H

RAFFLES INSTITUTION
2013 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9647/02

Paper 2 Structured Questions **18 September 2013**
2 hours

Candidates answer on the Question Paper.

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 in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

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

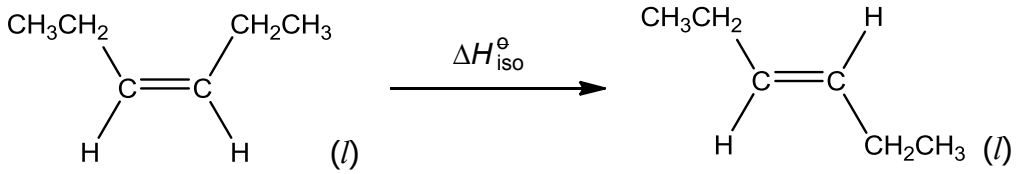
For Examiner's Use	
1	**/ 12**
2	**/ 13**
3	**/ 11**
4	**/ 10**
5	**/ 18**
6	**/ 8**
Total	**/ 72**

This document consists of **22** printed pages.

For Examiner's Use

1 Planning (P)

The standard enthalpy change of isomerisation, $\Delta H^{\ominus}_{iso}$, measures the enthalpy change when 1 mole of a *cis*–alkene isomerises to 1 mole of the corresponding *trans*–alkene under standard conditions:



cis–hex–3–ene *trans*–hex–3–ene

However, this enthalpy change cannot be measured directly by experiment.

A student decided to determine the standard enthalpy change of isomerisation of *cis*–hex–3–ene to *trans*–hex–3–ene using their respective standard enthalpy changes of combustion, $\Delta H^{\ominus}_{c}$. Both alkenes are volatile liquids at 298 K.

From his literature review, the student found the $\Delta H^{\ominus}_{c}$ of *cis*–hex–3–ene to be –3733 kJ mol^{-1}. However, the $\Delta H^{\ominus}_{c}$ of *trans*–hex–3–ene was not available.

(a) Write a balanced equation, with state symbols, to describe the standard enthalpy change of combustion, $\Delta H^{\ominus}_{c}$, of *cis*–hex–3–ene, C_6H_{12}.

…….. [1]

(b) To determine the standard enthalpy change of combustion of *trans*–hex–3–ene, the student decided to conduct a flame calorimetric experiment. There are two stages to this experiment:

Stage I

Calibration of calorimeter set-up (i.e. container and water).

In the experiment, the calorimeter set-up must first be calibrated by determining its heat capacity, ***C***, which is the amount of heat required to raise its temperature by 1 K.

Stage II

Determination of the standard enthalpy change of combustion of trans–hex–3–ene using the calibrated calorimeter set-up.

3

For Examiner's Use

The student carried out the flame calorimetric experiment using a copper can. Part of his results is shown below.

For *cis*–hex–3–ene:		
mass of water	=	250 g
change in temperature of water	=	5.0 °C
change in mass of spirit lamp with *cis*–hex–3–ene	=	0.20 g
For *trans*–hex–3–ene:		
mass of water	=	250 g
change in temperature of water	=	5.4 °C
change in mass of spirit lamp with *trans*–hex–3–ene	=	0.22 g

(i) Given that $\Delta H_c^{\ominus}$ [*cis*–hex–3–ene] = –3733 kJ mol^{-1}, calculate the heat capacity, ***C***, of the calorimeter set-up based on the above experimental results. Show the units of ***C*** clearly.

heat capacity, ***C*** = ...

(ii) Hence estimate a value for the standard enthalpy change of combustion of *trans*–hex–3–ene, $\Delta H_c^{\ominus}$ [*trans*–hex–3–ene].

$\Delta H_c^{\ominus}$ [*trans*–hex–3–ene] = ...

(iii) Using results from **(b)(i)** and **(b)(ii)**, calculate the standard enthalpy change of isomerisation, $\Delta H_{iso}^{\ominus}$, of *cis*–hex–3–ene to *trans*–hex–3–ene.

$\Delta H_{iso}^{\ominus}$ [*cis*–hex–3–ene] = ...

[3]

For Examiner's Use

(c) Using information from **(b)**, write a plan which will allow you to estimate a value for the standard enthalpy change of combustion of *trans*–hex–3–ene in your school laboratory.

You are **not** given a copper can.
However, you may assume that you are provided with the following:

- *cis*–hex–3–ene ($\Delta H_c^{\ominus}$ = –3733 kJ mol^{-1})
- *trans*–hex–3–ene
- 250 cm^3 beaker
- two spirit lamps with a 5 cm-wick each
- deionised water
- a lighter
- thermometer
- apparatus normally found in a school or college laboratory

Your plan should contain the following:

- a diagram of the experimental set-up
- appropriate quantities of chemicals and solutions
- all essential experimental details

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For Examiner's Use

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…… [7]

(d) Identify **one** potential safety hazard in this experiment and state how you would minimise this risk.

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…… [1]

[Total: 12]

For Examiner's Use

2 Hydrazine, N_2H_4, is a colourless flammable liquid with an ammonia-like odour.
It boils at 114 °C, and gaseous hydrazine can decompose to form hydrogen and nitrogen gases.

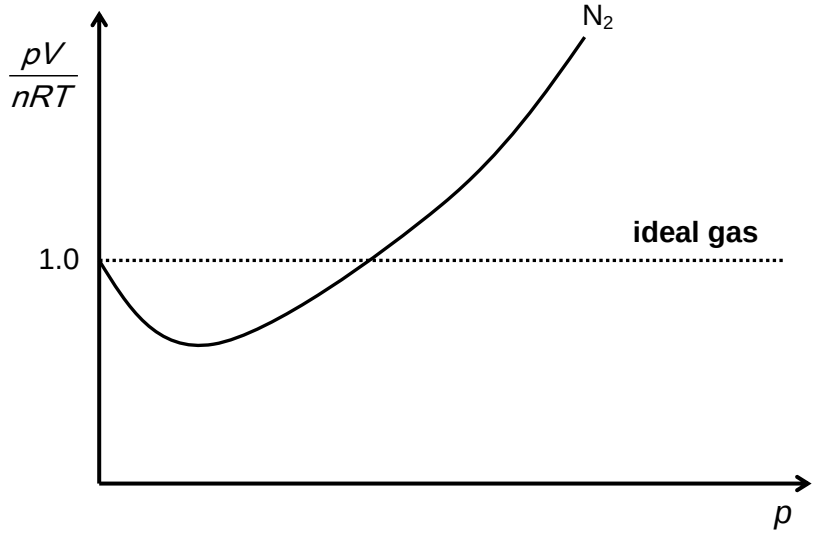
(a) Draw the dot-and-cross diagram of N_2H_4.

[1]

(b) State the hybridisation of the N atom and suggest what the H–N–H bond angle is in N_2H_4.

hybridisation …… bond angle …… [2]

A graph of $\frac{pV}{nRT}$ against p for N_2(g) is given below.



(c) On the axes above, sketch the corresponding graphs for H_2(g) and N_2H_4(g).

[2]

7

For Examiner's Use

In a closed reaction vessel of 10 dm^3 maintained at a temperature of 150 °C, gaseous hydrazine decomposes into nitrogen and hydrogen. The system reaches equilibrium with a total pressure of 1 atm. (Take 1 atm = 101 kPa.)

$$N_2H_4(g) \quad \textit{f} \quad N_2(g) + 2H_2(g)$$

The average M_r of the equilibrium gas mixture in the 10 dm^3 vessel is found to be 20.

(d) Calculate the mass of the gaseous mixture inside the reaction vessel at the given temperature and pressure.

mass of gaseous mixture = ... [2]

The average M_r for this gas mixture can be expressed as

$$M_r \text{ (average)} = \chi_{N_2H_4} \times M_r(N_2H_4) + \chi_{N_2} \times M_r(N_2) + \chi_{H_2} \times M_r(H_2)$$

where $\chi_{N_2H_4}$, χ_{N_2} and χ_{H_2} are the mole fractions of N_2H_4, N_2 and H_2 respectively.

(e) **(i)** Show that the degree of dissociation, α, under these conditions has a value of 0.30.

For Examiner's Use

(ii) Using **(e)(i)**, calculate the partial pressure (in atm) of N_2H_4 present at equilibrium.

Hence calculate the value of the equilibrium constant, K_p, of the system. Show the units of K_p clearly.

$p_{N_2H_4}$ = …… atm

K_p = ……

(iii) What will be the effect on the degree of dissociation, α, at 300 °C, given that the dissociation reaction of N_2H_4 is highly exothermic?

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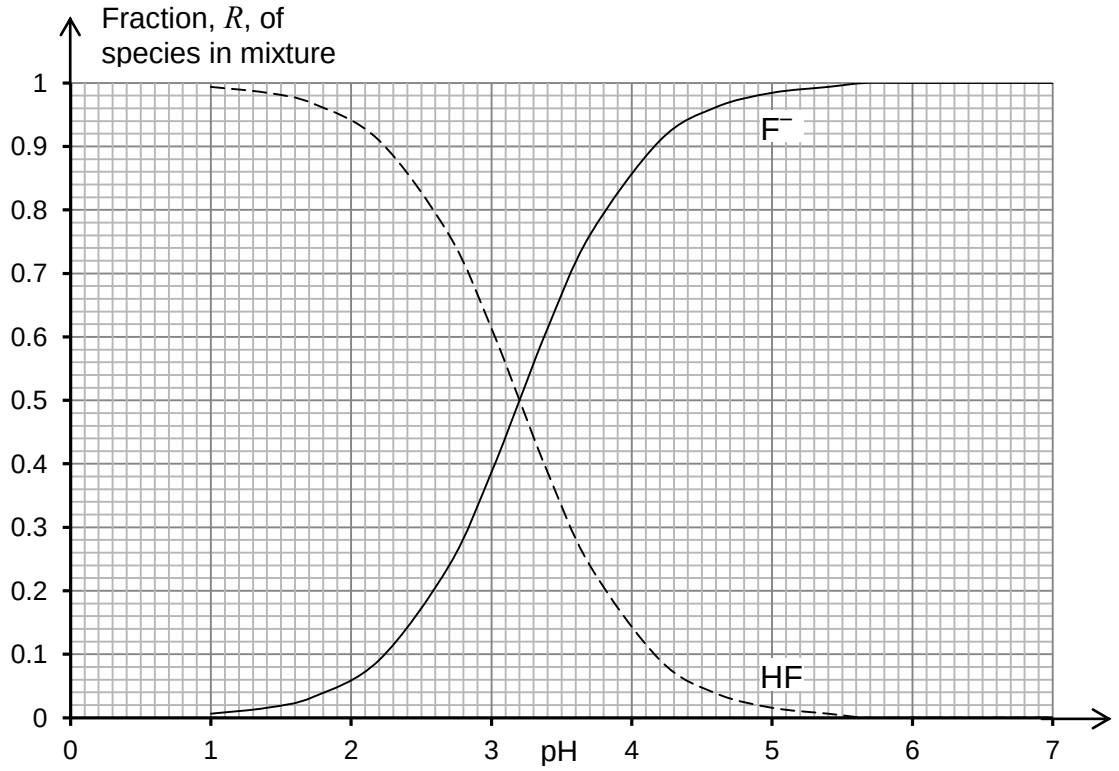
[6]

[Total: 13]

3 The following graph shows how the fraction, R, of an equilibrium mixture of a weak acid, HF, and its conjugate base, F^-, varies with pH.

For Examiner's Use



R, is defined for HF and F^- as follows:

$$R_{HF} = \frac{[HF]_{eqm}}{[HF]_{eqm}+[F^-]_{eqm}} \quad ; \qquad R_{F^-} = \frac{[F^-]_{eqm}}{[HF]_{eqm}+[F^-]_{eqm}}$$

where ($[HF]_{eqm} + [F^-]_{eqm}$) is the total concentration of all fluorine-containing species.

(a) The graph shows that the fraction of HF decreases with increasing pH. By applying *Le Chatelier's Principle* to the following equilibrium,

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq),$$

explain why the fraction of HF decreases with increasing pH.

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……

……

…… [2]

For Examiner's Use

(b) By considering the values of $_{HF}$ and $_{F^-}$ at the intersection point of the two curves, calculate the acid dissociation constant, K_a, of HF. Show your working clearly.

K_a of HF = ... [2]

(c) An excess of a sparingly soluble salt, CaF_2, was added to a beaker of water to form a saturated solution.

$$CaF_2(s) \; f \; Ca^{2+}(aq) + 2F^-(aq) \quad \text{——————} \; ①$$

(i) In the above system, $[Ca^{2+}]$ can be expressed in terms of $[F^-]$ by the following equation:

$$[Ca^{2+}] = a\,[F^-]$$

State the value of a.

a = ...

The mixture was then acidified by adding $H^+(aq)$, establishing a second equilibrium:

$$H^+(aq) + F^-(aq) \; f \; HF(aq) \quad \text{——————} \; ②$$

(ii) Explain how the $[Ca^{2+}]$ changes as H^+ is added to the saturated solution of CaF_2.

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For Examiner's Use

After acidification, it was found that the pH of the equilibrium mixture is 3.0 and [HF(aq)] = 4.63 x 10^{-4} mol dm^{-3}.

(iii) By obtaining the values of $_{HF}$ and $_{F^-}$ at pH 3.0 from the graph on page 9, determine the value of $\frac{[F^-(aq)]}{[HF(aq)]}$.

Hence calculate the $[F^-]$ at pH 3.0.

$\frac{[F^-(aq)]}{[HF(aq)]}$ = …….

$[F^-]$ = …….

(iv) By considering your answers in **(c)(i)** and **(c)(ii)**, express $[Ca^{2+}]$ at pH 3.0 in terms of $[F^-]$ and [HF] in the saturated solution.

(v) Using your answers to **(c)(iii)** and **(c)(iv)**, calculate the $[Ca^{2+}]$ at pH 3.0, and hence determine the solubility product, K_{sp}, of CaF_2.

$[Ca^{2+}]$ = …….

K_{sp} = …….

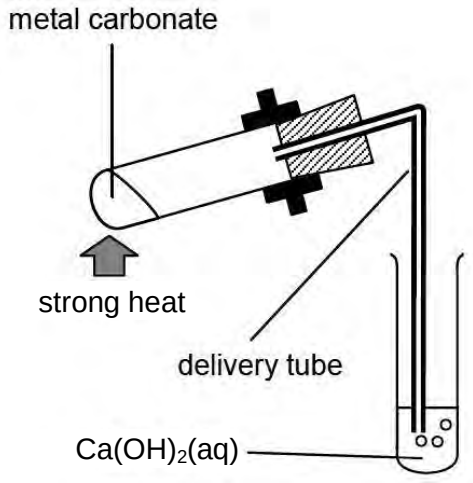
[7]

[Total: 11]

For Examiner's Use

4 The thermal decomposition of three solid anhydrous metal carbonates, **X**CO_3, **Y**CO_3 and **Z**CO_3 was investigated.

A pure 1.0 g sample of each carbonate was separately heated using the set-up shown below.



Appropriate mass measurements were made, and the following observations were noted during the experiment.

carbonate	observations
XCO_3	• white solid remains white • white ppt observed with $Ca(OH)_2(aq)$ after some time
YCO_3	• white solid remains white • no ppt observed with $Ca(OH)_2(aq)$
ZCO_3	• white solid turns orange brown then black almost immediately • white ppt observed in $Ca(OH)_2(aq)$ almost immediately

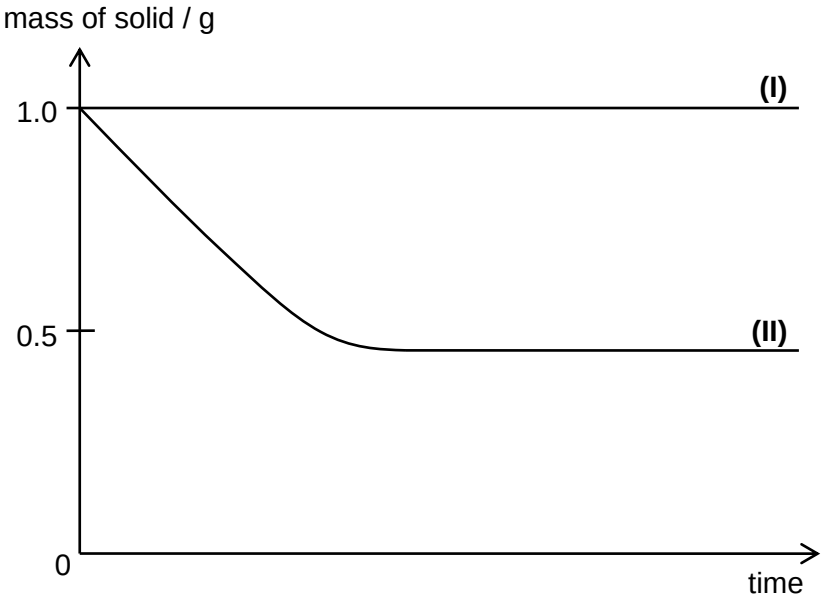
(a) Write a balanced equation, with state symbols, for the formation of the white precipitate in $Ca(OH)_2(aq)$.

…….. [1]

13

For Examiner's Use

From the experiment, decomposition profiles of these metal carbonates were plotted. Two of these plots are shown below.



It is known that these two plots correspond to those of magnesium carbonate and barium carbonate.

(b) (i) Which metal carbonate is represented by plot **(II)**?

……

(ii) With reference to your answer in **(b)(i)**, explain the relative ease of decomposition of these two carbonates.

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(iii) Give the electronic configuration of Mg^{2+} and explain why the ionic radius of Mg^{2+} is smaller than the atomic radius of Mg.

electronic configuration of Mg^{2+} ……

explanation ……..……..

……

[6]

For the boiling tube containing **Z**CO_3, it was found that the total decrease in mass was 0.333 g.

For Examiner's Use

(c) Sketch as accurately as possible, on the axes given on page 13, the decomposition profile for **Z**CO_3. Show all relevant information and label your sketch as "**(III)**".

[1]

(d) The black solid that finally remains has the formula $\mathbf{Z}_3O_4$. This solid is the only product containing **Z**.

From the experimental data, determine a value for the relative atomic mass of **Z**, and hence suggest the identity of **Z**.

A_r of **Z** = ……

identity of **Z** ……

[2]

[Total: 10]

For Examiner's Use

5 **(a)** Benzyl iodide was once used by the French army as tear gas in World War I. To synthesise benzyl iodide, one suggestion is to replace the chloride ion with an iodide ion. This reaction occurs but it does not go to completion.

$$C_6H_5CH_2Cl + I^- \; f \quad C_6H_5CH_2I + Cl^-$$

By quoting relevant values from the *Data Booklet*, suggest an explanation in terms of thermodynamics as to why this reaction does not go to completion. Assume that the entropy change of this reaction is close to zero.

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…… [2]

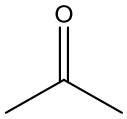
(b) The Finkelstein reaction, discovered by the German chemist, Hans Finkelstein, is used in the laboratory to synthesise benzyl iodide.

During the procedure, benzyl chloride is refluxed with sodium iodide using propanone as a solvent.

$$C_6H_5CH_2Cl + NaI \; f \quad C_6H_5CH_2I + NaCl$$

In propanone, the reaction proceeds at a faster rate and to near completion. Solid sodium chloride is produced as a by-product.

(i) Propanone is a polar solvent.



propanone

Draw a diagram to show the interaction between a sodium ion and a propanone molecule. State clearly the type of interaction involved.

For Examiner's Use

(ii) The table below shows the solubility of sodium halides in propanone.

compound	mass (in g) per 100 g of propanone
NaC*l*	0.00042
NaI	28.0

Hence suggest a reason why the Finkelstein reaction goes to near completion.

……

……

[3]

(c) Benzyl iodide is converted to its alcohol readily by heating with aqueous sodium hydroxide.

$$C_6H_5CH_2I + NaOH \longrightarrow C_6H_5CH_2OH + NaI$$

The rate equation is rate = k [$C_6H_5CH_2I$].

(i) Describe the mechanism of this reaction. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

(ii) Explain why benzyl iodide undergoes a unimolecular reaction with NaOH(aq) whereas (2–iodoethyl)benzene, $C_6H_5CH_2CH_2I$, undergoes a bimolecular reaction with NaOH(aq).

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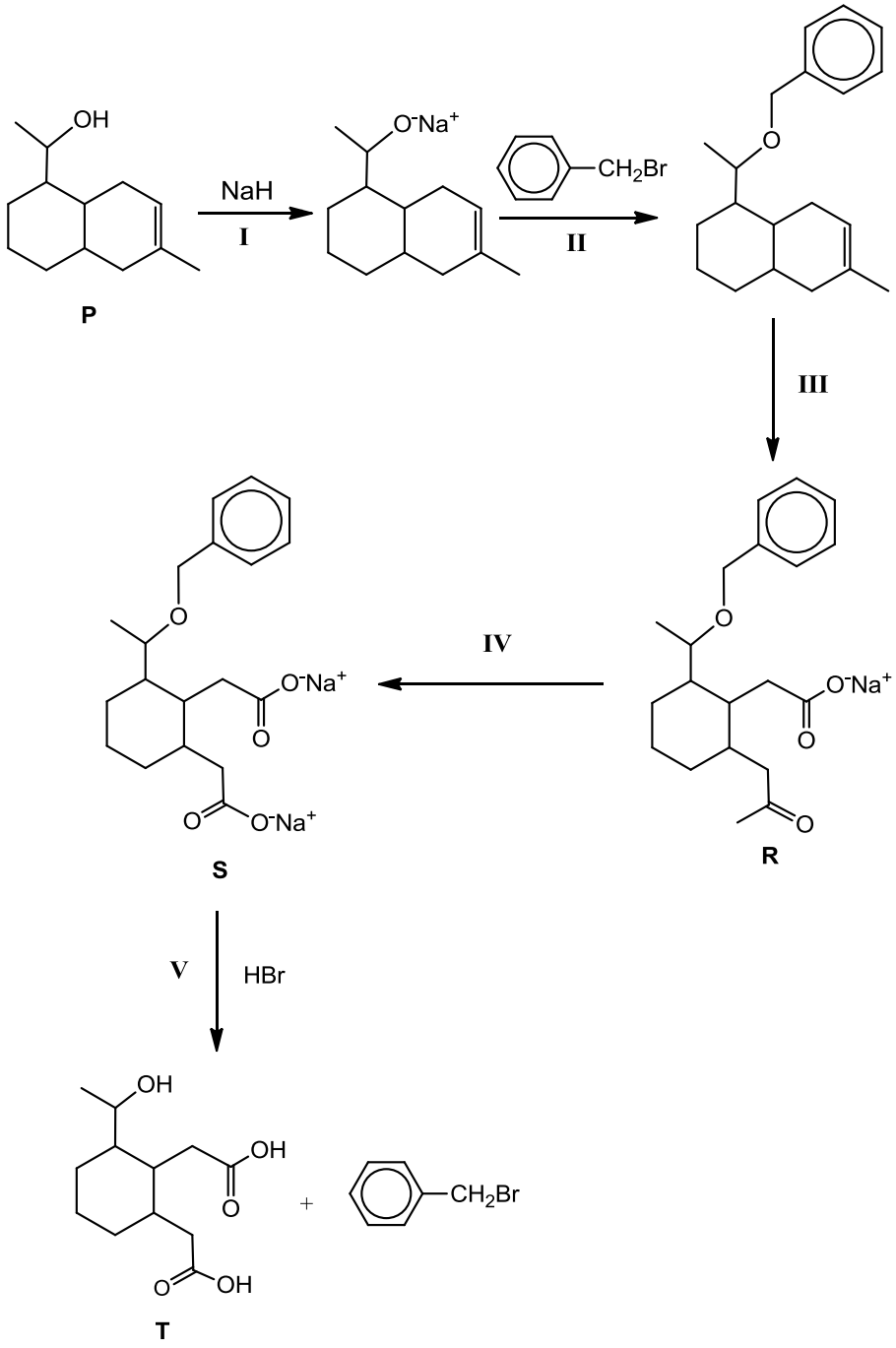
[5]

For Examiner's Use

(d) Benzyl bromides are often used to form benzyl ethers ($C_6H_5CH_2$–O–R), which are known to be good protecting groups in multi-step organic syntheses. The benzyl ethers formed will protect reactive functional groups from further reactions. These protecting groups can subsequently be removed to recover the originally unprotected functional groups.

The following illustrates a synthetic scheme in which a benzyl ether is acting as the protecting group.



(i) Name the functional groups present in compound **P**.

……..……

For Examiner's Use

(ii) State the role of NaH in step **I**.

……..……

(iii) State the reagents and conditions needed for steps **III** and **IV**.

step **III** ……

step **IV** ……

(iv) In this synthesis, benzyl bromide was added to protect a particular functional group in compound **P** from further reaction.

Identify this particular functional group in **P** and explain what would have happened instead in the reaction scheme if this functional group was not protected.

functional group in **P** ……

explanation ..……..……

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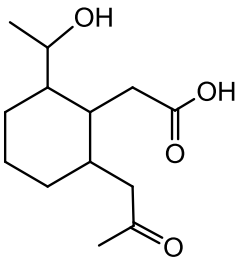
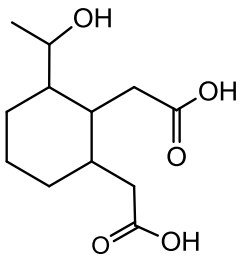
……..……...……

For Examiner's Use

(v) Intermediate **R** is reacted with $H_2SO_4(aq)$ to form compound **U**.



U



T

State how compound **U** can be distinguished from product **T** by a simple chemical test, and draw the structure of the organic product that would be produced during this test.

test ..……...……...…….

observations ..……...……...

……..……..……...……

organic product

[8]

[Total: 18]

For Examiner's Use

6 **(a)** Trioxanes are structures made up of three carbon atoms and three oxygen atoms in a six-membered ring.

Compound **A**, of molecular formula $C_3H_6O_3$, can form only **one** mono-bromo derivative when reacted with Br_2 under light.

(i) Draw the structural formula of trioxane, **A**.

There are three possible structural isomers of trioxane.

The other two trioxane structural isomers are known to be hypothetical structures and cannot be isolated.

(ii) Draw the structural formulae of the other two "trioxane" isomers.

(iii) Suggest a reason why the above two "trioxane" isomers cannot be isolated.

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[4]

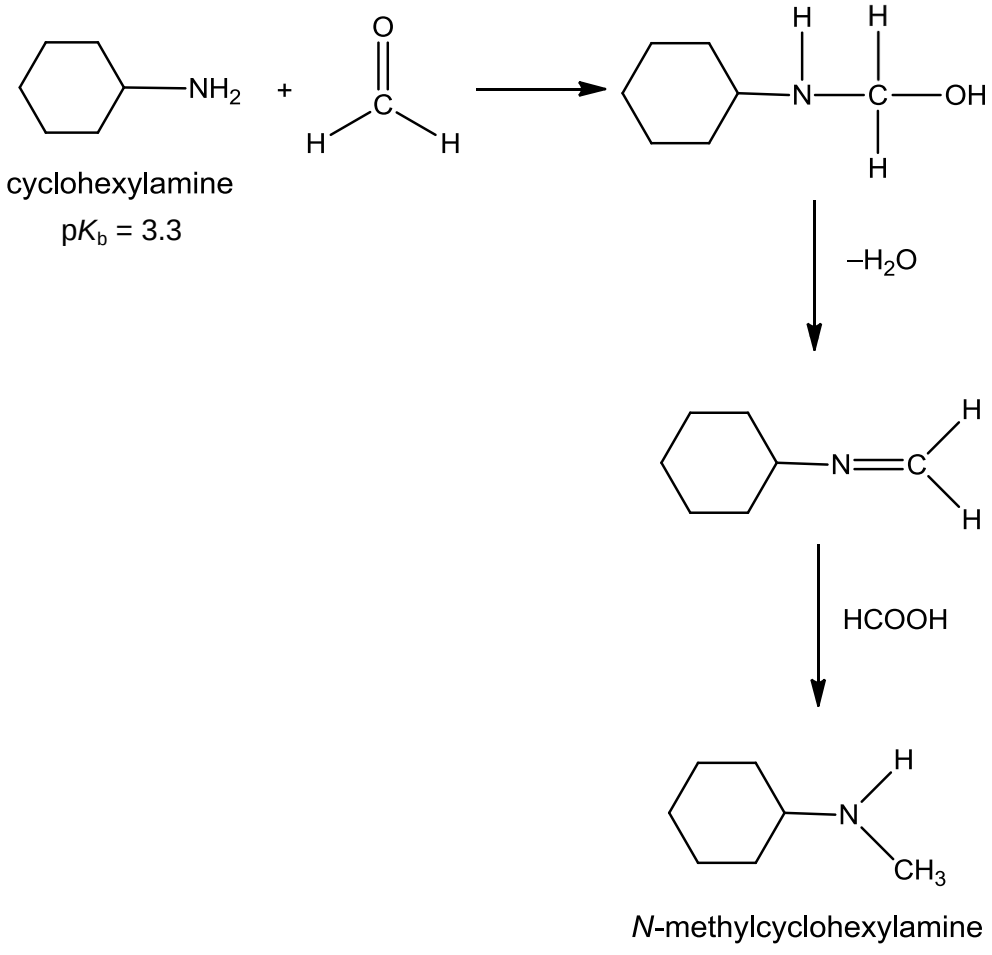
21

For Examiner's Use

(b) In the Leuckart reaction, a carbonyl compound reacts with primary amines to form substituted amines.

The first step of the reaction involves the nucleophilic addition of amines to a carbonyl compound, forming an intermediate that can be reduced by methanoic acid.

One example of the Leuckart reaction using methanal, HCHO, is shown as follows.



(i) Cyclohexylamine has a pK_b value of 3.3.

Predict a pK_b value for *N*-methylcyclohexylamine.
Briefly explain your prediction.

pK_b ……

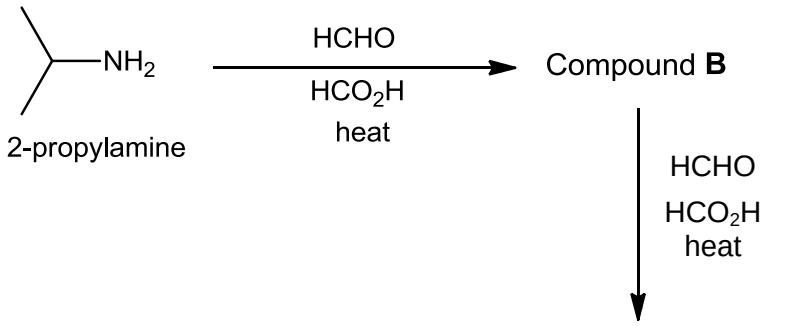
explanation ……

……

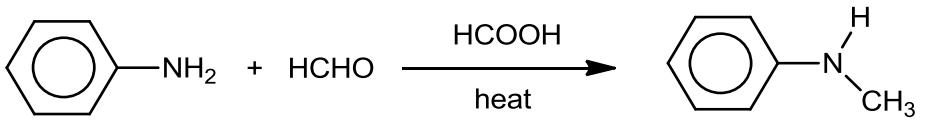
……

For Examiner's Use

(ii) Draw the full structural formula of the organic product formed in the box below when 1 mole of 2–propylamine reacts with 2 moles of methanal via the Leuckart reaction.



(iii) When phenylamine undergoes the Leuckart reaction with methanal, the yield of the product, *N*-methylphenylamine, is only 10.1%.



phenylamine

N-methylphenylamine

yield = 10.1%

Suggest a reason why the yield of *N*-methylphenylamine is poor.

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[4]

[Total: 8]

– END OF PAPER –