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# **CHEMISTRY**

**9647/03**

Paper 3      Free Response

**13 September 2011**

Candidates answer on separate paper.

**2 hours**

Additional Materials:      Writing Paper  
                                         Data Booklet

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## **READ THESE INSTRUCTIONS FIRST**

**DO NOT open this question booklet until you are told to do so.**

Write your name, class and index number in the spaces provided on the cover page.

Write in dark blue or black pen on both sides of paper.

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 any **four** questions.

Begin each question on a fresh sheet of paper.

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.

At the end of the examination, fasten all your work securely together, with the cover page on top.

Answer any **four** questions.  
Begin each question on a **fresh sheet of paper**.

1 This question is about the chemistry of halogens and their compounds.

(a) Many compounds of chlorine are manufactured from brine, concentrated NaCl(aq). The electrolysis of brine produces Cl<sub>2</sub>(g) and NaOH(aq). In some industrial electrolytic cells, these two substances are allowed to react further. The products formed in this second reaction depend on the operating conditions used.

- (i) Write balanced equations for the reaction between Cl<sub>2</sub>(g) and
- cold aqueous NaOH,
  - hot aqueous NaOH.

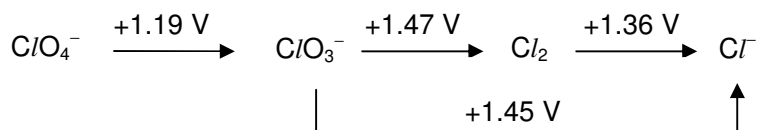
(ii) Suggest why F<sub>2</sub>(g) **cannot** be manufactured in a similar way using concentrated NaF(aq).

[3]

(b) The standard electrode potentials,  $E^\ominus$ , and standard Gibbs free energy changes,  $\Delta G^\ominus$ , of different chlorine-containing species are tabulated below.

|   | Half-equation                                                                                        | $E^\ominus / \text{V}$ | $\Delta G^\ominus / \text{kJ mol}^{-1}$ |
|---|------------------------------------------------------------------------------------------------------|------------------------|-----------------------------------------|
| 1 | $\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O}$  | +1.19                  | -230                                    |
| 2 | $2\text{ClO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightleftharpoons \text{Cl}_2 + 6\text{H}_2\text{O}$ | +1.47                  | ?                                       |
| 3 | $\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$                                          | +1.36                  | -262                                    |

These electrode potentials can be summarised using the Latimer diagram shown below. In a Latimer diagram, the most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

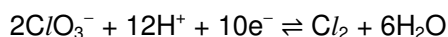


$\Delta G^\ominus$  and  $E^\ominus$  are related by the following equation.

$$\Delta G^\ominus = -zFE^\ominus$$

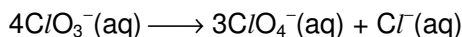
where  $\Delta G^\ominus$  is the standard Gibbs free energy change in **joules per mole**,  $z$  is the number of moles of electrons transferred during the redox reaction and  $F$  is the Faraday constant.

(i) Calculate  $\Delta G^\ominus$  for half-reaction 2.



- (ii) The standard electrode potential of converting  $\text{C/O}_3^-$  to  $\text{Cl}^-$  is **not** the summation of +1.47 V and +1.36 V. This is because the number of electrons transferred in each step must be taken into account.

- ① Write a half-equation for the conversion of  $\text{C/O}_3^-$  to  $\text{Cl}^-$ .
  - ② Using your knowledge of Hess' Law for  $\Delta G^\ominus$  and your answers to **(b)(i)**, show with the aid of an energy cycle that the  $E^\ominus$  for the conversion of  $\text{C/O}_3^-$  to  $\text{Cl}^-$  is +1.45 V.
- (iii) With the help of the Latimer diagram provided, calculate  $E^\ominus_{\text{cell}}$  of the reaction below and hence determine its  $\Delta G^\ominus$ .



[7]

- (c) Halogens and their compounds are commonly used in organic reactions to synthesise new compounds. 6.7 g of compound **A**,  $\text{C}_9\text{H}_{10}\text{O}$ , reacts with  $1.2 \text{ dm}^3$  of chlorine gas (at r.t.p.) to give compound **B**. On addition of  $\text{PCl}_5$ , **A** gives white fumes. Treatment of **A** with  $\text{NaBr}$  and concentrated  $\text{H}_2\text{SO}_4$  under reflux gives compounds **C** and **D**. Both **C** and **D** have the same molecular formula  $\text{C}_9\text{H}_{10}\text{Br}_2$  and each contains only *one* chiral centre.

- (i) Use the information to deduce the structural formulae of **A** – **D**. Explain the reactions that occur.

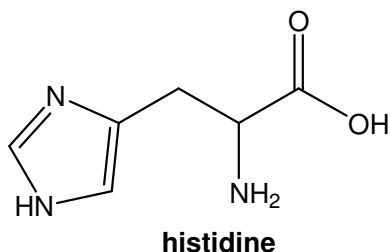
In particular, state clearly the type of reaction(s) undergone by **A** with  $\text{NaBr}$  and concentrated  $\text{H}_2\text{SO}_4$  described above.

- (ii) State and explain which compound, **C** or **D**, is produced in greater quantity.
- (iii) Describe the mechanism of the reaction between **A** and  $\text{Cl}_2$ , including curly arrows showing the movement of electrons, and all charges.

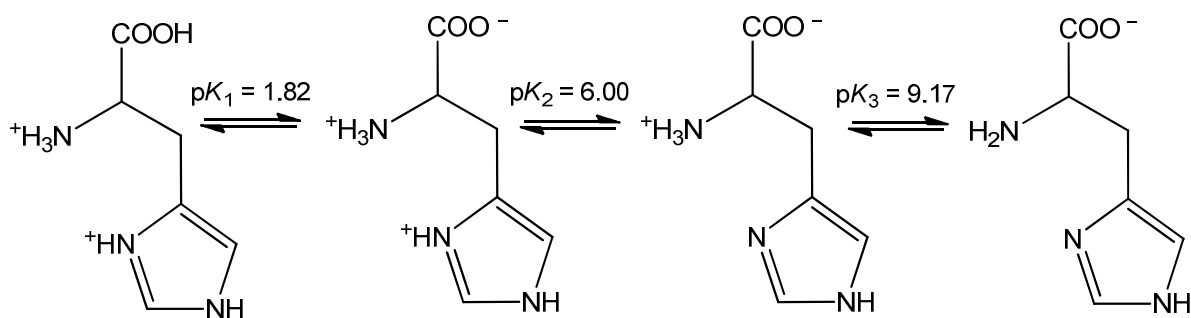
[10]

[Total: 20]

- 2 (a) Histidine, an essential amino acid, is present in many proteins and enzymes and plays a vital role in the structure and oxygen-binding function of haemoglobin.



There are three  $pK_a$  values associated with histidine:  $\alpha$ -carboxyl = 1.82, R group = 6.00 and  $\alpha$ -amino = 9.17.



- (i) Sketch the titration curve when 25 cm<sup>3</sup> of protonated form of histidine is being titrated with 75 cm<sup>3</sup> of NaOH(aq) of the same concentration. Your sketch should show clearly where the three  $pK_a$  values occur.
- (ii) Indicate clearly the isoelectric point of histidine on your sketch with an "X".
- (iii) Histidine is considered one of the best amino acid buffers under physiological condition.

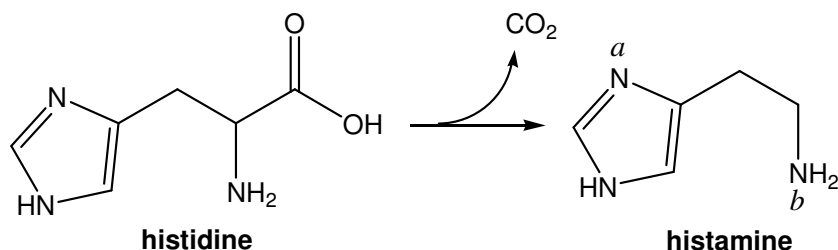
Write an equation to illustrate how histidine can maintain the pH of a solution at pH 6 when a small amount of OH<sup>-</sup>(aq) is added. Show the structure of histidine clearly in your equation.

- (iv) Calculate the final pH of a 100 cm<sup>3</sup> solution of 0.1 mol dm<sup>-3</sup> histidine at pH 6 if 1 dm<sup>3</sup> of 0.001 mol dm<sup>-3</sup> HCl was added.

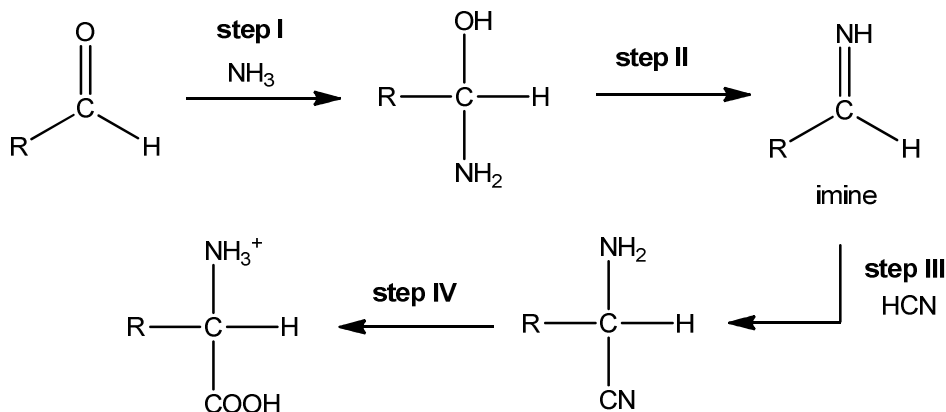
You may represent the acid as HA and the conjugate base as A<sup>-</sup> in your working.

[9]

- (b) Decarboxylation is an important reaction of amino acids in many biological processes. Histamine, which causes runny noses and itchy eyes, is synthesised in the body by decarboxylation of histidine with the aid of an enzyme catalyst, L-histidine decarboxylase.



- (i) State the hybridisation of the nitrogen, labelled *a*, in histamine. Hence, explain why it is less basic than the nitrogen, labelled *b*.
- (ii) Sketch a graph to illustrate the relationship between histidine concentration and the rate of reaction using a fixed amount of L-histidine decarboxylase. [4]
- (c) The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker.



- (i) Name the types of reactions in **step I** and **step II**.
- (ii) Suggest suitable reagents and conditions for **step IV**.
- (iii) In **step III**, the reaction proceeds via 2 parts:
- ① Acid-base reaction between N in imine and HCN
  - ② Followed by a nucleophilic attack on C by  $\text{CN}^-$

Propose a mechanism for **step III**, showing clearly the movement of electrons using curly arrows.

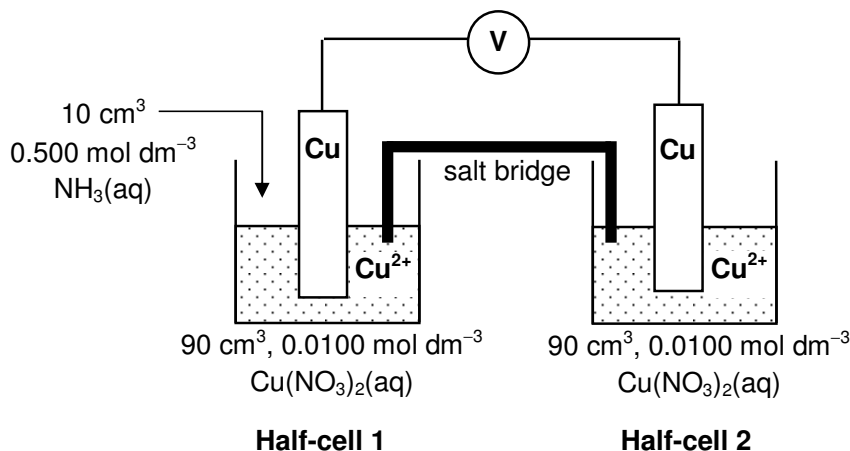
- (iv) Suggest, with a reason, if there is any difference in the optical activity of a sample of amino acid synthesised by Strecker's method and that of a naturally occurring amino acid.

[7]

[Total: 20]

- 3 (a) The Nernst equation was developed by the German chemist, Walter Hermann Nernst, to calculate the cell potential under non-standard conditions.

Two identical concentration half-cells, each consisting of a copper electrode immersed in 90 cm<sup>3</sup> of 0.0100 mol dm<sup>-3</sup> of copper(II) nitrate, are prepared.



10 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> NH<sub>3</sub>(aq) is added to half-cell 1 and the colour of the solution changes from blue to deep blue. The  $E_{\text{cell}}$  measured is +0.129 V.

In your calculations, you may apply the following Nernst equation which has been derived for the above electrochemical cell.

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.0592}{2} \lg \frac{[\text{Cu}^{2+}]_{\text{half-cell 1}}}{[\text{Cu}^{2+}]_{\text{half-cell 2}}}$$

where

$E_{\text{cell}}$  is the cell potential under non-standard conditions,

$E_{\text{cell}}^{\ominus}$  is the standard cell potential, taken to be 0.00 V before the addition of NH<sub>3</sub>(aq),

$[\text{Cu}^{2+}]_{\text{half-cell 1}}$  is the concentration of copper ions left in the solution of half-cell 1 after the addition of NH<sub>3</sub>(aq),

$[\text{Cu}^{2+}]_{\text{half-cell 2}}$  is the original concentration of copper ions in half-cell 2.

- (i) Write an equation to account for the formation of the deep blue solution.
- (ii) Deduce and explain which half-cell contains the negative electrode.
- (iii) Give the expression, including its units, for the equilibrium constant,  $K_f$ , for the formation of the complex ion formed in (a)(i).
- (iv) Using the Nernst equation given, calculate the  $[\text{Cu}^{2+}]$  in half-cell 1 after the addition of NH<sub>3</sub>(aq).
- (v) Hence, calculate  $K_f$  for the formation of the complex ion in half-cell 1.

[8]

- (b) When a few drops of NaOH(aq) are added to a solution containing a transition metal ion, a grey-green precipitate **F** is observed. Addition of excess NaOH(aq) results in the formation of a deep green solution **G**. On warming **G** with H<sub>2</sub>O<sub>2</sub>(aq), a yellow solution **H** is obtained. On boiling solution **H** until no more bubbles are given out, followed by acidification, an orange solution **J** is obtained.

Identify **F**, **G**, **H** and **J**.

[3]

- (c) By considering relevant  $E^\ominus$  values from the *Data Booklet*, suggest a mechanism for the catalysis of the decomposition of H<sub>2</sub>O<sub>2</sub>(aq) by Fe<sup>3+</sup> ions.

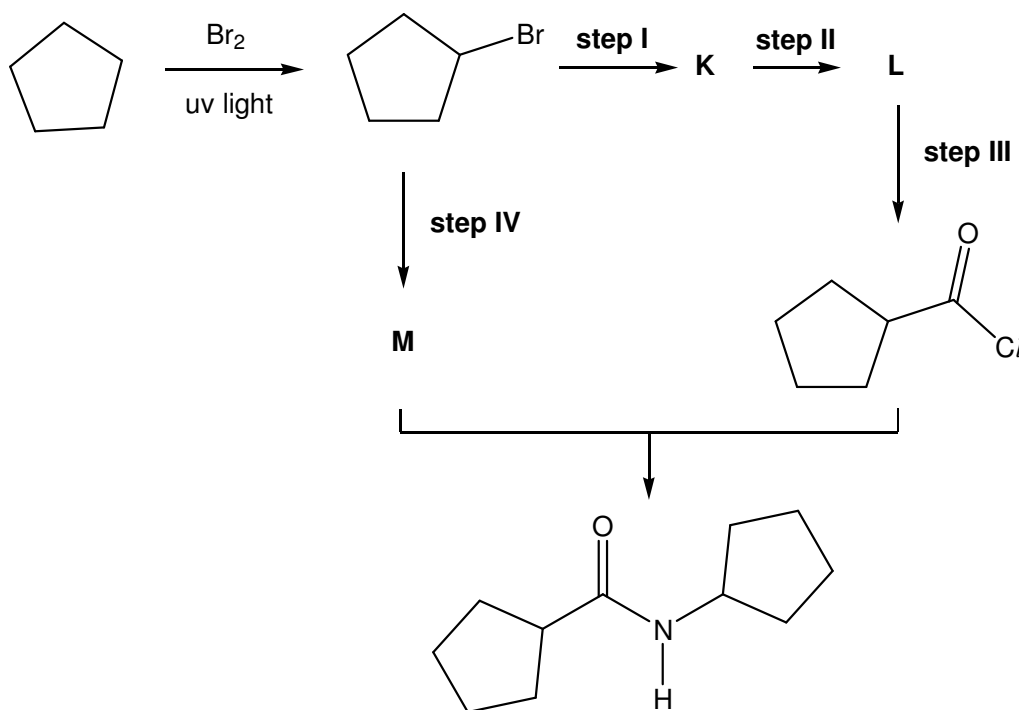
[2]

- (d) A cycloalkane, C<sub>5</sub>H<sub>10</sub>, gives only two mono-brominated products (ignoring any stereoisomers) with Br<sub>2</sub> under uv light.

- (i) Give the structural formulae of the cycloalkane and the two mono-brominated products formed.

- (ii) Suggest the ratio in which the two mono-brominated products will be formed.

- (iii) Cyclopentane is an isomer of the cycloalkane identified in (d)(i). It can be used to synthesise a secondary amide as shown in the reaction scheme:



Suggest suitable reagents and conditions required for **steps I, II, III** and **IV**.

[7]

[Total: 20]



- 4 (a) Aluminium is the most common metallic element in the earth's crust and occurs in rocks such as feldspars and micas. Its only oxide is aluminium oxide,  $\text{Al}_2\text{O}_3$ , commonly known as alumina.

Use the following data, together with appropriate data from the *Data Booklet*, to construct a Born-Haber cycle to determine the lattice energy of aluminum oxide.

enthalpy change of formation of aluminium oxide =  $-1676 \text{ kJ mol}^{-1}$

enthalpy change of atomisation of aluminium =  $+322 \text{ kJ mol}^{-1}$

first electron affinity of oxygen =  $-142 \text{ kJ mol}^{-1}$

second electron affinity of oxygen =  $+744 \text{ kJ mol}^{-1}$

[4]

- (b) The oxides,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , are all used as refractory materials due to their high melting points. If a sample of one of the oxides was provided as a white powder, describe the reactions you could carry out on the powder to determine which of the three oxides it was.

[3]

- (c) Aluminium oxide is employed industrially for many organic reactions. Compound **N** is obtained when propan-2-ol is heated over  $\text{Al}_2\text{O}_3$ .

(i) Identify compound **N**.

(ii) Suggest reagents and conditions to convert **N** into 2-hydroxypropanoic acid (commonly known as lactic acid) in no more than 3 steps.

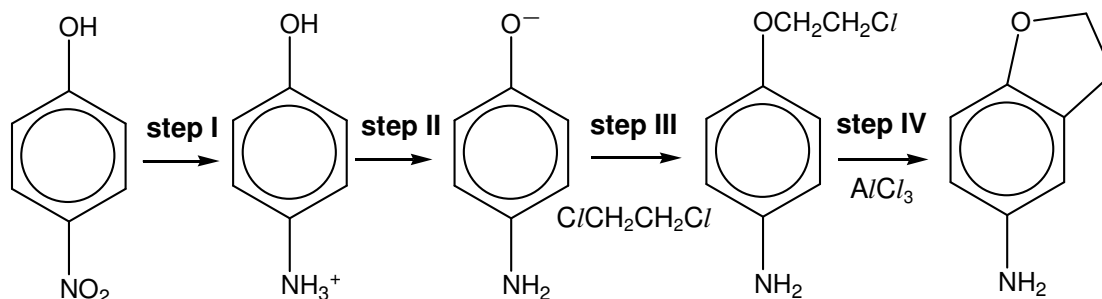
[4]

- (d) Compounds of beryllium and aluminium share certain chemical properties. Beryllium salts, probably from rocks such as feldspars, may sometimes be found in drinking water.

An aqueous solution of beryllium sulfate is known to irritate the skin. With the aid of relevant equation(s), explain why that is so.

[2]

- (e) Another aluminium compound that has important uses in organic chemistry is aluminium chloride.  $AlCl_3$  is produced when dry chlorine is passed over heated aluminium foil in a hard glass tube.



- (i) State the reagents and conditions for **step I** and **step II**.
- (ii) With the aid of an equation, explain why aluminium chloride can act as a Lewis acid catalyst in **step IV**.
- (iii) Using your answer to (e)(ii), describe the mechanism of the reaction in **step IV**.
- (iv) Suggest why the yield might be low in **step IV**.

[7]

[Total: 20]

5 This question is about the chemistry of two transition metals, iron and nickel.

- (a) Iron is a silvery grey metal and forms stable coloured ions of mainly +2 and +3 oxidation states.

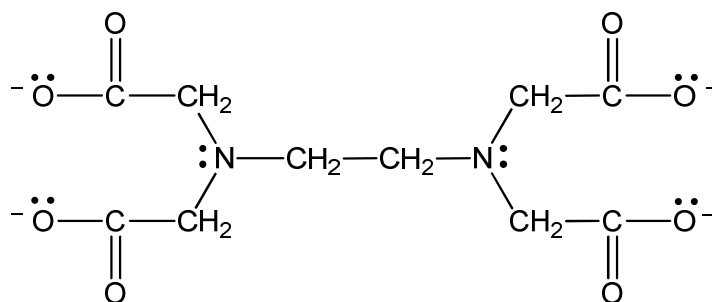
In an experiment, a student added aqueous potassium fluoride to a sample of yellow iron(III) chloride solution. It was noted that the solution decolourised, forming  $[\text{FeF}_5(\text{H}_2\text{O})]^{2-}$ .

(i) Explain why an aqueous solution of  $\text{Fe}^{3+}$  is yellow.

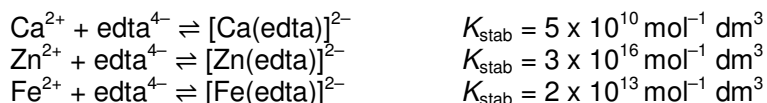
(ii) Suggest a reason why  $[\text{FeF}_5(\text{H}_2\text{O})]^{2-}$  is colourless.

[4]

- (b) Chelation therapy is commonly used to remove excess iron from the body. Ethylenediaminetetraacetate or  $\text{edta}^{4-}$  is an example of such a chelating agent.



The stability constants,  $K_{\text{stab}}$ , of three edta complexes are given below.



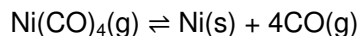
Given that calcium and zinc are essential for health, explain what problem might arise during the treatment and how it can be overcome.

[2]

- (c)  $\text{Ni(CO)}_4$  is a compound formed by the reaction between nickel and carbon monoxide.

- (i) Sketch the shapes of the hybrid orbitals around the C atom in carbon monoxide.

The Mond process was developed by Ludwig Mond to extract and purify nickel from its ores. One of the stages of this process involves the decomposition of  $\text{Ni(CO)}_4$  at 227 °C to give nickel.



The equilibrium constant,  $K_p$ , for the equilibrium at 227 °C is 1.01 atm<sup>3</sup>.

- (ii) Write an expression for  $K_p$ .

A sample of gaseous  $\text{Ni(CO)}_4$  was placed in a 2 dm<sup>3</sup> evacuated container at 227 °C. At equilibrium, the partial pressure of CO was 2.00 atm.

- (iii) Calculate the total pressure of the system at equilibrium.

- (iv) Calculate the mass of  $\text{Ni(CO)}_4$  placed in the container initially.

[7]

- (d) Ni is commonly used in catalytic hydrogenation reactions. One such example is given below.

Compound **P**,  $\text{C}_{10}\text{H}_{12}\text{NOCl}$ , has a chiral centre and dissolves in dilute sulfuric acid. It reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate, but does not react with Tollens' reagent. **P** reacts with  $\text{H}_2$  in the presence of Ni catalyst followed by addition of aqueous bromine to form **Q**,  $\text{C}_{10}\text{H}_{12}\text{NOCl/Br}_2$ . When compound **Q** is heated under reflux with aqueous iodine and excess alkali, followed by careful acidification, compound **R**,  $\text{C}_9\text{H}_9\text{NO}_3\text{Br}_2$ , and a yellow precipitate are formed.

Deduce the structures of compounds **P**, **Q** and **R**, giving reasons for your answer.

[7]

[Total: 20]



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