Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Write in dark blue or black pen.
3 You may use an HB pencil for any diagrams or graphs.
4 Do not use staples, paper clips, glue or correction fluid.
5 Answer **all** questions in the spaces provided on the Question Paper.

The number of marks is given in brackets [ ] at the end of each question or part question.
You are advised to show all workings in calculations.
You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
Question No.	**Marks**
1	**/ 13**
2	**/ 12**
3	**/ 25**
4	**/ 10**
5	**/ 15**
Total	**/ 75**

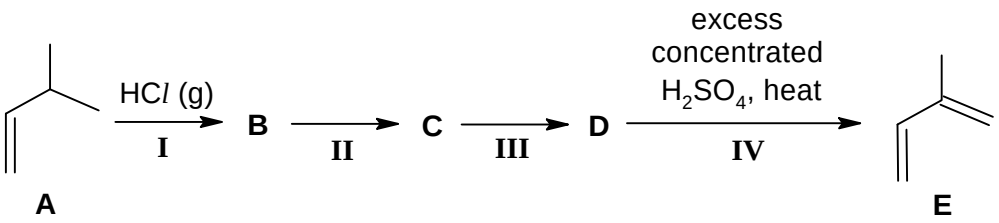
This question paper consists of **21** printed pages and **1** blank page.

[Turn over

Answer **all** questions in the spaces provided.

1 Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.

(a) **E** can be synthesised from 3–methylbut–1–ene, **A**, in a 4–step process as follows.



(i) **B** is a major product of step **I**.

Draw the structures of compounds **B**, **C** and **D**.

B	C	D

[3]

(ii) Suggest the reagents and conditions for steps **II** and **III**.

step **II** : ……[1]

step **III** : ……[1]

(iii) Predict, with reasoning, whether the mixture of products formed in step **I** is optically active.

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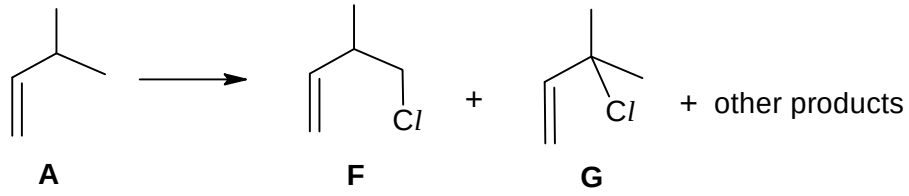
……[2]

(b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



A **F** **G**

(i) State the reagents and conditions used to form **F** and **G** from **A**.

……[1]

(ii) Predict the ratio in which **F** and **G** will be formed.

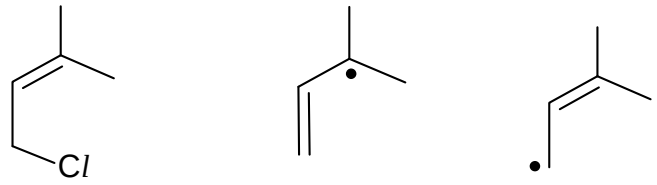
……[1]

(iii) **Z** was one of the other products formed in the reaction in **(b)**. It was suggested that the radical, **•G**, is involved in the formation of **Z**.

The mechanism of **•G** converting to **Z** is thought to involve 2 steps.

1. Delocalisation of unpaired electron forming **•Z**.
2. **•Z** reacts with Cl_2 to form **Z** and a radical.

The structures of **Z**, **•G** and **•Z** are as follows.



Z **•G** **•Z**

Use the information above to draw out the mechanism for the conversion of **•G** to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). Use curly half-arrows to indicate the movement of unpaired electrons.

[2]

(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

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……[2]

[Total: 13]

2 (a) Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (**J** to **R**) in Periods 2 and 3 of the Periodic Table.

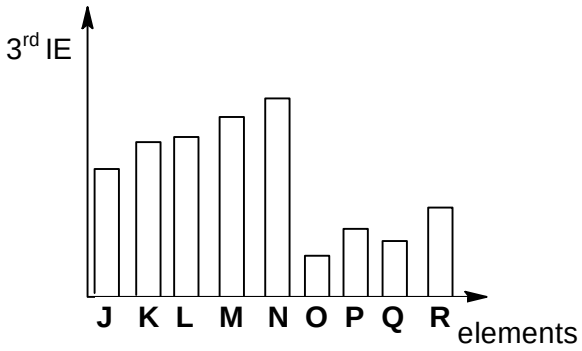

Fig 2.1

(i) Write an equation for the third ionisation energy of element **J**.

……[1]

(ii) Identify element **N**.

……[1]

(iii) Using your answers in **(a)(i)**, **(a)(ii)** and the electronic configurations of the species involved, explain the following features of Fig 2.1.

1. The significantly higher 3rd IE of **N** compared to **O**.

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……[2]

2. The lower 3rd IE of **Q** than **P**.

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……[2]

(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, log (IE), of an element **S** against the number of electrons removed.

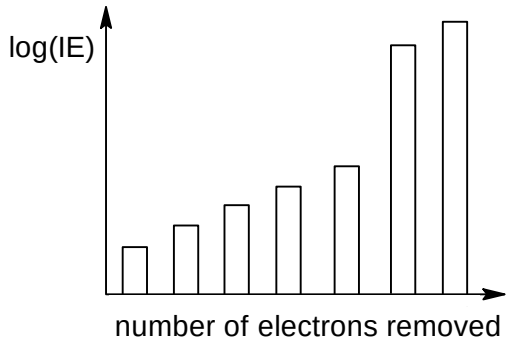

Fig 2.2

(i) Explain the general trend shown in Fig 2.2.

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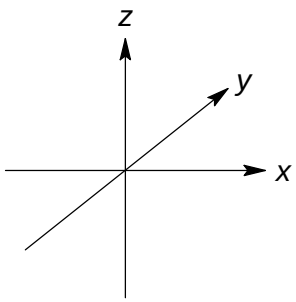
……[2]

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.



[1]

(c) The Periodic Table shows helium placed at the top of Group 18.

(i) Suggest why the element helium could be placed at the top of Group 2.

……[1]

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

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……[2]

[Total: 12]

3 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) **(i)** State what is meant by the terms:

- *Complex*

……

……

……[1]

- *Ligand*

……

……

……[1]

(ii) Two of the complexes formed by copper are $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$ and $CuCl_4^{2-}$. Draw three–dimensional diagrams of their structures in the boxes below and name their shapes.

$Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$	$CuCl_4^{2-}$
Shape:	Shape:

[3]

(iii) State the oxidation number of Cu in $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$.

……[1]

(iv) Platinum forms square–planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$. Suggest the structures of the two isomers.

isomer 1	isomer 2

[3]

By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Type of isomerism: ……[1]

(b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

(i) Complete the electronic configuration of these species.

Cu: [Ar]……[1]

Cu(I): [Ar]……[1]

(ii) Explain why the following statements are true.

- Copper metal is a better electrical conductor than calcium metal.
- Copper(II) salts are generally coloured.

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……[3]

(c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

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

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
Cu_2O (s)	–168.6
CuO (s)	–157.3
$Cu(NO_3)_2$ (s)	–302.9
NO_2 (g)	+33.2

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable $\Delta H_f^{\ominus}$ values from the table to calculate the $\Delta H_r^{\ominus}$ for this reaction.

$$Cu(NO_3)_2\ (s) \rightarrow CuO\ (s) + 2NO_2\ (g) + \tfrac{1}{2}O_2(g)$$

[1]

(ii) Copper(I) oxide can be produced from copper(II) oxide.

$$2CuO\ (s) \rightleftharpoons Cu_2O\ (s) + \tfrac{1}{2}O_2(g) \quad \text{reaction 1}$$

Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

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……[2]

(iii) For reaction 1, $\Delta S^{\ominus}$ = +93.6 J K^{-1} mol^{-1}. Use this value and your answer in **(c)(ii)** to calculate $\Delta G^{\ominus}$.

[1]

(iv) Write the expression of the equilibrium constant, K_c, for reaction 1. State the units.

[2]

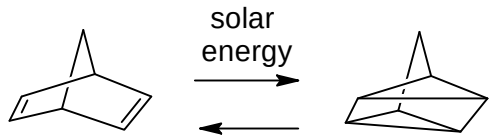
(v) For any reaction, $\Delta G^{\ominus}$ and the equilibrium constant, K_c, are related according to the equation,

$$\Delta G^{\ominus} = -2.303RT \log K_c$$

Use this equation to calculate a value of K_c for reaction 1.

[1]

(d) In 1977, Kutal *et al*. conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



norbornadiene quadricyclene

In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

(i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

……[1]

(ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.

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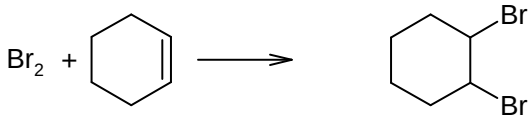
……[2]

[Total: 25]

4 (a) Cyclohexene can react with Br_2 to form 1,2–dibromocyclohexane as shown below.



cyclohexene 1,2–dibromocyclohexane

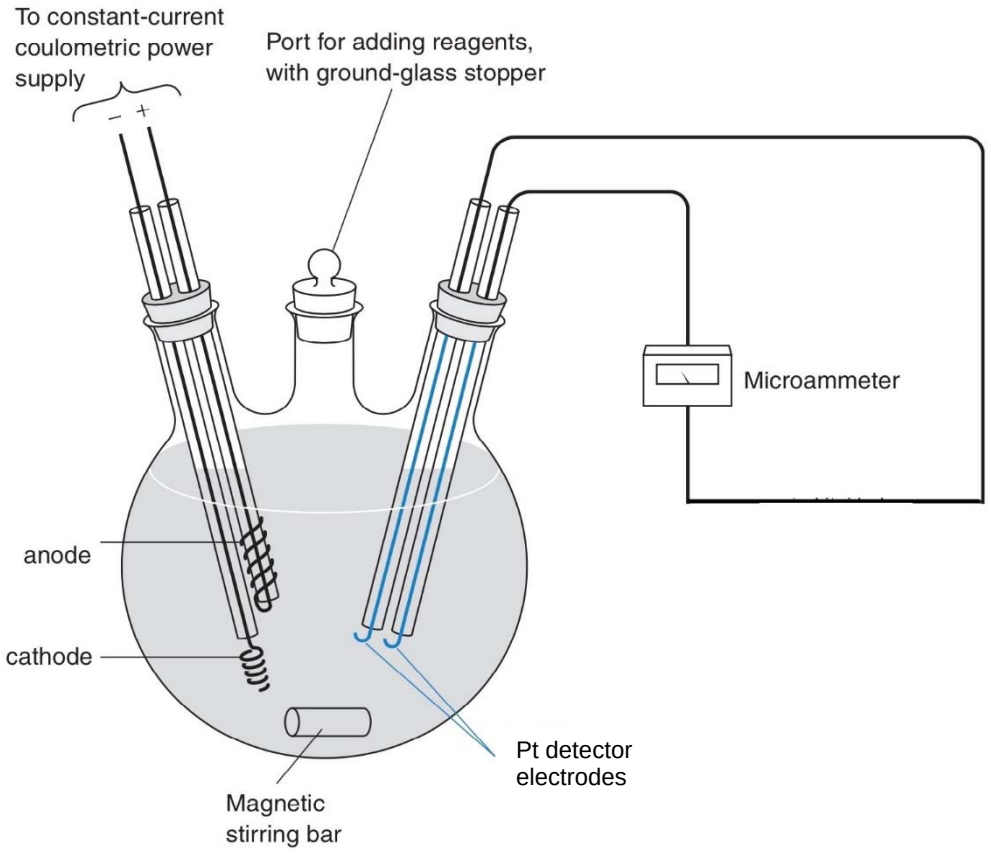
An experiment was carried out where the cyclohexene was titrated with the Br_2 generated by the oxidation of Br^- in the electrolytic cell:

$$2Br^- \rightarrow Br_2 + 2e^-$$

The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br^- dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left–hand and right–hand sides respectively.



Br_2 generated from electrolysis, reacts with the cyclohexene. At the end–point, all the cyclohexene has reacted and the concentration of Br_2 suddenly rises, signalling the end of the reaction.

(i) State whether Br_2 is generated at the cathode or anode of the electrolytic cell.

……[1]

(ii) The rise in the concentration of Br_2 is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:

Detector anode: $2Br^- \rightarrow Br_2 + 2e^-$

Detector cathode: $Br_2 + 2e^- \rightarrow 2Br^-$

Suggest why there is no current detected before equivalence point is reached.

……

……

……[1]

In an experiment, 2 cm^3 of 0.600×10^{-3} g cm^{-3} cyclohexene is to be titrated.

(iii) Calculate the amount, in moles, of the cyclohexene used.

[1]

(iv) The experiment was carried out with a constant current of 5×10^{-3} A for the electrolytic cell. Determine the time taken for complete titration.

[2]

(b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + I_2 + 2OH^-$$

The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

$E = 0.32 + 0.029 \log_{10} [I_2]$, where $[I_2]$ is expressed in mol dm^{-3}.

To determine ozone in the atmosphere, a light–weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm^3 of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

(i) Calculate the concentration of iodine liberated.

[1]

(ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

(c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

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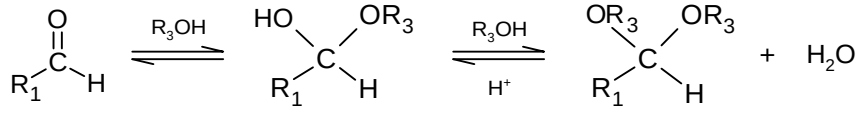
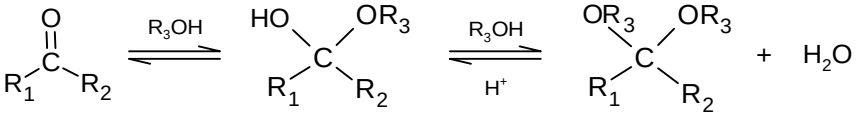
……[2]

[Total: 10]

5 (a) Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.

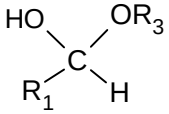


aldehyde hemiacetal acetal



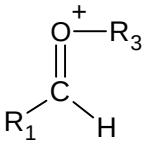
ketone hemiacetal acetal

The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



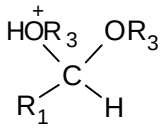
hemiacetal

1. Protonation of the hydroxyl group of the hemiacetal.
2. Loss of water leads to an unstable and highly reactive oxonium ion.



oxonium ion

3. Nucleophilic attack of alcohol, R_3OH, on the oxonium ion to give



4. Loss of a proton to give the acetal.

(i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

(ii) State the purpose of removing water from the reaction mixture.

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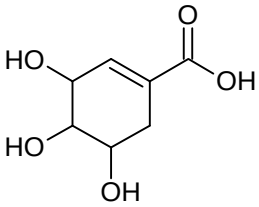
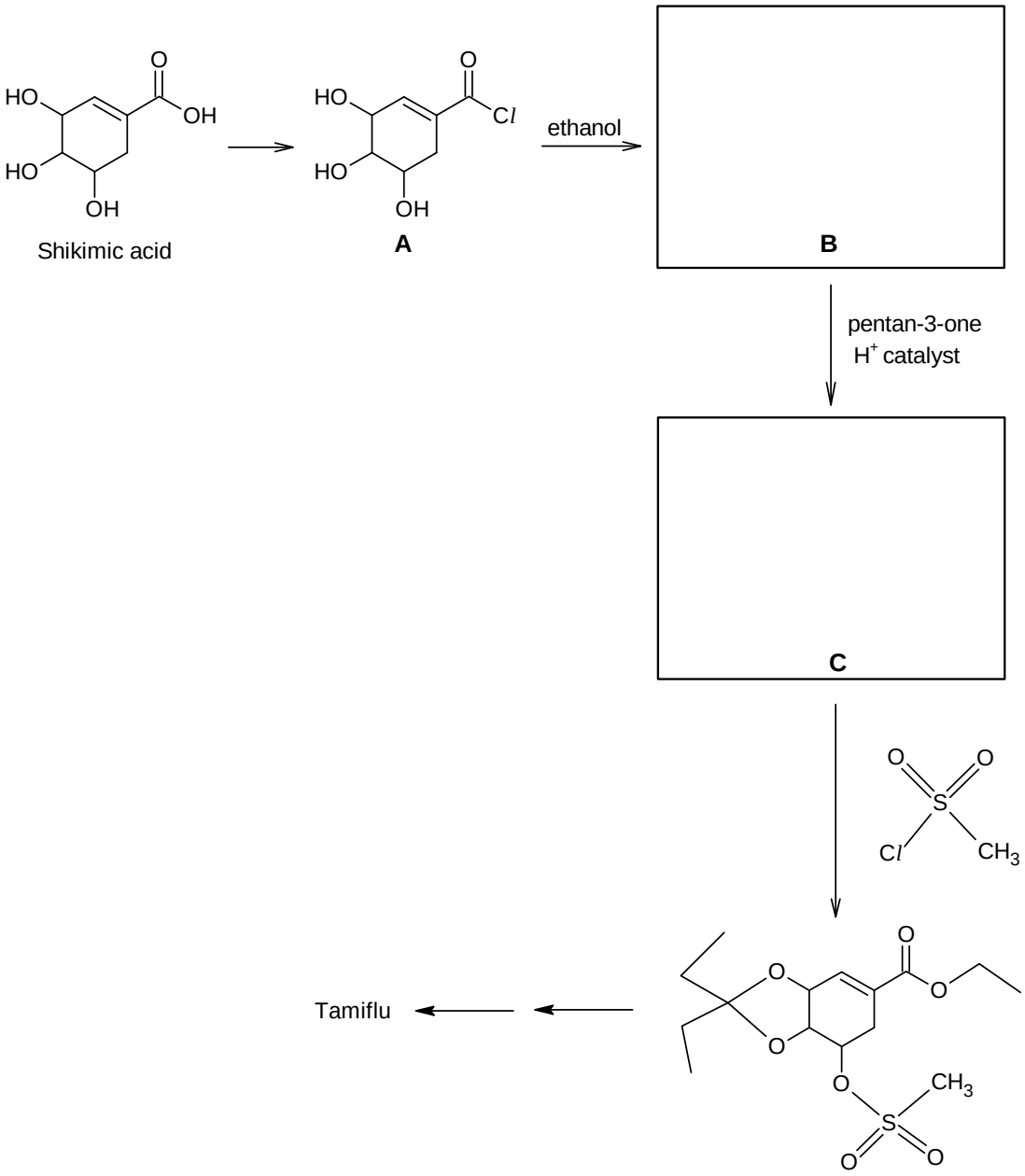
……[1]

(b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird–flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

Part of the synthetic route is shown below. Formation of acetals between selected –OH groups of Shikimic acid and ketones helps to control which of the –OH groups reacts to synthesise **C** from **B**.



(i) Draw the structures of **B** and **C** in the boxes provided above.

[2]

(ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

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……[1]

(c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.

$HCOOH\ (aq) \rightleftharpoons HCOO^-\ (aq) + H^+\ (aq) \qquad K_a = 1.60 \times 10^{-4}\ mol\ dm^{-3}$

(i) Explain what is meant by the term pK_a as applied to methanoic acid.

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……[2]

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm^3 of water.

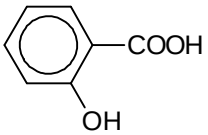
(ii) Calculate the pH of this solution.

[2]

(iii) Hence, calculate the degree of dissociation, α, of methanoic acid in this solution.

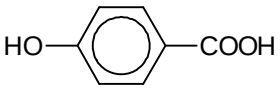
[1]

(d) Salicylic acid occurs naturally in plants.



salicylic acid

pK_{a1} = 2.97



isomer of salicylic acid

pK_{a1} = 4.54

Explain why salicylic acid is more acidic than its isomer.

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……[2]

[Total: 15]

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