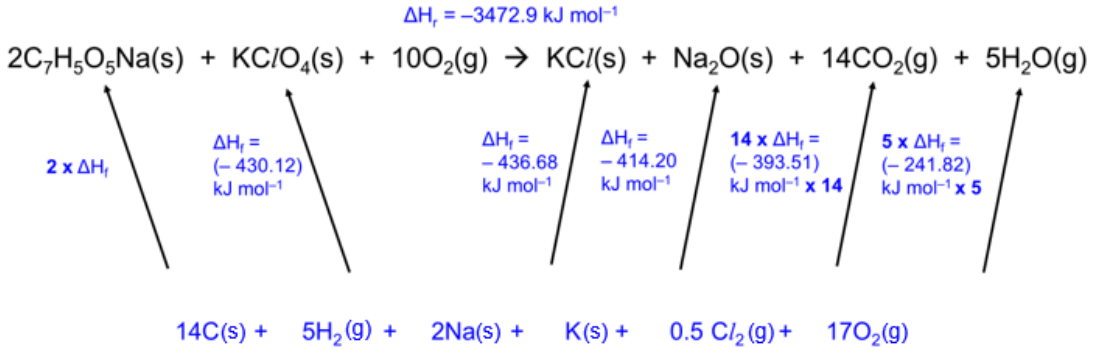
$$2C_7H_5O_5Na(s) + KClO_4(s) + 10O_2(g) \rightarrow KCl(s) + Na_2O(s) + 14CO_2(g) + 5H_2O(g)$$

The standard enthalpy change of the above reaction is –3472.9 kJ mol^{-1}.

The table lists some $\Delta H_f^{\ominus}$ values.

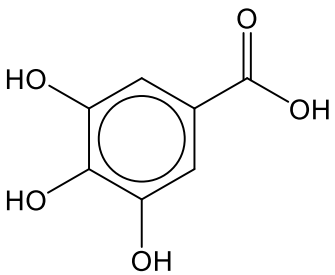
compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$KClO_4(s)$	–430.12
$KCl(s)$	–436.68
$Na_2O(s)$	–414.20
$CO_2(g)$	–393.51
$H_2O(g)$	–241.82

Use the data above to calculate the standard enthalpy change of formation of $C_7H_5O_5Na$. [3]



$2\Delta H_f$ ($C_7H_5O_5Na$) + (- 430.12) + (- 3472.9) = (- 436.68) + (-414.20) + 14 (– 393.51) kJ mol^{-1} + 5 (- 241.82)
$2\Delta H_f$ ($C_7H_5O_5Na$) = - 3666.10
ΔH_f ($C_7H_5O_5Na$) = -1833.05 = - 1830 kJ mol^{-1} (3.s.f)

(c) One of the aromatic compounds present in whistling pyrotechnics is gallic acid. Gallic acid belongs to a class of polyphenols and are a constituent of tannins, found in plants.

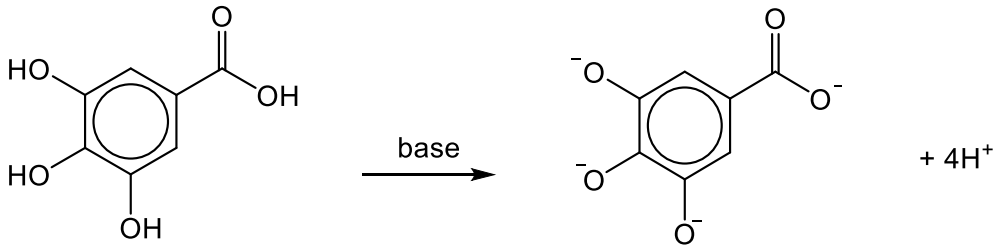


Gallic acid

Polyphenols can undergo reactions with halogenoalkanes in the Williamson Ether synthesis.

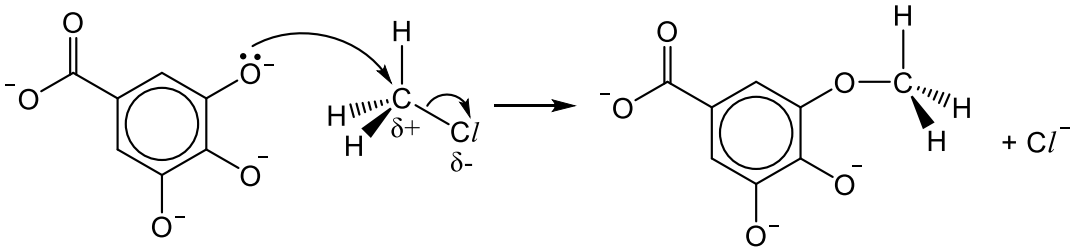
Gallic acid can react with excess chloromethane in the presence of a base to form gallic acid trimethyl ether via Williamson Ether synthesis. The mechanism is as follows:

Step 1:



Gallic acid

Step 2:



**Step 2* will take place until all three phenoxide ions have reacted.

(i) Explain the significance of the use of base in the synthesis of the ether. [1]

A base is required to react with the phenol to form phenoxides, which are stronger nucleophiles to approach the partial positive carbon in the alkyl halide.

(ii) Name the type of mechanism for Step 2. [1]

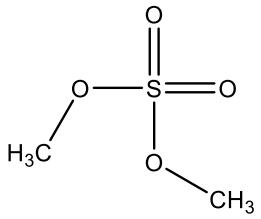
Nucleophilic substitution (S_N2)

(iii) Explain whether primary or tertiary halogenoalkanes are more suitable in the synthesis of ethers via the mechanism. [2]

Primary halogenoalkanes.

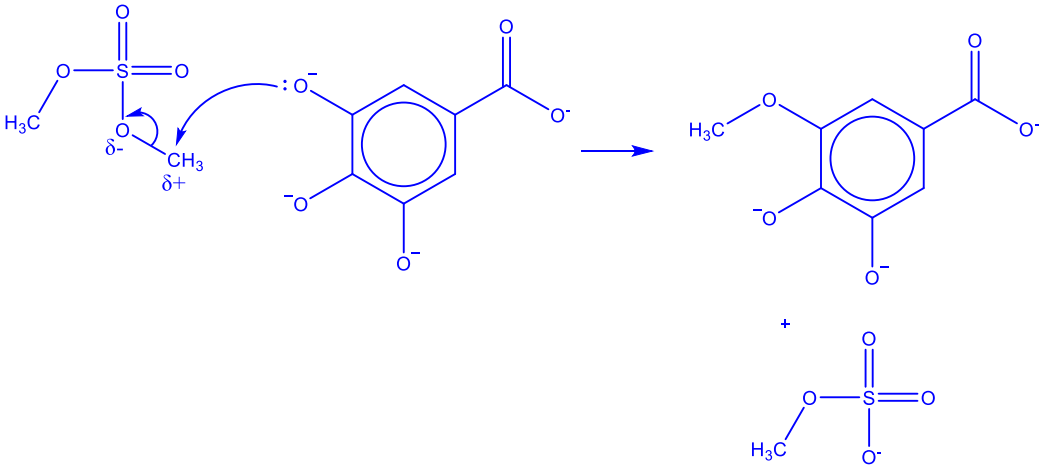
Primary halogenoalkanes are more suitable for reaction via this mechanism. In primary halogenoalkane, there is less steric hindrance around the partial positive carbon with only 1 R-group compared to tertiary halogenoalkanes with 3 R-groups around its partial positive carbon, making it more feasible for the incoming phenoxide nucleophile to approach.

(iv) Dimethyl sulfate (DMS) can also replace chloromethane to add methyl groups to the phenolic group in the ether synthesis.

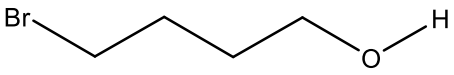


Dimethyl sulfate (DMS)

With reference to the mechanism, use curly arrows to show the electron movement on how DMS can react with gallic acid in Step 2 of the synthesis mechanism to form 1 ether functional group. [2]

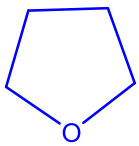


Another molecule, 4-bromo-1-butanol, also undergoes the Williamson Ether synthesis to form an ether, in the presence of a base such as sodium hydride, NaH.

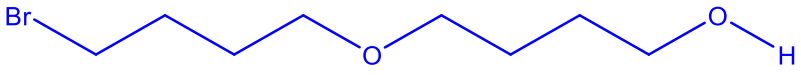


4-bromo-1-butanol

(v) Draw the structure of the ether product formed via Williamson Ether synthesis. [1]



(vi) Suggest the structure of another possible bromine-containing ether product, other than the structure drawn in **(v)**. [1]



(d) Different compounds are packed into small pellets in the rocket body, known as "stars", to create fireworks of different colours. This is through the incorporation of inorganic compounds which will be coated with gunpowder to produce coloured sparks upon ignition.

Carbonates of the Group 2 elements are often used to produce different colours. The corresponding colours of the sparks and their decomposition temperatures are shown below.

Compound	Colour	Decomposition temperature / °C
$CaCO_3$	Orange	900
$SrCO_3$	Red	1290
$BaCO_3$	Green	1350

(i) Quote relevant data from the *Data Booklet* to explain the trend in decomposition temperature from $CaCO_3$ to $BaCO_3$. [3]

Down Group 2 from Ca to Ba,
Ionic radii:
Ca^{2+}: 0.099nm
Sr^{2+}: 0.113nm
Ba^{2+}: 0.135nm

- the charges stay the same but the ionic radii of the Group 2 cations, M^{2+} increases from Ca to Ba.
- As charge density = $\frac{q}{r}$, there is a decrease in the charge density of the Group 2 cations. Hence, the polarising power of the Group 2 cations decreases
- This results in the electron cloud of the large CO_3^{2-} anion to be distorted (or polarised) to a smaller extent and a smaller weakening effect on the C–O bonds within the CO_3^{2-} by the M^{2+}.
- As more energy is required for decomposition (breaking down of the anion), the decomposition temperature increases from $CaCO_3$ to $BaCO_3$.

(ii) A solid sample is known to be either $MgCO_3$ or $BaCO_3$. Its identity can be identified by adding **one common** laboratory reagent.

State the reagent used, and the expected observations for each carbonate. [2]

Add aqueous H_2SO_4.

Both will give effervescence of CO_2, but only $MgCO_3$ will form a clear colourless solution while $BaCO_3$ will leave behind a white ppt of $BaSO_4$.

[Total: 20]