HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**14S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9647/02

Paper 2 Structured Questions

2 September 2015

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1) Write your **name**, **CT group, centre number** and **index number** clearly in the spaces at the top of this page.
2) Answer **all** questions in the spaces provided in this Question Paper.

INFORMATION FOR CANDIDATES

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

A Data Booklet is provided.

Do not use staples, paper clips, highlighters, glue or correction fluid.

You may use a calculator.

You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
1	**/ 12**
2	**/ 10**
3	**/ 17**
4	**/ 9**
5	**/ 9**
6	**/ 15**
Deductions	
Total	**/ 72**

Calculator Model:

1 Planning (P)

When excess ammonia is added to an aqueous solution containing transition metal ion M^{2+}, a complex ion $[M(NH_3)_n]^{2+}$, where *n* has a maximum value of 6, is formed.

When this solution is shaken with trichloromethane (density = 1.49 g cm^{-3}), an equilibrium mixture consisting of two immiscible layers is obtained. The aqueous layer contains the complex ion and uncomplexed 'free' ammonia while the organic layer contains only 'free' ammonia.

The ratio of the concentrations of 'free' ammonia in the two immiscible layers at equilibrium is a constant, known as the partition ratio, *K*.

$$NH_3(aq) \rightleftharpoons NH_3(\text{trichloromethane}) \qquad K = \frac{[NH_3(\text{trichloromethane})]}{[NH_3(aq)]} = 0.4$$

To determine the value of *n* in $[M(NH_3)_n]^{2+}$, the equilibrium mixture is prepared. A sample is withdrawn from the organic layer and the 'free' ammonia is titrated with standard hydrochloric acid. As the aqueous acid is unable to dissolve in the organic layer, an equal volume of water is added to the organic layer before titration so that the 'free' ammonia can be neutralised by the acid.

The titration results can be used to determine the concentration of 'free' ammonia in the organic and aqueous layers. The amount of ammonia used to form the complex ion and hence the value of *n* can then be determined.

(a) Explain why the value of the partition ratio, *K*, of ammonia between trichloromethane and water is less than 1.

....

....[1]

(b) With the aid of an equation, explain why the concentration of 'free' ammonia in the aqueous layer cannot be determined by titrating the aqueous layer with standard hydrochloric acid.

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....[2]

(c) You are required to write a plan to determine the formula of the complex ion, $[M(NH_3)_n]^{2+}$.

You are provided with:

- aqueous ammonia, of concentration 1.0 mol dm^{-3}
- aqueous M^{2+}, of concentration 0.10 mol dm^{-3}
- hydrochloric acid, of concentration 0.050 mol dm^{-3}
- trichloromethane
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should give details of:

- the preparation of the equilibrium mixture containing the complex ion using **50.0 cm³** of 0.10 mol dm^{-3} M^{2+} and appropriate volumes of aqueous ammonia and trichloromethane;
- withdrawal of sample(s) from the organic layer;
- the titration of the 'free' ammonia in the organic layer.

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……………………………………………………………………………………………………[7]

(d) In one experiment, an equilibrium mixture was prepared using 1 dm^3 of 1.0 mol dm^{-3} aqueous ammonia, 1 dm^3 of 0.10 mol dm^{-3} aqueous M^{2+} and 1 dm^3 of trichloromethane. The concentration of 'free' ammonia in the organic layer was found to be x mol dm^{-3}.

Express the concentration of 'free' ammonia in the aqueous layer and the value of n in terms of x.

[2]

[Total: 12]

For Examiner's use

2 This question is about the chemistry of Kuro Tamago (lit. “black eggs”), a local specialty of egg hard-boiled in the hot springs of Owankundai, Japan.

When raw eggs are boiled in hot spring water of Owankundai (pH = 9.2), a chemical reaction between aqueous iron(II) and sulfide ions (from hydrogen sulfide, H_2S), produces a black solid, FeS, that adheres to the porous egg shells.

Iron sulfide is precipitated by the following reaction.

reaction 1: $Fe^{2+}(aq) + S^{2-}(aq) \rightarrow FeS(s) \qquad \Delta H^{\ominus}_{ppt}$

Hydrogen sulfide gas from volcanic systems is released into the hot spring water and behaves as a dibasic (diprotic) weak acid.

$$H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

In a saturated solution of hydrogen sulfide,

$$[H^+]^2[S^{2-}] = 1.0 \times 10^{-23}\ mol^3\ dm^{-9}$$

(a) **(i)** Calculate the maximum concentration of sulfide ions present in hot spring water.

[2]

(ii) Hence, calculate the minimum concentration of Fe^{2+} present in hot spring water in order for precipitation to occur.

(K_{sp} of FeS = $4.9 \times 10^{-18}\ mol^2\ dm^{-6}$)

[1]

(b) Use the following data, together with relevant data from the *Data Booklet*, to calculate the $\Delta H^{\ominus}_{\text{ppt}}$ for reaction 1.

standard enthalpy change of formation of FeS(s)	–102 kJ mol^{-1}
standard enthalpy change of atomisation of Fe(s)	+415 kJ mol^{-1}
standard enthalpy change of atomisation of S(s)	+279 kJ mol^{-1}
sum of first two electron affinities of sulfur	+337 kJ mol^{-1}
enthalpy change of hydration of Fe^{2+}(g)	–1981 kJ mol^{-1}
enthalpy change of hydration of S^{2-}(g)	–1372 kJ mol^{-1}

[2]

(c) When a precipitate is formed, $\Delta G^{\ominus}_{\text{ppt}}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{\text{ppt}} = 2.303RT \log K_{\text{sp}}$$

(i) Use the data given in **(a)(ii)** to calculate $\Delta G^{\ominus}_{\text{ppt}}$, in kJ mol^{-1}, for FeS.

[1]

(ii) Use your answer in **(b)** and **(c)(i)** to calculate $\Delta S^{\ominus}_{\text{ppt}}$, in J mol^{-1} K^{-1}, for the formation of the precipitate FeS(s) at 298 K.

[2]

(iii) Explain the significance of the sign of your answer in **(c)(ii)**.

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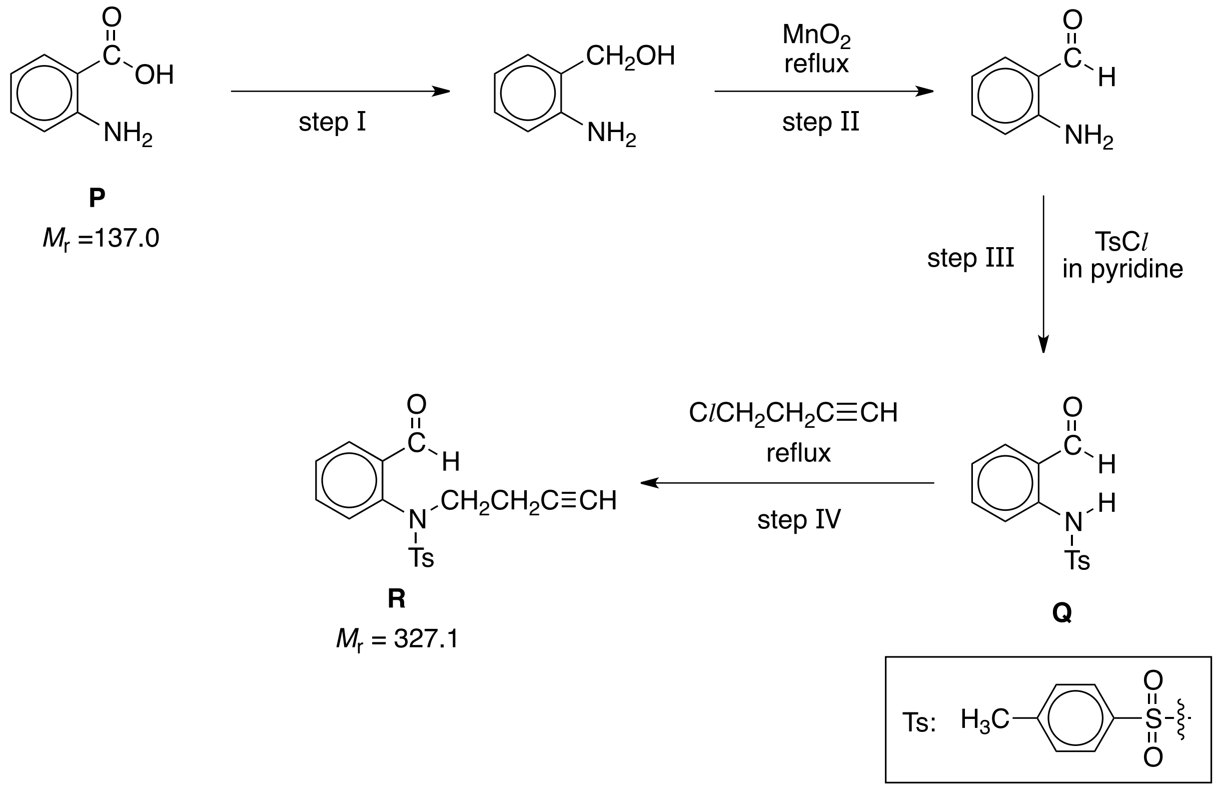
[Total: 10]

3 A student synthesised compound **R** using the following scheme.



(a) Given that each step gave a yield of 50.0%, determine the mass of compound **P** required to produce 1.00 g of compound **R**.

[1]

(b) State the reagents and conditions for step I.

....[1]

(c) MnO_2 was used as an oxidising agent in step II.

(i) State the oxidation state of Mn in MnO_2.

....[1]

(ii) At the end of the reaction in step II, MnO_2 was converted to Mn^{2+}.

State the full electronic configuration of Mn^{2+}.

……………………………………………………………………………………………[1]

(iii) The oxidation states of Mn in MnO_2 and Mn^{2+} are different.

Explain briefly why Mn exhibits variable oxidation states.

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……………………………………………………………………………………………[1]

(iv) $KMnO_4$ cannot be used as the oxidising agent in step II in place of MnO_2.

Explain the above statement, supporting your answer with relevant values from the *Data Booklet*.

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……………………………………………………………………………………………[2]

(v) Suggest another set of reagents and conditions that could be used in step II.

……………………………………………………………………………………………[1]

(d) **(i)** Given that the mechanism in step IV is a nucleophilic substitution, draw the mechanism, showing clearly any curly arrows, charges, dipoles and lone pairs where relevant.

[2]

(ii) No significant reaction was detected when step IV was carried out at room temperature. The student observed that the increase in temperature increased the rate of reaction in step IV.

With the aid of a sketch of the Boltzmann distribution, explain these observations.

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…………………………………………………………………………………………………[4]

(iii) Predict the effect on the rate of reaction when $BrCH_2CH_2C{\equiv}CH$ was used in place of $C\textit{l}CH_2CH_2C{\equiv}CH$ in step IV. Explain your answer.

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…………………………………………………………………………………………………[1]

(e) The student found the addition of K_2CO_3 in step IV reduced the amount of time required for the reaction.

(i) Given that K_2CO_3 reacted with compound **Q** in an acid–base reaction, write an ionic equation for this reaction.

…………………………………………………………………………………………………[1]

(ii) It was known that the nature of the nucleophile affected the rate of the reaction in step IV.

Based on your answer for **(e)(i)**, explain how the addition of K_2CO_3 in step IV increased the rate of reaction.

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…………………………………………………………………………………………………[1]

[Total: 17]

4 **(a)** A zinc-air battery uses oxygen gas in the air as an oxidising agent and zinc metal as a reducing agent. Zinc is oxidised to a soluble zincate, $Zn(OH)_4^{2-}$. The electrolyte circulated through the battery is NaOH(aq).

(i) Give the equation for the reactions which occur at the anode and cathode respectively.

Anode: ……………………………………………………………………………………

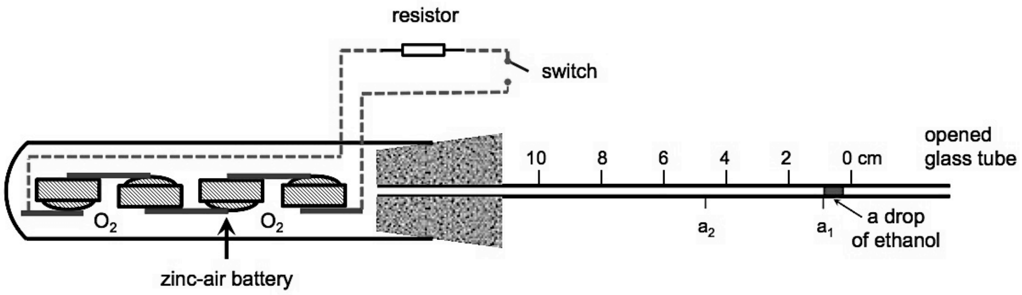
Cathode: …………………………………………………………………………………

[2]

(ii) Given that the standard cell potential is +1.65V, calculate the standard electrode potential, $E^{\ominus}_{Zn(OH)_4^{2-}/Zn}$.

[1]

(iii) Professor Kamata from Gakugei University studied the volume of oxygen consumed by the zinc-air battery using the set-up below. The experiment was conducted under room temperature and pressure.



When the switch was closed, the drop of ethanol began to move from a_1 to a_2.

The following data was collected during the experiment:

Cross sectional area of glass tube = 0.0314 cm^2
Initial glass tube reading, a_1 = 1.00 cm
Current produced, I = 0.0384 A
Time taken for the ethanol to travel from a_1 to a_2, t = 50 s

Calculate the final glass tube reading a_2, in the experiment.

[3]

(b) If present in sufficient concentration in the air, carbon dioxide can cause the formation of zinc carbonate, which can clog the electrode and add resistance to the zinc-air battery. Zinc carbonate and barium carbonate decompose when heated to give similar products.

By quoting appropriate data from the *Data Booklet*, deduce whether zinc carbonate would decompose at a higher or lower temperature than barium carbonate. Explain your answer.

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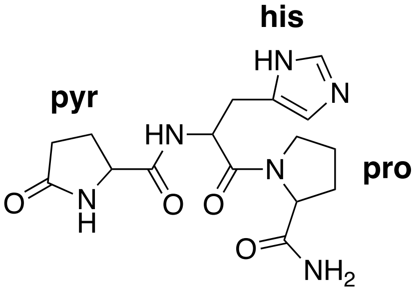
[Total: 9]

5 Thyroliberin and tyrocidine are molecules consisting of amino acids joined together.

(a) The hormone thyroliberin is a tripeptide made up of proline (pro), pyroglutamic acid (pyr) and histidine (his). Interestingly, there are no free carboxylic acid or amine groups at the carbon and nitrogen termini.



thyroliberin

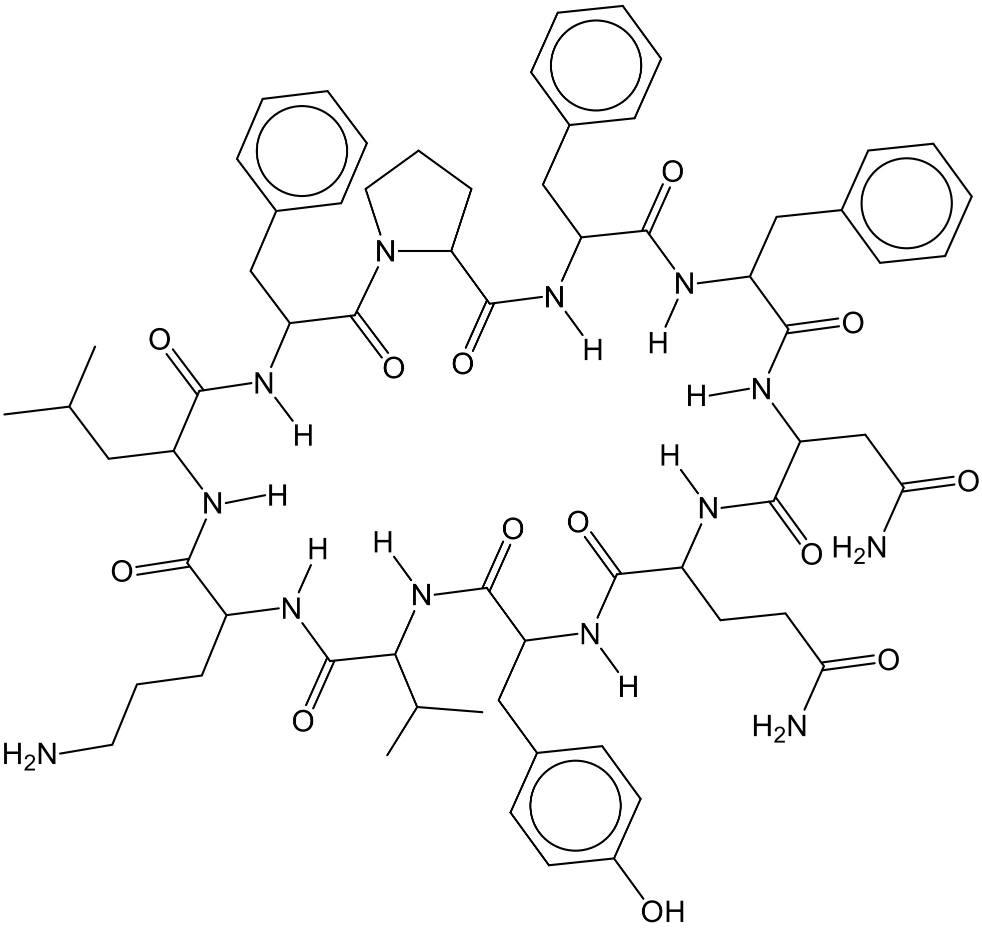
(i) Identify the residue (proline, pyroglutamic acid or histidine) at the carbon terminus.

……………………………………………………………………………………………[1]

(ii) Draw the structure of all nitrogen-containing products when thyroliberin is subjected to prolonged heating with sodium hydroxide.

[3]

(b) Tyrocidine is an antibacterial drug. It was discovered more than 60 years ago.

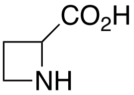


tyrocidine

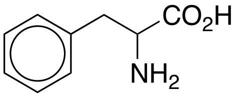
(i) It is suggested that each tyrocidine molecule is folded into a beta-pleated sheet-like structure. In the diagram above, draw and fully annotate an example of the stabilising interaction in the **interior** of the molecule.

[1]

(ii) A drug designer proposes to alter the structure of the tyrocidine molecule by incorporating residues of azetidine-2-carboxylic acid (aze) in place of all phenylalanine residues (phe).



azetidine-2-carboxylic acid (aze)



phenylalanine (phe)

By considering your answer in **(b)(i)**, explain the likely effect that this change will have on the stability of the folded structure.

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…………………………………………………………………………………………[2]

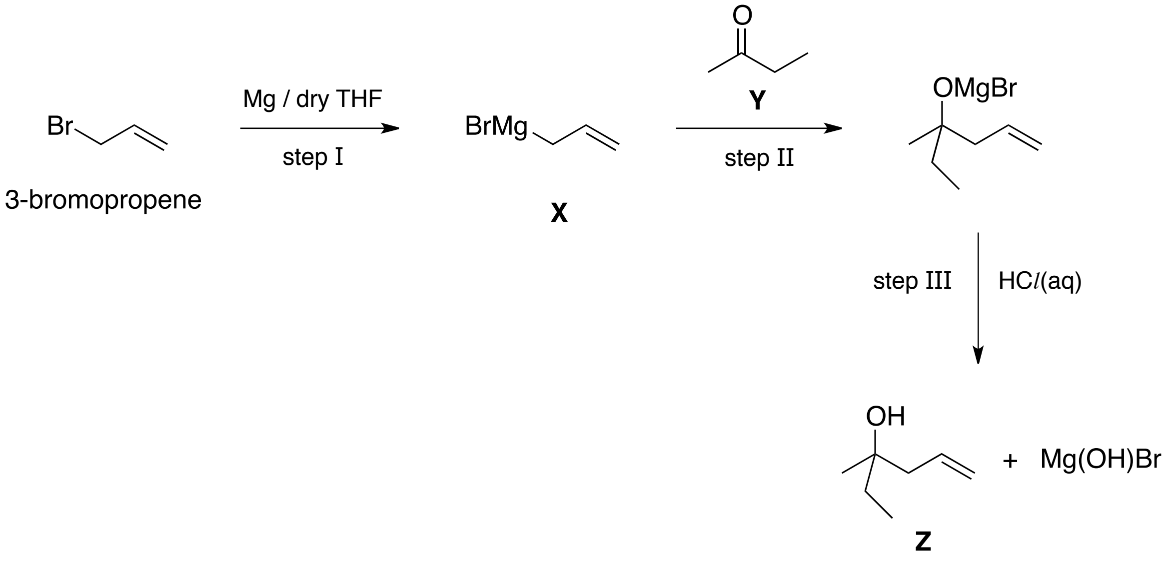
(iii) Tyrocidine works by diffusing into the hydrophobic bacterial cell membrane, thus disrupting the membrane’s integrity. In the diagram on the previous page, circle **one** R group of the molecule which will interact with the membrane to make the disruption possible. State the type of interaction occurring.

Type of interaction: ………………………………………………………………………[2]

[Total: 9]

6 Compound **Z** is an important starting material in the synthesis of antibiotics.

Z could be made from 3-bromopropene and compound **Y** via the Grignard reaction through the following scheme.



(a) The carbon atom bonded to Br in 3-bromopropene is electrophilic in nature. After reacting with Mg in step I to form **X**, it becomes nucleophilic in nature.

Explain why the carbon atom becomes nucleophilic after reacting with Mg in step I.

…………………………………………………………………………………………………[1]

(b) Suggest the type of reaction which occurs in steps II and III.

Step II: …………………………………………………………………………………………..

Step III: ………………………………………………………………………………………

[2]

(c) A small amount of 3-bromopropene, **Y** and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish **Z** from the other two compounds. State what you would observe.

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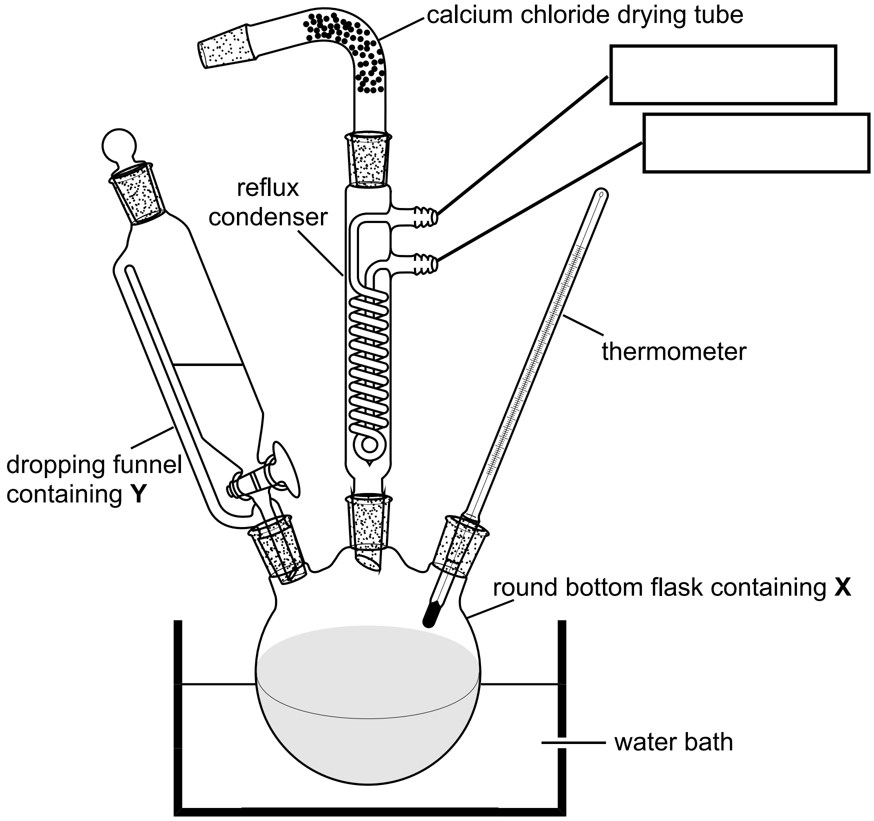
…………………………………………………………………………………………………[2]

The experimental set-up in the synthesis of **Z** is shown below.



(d) **(i)** Fill in the boxes near the reflux condenser with the following two terms:

- water in
- water out

[1]

(ii) A student suggested replacing the calcium chloride drying tube with a stopper cap. Explain briefly whether this is a wise suggestion.

………………………………………………………………………………………………

………………………………………………………………………………………………[1]

(e) Compounds **V** and **W** are structural isomers of **Z**.

The table below shows the results of tests being carried out on **V** and **W**.

Test	Reagents and conditions	Observations	
		V	**W**
1	Fehling's solution	Brick red precipitate formed	Brick red precipitate not formed
2	Aqueous bromine	Orange solution remained	Orange solution remained

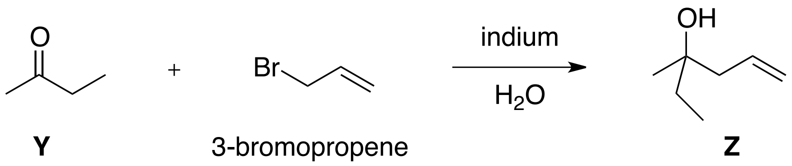
When **V** and **W** were separately subjected to chlorine in the presence of sunlight, the number of monochlorinated products (not including stereoisomers) was found to be three and two respectively.

Suggest a possible structure for **V** and **W** in the boxes below.

V	**W**

[2]

Z could also be produced by the Barbier reaction using indium.



The above reaction takes around 60 min for completion. When zinc is used instead of indium, a much longer reaction time under more vigorous conditions is required.

(f) **(i)** It was postulated that the rate-determining step of the reaction involved the transfer of an electron from the metal surface to 3-bromopropene.

Given that the first ionisation energy of indium is 558 kJ mol^{-1} and together with relevant data from the *Data Booklet*, suggest why a more vigorous reaction condition is required when zinc is used.

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……………………………………………………………………………………………[1]

(ii) A student suggested using sodium metal as the alternative source of metal for the Barbier reaction since its first ionisation energy is close to that of indium. Explain whether the suggestion is feasible.

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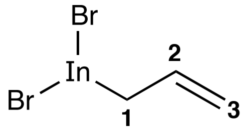
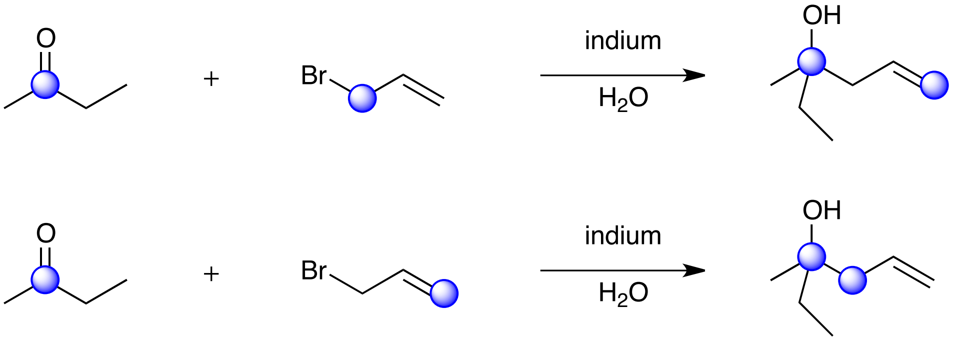
……………………………………………………………………………………………[1]

(iii) The reactive intermediate in the Barbier reaction is thought to have the structure shown below. The carbon atoms have been numbered.



In an attempt to locate the nucleophilic carbon, a ^{13}C isotopic labeling experiment was performed with the following results:

● refers to ^{13}C



Based on the above results, suggest which carbon (1, 2 or 3) in the intermediate is the nucleophilic carbon.

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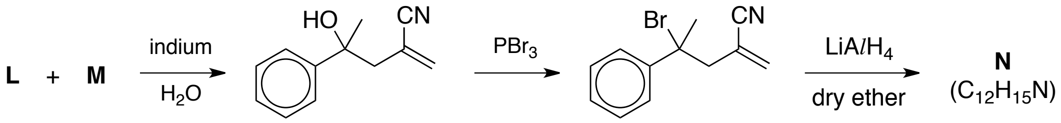
(iv) The reaction scheme below shows a three-step synthesis of compound **N** from compounds **L** and **M**.



Suggest the structures of **L**, **M** and **N** in the boxes below.

L	**M**	**N**

[3]

[Total: 15]