Name:	Index No.:	CT Group: 12

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CHEMISTRY **9647/03**

Paper 3 Free-Response **23 September 2013**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any four questions.
A Data Booklet is provided.
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.

Answer any four questions.

1 **(a)** With the aid of a diagram, describe how a polypeptide chain is held in the shape of an alpha helix. [3]

(b) Haemoglobin is the oxygen-carrying protein in red blood cells.

(i) With reference to the haemoglobin molecule, describe and explain what is meant by the term *quaternary structure* of proteins. In your answer, you should state the type of bonding or interaction involved.

(ii) A typical polypeptide chain of haemoglobin consists of 141 amino acids.

The R groups of 3 of the amino acids are given below.

amino acid	**formula of side chain (R in $RCH(NH_2)CO_2H$)**
glutamic acid	$-CH_2CH_2CH_2CO_2H$
valine	$-CH(CH_3)_2$
lysine	$-CH_2CH_2CH_2\ CH_2NH_2$

Use **all three** amino acids above to construct the displayed formula of a possible section of the polypeptide.

(iii) Uncoiling of the protein structure is favoured when temperature is higher than physiological conditions. With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

suggest why this process is favoured at higher temperatures.

[8]

(c) One molecule of haemoglobin can bind up to four molecules of oxygen, according to the following equation.

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq) \qquad K_c = 3 \times 10^{20}\ mol^{-4}\ dm^{12}$$

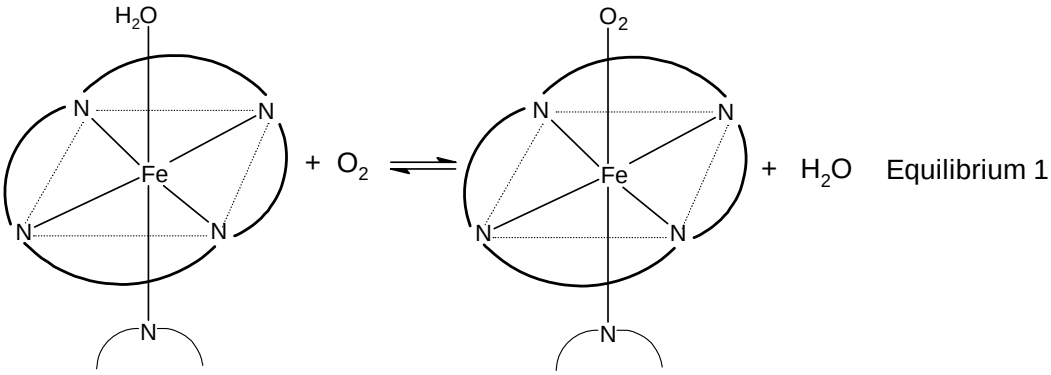
(i) Write an expression for K_c for this reaction.

(ii) Calculate the percentage of $Hb(O_2)_4$ in an $Hb\text{-}Hb(O_2)_4$ mixture when $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}.

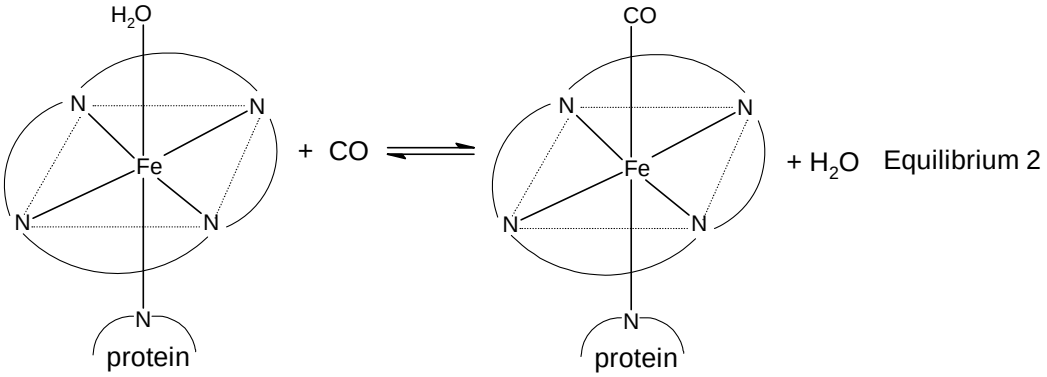
[3]

(d) **(i)** Carbon monoxide, CO, mainly causes adverse effects in humans by combining with haemoglobin to form carboxyhaemoglobin in the blood. This prevents haemoglobin from releasing oxygen in tissues, effectively reducing the oxygen-carrying capacity of the blood.

The equations below show the reactions of haemoglobin with oxygen and carbon monoxide respectively.



haemogloblobin oxyhaemoglobin



haemoglobin carboxyhaemoglobin

CO is found to have 245 times more affinity for haemoglobin than O_2. Explain how excessive inhalation of CO will give rise to poisoning in the blood.

(ii) Suggest a method for the treatment of carbon monoxide poisoning.

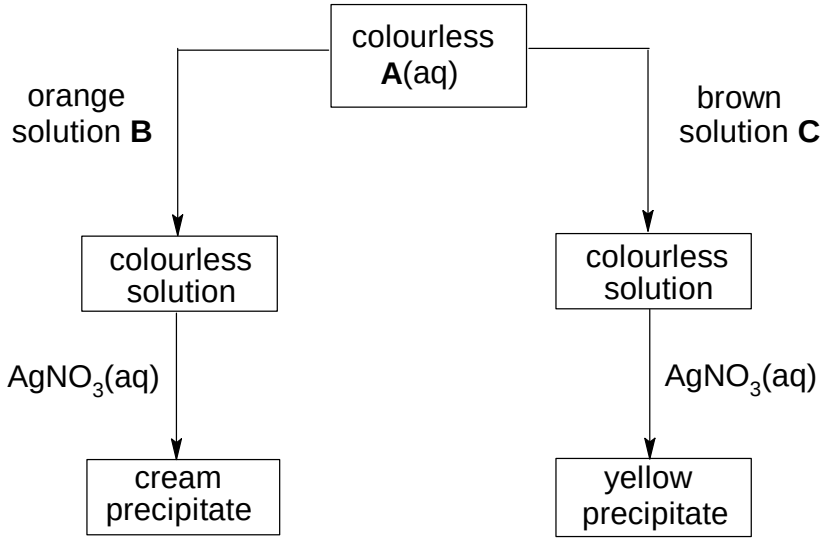
[3]

(e) Oxygen can be liquefied by pressure alone if its temperature is below the 'critical temperature' of -118°C. Above this critical temperature no amount of pressure will liquefy oxygen. Suggest a suitable value for the critical temperature of ammonia. Give your reasoning.

[3]

[Total: 20]

2 **(a)** The diagram below shows the reactions of a salt, **A**, in aqueous medium.



A has the following composition by mass:

K, 41.1%; S, 33.7%; O, 25.2%.

The relative formula mass, M_r, of **A** is 190.4. One formula unit of **A** contains only one type of anion.

(i) Determine the formula of the salt **A**.

(ii) Suggest the identities of **B** and **C**.

(iii) By means of two ionic equations, show how the yellow precipitate is formed from **C**.

(iv) For the reaction of **A** and **B**, a titration was carried out to determine if the sulfur-containing product is $S_4O_6^{2-}$ or SO_4^{2-}.

It was found that 25.0 cm^3 of 0.200 mol dm^{-3} of **B** required 10.0 cm^3 of 0.125 mol dm^{-3} of **A** for complete reaction.

Use the data to determine the final oxidation state of sulfur in the product. Hence, write a balanced equation for the reaction of **A** and **B**.

(v) Construct a balanced equation for the reaction of **B** with hot aqueous potassium hydroxide.

[8]

(b) Pseudohalogens are a family of inorganic compounds which possess chemical properties similar to the halogens. Two examples of pseudohalogens are cyanogen $(CN)_2$ and thiocyanogen $(SCN)_2$.

The equations below represent the standard reduction potentials of cyanogen and thiocyanogen.

$(CN)_2 + 2H^+ + 2e^- \rightleftharpoons 2HCN$ $\quad E^\ominus = +0.37$ V
$(SCN)_2 + 2e^- \rightleftharpoons 2SCN^-$ $\quad E^\ominus = +0.77$ V

(i) Use the *Data Booklet* to predict what you would expect to observe when the following solutions are mixed. Write balanced equations for any reaction that occurs.

I $(CN)_2(aq)$ and $Br_2(aq)$

II KSCN(aq) and acidified $KMnO_4(aq)$

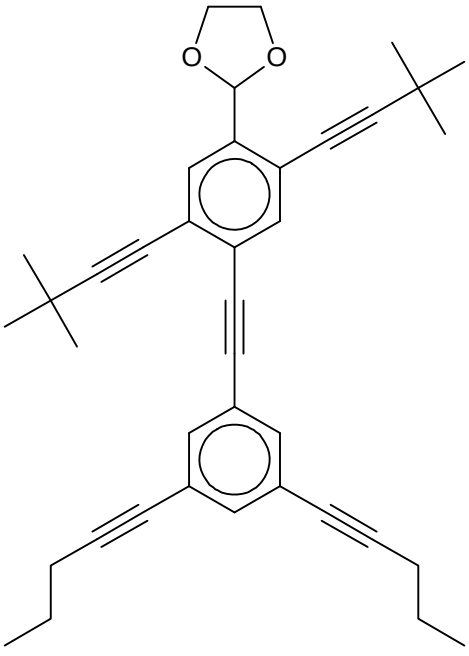
(ii) A reaction occurs when an unknown metal, **D**, is added to $(SCN)_2$. The standard cell potential of the reaction is determined to be +0.43 V.

Use the *Data Booklet* to deduce the identity of metal **D**, showing your working clearly.

[5]

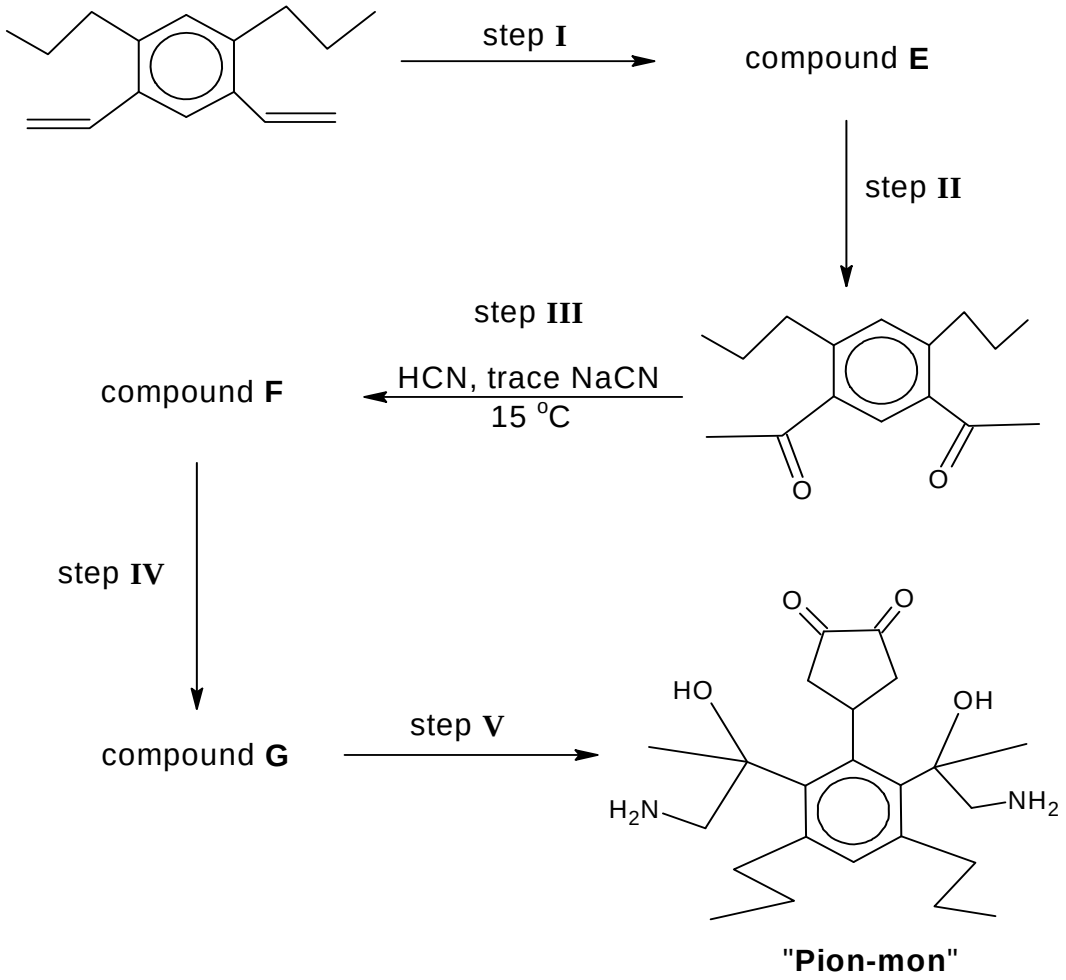
(c) NanoPutians are a family of organic molecules whose structural formulae resemble human forms. These compounds were designed and created by Dr James Tour from Rice University in 2003 as a part of a sequence of chemical education for young students.

One such molecule, named the NanoKid, is shown below.



6

Inspired by their discovery of the NanoPutians and a motivation to create a digital mascot for the school, a team of year two chemistry students from Pioneer Junior College devised the following reaction scheme to form "**Pion-mon**".



"**Pion-mon**"

(i) Suggest reagents and conditions for steps **I**, **II**, **IV** and **V**.

(ii) Draw the structural formulae of compounds **E**, **F** and **G**.

[7]

[Total: 20]

3 **(a)** **(i)** Describe what you would see when separate samples of sodium and sulfur are burnt in air.

(ii) The oxides of sodium and sulfur resulting from the reactions in **(i)** both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution.

[4]

(b) Sulfurous acid is an aqueous solution of sulfur dioxide. Sulfurous acid, H_2SO_3, is a weak dibasic acid with pK_1 = 2.15 and pK_2 = 7.21.

(i) Calculate the pH of a 0.80 mol dm^{-3} solution of sulfurous acid (ignore the effect of pK_2 on the pH).

(ii) An amphiprotic species is one that reacts with an acid and a base. The pH of a solution containing an amphiprotic species is given by the following expression.

$$pH = \tfrac{1}{2}(pK_1 + pK_2)$$

In the titration of H_2SO_3 with NaOH, an amphiprotic species is formed. Identify the amphiprotic species formed and calculate the pH of the solution.

(iii) Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 0.40 mol dm^{-3} NaOH is added to 10.0 cm^3 of 0.80 mol dm^{-3} H_2SO_3. On your sketch, clearly mark the points you have calculated in **(i)** and **(ii)**.

(iv) Suggest a suitable indicator from the following table to be used to detect the first equivalence point and state the colour change of the solution at this equivalence point.

indicator	pH range	acid solution	basic solution
bromocresol green	4 – 6	yellow	blue
bromothymol blue	6 – 8	yellow	blue
phenolphthalein	8 - 10	colourless	red

(v) Draw the dot-and-cross diagram showing the electrons (outer shells only) in SO_3^{2-}, and use the VSEPR (valence shell electron pair repulsion) theory to predict its shape.

[9]

(c) The following two experiments (**I**) and (**II**) were carried out separately to determine enthalpy changes of neutralisation, ΔH_{neut}.

(I) 50 cm^3 of 0.80 mol dm^{-3} NaOH is mixed with 25 cm^3 of 0.80 mol dm^{-3} H_2SO_3 and the temperature rise was recorded as 6.7 ^oC.

(II) 50 cm^3 of 0.80 mol dm^{-3} NaOH is mixed with 50 cm^3 of 0.80 mol dm^{-3} HC*l* and the temperature rise was recorded as 5.5 ^oC.

Given that the specific heat capacity of solution is 4.18 J cm^{-3} K^{-1}, calculate the ΔH_{neut} for each of the two reactions and account for the difference between the two values.

[4]

(d) State and explain how the acidities of propan-1-ol, propanoic acid and phenol compare with each other.

[3]

[Total: 20]

4 Data concerning some elements of Group II of the Periodic Table, at 298 K, are given in the table. Further data may be found in the *Data Booklet*.

	Mg	Ca	Sr
$\Delta H_{hydration}$ of M^{2+} / kJ mol^{-1}	–1980	–1650	–1480
$\Delta S_{hydration}$ of M^{2+} / J mol^{-1} K^{-1}	–293	–238	–222
solubility of sulfate / mol dm^{-3}	1.8	4.7×10^{-2}	7.5×10^{-4}

(a) **(i)** Using the data provided, account for the trend of solubility of the Group II sulfates down the group.

(ii) Calculate $\Delta G_{hydration}$ of Mg^{2+}, leaving your answer in kJ mol^{-1}.

[4]

(b) To separate the two Group II metal ions, Mg^{2+} and Sr^{2+}, a student added solid sodium carbonate, Na_2CO_3, slowly to a solution, which contains a mixture of 0.100 mol dm^{-3} $MgCl_2$ and 0.100 mol dm^{-3} $SrCl_2$.

[K_{sp} of $MgCO_3 = 3.5 \times 10^{-8}$ mol^2 dm^{-6}; K_{sp} of $SrCO_3 = 1.1 \times 10^{-10}$ mol^2 dm^{-6}]

(i) State which metal ion is precipitated first. Hence, calculate the concentration of carbonate ion in the solution, in mol dm^{-3}, needed for the first trace of precipitate to be seen.

(ii) Determine the concentration of this metal ion, in mol dm^{-3}, remaining in the solution when the other metal ion just starts to precipitate.

(iii) For an effective separation, less than 1% of this metal ion should remain in solution.
By means of calculation, determine if the above separation is effective.

[4]

(c) When magnesium chloride is added to water, a solution is formed which has a pH of 6.5. When aluminium chloride is added to water, the resulting solution has a pH of 3. With the aid of equations, explain the difference in observations.

[3]

(d) Compound **L**, $C_5H_7O_2N$, is a cyclic compound which is optically active and neutral.

On heating **L** with aqueous NaOH, a pungent gas that turned moist red litmus blue was liberated. Upon acidification of the reaction mixture with aqueous HC*l*, **M**, $C_5H_8O_4$, was formed.

M reacts with Li$Al$$H_4$ to form **N**, $C_5H_{12}O_2$. On passing over hot Al_2O_3, **N** forms **P**, C_5H_8. **P** decolourises aqueous Br_2. When **P** is heated with acidified $KMnO_4$ solution, **Q,** $C_3H_4O_3$ is formed, together with effervescence that forms a white precipitate with limewater.

Q reacts with aqueous Na_2CO_3 with effervescence and forms a yellow precipitate when warmed with alkaline aqueous I_2.

Given that compounds **M, N, P** are **Q** are all non-cyclic compounds, deduce the structures of compounds **L, M, N, P,** and **Q**, and explain the chemistry of the reactions described.

[9]

[Total: 20]

5 **(a)** Phosphorus trichloride can be prepared by the reaction of white phosphorus with chlorine. Some related thermochemical data are shown below.

enthalpy change of formation of $PCl_3(l)$	–320 kJ mol^{-1}
bond energy of P−C*l* bond in PCl_3	+323 kJ mol^{-1}
enthalpy change of atomisation of phosphorus	+314 kJ mol^{-1}

Using the above data, together with relevant data from the *Data Booklet*, construct an energy level diagram to determine the enthalpy change of vaporisation of $PCl_3(l)$.

[4]

(b) **(i)** Carbon and silicon are both elements of Group IV. Each forms a tetrachloride. CCl_4 has no reaction with water while $SiCl_4$ reacts violently with water. Briefly account for the difference in behaviour with water.

(ii) Tin is another element in Group IV.

When tin(IV) chloride reacts with potassium hydroxide in a small amount of water, potassium chloride is produced, together with an anhydrous salt **R** having the molecular formula of $K_2SnCl_3O_3H_3$.

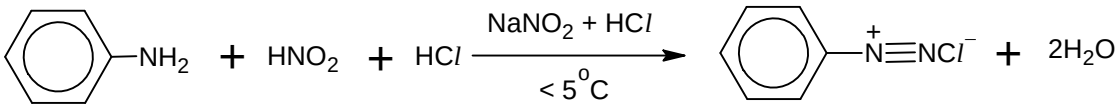
R is an ionic salt. One formula unit of **R** contains one type of anion and one type of cation.

Suggest the formula of the anion present in **R**. Hence, draw a possible structure of the anion.

[3]

(c) Diazonium salts are important intermediates in the synthesis of many other substituted aromatic compounds. The following equation shows the formation of phenyldiazonium chloride.

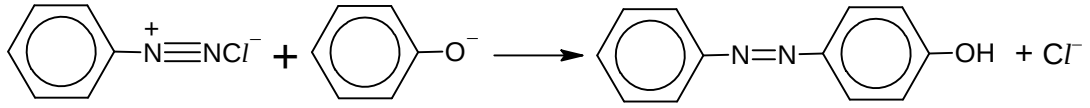
reaction **1**



phenyldiazonium chloride

Azo dyes are common organic compounds which can be synthesised from diazonium salts. They are often brightly coloured due to the presence of the chromophore functional group, -N=N-. The following reaction shows how one such azo dye can be manufactured.

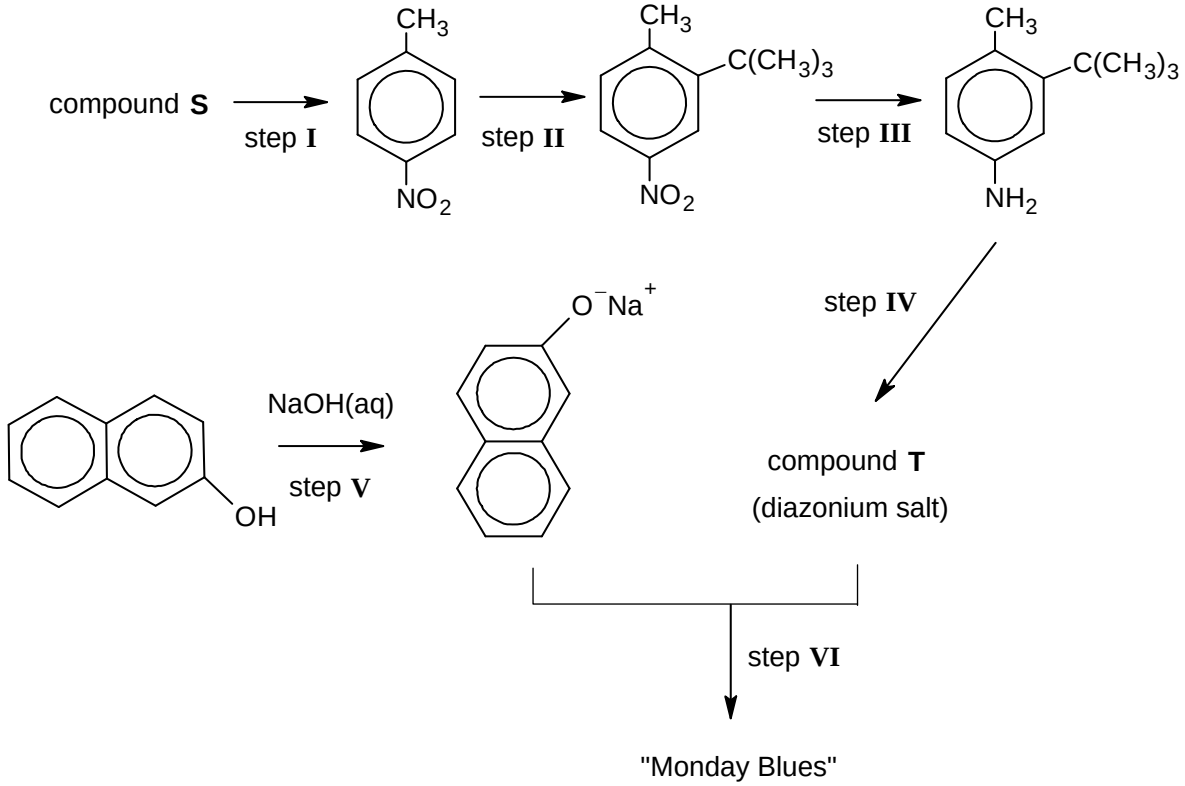
reaction **2**



azo compound

(i) State the type of reaction that occurs in reaction **2**.

A research chemist is tasked to create new azo dyes. Using reaction **1** and **2**, he proposed the following reaction scheme to a new azo dye named “Monday Blues”.



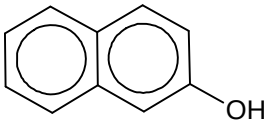
(ii) Suggest the structures of compounds **S**, **T**, and “Monday Blues”.

(iii) Give the reagents and conditions for steps **I**, **II** and **III**.

(iv) Give a mechanistic account for the reaction in step **II**.

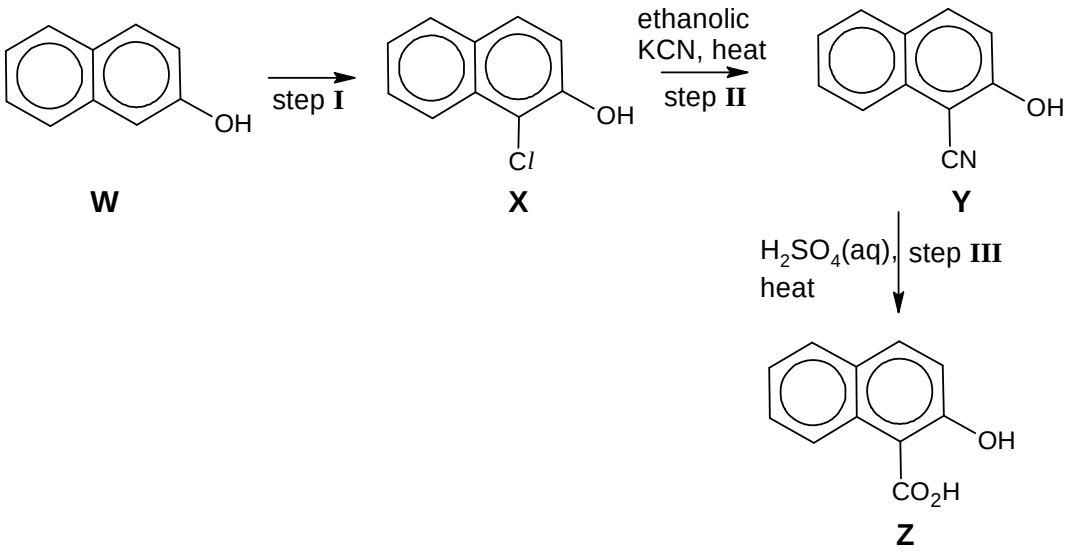
[9]

(d) 2-naphthol is a compound used in the synthesis of “Monday Blues” in **(c)**.



2-naphthol

A research assistant proposed to synthesise compound **Z**, a precursor to a drug, starting from 2-naphthol, compound **W**, by the following route.



W **X** **Y** **Z**

(i) Give the reagents and conditions for step **I**.

(ii) The reaction scheme proposed by the research assistant above failed to give the desired product. Suggest an explanation for this.

(iii) Suggest a 2-step synthetic route to form compound **Z,** starting from compound **W**, 2-napthol.

[4]

[Total: 20]

End of paper