EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2023
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CIVICS GROUP	2	2	–			

INDEX NUMBER		

CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2023

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staplers, 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** questions.

Section B
Answer **one** question.

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

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	
Paper 3	
A1	**/ 19**
A2	**/ 23**
A3	**/ 18**
B4 or 5	**/ 20**
Total	**/ 80**

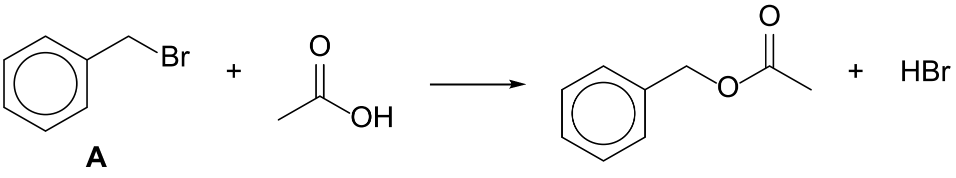
This document consists of **32** printed pages.

Section A

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

1 **(a)** Solvolysis is a reaction in which the solvent is one of the reagents and is also present in great excess of that required for the reaction. Usually, the electron-rich solvent molecule substitutes an atom or group in the reactant molecule.

One example of solvolysis is the reaction of compound **A**, $C_6H_5CH_2Br$, with ethanoic acid as the solvent.



This reaction happens *via* an S_N1 mechanism.

(i) Describe the mechanism for the reaction between compound **A** with ethanoic acid. Show relevant lone pairs of electrons, dipoles and curly arrows. [4]

(ii) Explain why this reaction mainly proceeds *via* the S_N1 mechanism. [1]

(iii) Given that the enthalpy change of the reaction is endothermic, draw a labelled reaction pathway diagram for the reaction involving compound **A** and ethanoic acid. [2]

Another reaction was carried out using $C_6H_5CHBrCH_3$ with ethanol as the solvent, in the presence of trace amount of sodium hydroxide. This reaction undergoes the same mechanism as the reaction between compound **A** and ethanoic acid.

(iv) Predict the major organic product formed from the reaction of optically pure $C_6H_5CHBrCH_3$ with ethanol, and comment on the optical activity of the product formed. Briefly explain your answer. [3]

(v) By-products are formed during the preparation of many organic compounds. This usually occurs because the reagents can react in more than one way.

Suggest a possible by-product, in full structural formula, that can be formed from the above reaction. [1]

....

....

....

....

....

....

....

....

....

....

....

....

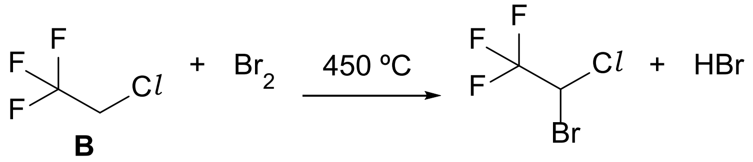
....

....

....

(b) One of the possible methods to produce compound **A** is free radical substitution. This method can also be used to produce halothane, $CF_3CHBrCl$, a general anaesthetic.

(i) Halothane is formed from compound **B** via the following reaction.



With reference to data from the *Data Booklet*, calculate the enthalpy change of the above reaction. [1]

(ii) Suggest why the reaction can be carried out in the absence of uv light. [1]

(iii) Suggest a simple chemical test to distinguish compound **A** from compound **B**. [2]

In free radical reactions of organic compounds, side products such as hydrogen halides are often formed.

(iv) Explain why HF is less volatile than HBr. [2]

(v) With reference to data from the *Data Booklet*, explain the relative stability of HCl and HI when subjected to heat. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 19]

2 This question deals with the chemistry of iron and its compounds.

(a) When iron metal is exposed to water and air, it undergoes a series of redox processes, forming rust, which contains mainly a hydrated form of iron(III) oxide.

Rusting occurs in 2 steps. In the first step, iron is initially oxidised to iron(II) ions by oxygen in the air.

equation 1 $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

(i) State the relationship between the standard Gibbs free energy change, $\Delta G^\ominus$, and standard cell potential, $E^\ominus_{cell}$. Use this relationship to calculate $\Delta G^\ominus$ for the reaction in equation 1 and show that this step occurs spontaneously. [3]

(ii) A method of preventing corrosion is galvanisation, in which iron is coated with a thin layer of zinc.

Explain, with the help of relevant $E^\ominus$ values, how galvanisation helps to prevent the corrosion of iron. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(b) When carbon steel corrodes in an environment that contains carbon dioxide and calcium ions, a product mixture of $FeCO_3$ and $CaCO_3$ is obtained.

The thermal decomposition of anhydrous metal carbonates, $CaCO_3$ and $FeCO_3$ was investigated. A pure 1.0 g sample of each carbonate was separately heated using the set-up in Fig. 2.1.

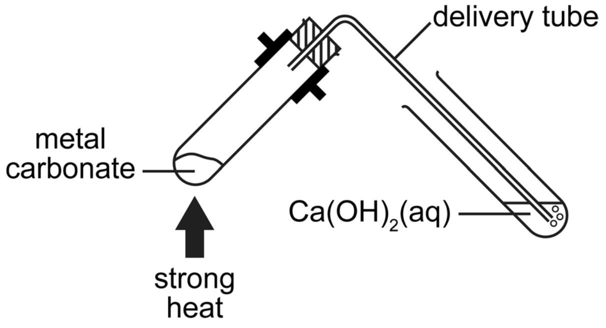


Fig. 2.1

The following observations were noted during the experiment.

carbonate	observations
$CaCO_3$	• white solid remains white • white ppt observed with $Ca(OH)_2(aq)$ after some time.
$FeCO_3$	• greenish brown solid turns black. • white ppt observed in $Ca(OH)_2(aq)$ after some time.

(i) Write a balanced equation, with state symbols, for the formation of the white precipitate in $Ca(OH)_2(aq)$. [1]

(ii) With the aid of suitable data from the *Data Booklet,* explain the relative ease of decomposition of these two carbonates. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(c) Fig. 2.2 shows an electrolytic cell which is used to prepare potassium ferrate(VI), K_2FeO_4, a powerful oxidising agent.

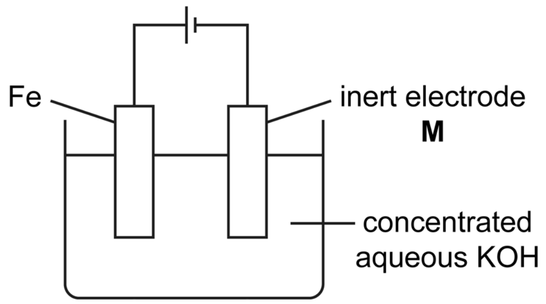


Fig. 2.2

(i) During the reaction, hydrogen gas is evolved at inert electrode **M** while the iron electrode is oxidised to ferrate(VI) ion as shown in the half equation below.

$$Fe(s) + 8OH^-(aq) \rightarrow FeO_4^{2-}(aq) + 4H_2O(l) + 6e^-$$

Construct the overall reaction occurring in the electrolytic cell, showing your working. [1]

(ii) 0.28 g of Fe was consumed when a current of 0.98 A was drawn from the battery for 50 minutes. By calculating the total electrical charge transferred, determine a value for the Avogadro's constant. [2]

(d) Fig. 2.3 shows some reactions involving potassium ferrate(VI).

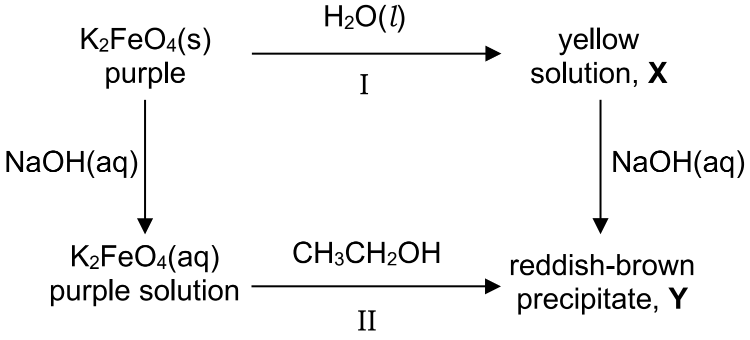


Fig. 2.3

Precipitate **Y** and the complex ion in solution **X** both contain iron, oxygen and hydrogen. The oxidation number of iron in **X** is the same as that in **Y**.

(i) Suggest the formula of the precipitate **Y** and the complex ion in solution **X**. [2]

(ii) Explain why solution **X** is yellow in colour. [3]

(iii) Vigorous effervescence of a colourless gas is observed in step I.
Suggest the identity of the gas evolved in this step. [1]

(iv) Given that step II also produces **Z**, C_2H_4O, state the role of K_2FeO_4 in step II.
Hence, suggest the structure of **Z**. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(e) The pentane-2,4-dionate ion, $[CH_3COCHCOCH_3]^-$, is a bidentate ligand and is commonly known as acetylacetonate (acac$^-$).

(i) Explain the meaning of the term *bidentate ligand*. [1]

(ii) Fe^{3+} reacts with acac$^-$ ligands to form a chiral complex, $[Fe(acac)_3]$, which exists as a pair of enantiomers. Complete Fig. 2.4 to show the two enantiomeric complexes, illustrating the stereochemical relationship between them.

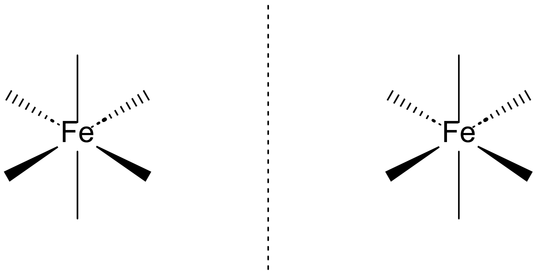


Fig. 2.4

You may use O⌒O to represent the acac$^-$ ligand. [2]

....

....

....

....

....

....

....

[Total: 23]

3 **(a)** Aqueous bromine reacts with methanoic acid to produce carbon dioxide gas, as shown in the equation below.

$$Br_2(aq) + HCO_2H(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

20 cm^3 of 0.25 mol dm^{-3} of aqueous bromine was reacted with 20 cm^3 of 3 mol dm^{-3} methanoic acid. The reaction was monitored by measuring the volume of carbon dioxide gas over time, at room temperature, as shown in Fig. 3.1.

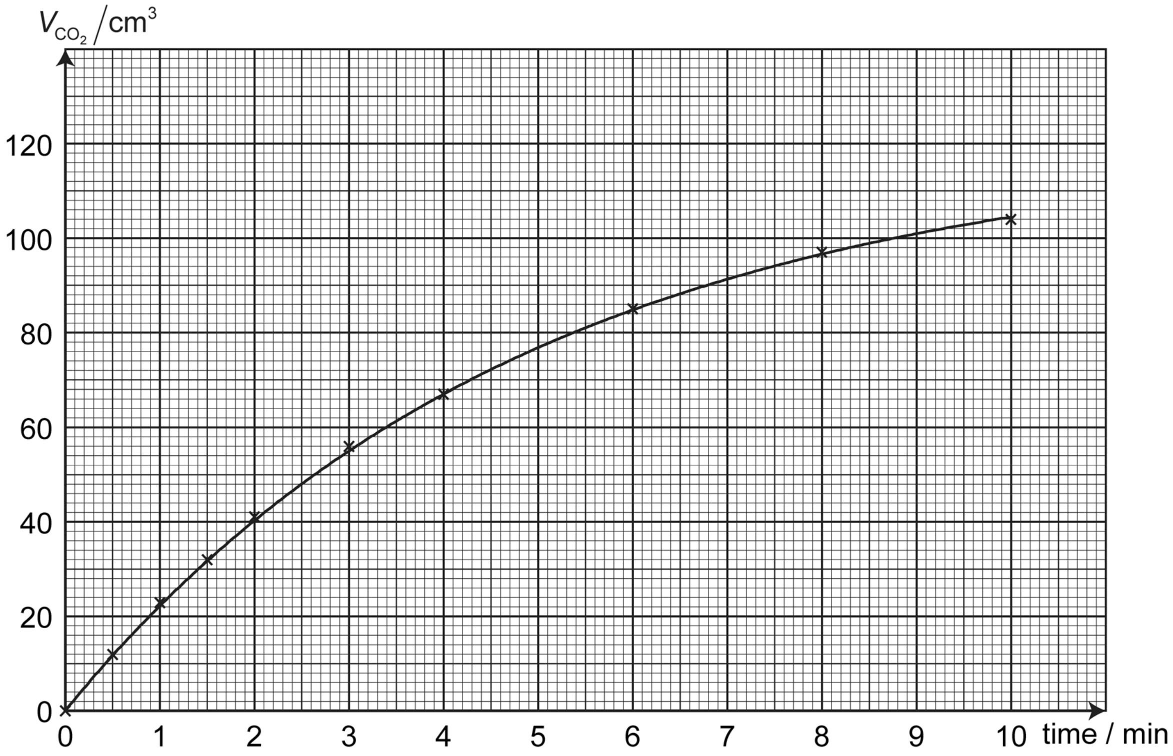


Fig. 3.1

(i) Prove that the order of reaction with respect to Br_2 is one, showing your working clearly on Fig. 3.1. [2]

(ii) Given the order of reaction with respect to HCO_2H is one, calculate the value of the rate constant k, stating its units clearly. [1]

(iii) Explain, with the aid of a labelled Maxwell-Boltzmann distribution curve, the effect on the rate constant, k, when temperature of the reaction was increased. [3]

(iv) Apart from measuring the volume of CO_2 gas produced, there are other methods to monitor the rate of reaction between aqueous bromine and methanoic acid.

Outline another experiment to monitor the progress of reaction over time. [2]

....

....

....

....

....

....

....

....

....

(b) Both silver iodide and silver iodate(V) are sparingly soluble salts.

salt	K_{sp}	$\Delta G^{\ominus}$ / kJ mol^{-1}
silver iodide, AgI	8.52×10^{-17}	+91.5
silver iodate(V), $AgIO_3$	–	+42.7

(i) The value of the solubility product, K_{sp}, is related to the standard Gibbs free energy change, $\Delta G^{\ominus}$, by the mathematical expression shown, where R is the molar gas constant and T is the temperature measured in K.

$$K_{sp} = 10^{-\frac{\Delta G^{\ominus}}{2.3RT}}$$

Write the expression for the solubility product, K_{sp}, of $AgIO_3$, and calculate its value at 25 °C, stating its units. [2]

(ii) An aqueous solution of silver nitrate was added to a mixture containing 0.001 mol dm^{-3} each of sodium iodide and sodium iodate(V).

Calculate the concentration of iodide ions in the solution when the first trace of silver iodate(V) appears. [2]

(iii) Silver ions and thiosulfate ions react to form a soluble complex, $[Ag(S_2O_3)_2]^{3-}$.

Explain, with the aid of equations, how the solubility of silver iodide would be affected when solid sodium thiosulfate is added to an aqueous solution of silver iodide. [2]

(c) When aqueous silver nitrate was shaken with excess aqueous potassium bromide, a pale cream solid **X** was observed.

This solid **X** readily dissolves in excess aqueous sodium cyanide, NaCN, forming a colourless solution of a complex anion. When more aqueous silver nitrate was added to the colourless solution, a white solid **Y**, was formed with the following composition by mass:

Ag: 80.6%; C: 8.96%; N: 10.5%

(i) Identify solid **X**. [1]

(ii) Given **Y** has a molecular mass of 268 and is an ionic compound containing one cation and one complex anion, deduce the formula of **Y** and suggest the formulae of its cation and anion. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

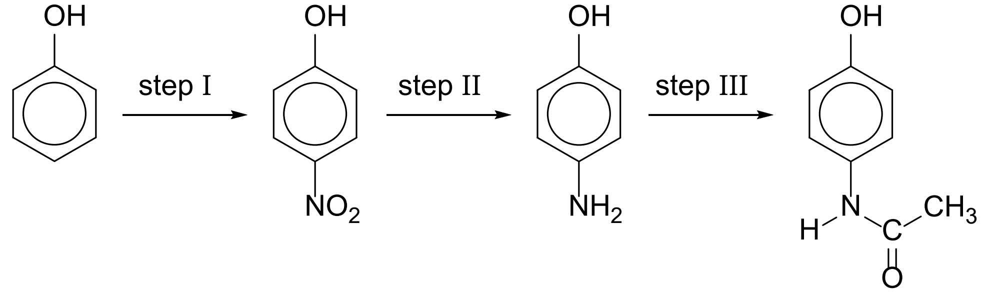
....

[Total: 18]

Section B

Answer **one** question from this section.

4 Phenol can be used to synthesise drugs such as paracetamol as shown in Fig. 4.1.



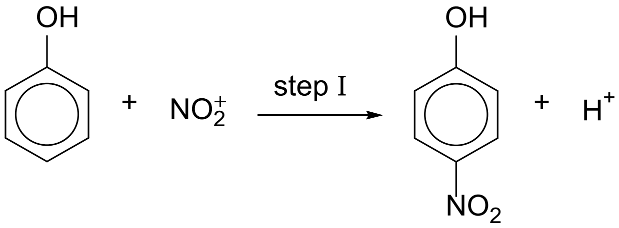
paracetamol

Fig. 4.1

(a) **(i)** State the reagents and conditions for each of steps I and II in Fig. 4.1 [2]

(ii) Predict whether the reagents and conditions used will be different from what you have suggested in **(a)(i)** if methylbenzene is nitrated instead of phenol. Explain your answer clearly. [1]

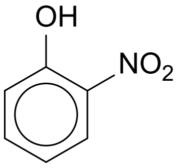
(b) The species that reacts directly with phenol to form 4-nitrophenol in step I is NO_2^+.



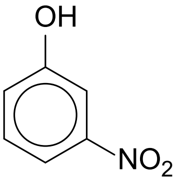
(i) Draw a dot-and-cross diagram showing the bonding in NO_2^+. [1]

(ii) Describe the mechanism for the reaction of phenol with NO_2^+ using curly arrow notation. [3]

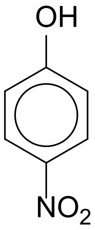
A mixture of three isomers **X**, **Y** and **Z** can be formed in step I.



X



Y



Z

(iii) Suggest why the concentration of **Z** formed is higher than that of **X** and **Y**. [2]

(iv) The boiling point of **X** is lower than that of **Z**. Explain the difference with the aid of clearly labelled diagrams. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

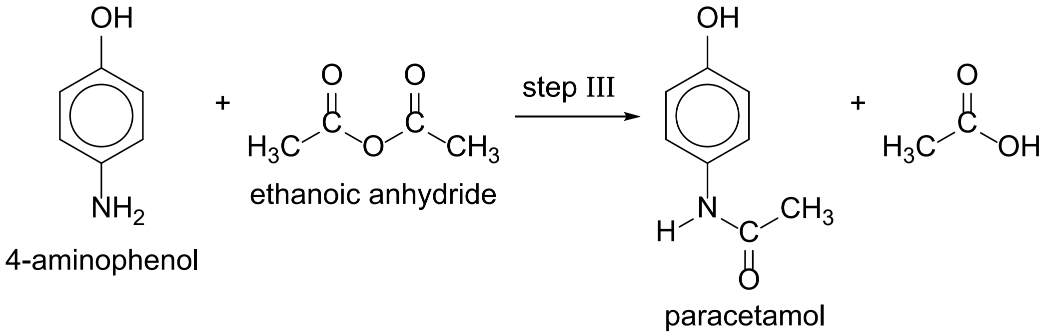
....

....

....

....

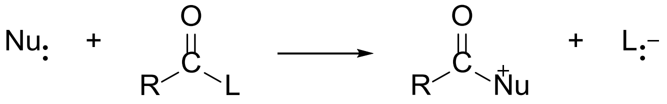
(c) Step III is a nucleophilic acyl substitution involving ethanoic anhydride, $(CH_3CO)_2O$ and the amino group of 4-aminophenol to form an amide.



(i) Phenols can also react with ethanoic anhydride. However, in Step III, the amino group of 4-aminophenol reacts faster with ethanoic anhydride than the hydroxy group, and the paracetamol product is isolated before the hydroxy group reacts.

Suggest a reason why the amino group reacts faster than the hydroxy group in the reaction between 4-aminophenol and ethanoic anhydride. [1]

(ii) One of the factors that affect the rate of nucleophilic acyl substitution is the nature of the leaving group, L.



Leaving groups that form more stable anions, L^-, can be substituted more easily, leading to faster reactions.

Explain why step III should be carried out using ethanoic anhydride, $(CH_3CO)_2O$ instead of ethyl ethanoate. [2]

(iii) Suggest a reason why 4-aminophenol is soluble in aqueous ethanoic acid while paracetamol is not. [1]

....

....

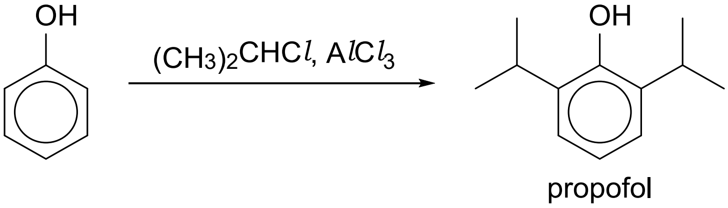
....

....

....

....

(d) Phenol can also form propofol *via* Friedel-Crafts alkylation.



(i) The first stage of the alkylation involves a reaction between $AlCl_3$ and $(CH_3)_2CHCl$.

$AlCl_3$ behaves an acid in the first stage. Identify the type of acid behaviour and explain why it is possible for $AlCl_3$ to play this role. [2]

(ii) When carrying out Friedel-Crafts alkylation, water cannot be introduced into the reaction mixture. With the aid of appropriate equations, explain why this is so. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

5 This question is about ethers and lactones.

Ethers have the general structure R_1–O–R_2 where R_1 and R_2 are hydrocarbon groups.

(a) An ether has the molecular formula $C_5H_{12}O$.

Draw the skeletal formulae for all six constitutional isomers of $C_5H_{12}O$ that contains an ether group. [2]

....

....

....

....

....

....

....

....

....

....

....

(b) Diethyl ether, $CH_3CH_2OCH_2CH_3$, is a common solvent used in reduction reactions involving lithium aluminium hydride, $LiAlH_4$, which is a source of the hydride ion, H^-.

(i) Suggest, with reasoning, the bond angle and shape around the O atom in diethyl ether. [2]

(ii) Suggest why $LiAlH_4$ dissolves well in diethyl ether. [1]

(iii) Apart from its role as a reducing agent, $LiAlH_4$ can also act as a strong base.

Water cannot be present in reactions involving $LiAlH_4$.
Suggest, with the aid of an equation involving H^-, why this is so. [1]

(iv) $LiAlH_4$ is commonly used to reduce many functional groups such as carboxylic acids, esters, and amides. However, it does **not** reduce alkenes.

Suggest why it can reduce the above-mentioned functional groups but not alkenes. [2]

(v) $LiAlH_4$ is a stronger reducing agent than $NaBH_4$ and both have similar structure and bonding. Suggest a reason for this difference in reducing strength. [1]

....

....

....

....

....

....

....

....

....

....

....

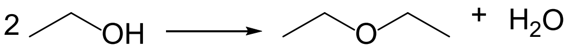
....

....

There are many ways to synthesise ethers.

(c) **(i)** One such way is when two alcohols react together as shown in equation 1.

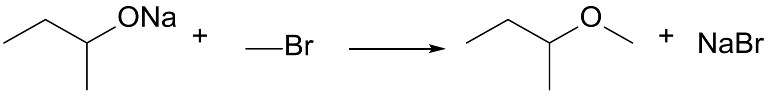
equation 1



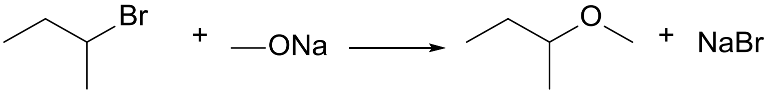
Suggest the type of reaction for the above reaction. [1]

(ii) Another way is the Williamson ether synthesis as shown in equations 2 and 3.

equation 2



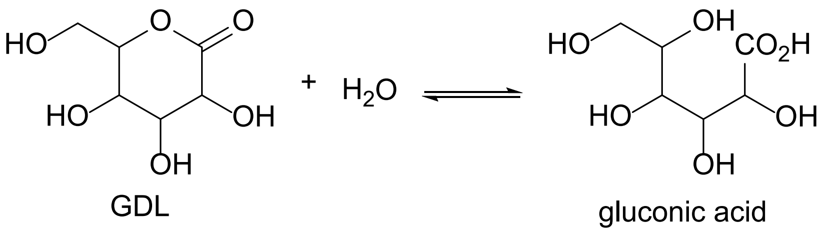
equation 3



Given that these reactions occur *via* S_N2 mechanism, explain why the reaction in equation 2 is preferred to form the desired product instead of the reaction in equation 3. [1]

Lactones are a class of organic compounds that contain an ester which is inside a ring (*i.e.* they are cyclic esters).

(d) The addition of glucono-delta-lactone, GDL, to soy milk produces a soft form of tofu due to a gradual acidification of the mixture. In aqueous solution the following equilibrium is slowly set up.



When 2.00 g of GDL (M_r = 178) was dissolved in 100.0 cm^3 water and the solution allowed to reach equilibrium, the concentration of gluconic acid was found to be 0.0670 mol dm^{-3}.

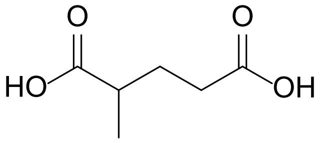
Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O]$ = 55.5 mol dm^{-3} throughout. [3]

(e) The Baeyer-Villiger oxidation reaction forms an ester from a ketone with a peroxyacid. An example is shown in equation 4 using peroxyethanoic acid, CH_3CO_3H.

equation 4 $RCOR' + CH_3CO_3H \rightarrow RCO_2R' + CH_3CO_2H$

Ketone **A** was reacted in this way to give **only one** cyclic ester **B**. When heated with HC*l*(aq), **B** gave compound **C** ($C_7H_{14}O_3$).

Compound **C** gave a yellow precipitate when treated with alkaline aqueous iodine and upon acidification, 2-methylpentanedioic acid was formed.



2-methylpentanedioic acid

Compound **C** produced three different alkenes, **D**, **E** and **F** of which two are *cis*-*trans* isomers, when heated with concentrated H_2SO_4.

(i) Explain what is meant by *cis-trans isomerism* in alkenes. [1]

(ii) Suggest the structures of **A**, **B**, **C**, **D**, **E**, and **F**. [5]

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

Additional answer space

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