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 **33** printed pages and **1** blank page.

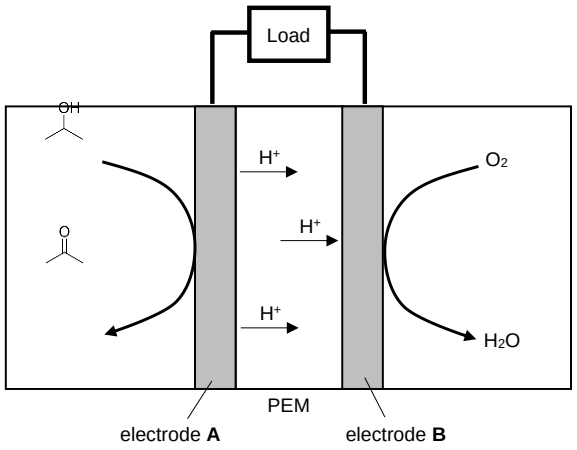
Section A

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]

(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]

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

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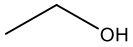
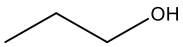
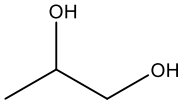
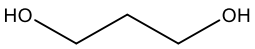
(b) The table below gives data on the boiling points of some alcohols.

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]

(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]

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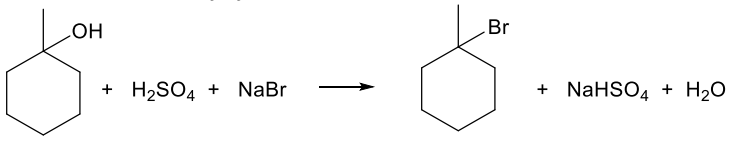
(c) Alcohols, such as ethanol, are soluble in water.

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.

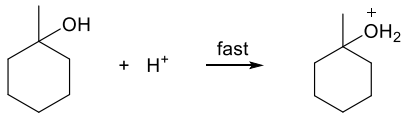


1-methylcyclohexanol 1-bromo-1-methylcyclohexane

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

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]

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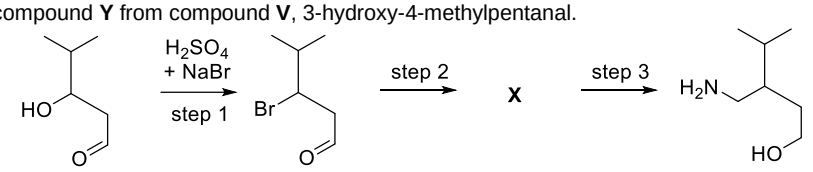
(e) The substitution reaction can be used as the first step in the following synthesis of compound **Y** from compound **V**, 3-hydroxy-4-methylpentanal.



V **W** **Y**

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

(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]

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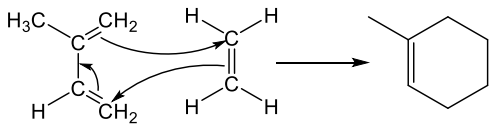
[Total: 19]

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:

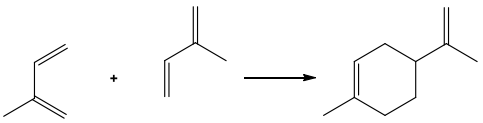


diene dienophile

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

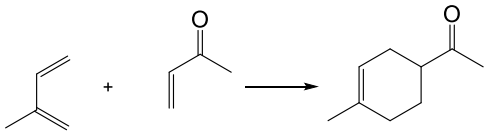
Isoprene, a diene, can be used to synthesise Limonene and **A** using the cycloaddition mechanism.

Reaction **I**:



Isoprene Limonene

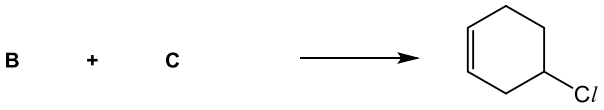
Reaction **II**:



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]

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

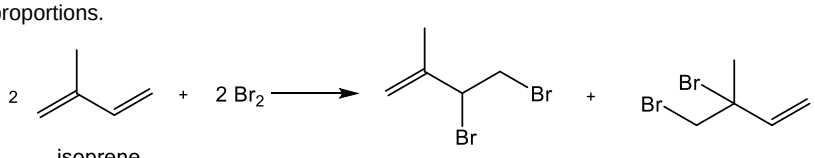


B + **C** **D**

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

(iii) Compound **D** has a chiral carbon but no effect on the plane of polarised light. Explain your reasoning. [1]

(b) When isoprene, is reacted with bromine, the following products may be formed in various proportions.



isoprene **E** **F**

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

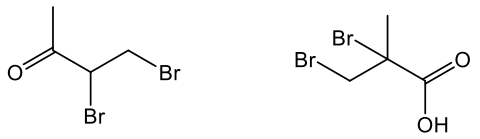
expt	concentration / mol dm^{-3}		initial rate / mol dm^{-3} s^{-1}
	isoprene	Br_2	
1	0.04	0.064	0.88×10^{-3}
2	0.08	0.064	1.76×10^{-3}
3	0.08	0.128	3.52×10^{-3}

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

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

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

(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]

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(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]

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]

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

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

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]

(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]

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

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[Total: 22]

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

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

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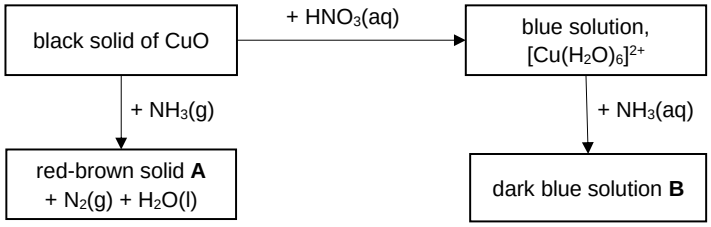
(b) The reactions involving copper(II) oxide, CuO, is shown in the following reaction scheme.



A is a good conductor of electricity.

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

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

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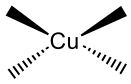
(c) Glycinate, an anion of glycine, can act as a ligand and form 2 dative bonds to a transition metal ion. It can be formed by adding glycine in a basic solution.

NH_2CH_2COOH
glycine

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

(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]

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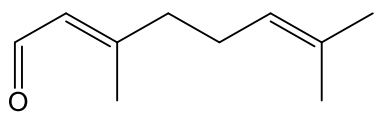
(e) The structure of citral, $C_{10}H_{16}O$, is as shown.



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.

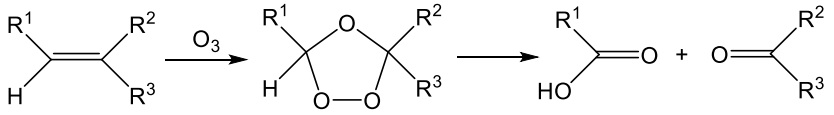


Fig. 3.1

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).

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

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

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[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 ^oC. 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 ^oC, stating its units. [2]

(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]

(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]

(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.

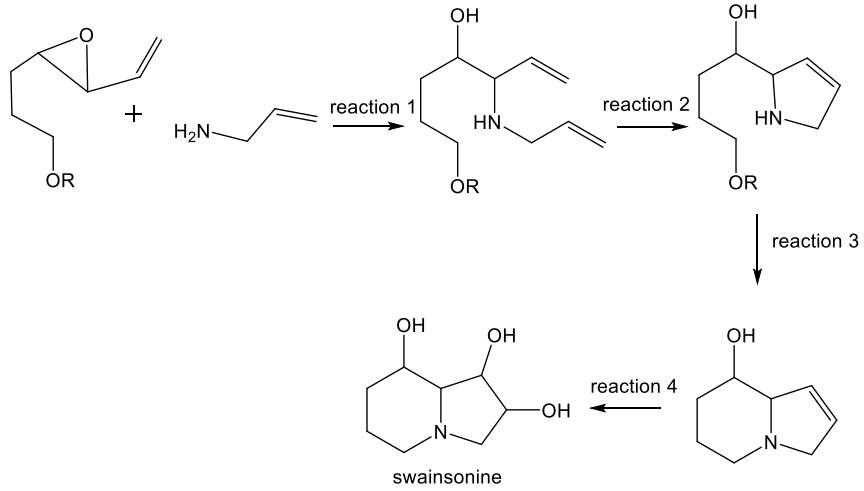
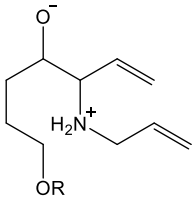


Fig. 4.1

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

(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]

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(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]

(ii) 10 cm^3 sample of saturated solution of Ag_2SO_4 is evaporated to dryness. Calculate the amount of solid produced. [2]

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(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]

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

$$Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l) \qquad \Delta G^{\ominus} = -241 \text{ kJ mol}^{-1}$$
$$\Delta H^{\ominus} = -301 \text{ kJ mol}^{-1}$$

Calculate, in J mol^{-1} K^{-1}, the standard entropy change of this reaction, and explain the significance of its sign. [3]

[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]

(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.

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

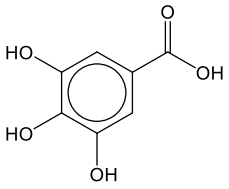
The standard enthalpy change of the above reaction is –3472.9 kJ mol^{-1}.

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]

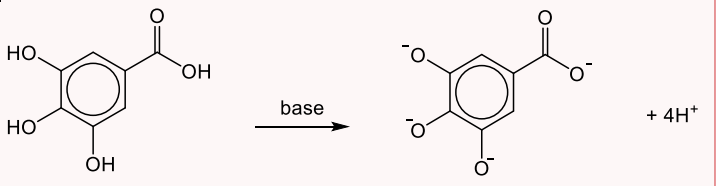
(c) One of the aromatic compounds present in whistling pyrotechnics is gallic acid. Gallic acid belongs to a class of polyphenols and are a constituent of tannins, found in plants.



Gallic acid

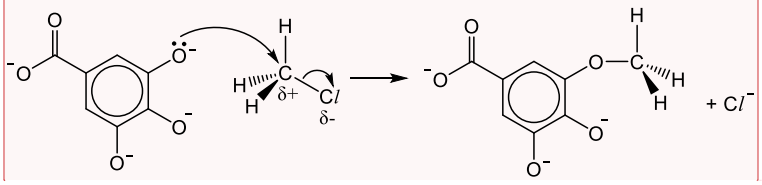
Polyphenols can undergo reactions with halogenoalkanes in the Williamson Ether synthesis. For example, gallic acid can react with excess chloromethane in the presence of a base to form gallic acid trimethyl ether via Williamson Ether synthesis. The mechanism is as follows:

Step 1:



Gallic acid

Step 2:



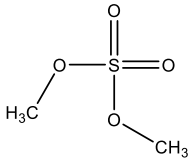
**Step 2* will take place until all three phenoxide ions have reacted.

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

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

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

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

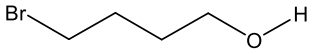


Dimethyl sulfate (DMS)

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]

Commented [ACK1]: flip

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]

(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]

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[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.