NAME _____ CLASS **22S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2023

CHEMISTRY 9729/02

Paper 2 Structured Questions

September 2023
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use a 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.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/13
2	/10
3	/10
4	/13
5	/16
6	/13
Penalty (delete accordingly)	
Lack **3sf** in final answer	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	/**75**

This document consists of **19** printed pages and **1** blank page.

[Turn Over

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

For Examiner's Use

1 (a) Halogens can react with alkanes to form halogenoalkanes.

The boiling points of a few halogenoalkanes, in Kelvin, are given in Table 1.1.

Table 1.1

compound	boiling point / K
CH_3F	195
CH_3Cl	249
CH_3CH_2F	236

(i) Comment on the relative bond polarity of C–F bond in CH_3F and C–C*l* bond in CH_3Cl.

……

…… [1]

(ii) Explain the difference in boiling point between CH_3F and CH_3Cl.

……

……

…… [1]

(iii) Both CH_3Cl and CH_3CH_2F are isoelectronic. Explain the difference in boiling point between CH_3Cl and CH_3CH_2F.

……

……

…… [1]

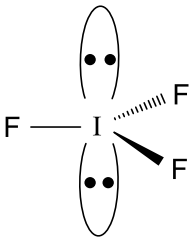
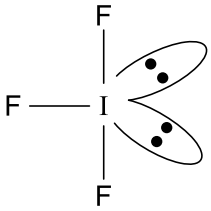
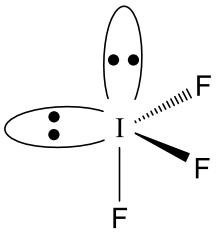
For Examiner's Use

(b) Halogens can react to form interhalogen compounds such as IF_3.

Consider a molecule of IF_3, the central atom is surrounded by five pairs of electrons in a trigonal bipyramidal arrangement. There are three electron pairs arranged on the same plane in equatorial positions and two electron pairs arranged perpendicular to the plane in axial positions.

Three possible different molecular arrangements of IF_3 are shown in Table 1.2.

Table 1.2

	 Lone pairs in axial positions.	 Lone pairs in equatorial positions.	 Lone pairs in axial and equatorial positions.
number of lone pairs at 90° relative to one another	0	0	1
number of bond pair and lone pair at 90° relative to one another			3
relative stability			

(i) For each structure, count the number of lone pair and bond pair that are 90° relative to one another. Fill the numbers in Table 1.2. [1]

(ii) Apply the principles of the Valence Shell Electron Pair Repulsion (VSEPR) theory to deduce the relative stability of these three possible arrangements. State the "**most stable**" structure and the "**least stable**" structure in Table 1.2. [2]

For Examiner's Use

(c) Peroxydisulfate ions, $S_2O_8^{2-}$, can react with iodide ions, I^-, to form sulfate ions, SO_4^{2-}, and iodine in a redox reaction.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

(i) Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure a E_{cell} value for this reaction.

In your answer, include the polarity of each electrode and the direction of electron flow in the external circuit.

[3]

(ii) Using relevant data from the *Data Booklet*, calculate ΔG , in kJ mol^{-1}, for the above reaction.

……

……

……

…… [2]

(iii) Using your answer in **(c)(ii)**, deduce whether the above reaction is exothermic or endothermic. Explain your answer as fully as you can.

……

……

……

……

…… [2]

[Total: 13]

For Examiner's Use

2 (a) Data concerning the Group 2 elements, at 298 K, are given in Table 2.1. Further data may be found in the *Data Booklet*. No calculation is required.

Table 2.1

	Mg	Ca	Sr	Ba
ΔH_{hyd} of M^{2+} / kJ mol^{-1}	−1980	−1650	−1480	−1365
solubility of MSO_4 / mol per 100 cm^3 water	1.8×10^{-1}	4.7×10^{-3}	7.1×10^{-5}	9.4×10^{-7}

(i) When a salt such as Group 2 sulfate dissolves in water, the lattice energy must be overcome. Explain how the magnitude of the lattice energy, ΔH_{LE}, of Group 2 sulfates will change from $MgSO_4$ to $BaSO_4$.

……

……

……

…… [2]

(ii) Explain why the ΔH_{hyd} of M^{2+} becomes less negative from Mg^{2+} to Ba^{2+}.

……

……

…… [1]

(iii) By considering the relationship between ΔH_{sol}, ΔH_{LE} and ΔH_{hyd}, suggest a reason to explain the trend in the solubility of the Group 2 sulfates.

……

……

……

…… [2]

(iv) 100 cm^3 of 0.0100 mol dm^{-3} aqueous calcium chloride was added to 100 cm^3 of 0.0200 mol dm^{-3} aqueous sodium sulfate. Use relevant data in Table 2.1 to deduce whether precipitation of calcium sulfate will occur.

[2]

For Examiner's Use

(b) The equation for the standard enthalpy change of formation of a gaseous sulfate ion is shown.

$$S(s) + 2O_2(g) + 2e^- \rightarrow SO_4^{2-}(g) \qquad \Delta H_f \ (SO_4^{2-}(g))$$

Using **relevant** data in Table 2.2 and the *Data Booklet*, complete the energy level diagram in Fig. 2.3 and use it to calculate $\Delta H_f \ (SO_4^{2-}(g))$.

Table 2.2

enthalpy change	value / kJ mol^{-1}
lattice energy of $BaSO_4(s)$	−2469
standard enthalpy change of formation of $BaSO_4(s)$	−1473
standard enthalpy change of atomisation of Ba(s)	+180
standard enthalpy change of atomisation of S(s)	+279
standard enthalpy change for $S(g) \rightarrow S^{2-}(g)$	+440
standard enthalpy change for $O(g) \rightarrow O^{2-}(g)$	+657

Fig. 2.3

[3]

[Total: 10]

3 The first stage of the Contact process for manufacturing concentrated sulfuric acid is to produce SO_3 from SO_2 and O_2.

For Examiner's Use

$$2SO_2(g) + O_2(g) \ll 2SO_3(g)$$

(a) (i) State **two** conditions necessary for an effective collision between reactant molecules.

……

…… [1]

(ii) Explain the effect of increasing total pressure, at constant temperature, on the rate of production of $SO_3(g)$ and the yield of $SO_3(g)$.

rate ……

…… [2]

……

yield ……..

……

……

(b) 2.00 mol of $SO_2(g)$ and 1.00 mol of $O_2(g)$ was introduced in a container with a suitable catalyst, at constant temperature and pressure.

The equilibrium mixture has a total volume of 40.0 dm^3 and the mole fraction of SO_3 is 0.82.

(i) Write the K_c expression for this reaction, giving its units.

[1]

(ii) Calculate a value for K_c.

[2]

(c) Vanadium(V) oxide, V_2O_5, acts as a catalyst in the Contact Process via the mechanism below:

For Examiner's Use

Step 1: $V_2O_5(s) + SO_2(g) \rightarrow V_2O_4(s) + SO_3(g)$ *slow*

Step 2: $V_2O_4(s) + ½O_2(g) \rightarrow V_2O_5(s)$ *fast*

(i) State the type of catalysis. Explain your answer.

……

…… [1]

(ii) Explain why V_2O_5 can behave as a catalyst.

…… [1]

……

……

(d) Fig. 3.1 shows the energy profile of the uncatalysed reaction between SO_2 and O_2.

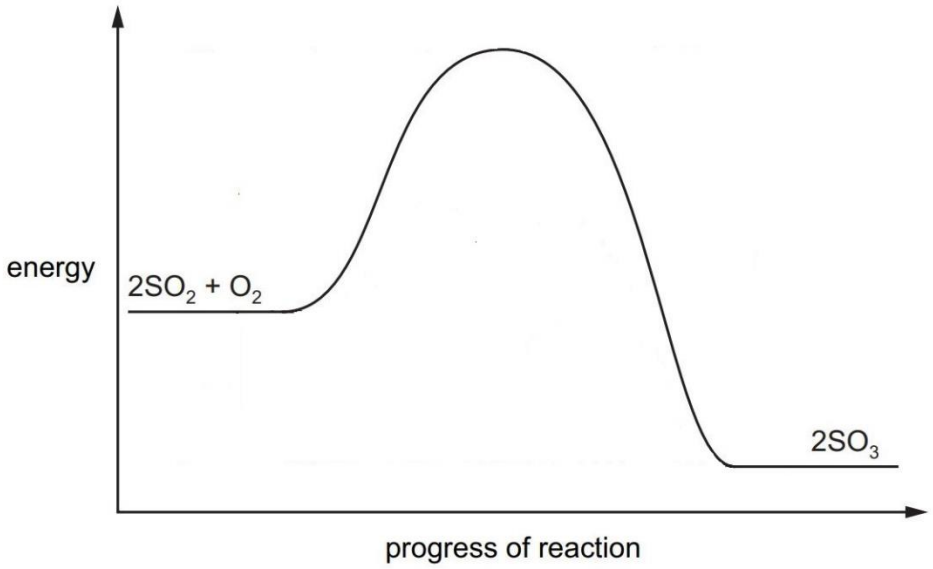


Fig. 3.1

(i) On Fig. 3.1, draw the energy profile of the reaction catalysed by V_2O_5. [1]

(ii) Indicate clearly on Fig. 3.1, the activation energy **E** for the first step in the **decomposition** of SO_3 in the presence of a catalyst. [1]

[Total: 10]

For Examiner's Use

4 **(a)** Concentrated sulfuric acid can react with solid halides. The reaction begins with the solid halide, NaX(s), reacting to form white fumes of HX(g) as shown in the equation below:

$$NaX(s) + H_2SO_4(l) \rightarrow HX(g) + NaHSO_4(s) \quad \text{where X = C}l\text{, Br, I}$$

However, the colour of the gas evolved changes as the reaction proceeds as shown below.

	observations with concentrated H_2SO_4
NaC*l*	white fumes of HC*l*
NaBr	reddish-brown fumes of Br_2
NaI	violet fumes of I_2

Upon further testing of the gaseous mixtures, it was found that both NaBr and NaI also produce SO_2.

It was also found that only the gaseous mixture from NaI turns moist lead(II) ethanoate paper from white to black, indicating the presence of $H_2S(g)$.

By considering the change in oxidation numbers for the reactions described above, explain the relative reducing power of the halides from chloride to iodide.

relative reducing power of halides: …… < ……< ……

explanation ……..

……

……

……

……

……

…… [3]

In the presence of acid, the reaction between iron(III) ions, $Fe^{3+}(aq)$, and iodide ions, $I^-(aq)$, occurs as shown below.

For Examiner's Use

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

Using an initial concentration of $Fe^{3+}(aq)$ of 0.150 mol dm^{-3}, the rate of this reaction can be followed by the change in the $I^-(aq)$ concentration as given in Fig. 4.1.

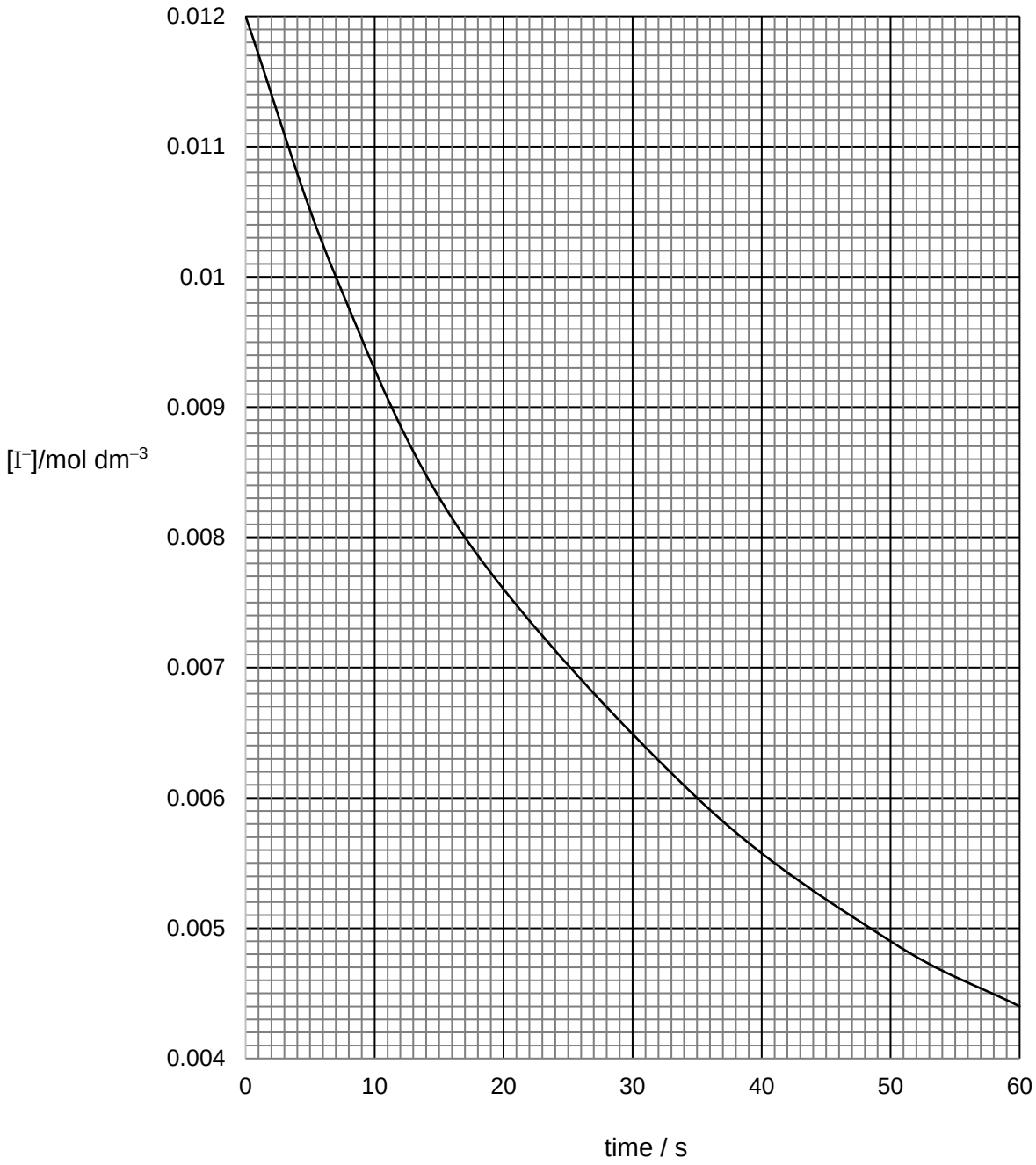


Fig. 4.1

(b) (i) Explain why it is important that the concentration of $Fe^{3+}(aq)$ is in large excess compared to the concentration of $I^-(aq)$ in this experiment.

For Examiner's Use

……

…… [1]

……

(ii) Use the graph in Fig. 4.1 to calculate the initial rate of reaction and the rate of reaction at 20 s. Show your working clearly on the graph.

……

……

……

……

……

…… [2]

(iii) Use the graph in Fig. 4.1 and your answer in **(b)(ii)** to show that the reaction is second order with respect to I^-(aq) ions.

……

……

……

……

……

…… [2]

(iv) The rate constant for this experiment is 15.4 $mol^{-2}\,dm^6\,s^{-1}$.

Write the rate equation for the reaction between Fe^{3+}(aq) and I^-(aq).

……

……

……

…… [1]

(v) Another experiment of the same reaction was performed at a different temperature. The results are shown in Table 4.2.

For Examiner's Use

Table 4.2

$[Fe^{3+}]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
0.040	0.080	5.38×10^{-3}

Deduce whether this experiment was carried out at a higher or lower temperature. Explain your answer.

……

……

……

……

…… [2]

(c) The following mechanism has been suggested for the reaction.

Step 1: $Fe^{3+} + I^- \ll FeI^{2+}$

Step 2: $FeI^{2+} + I^- \rightarrow Fe^{2+} + I_2^-$

Step 3: $Fe^{3+} + I_2^- \rightarrow Fe^{2+} + I_2$

Based on the rate equation you have derived in **(b)(iv)**, state which step is the rate-determining step. Explain your answer.

……

……

……

……

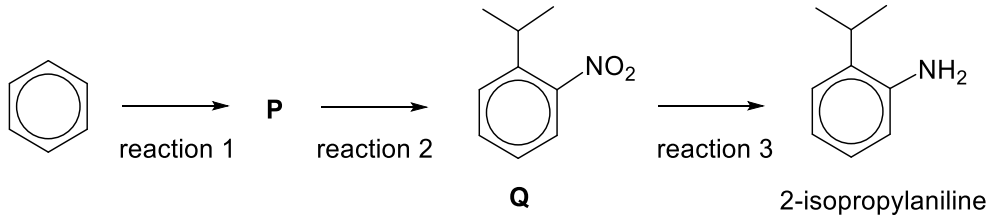
…… [2]

[Total: 13]

BLANK PAGE

5 **(a)** Benzene can be used to produce 2-isopropylaniline via a series of reactions as shown below.

For Examiner's Use



Q

2-isopropylaniline

(i) Draw the structure of **P**.

[1]

(ii) State the reagents and conditions for reactions 1 and 2.

reaction 1: ……..

reaction 2: ……. [2]

Q can be reduced to form 2-isopropylaniline via two steps in reaction 3.

During step I, granulated Sn and concentrated HC*l* are added to **Q** and the mixture is heated under reflux in a hot water bath for about half an hour. Sn acts as the reducing agent.

Step II involves the addition of concentrated sodium hydroxide to the resulting mixture.

(iii) Write a half-equation for the reduction of **Q** in acid solution in step I.

[1]

(iv) Explain why the acidic resulting mixture from step I is made alkaline before 2-isopropylalanine can be separated out and purified.

……

……

……

……

…… [2]

(v) Write an equation for the reaction of 2-isopropylaniline with aqueous Br_2.

[1]

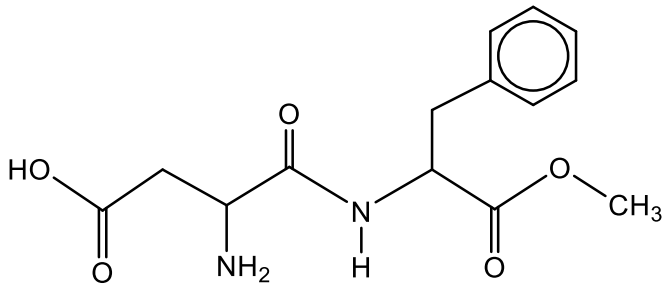
For Examiner's Use

(vi) When dilute HNO_3 is added to 2-isopropylaniline, compound **R**, $C_9H_{14}N_2O_3$, is formed.

Draw the structure of **R**.

[1]

(b) Aspartame is made up of amino acids and is widely used as a sweetener in 'diet' soft drinks. Its structure is shown in Fig. 5.1.



aspartame

Fig. 5.1

(i) Deduce the molecular formula of aspartame.

…… [1]

(ii) On the structure of aspartame in Fig. 5.1, circle the amide and ester functional groups in aspartame. [1]

(iii) Aspartame can be hydrolysed via a nucleophilic reaction.

In general, an amide functional group will take longer to hydrolyse as compared to an ester functional group under the same reaction conditions. Suggest a reason why this is so.

……

……

……

……

…… [1]

(iv) In the stomach, aspartame is hydrolysed by the acidic gastric juice.

Draw the structures of the products formed after complete acid hydrolysis of aspartame.

[3]

(c) An octapeptide contains the following amino acids:

arg, cys, ile, met, phe, pro, tyr, val

Analysis gave the following results:

The enzyme trypsin, which hydrolyses at the carboxylic group of *arg*, gave a dipeptide (containing *arg* and *cys*) and a hexapeptide.

On reaction with cyanogen bromide which hydrolyses at the carboxylic group of *met*, a hexapeptide and a dipeptide (having the sequence *pro*-*phe*) are obtained.

Another enzyme chymotrypsin, which hydrolyses at the carboxylic group of *tyr*, gave two tetrapeptides. The *N*-terminus of one of the tetrapeptides is *ile*.

Use these results to deduce the sequence of the octapeptide.

…… [2]

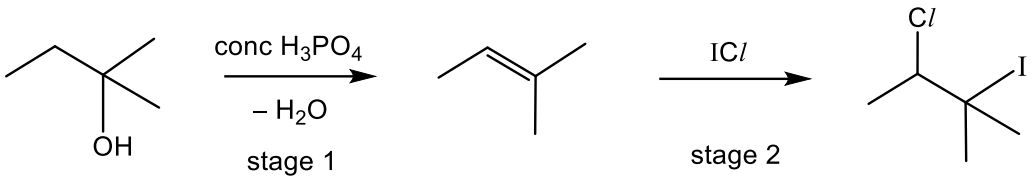
[Total: 16]

For Examiner's Use

6 A student devises an experiment to convert an alcohol to a dihalogenoalkane in two stages, as shown in the scheme below.

In stage 1, alcohol **S** is dehydrated to alkene **T**.

In stage 2, **T** is converted to a dihalogenoalkane **U**.



S **T** **U**

Physical properties and hazards of the materials are given in Table 6.1 below.

Table 6.1

substance	M_r	boiling point / °C	density / g cm^{-3}	hazards
alcohol **S**	88.0	102	0.81	moderate hazard, flammable, corrosive
alkene **T**	70.0	38	0.66	health hazard, flammable, hazardous to the aquatic environment
concentrated phosphoric acid	98.0	158	1.69	corrosive
iodine monochloride	162.4	98	3.10	corrosive

(a) **(i)** Give the systematic name for **S**.

……. [1]

(ii) Given that stage 1 has a yield of 85%, calculate the volume of **S** required to produce 12 g of **T**.

……

……

……

……

…… [2]

In stage 1, alcohol **S** is mixed with 6 cm^3 of concentrated phosphoric acid. The mixture is heated and the product, alkene **T**, collected by fractional distillation. The vessel that receives **T** sits in an ice bath.

(iii) Why is there a need to collect **T** in an ice bath?

……

…… [1]

(iv) Anhydrous calcium chloride granules, $CaCl_2$, are added to the distillate. Give one possible reason for this addition.

……

…… [1]

(v) The student considers a similar scheme to make 1,2-dibromopropane. What practical difficulty would arise when collecting the intermediate alkene?

……

…… [1]

(b) In stage 2, an interhalogen compound, iodine monochloride, ICl, commonly used as Wijs' reagent, reacts with alkene **T**.

(i) ICl reacts faster with alkenes than the pure halogens, Cl_2, Br_2 and I_2. Suggest a reason for this difference.

……

…… [1]

(ii) **U** is the minor product of the reaction in stage 2.

Draw the structure of the major product.

[1]

(iii) Describe the mechanism for the reaction that occurs between IC*l* and alkene **T**.

Explain why **U** is not the major product.

mechanism:

explanation ……

……

……

…… [3]

(c) The different reactivities of organic halogeno compounds and alcohols, can be exploited in successive reactions of dihalogeno compounds.

Predict the outcome of the following transformations as shown in Fig. 6.2, drawing the structures of **V** and **W** in the boxes provided.

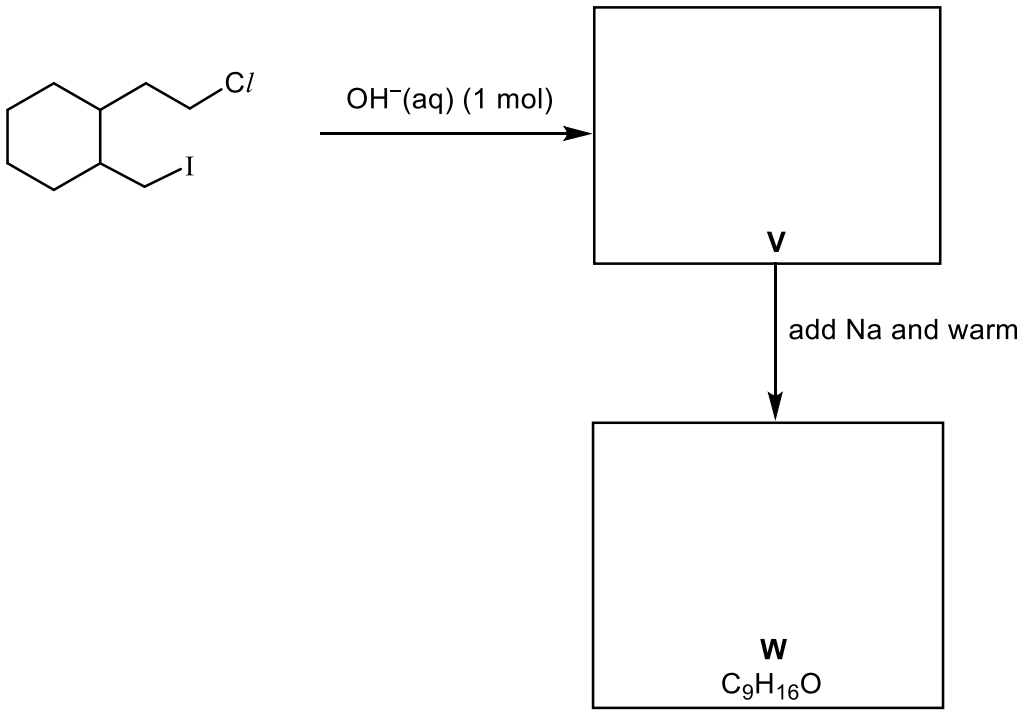


Fig. 6.2 [2]

[Total: 13]