Anglo-Chinese Junior College

JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME		FORM CLASS	
TUTORIAL CLASS		INDEX NUMBER	

CHEMISTRY

9729/03

Paper 3 Free Response

28 August 2023
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.
Circle the number of the question you have attempted.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

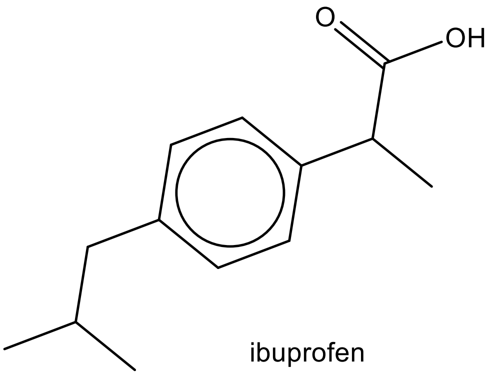
For Examiners' use only	
Section A	
1	/ 17
2	/ 18
3	/ 25
Section B	
4 / 5	/ 20
Total	/ 80

This document consists of **28** printed pages.

Section A

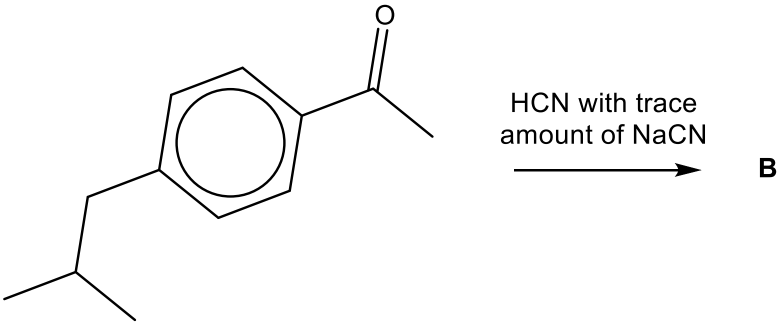
Answer **all** the questions in this section.

1 Ibuprofen belongs to a class of drugs called non-steroidal anti-inflammatory drugs (NSAIDs) used to reduce inflammation, pain and fever. Pain, fever, and inflammation are caused by the release in the body of chemicals called prostaglandins. Ibuprofen blocks the enzyme that makes prostaglandins resulting in lower levels of prostaglandins.



ibuprofen

The following diagram shows the first step in the synthesis route to form ibuprofen from compound **A**.



A

(a) A series of experiments were carried out at 25 °C to find the effect of initial concentration of hydrogen cyanide, cyanide ions and **A** on the initial rate of formation of **B**.

Table 1.1

experiment	initial concentration / mol dm^{-3}			initial rate of formation of **B** / mol dm^{-3} s^{-1}
	[**A**]	[HCN]	[CN$^-$]	
1	0.020	0.060	0.060	1.00
2	0.020	0.050	0.050	0.833
3	0.020	0.050	0.060	1.00
4	0.025	0.050	0.050	1.042

(i) Write a balanced equation for the reaction that produces compound **B**. [1]

(ii) Use the data in Table 1.1 to deduce the order of reaction with respect to each of the reactants. [3]

(iii) Write the rate equation for this reaction. Hence, calculate the value of the rate constant using the data in experiment 2. Include its units. [2]

(iv) Describe a mechanism that is consistent with the rate equation deduced in **(a)(iii)** and indicate which step in the mechanism is the rate determining step. Explain your reasoning. [3]

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(b) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on rate when the temperature is increased. [3]

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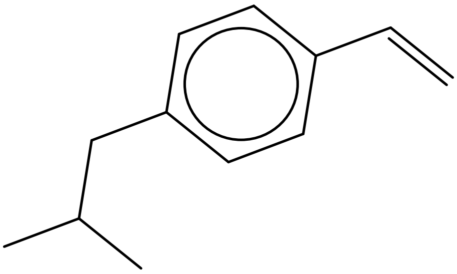
(c) Propose a 3-step synthesis of ibuprofen starting from the compound 1-isobutyl-4-vinylbenzene. Suggest the reagents and conditions, and draw the structure of the organic intermediate product in each step. [5]



1-isobutyl-4-vinylbenzene

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[Total: 17]

2 **(a)** Describe and explain the general trend in the first ionisation energy across Period 3. [3]

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(b) **(i)** Describe and explain the reactions, if any, of the chlorides $NaCl$, $AlCl_3$ and PCl_5 with water. Write equations for all reactions that occur and suggest the pH of the resulting solutions. [4]

(ii) At certain temperatures, aluminium chloride exists as Al_2Cl_6 molecules. Draw the structure of Al_2Cl_6. Label the co-ordinate bonds on your structure. [1]

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(c) PCl_5 reacts with ketones in a 1 : 1 molar ratio to give gem-dichlorides. A gem-dichloride contains two chlorine atoms bonded to the same carbon atom.

$$CH_3CH_2COCH_2CH_3 \longrightarrow CH_3CH_2CCl_2CH_2CH_3$$

(i) Heating the above gem-dichloride, 3,3-dichloropentane, with ethanolic KOH produces a compound **S**, C_5H_8. Treating **S** with hydrogen over a nickel catalyst produces pentane.

Draw the displayed formula of **S** and on it, suggest values of **all** C–C–C bond angles. [2]

(ii) If 1,1-dichlorocyclohexane is similarly heated with an excess of ethanolic KOH, a product **T**, C_6H_9Cl, is obtained and no further loss of chlorine occurs. **T** decolourises aqueous bromine.

Suggest the structure of **T** and suggest why the expected loss of both chlorine atoms does not occur. [2]

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(d) Group 2 nitrates such as magnesium nitrate and barium nitrate decompose on heating.

(i) Magnesium nitrate has a decomposition temperature of 330 °C while barium nitrate has a decomposition temperature of 592 °C.

Explain the difference in the decomposition temperatures. [2]

(ii) Compare the decomposition temperature of aluminium nitrate to that of magnesium nitrate.

Explain your answer using data from the *Data Booklet*. [2]

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(e) The value of the solubility product of barium sulfate is 1.08×10^{-10} at 25 °C.

Given that 100 cm^3 of 0.001 mol dm^{-3} barium nitrate and 100 cm^3 of 0.001 mol dm^{-3} sulfuric acid was mixed, calculate the mass of precipitate formed. [2]

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[Total: 18]

3 **(a)** **(i)** State and explain the conditions needed for a gas to behave ideally. [2]

(ii) Sketch and label a graph showing how the volume for a given mass of an ideal gas varies with temperature in Kelvin at constant pressure. [1]

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(b) Globally, ammonia is the second most produced chemical. The equation for the Haber process for manufacturing ammonia is shown.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\ \text{kJ mol}^{-1}$$

A mixture of H_2 and N_2 in the molar ratio 3:1 is added to a sealed vessel and heated to 450 ^{o}C with an iron catalyst. At equilibrium, 40% of the nitrogen had reacted. The total pressure in the vessel is 2.80×10^4 kPa at equilibrium.

(i) Write the expression for the equilibrium constant, K_p, for this reaction. Use your expression to calculate the value of K_p for this reaction. Include its units. [4]

(ii) Given that the Haber process is typically carried out at 450 ^{o}C and 200 atm, explain the rationale behind the conditions used in the Haber process for manufacturing ammonia. [2]

(c) 80% of ammonia produced by the industry is used in agriculture as fertiliser, commonly sold in the form of ammonium nitrate, NH_4NO_3.

On 4th August 2020, in Beirut, Lebanon, approximately 2 750 tonnes of ammonium nitrate which had been improperly stored in a warehouse ignited and this led to significant loss of life, injuries, and destruction. This was the largest non-nuclear explosion in history, leaving a blast radius, *r*, of 62 m.

The decomposition of solid ammonium nitrate is shown.

$$2NH_4NO_3(s) \longrightarrow 2N_2(g) + O_2(g) + 4H_2O(g)$$

1 tonne = 1 000 kg

(i) Assuming that the explosion expands outwards in a hemisphere where volume = $\frac{2}{3}\pi r^3$ and reaches 15 atm pressure at the edge of the blast radius, calculate the temperature of the gases within the blast radius. [2]

(ii) During the decomposition of solid ammonium nitrate, a side reaction occurs as shown.

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

Draw the 'dot-and-cross' diagram for N_2O. [1]

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(d) Ammonium nitrate can also be found in instant cool packs for treating sports injuries. A typical instant cool pack contains 150 cm^3 of water which is separated from the solid ammonium nitrate by a thin film. When the film is broken, the ammonium nitrate dissolves, and the water reaches a temperature of 0 ^oC.

The equation for the dissolution of ammonium nitrate is shown.

$$NH_4NO_3(s) + aq \longrightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +25.7 \text{ kJ mol}^{-1}$$

(i) Define the term *enthalpy change of solution*. [1]

(ii) Calculate the mass of ammonium nitrate needed to bring an instant cool pack from 25 ^oC to 0 ^oC. [2]

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(e) Lebanon exports perfumes. Geraniol, **E**, $C_{10}H_{18}O$, is commonly found in essential oils used in perfumes.

E does not react with 2,4-dinitrophenyhydrazine but reacts with hydrogen in the presence of heated nickel catalyst to form **F**, $C_{10}H_{22}O$. **E** reacts with warm acidified $K_2Cr_2O_7$ to form **G**, which when purified, forms a gas **H** with aqueous sodium carbonate.

E reacts with hot acidified $KMnO_4$ to form **J**, C_3H_6O, and **K**, $C_5H_8O_3$ as the only organic products. **J** and **K** both give a yellow precipitate with alkaline aqueous iodine. **K** forms **H** with aqueous sodium carbonate and does not rotate plane polarised light.

Deduce the structures of **E** to **K**, identify the reactions involved and explain your reasoning. [10]

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[Total: 25]

Section B

Answer **one** question from this section.

4 Copper, nickel, manganese and iron are transition elements.

(a) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with nickel and silver as minor impurities. It contained no other metal.

In order to purify it, this alloy was made the anode of an electrolytic cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

(i) Explain, with reference to relevant $E^\ominus$ values, what happens to the nickel and silver impurities during the purification procedure. [2]

A current of 3.50 A was passed through the cell for 11 minutes 47 seconds, and the electrodes were removed, washed, dried and finally weighed. It was found that anode had lost 0.947 g.

After filtering it off and drying it, the deposit under the anode weighed 0.0497 g.

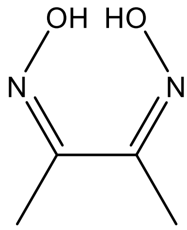
On adding an excess of dimethylglyoxime to the electrolyte, the highly insoluble red complex with formula $Ni(C_4H_7N_2O_2)_2$, molar mass 288.7 g mol^{-1}, was precipitated. Its mass was 0.587 g.

(ii) Calculate the maximum increase in mass of the cathode. [1]

(iii) Calculate the actual masses of copper, nickel and silver removed from the alloy. [3]

In 1905, L. A. Chugaev suggested the use of dimethylglyoxime as a specific reagent for the qualitative and quantitative determination of nickel, earning dimethylglyoxime the nickname of “Chugaev’s reagent”. It is a bidentate ligand.

The structure of Chugaev’s reagent is given below.



(iv) Suggest a reagent that reacts with butanedione to form Chugaev’s reagent. [1]

(v) State the coordination number of Ni in the $Ni(C_4H_7N_2O_2)_2$ complex. [1]

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(b) Potassium manganate(VII) plays an important role in analytical chemistry.

The figures below show the standard electrode potentials, $E^\ominus$, of various redox half reactions. For example, in Fig. 4.1, the line shows that the $E^\ominus$ for MnO_4^-/Mn^{2+} half-cell is +1.52 V.

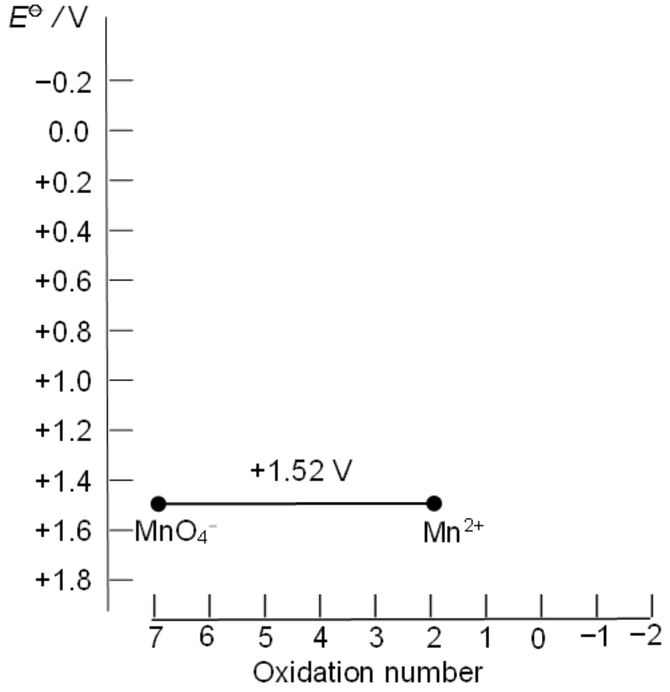

Fig. 4.1

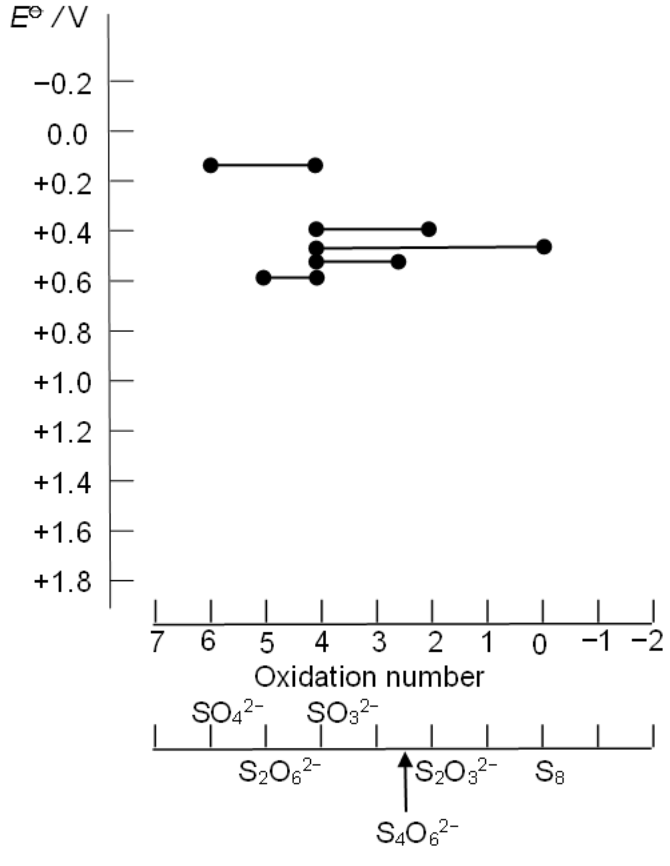

Fig. 4.2

(i) Use Fig. 4.2 to predict what sulfur-containing species might be formed from sodium sulfite, Na_2SO_3, when it is titrated with acidified potassium manganate(VII) solution. Give a reason for your prediction. [2]

(ii) Given that the two sulfur atoms in $S_2O_6^{2-}$ are indistinguishable, draw the structure of $S_2O_6^{2-}$. [1]

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(c) In another experiment, a solution of iron(II) sulfate was titrated against 0.020 mol dm^{-3} acidified potassium manganate(VII), maintaining a constant pH throughout the titration. The electrode potential was measured against a standard hydrogen electrode and the following data was obtained.

volume of $KMnO_4$(aq) added / cm^3	$E^{\ominus}$ at 25 °C / V
20.0	+0.734
40.0	+0.760
60.0	+0.780
80.0	+0.806
120.0	+1.512
140.0	+1.515

The electrode potential of the mixture at 25 °C, $E^{\ominus}$, is given by the expression

$$E \;=\; E^{\ominus}(Fe^{3+}/Fe^{2+}) \;+\; 0.0257 \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

(i) Using the given expression and relevant information from the *Data Booklet*, determine the value of E when $[Fe^{2+}]$ and $[Fe^{3+}]$ are equal. [1]

(ii) Estimate the volume of $KMnO_4$ added which corresponds to your value of E in **(c)(i)**. [1]

(iii) Explain why there is a rapid increase in the value of E between 80.0 cm^3 and 120.0 cm^3 of $KMnO_4$. [1]

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(d) Lanthanum is a Period 6 transition element. It exhibits an oxidation state of +3 in all of its compounds. Lanthanum iodate(V) is stable at room temperature, but when heated to 560 °C it decomposes, as shown in reaction 1.

Reaction 1 lanthanum iodate(V) ⟶ lanthanum periodate(VII) + oxygen + iodine

There are three common periodate(VII) ions that occur in compounds: IO_4^-, IO_5^{3-} and IO_6^{5-}. The ion contained in the lanthanum periodate(VII) product of reaction 1 can be deduced by determining the stoichiometry of the reaction in the following way.

- A 1.50 g sample of lanthanum iodate(V) was heated at 560 °C in a closed vessel until no further reaction takes place.
- The iodine produced was dissolved in hexane and titrated against 0.300 mol dm^{-3} sodium thiosulfate solution.

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

The end-point occurs when 18.10 cm^3 of 0.300 mol dm^{-3} sodium thiosulfate was added.

(i) State the shape of IO_4^-. [1]

(ii) State the colour of iodine dissolved in hexane. [1]

(iii) Use the titration results to show that the IO_3^- : I_2 molar ratio in this reaction is 5:2. Hence write a balanced ionic equation showing the decomposition of IO_3^- to I_2, O_2 and the appropriate periodate(VII) ion. [3]

(iv) Construct the full chemical equation for the decomposition of lanthanum iodate(V). [1]

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5 Cobalt and chromium are transition elements.

(a) A cobalt-chrome alloy is a metal alloy of cobalt and chromium.
A sample of this alloy was dissolved in dilute HC*l* to form a solution containing 1.55×10^{-2} mol dm^{-3} of Cr^{3+}(aq) and 5.77×10^{-3} mol dm^{-3} of Co^{2+}(aq).
Aqueous NaOH was then added slowly to 25 cm^3 of the solution.

Using the K_{sp} information below, show that the addition of NaOH will not allow for the separation of the Cr^{3+} and Co^{2+} metal cation ions in the above solution.

compound	K_{sp}
$Cr(OH)_3$	1.60×10^{-20}
$Co(OH)_2$	5.92×10^{-15}

[3]

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(b) Given that

$$Co(NH_3)_6^{3+} + e^- \rightleftharpoons Co(NH_3)_6^{2+} \quad E^\ominus = +0.11\ V$$

Explain why the reducing power of Co(II) increases in the presence of excess aqueous ammonia. [1]

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(c) There exists two cobalt-containing compounds, **X** and **Y**, which have the same relative formula mass of 259.3. Both contain ammonia and two different halides associated with the cobalt(II) ion.

When excess silver nitrate solution was added to equal masses of each of them, **X** produced 1.31 g of precipitate while **Y** produced 1.00 g of another precipitate.

By considering the ratio of the M_r of AgBr to the M_r of AgC*l*, deduce the molecular formula of the cobalt-containing compound and hence, determine the formula of the cation in **Y**. [3]

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(d) The simplest aldehyde, methanal, HCHO, can readily be oxidised to methanoic acid by acidified potassium manganate(VII).

$$5HCHO(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow 5HCOOH(aq) + 2Mn^{2+}(aq) + 6H_2O(l)$$

The reaction proceeds very slowly at room temperature. A small amount of vanadium(III) ions, V^{3+}, are added to the mixture to speed up the reaction.

The half-equation for the reduction of methanoic acid is shown.

$$HCO_2H + 2H^+ + 2e^- \rightleftharpoons HCHO + H_2O \qquad E^\ominus = -0.03\text{ V}$$

Use data from the *Data Booklet* and the half-equation given to construct equations and justify the two-step mechanism of the reaction. [3]

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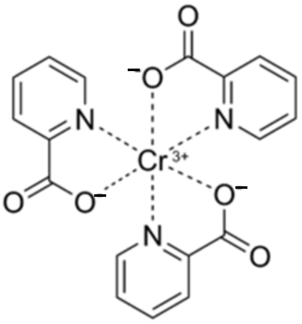
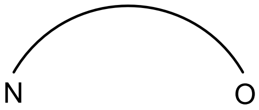
(e) Chromium is used in certain nutritional supplements.

(i) Chromium(III) picolate is sold as a nutritional supplement to treat type 2 diabetes and promote weight loss.



chromium(III) picolate

It exists as two stereoisomers. Specify the type of stereoisomerism and draw either stereoisomer. You may represent each ligand as shown below.



[2]

(ii) By quoting and using relevant $E^\ominus$ values from the *Data Booklet*, explain why the blue solution, containing Cr^{2+}(aq), obtained by dissolving chromium metal in dilute sulfuric acid slowly turns green even in the absence of air. [2]

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(f) Copper is also used in certain nutritional supplements.

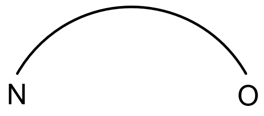
Copper(II) glycinate is used as a dietary supplement for copper in animal feeds.

Copper(II) glycinate is formed when the α-amino acid glycine (R = H) is added to an aqueous solution of copper(II) ethanoate.

A blue precipitate of the square pyramidal copper(II) glycinate ($C_4H_{10}CuN_2O_5$) is formed which contains one coordinated water molecule.

When heated, this precipitate undergoes isomerisation between three different stereoisomers. However, throughout the isomerisation, the water molecule remains in the axial position.

Draw all three stereoisomers and specify which is the pair of cis-trans isomers. You may represent each glycine ligand as shown below.



[3]

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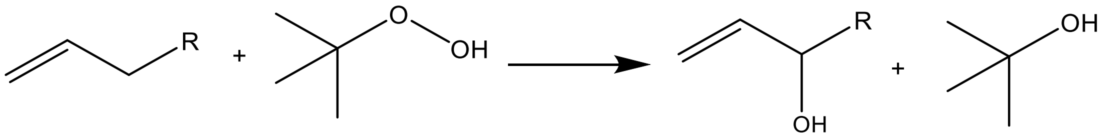
(g) The Kharasch–Sosnovsky reaction is the radical oxidation of an allylic alkene to an allylic alcohol using a copper catalyst and a peroxide.



The mechanism is believed to involve radical intermediates and copper in its +1, +2 and +3 oxidation states, via four steps.

The first two steps of the mechanism are provided below.

Step 1: $Cu(I) + HO–OC(CH_3)_3 \rightarrow Cu(II)–OH + (CH_3)_3CO\bullet$

Step 2: $(CH_3)_3CO\bullet + CH_2=CH–CH_2R \rightarrow (CH_3)_3COH + CH_2=CH–\overset{\bullet}{C}HR$

(i) Draw step 2 of the mechanism. Show all relevant curly arrows. [1]

(ii) $CH_2=CHCHR–Cu(III)–OH$ is an intermediate formed in step 3, and reacts in step 4.

Write the equations for steps 3 and 4. [2]

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.