Calculator Model / No.

Name: ____________________ Class: 15S_________ Reg Number: ______

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry 9647/02

Paper 2 Structured Questions **19 September 2016**

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

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

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

Examiner's Use		
Paper 1	MCQ	/ 40
Paper 2	Q1	/ 12
	Q2	/ 17
	Q3	/ 15
	Q4	/ 9
	Q5	/ 7
	Q6	/ 12
	Total	/ 72
Paper 3		/ 80
Total		/ 192
Percentage		
Grade		

This document consists of **28** printed pages

1 Planning (P)

Lead iodide, PbI_2, is a sparingly soluble salt.

$$PbI_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2I^-\,(aq)$$

One method of determining the relative solubility and an approximate value of the solubility product of the salt, K_{sp}, would be through direct observation. Two standard solutions (one of a soluble lead(II) salt, and the other of a soluble iodide salt) in different proportions are mixed and allowed to stand and reach an equilibrium. In some mixtures, the ionic product of the particular solution exceeds the K_{sp} value and precipitation of PbI_2 crystals will occur. In other mixtures, the final concentrations of lead and iodide ions will be such that precipitation does not occur.

The experimental ionic product can be determined for each solution. In the experiment, the value of K_{sp} lies between the ionic product values for solutions with precipitate and those values for solutions without precipitate. The value for K_{sp} can be given as:

Maximum ionic product that does not gives *ppt*	<	K_{sp}	<	*Minimum* ionic product that gives *ppt*

The value for K_{sp} can be estimated by determining the mean between the above two ionic products. In order for a more precise determination of K_{sp}, the concentration of the solution mixtures should be prepared in a manner that would result in a relatively small range of ionic products.

In the experiment, two standard solutions of lead(II) nitrate and potassium iodide are prepared and then diluted appropriately using relevant volumes of the solutions and water. To avoid localised supersaturation that brings about erroneous precipitation, water has to be mixed in first.

In order to predetermine the concentrations required, a student prepared two solutions, **A** and **B**.

Solution **A** contains 2.50 cm^3 of 0.0100 mol dm^{-3} lead(II) nitrate, $Pb(NO_3)_2$ with 5.50 cm^3 of deionised water added.

Solution **B** contains 2.00 cm^3 of 0.0100 mol dm^{-3} potassium iodide, KI.

Mixing these above solutions (at 25°C) produced the yellow precipitate of PbI_2. These solutions provide an ionic product which **just exceeds** the K_{sp} of PbI_2.

(a) Calculate the ionic product of PbI_2 in this given mixture to determine a rough estimate of the K_{sp} value of PbI_2.

[1]

(b) Consider the description of the precipitation experiment given in this question.

Write a plan for such a series of **four** experiments to determine a value for the K_{sp} of PbI_2. In your plan, you should use the same total volume as described when solutions **A** and **B** are mixed.

Your plan should ensure that

- at least two of your experiments do not produce a precipitate
- the estimated range for the value of K_{sp} is relatively small. *(< 10% deviation from the estimated ionic product in* **(a)***).*

You should use the quantities specified in **(a)** *in one of your experiments.*

You may assume that you are provided with

- solid lead nitrate, $Pb(NO_3)_2$
- 0.0400 mol dm^{-3} aqueous potassium iodide, KI,
- deionised water,
- the equipment and materials normally found in a school or college laboratory.

Your plan should include the following.

- details, including quantities, for the preparation of a 100 cm^3 stock solution of 0.0100 mol dm^{-3} of $Pb(NO_3)_2$
- details, including quantities for the preparation of a 100 cm^3 stock solution of 0.0100 mol dm^{-3} of KI
- suitable format summarising appropriate quantities of solutions to be used in each experiment (for four experiments), the corresponding concentrations and calculated ionic products
- outline of all essential experimental procedures
- brief, but specific details on how the K_{sp} value can be estimated from the experiment.

[8]

(c) Explain how the solubility of PbI_2 would change if PbI_2 is dissolved in a solution of hydroiodic acid, HI.

[1]

(d) Lead(II) salts are toxic and prolonged exposure affects the mental development in children. Pb^{2+} ions can be removed from contaminated water through precipitation by adding a soluble salt solution containing the appropriate anion.

The solubility products of some sparingly soluble lead(II) salts, at 25 °C are given in the table below.

Salt	K_{sp}
$PbCO_3$	7.4×10^{-14} mol^2 dm^{-6}
$Pb(IO_3)_2$	3.7×10^{-13} mol^3 dm^{-9}
$Pb_3(PO_4)_2$	7.9×10^{-43} mol^5 dm^{-15}

Calculate the solubility of the above lead(II) salts in *mol dm^{-3}* at 25°C. Hence, state the most effective anion in removing Pb^{2+} from the contaminated water sample.

[2]

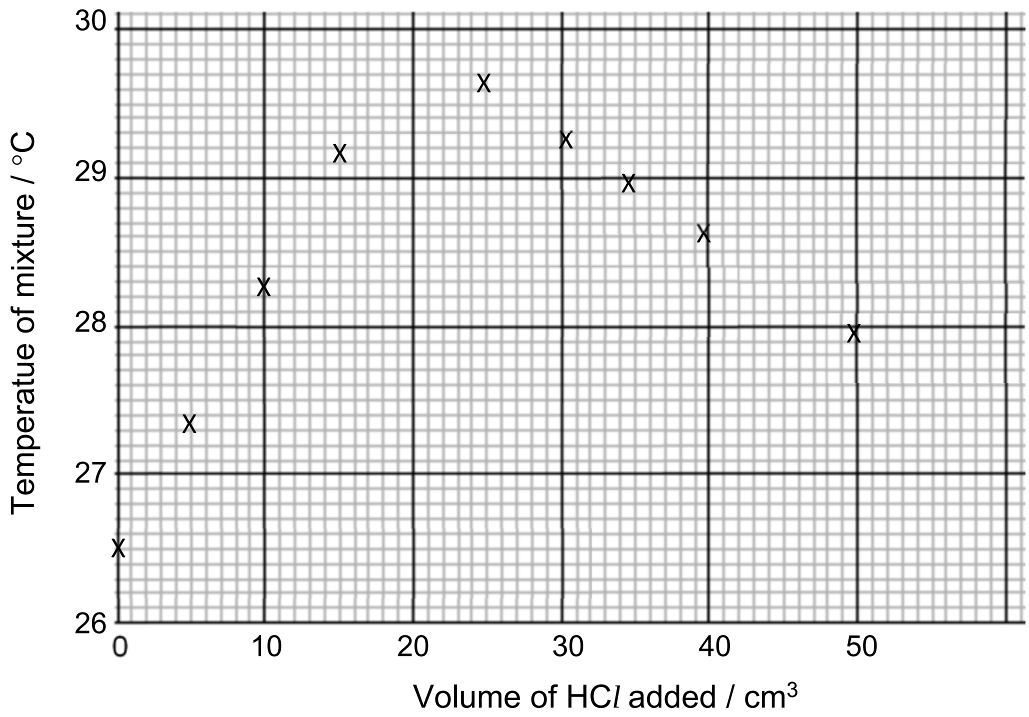
[Total: 12]

2 Amines are a class of compounds that are widely used in both the pharmaceutical and agricultural industry. An amine–containing drug, *Tamiflu* is an effective drug against the H1N1 strain of influenza A virus. Another amine, ethylamine, $CH_3CH_2NH_2$, is widely used in the production of herbicides.

(a) In order to determine the standard enthalpy change of neutralisation, 60.0 cm^3 of 0.370 mol dm^{-3} aqueous ethylamine was placed in a polystyrene cup. Dilute HC*l* was added and after each addition, the mixture was stirred and the temperature noted.

The highest temperature reached was recorded and plotted on the graph below.

Graph of temperature of mixture against volume of HC*l* added



(i) Calculate the initial pH of aqueous ethylamine in the polystyrene cup.

Base dissociation constant of ethylamine is 5.6×10^{-4} mol dm^{-3}.

[1]

(ii) Calculate the concentration of dilute HC*l* used in the experiment.

[1]

(iii) Calculate the enthalpy change of neutralisation for the reaction between HC*l* and ethylamine.

(You may assume the density of the solutions is 1.00 g cm^{-3} and their specific heat capacity is 4.18 J g^{-1} K^{-1}.)

[2]

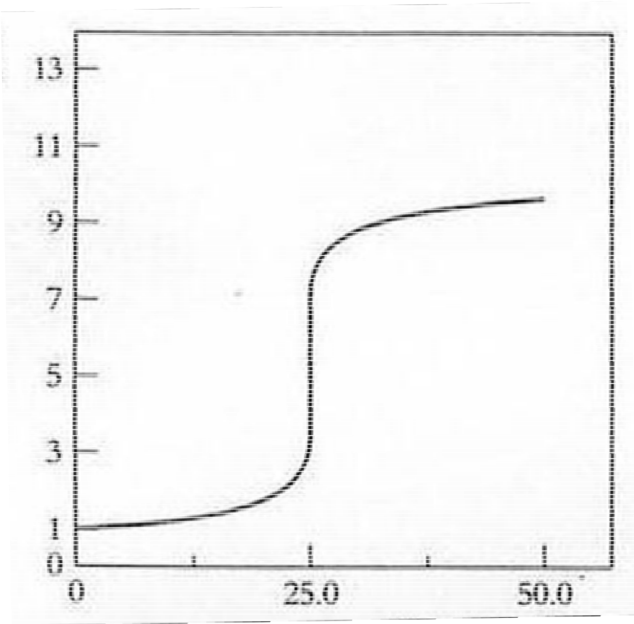
(iv) With reference to your answer in **(a)(iii)**, explain why the temperature of the mixture was reported to be higher when the above experiment was repeated using an aliquot of aqueous potassium hydroxide of the same concentration as that of the ethylamine sample.

[1]

(b) In another experiment, a sample of 0.640 mol dm^{-3} aqueous ethylamine was added to 10.0 cm^3 dilute HNO_3 in a conical flask. The equivalence point can be detected by a distinct colour change brought about by the use of a suitable indicator.

The graph below shows the change in pH of the reaction mixture against the volume of ethylamine added.

pH



Volume of ethylamine added / cm^3

(i) Suggest a suitable indicator for this acid–base titration and state the colour change observed at the equivalence point.

[1]

Indicator: ....

Colour change: ....

(ii) Circle clearly on the graph, the region within which the mixture is acting as a buffer.

[1]

(iii) Write an equation to suggest how the solution in **(b) (ii)** acts a buffer upon the addition of a small amount of aqueous sodium hydroxide.

[1]

(c) An agricultural chemist synthesised ethylamine from ethanal in an industrial laboratory via a two–step procedure as shown in the scheme below.

$$CH_3CHO \xrightarrow[NH_2OH,\ H^+]{\textbf{I}} CH_3CH{=}NOH \xrightarrow{\textbf{II}} CH_3CH_2NH_2$$

(i) Suggest the type of reactions for both steps and the reagents and conditions for step **II**.

[2]

Step	Type of reaction	Reagents and conditions
I		
II		

(ii) Suggest a chemical test that the chemist can perform to confirm that the procedure is complete.

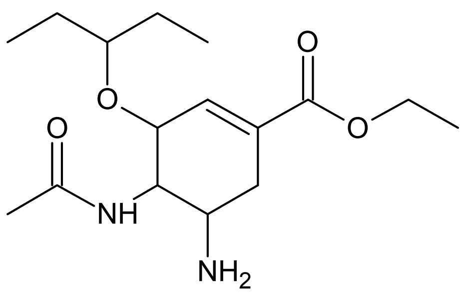
[1]

(d) Use the following data and relevant data from the *Data Booklet* to construct an energy cycle to calculate the enthalpy change of formation of $CH_3CH_2NH_2(l)$.

Enthalpy change of vapourisation of $CH_3CH_2NH_2(l)$ = +29 kJ mol^{-1}
Enthalpy change of atomisation of C(s) = +715 kJ mol^{-1}

[3]

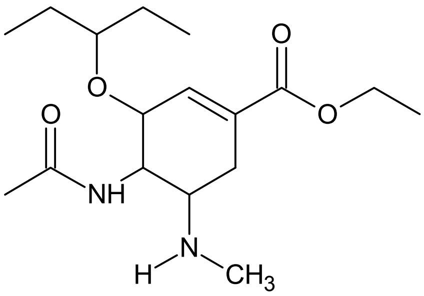
(e) The structure of *Tamiflu* is shown below.



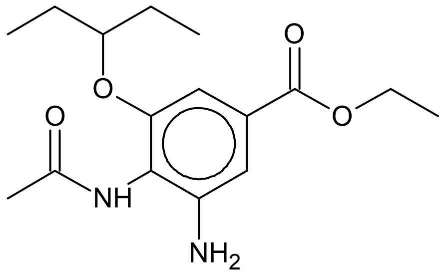
(i) Name the two nitrogen–containing functional groups present in *Tamiflu.*

[1]

(ii) Compound **Q** is a derivative of *Tamiflu* while compound **R** is an aromatic compound with similar functional groups as *Tamiflu*.



compound **Q**



compound **R**

Describe and explain the relative basicities of the following compounds:

- Compound **Q** and *Tamiflu*

[1]

- Compound **R** and *Tamiflu*

[1]

[Total: 17]

3 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) When potassium iodide reacts with concentrated sulfuric acid, violet vapour is observed and a pungent gas is detected.

(i) Write a chemical equation for the reaction to account for the formation of the violet vapour.

[1]

(ii) When potassium bromide reacts with concentrated sulfuric acid, different observations are made.

By quoting suitable values from the *Data Booklet*, explain the difference in the observations.

[2]

(iii) In order to prepare HBr as the only bromine–containing product from KBr, concentrated H_3PO_4 should be used instead of concentrated H_2SO_4.

Suggest a plausible reason for this. Write a balanced equation for this reaction.

[2]

(b) Precipitates are formed when aqueous silver nitrate is added to separate tubes containing aqueous potassium chloride, aqueous potassium bromide and aqueous potassium iodide.

(i) Describe the effect of adding concentrated NH_3 to **each** of the resulting mixtures.

[1]

Tube containing KCl ______________________________

Tube containing KBr ______________________________

Tube containing KI ______________________________

(ii) Provide a qualitative explanation to substantiate your answer for observations in the tube containing KI.

[2]

(c) 5.0×10^{-4} mol of a bromate salt containing the $BrO_4^{\boldsymbol{n}-}$ anion was added to 20.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions. The remaining solution was made up to 250 cm^3 with distilled water.

A 25.0 cm^3 aliquot of the resultant solution required 40.0 cm^3 of 0.010 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Calculate the value of ***n***.

[2]

(d) When heated in chlorine, magnesium forms magnesium chloride. Magnesium can also be heated in air to give magnesium oxide. Similarly, aluminium and zinc can be vapourised and reacted with air to form the respective oxides.

(i) Describe the reactions, if any, of magnesium chloride and magnesium oxide with water, suggesting the pH of the resulting solutions and writing equations where appropriate.

[3]

(ii) Zinc oxide has acid–base properties that are similar to aluminium oxide. Write equations for **two** reactions which demonstrate these properties of zinc oxide.

[2]

[Total: 15]

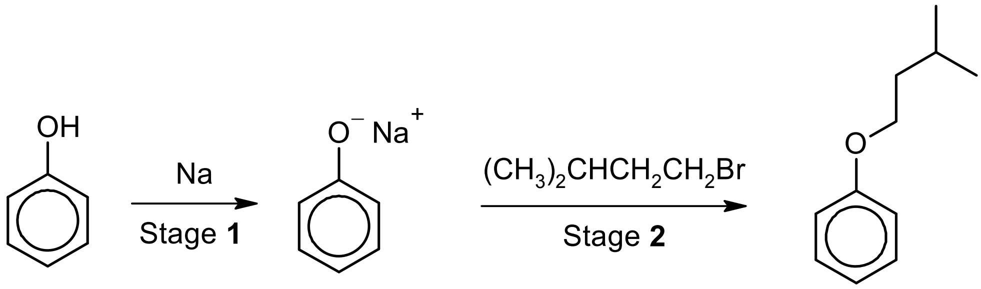
4 The *Williamson* reaction is widely used in the laboratory and industrial synthesis of ethers. It is the simplest and most popular method of preparing ethers.

In a typical *Williamson* reaction, an alkoxide ion is prepared *in situ* and is reacted with a halogenoalkane according to the general equation shown below.

$$RO^{-}Na^{+} + R'X \longrightarrow ROR' + NaX$$

where R,R' are alkyl groups and X is Br or C*l*.

The following experimental procedure details the synthesis of (3–methylbutoxy)benzene using the *Williamson* reaction.

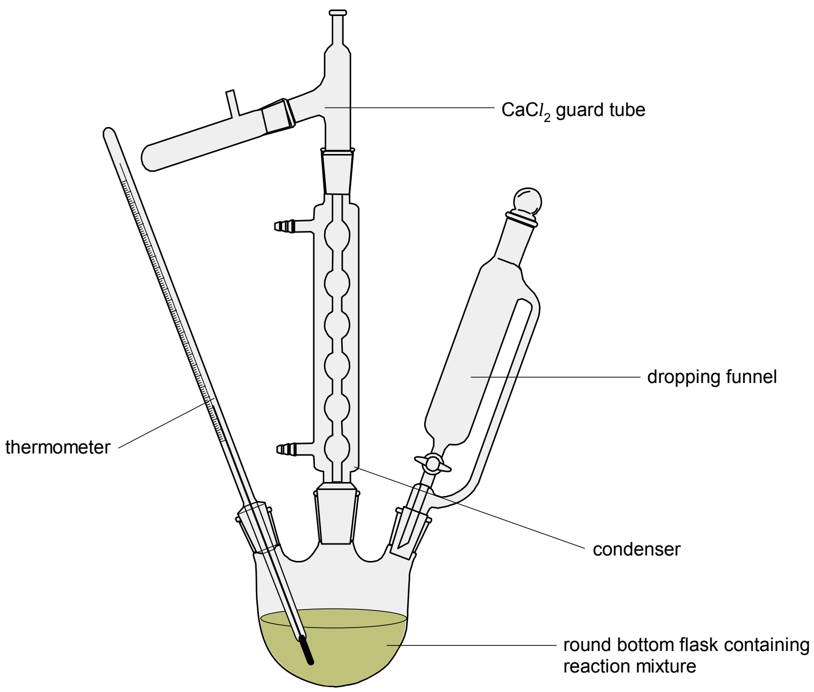


(3-methylbutoxy)benzene

PROCEDURE:

Preparation of (3-methylbutoxy)benzene

1 2.90 g of sodium metal is added to a dry round-bottom flask equipped with a dropping funnel and a condenser. This apparatus set-up is shown below. The set-up is protected from atmospheric moisture with the use of a calcium chloride guard tube.



2 Prepare an ethanolic solution containing 11.8 g of phenol. Add dropwise to the reaction mixture using the dropping funnel. If the reaction becomes too vigorous, cool the flask with a cold towel until the reaction is again under control.

3 Transfer 20.0 cm^3 of 1-bromo-3-methylbutane to the dropping funnel and add it to the flask slowly over 3 – 4 minutes.

4 Boil the reaction mixture gently over a water bath for 30 minutes.

5 Evaporate as much of the ethanol solvent as possible.

Purification of (3-methylbutoxy)benzene

6 Add about 20 cm^3 of water to the residue in the flask and separate the organic layer using a separating funnel.

7 Wash the organic layer with sodium hydroxide.

8 Then, wash the organic layer with dilute sulfuric acid and water again.

9 Add anhydrous magnesium sulfate to the organic layer.

10 Distill the organic layer to purify (3-methylbutoxy)benzene at a suitable temperature.

Table 4: Physical Properties of the reagents and the organic product

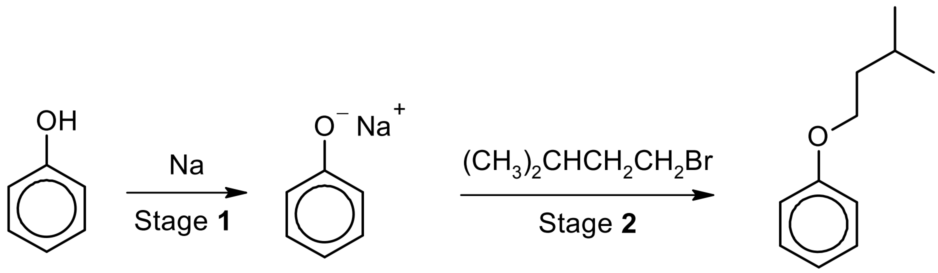
substance	formula	molar mass / g mol^{-1}	physical state at r.t.p.	density / g cm^{-3}	solubility in water	boiling point / °C
ethanol	C_2H_5OH	46	liquid	0.789	soluble	78
phenol	C_6H_5OH	94	solid	1.07	insoluble	182
1–bromo–3–methylbutane	$C_5H_{11}Br$	151	liquid	1.21	insoluble	120
(3–methylbutoxy)benzene	$C_{11}H_{16}O$	164	liquid	0.91	insoluble	216
sodium bromide	NaBr	103	solid	3.21	soluble	–
water	H_2O	18	liquid	1.00	–	100

(a) **(i)** Suggest why it is necessary to protect the apparatus set–up from moisture using the calcium chloride guard tube in step **1**.

[1]

(ii) Determine the theoretical yield (in g) of (3–methylbutoxy)benzene for this reaction. You may assume that the reaction between sodium and phenol to form phenoxide in stage **1** is complete.

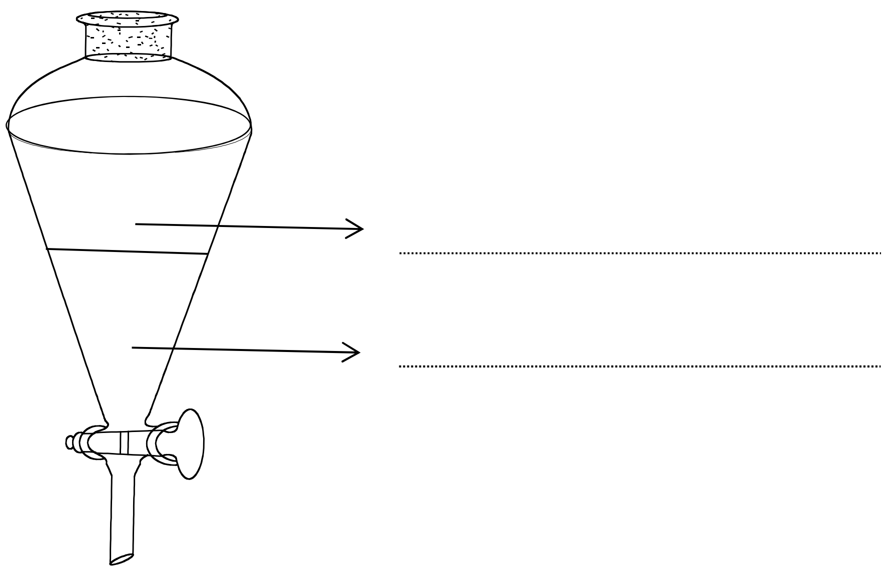
[2]



(3-methylbutoxy)benzene

(iii) On the diagram of the separating funnel below, label the two layers that will be observed after step **6.**

[1]



(b) Other than the crude product, the organic layer (Step **6**) also contains several impurities. These impurities comprises of unreacted reactants, by–products or products from undesired reactions.

In the purification of the crude product (Steps **6** – **9**), the impurities are removed from the crude product with each subsequent addition of chemicals.

(i) Suggest the impurity removed by each of the chemicals below.

[1]

1 sodium hydroxide ____________________

2 anhydrous magnesium sulfate ____________________

(ii) With reference to the data provided in **Table 4**, account for the observed boiling points of ethanol and the product, (3–methylbutoxy)benzene.

In your answer, you should state the predominant type of interactions present in the two compounds.

[2]

(iii) The final stage in the purification process is the distillation of the crude product (Step **10**).

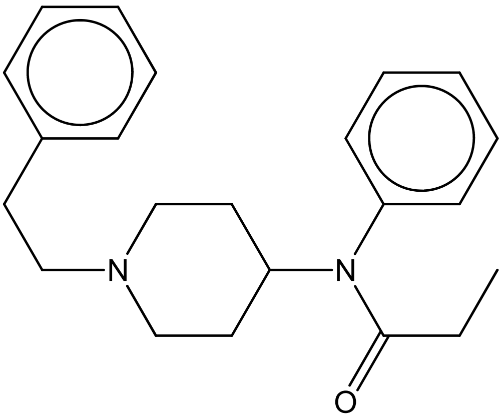
Suggest why distillation is a suitable technique to obtain a pure sample of (3–methylbutoxy)benzene. Propose a suitable range of temperature for the distillation set–up.

[2]

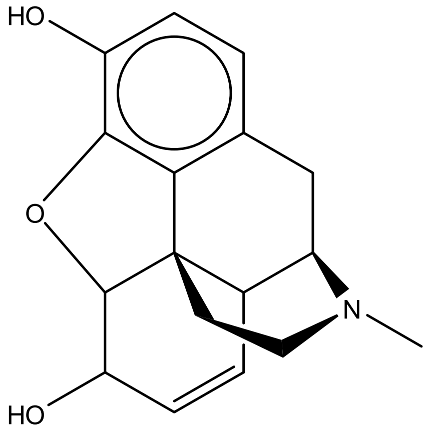
[Total: 9]

5 On 21st April 2016, famed American pop artiste, Prince Rogers Nelson died of an accidental overdose of the drug, *fentanyl*.

Fentanyl, an opioid analgesic was first synthesised in 1960. It was primarily used for pain relief in clinical practice. Its efficacy is about 100 times that of *morphine*.

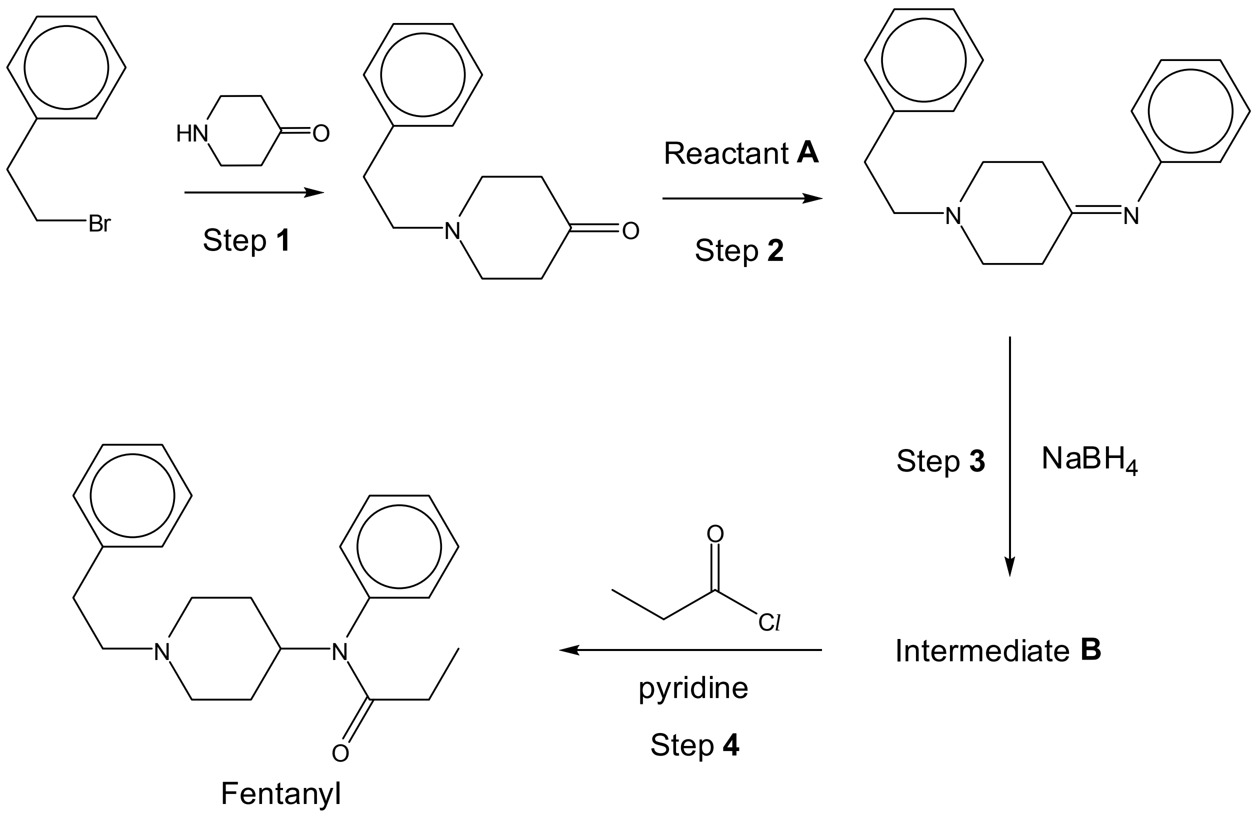


Fentanyl



Morphine

Fentanyl can be synthesised from 2–bromoethylbenzene following the reaction scheme below.



(a) Name and outline the mechanism for the reaction in step **1**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

(b) Suggest the displayed formula of reactant **A** in Step **2**.

[1]

(c) Propose the structure of intermediate **B**.

[1]

(d) Propanyl chloride is used in step **4** in the synthesis of *fentanyl*.

Explain why the use of propanoic acid as a replacement in step **4** is not suitable.

[1]

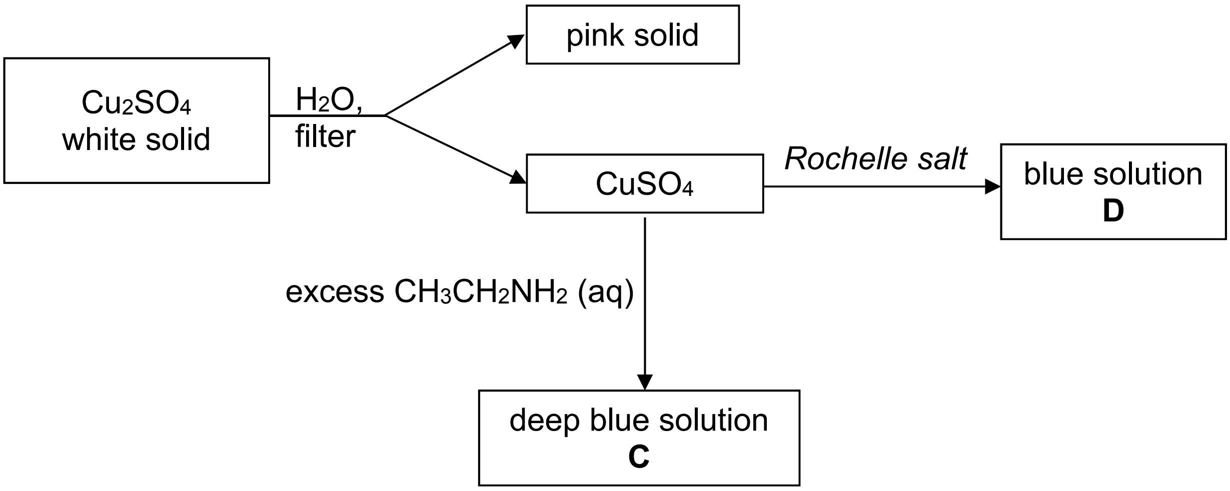
(e) Suggest a chemical test that can be used to distinguish between *fentanyl* and *morphine*.

[2]

[Total: 7]

6 Copper forms compounds with variable oxidation states and these compounds are used in numerous industries such as in wastewater treatment and as mineral supplements.

(a) The following scheme illustrates the reactions between different compounds of copper.



(i) State the full electronic configuration of copper in the white solid. **[1]**

....

(ii) With reference to relevant E^θ *data* from the *Data Booklet*, describe and explain the type of reaction undergone when the white solid dissolves in water. **[2]**

(iii) Identify the species in solution **C** that is responsible for the deep blue colour and account for its formation from $CuSO_4$. Include a relevant equation in your answer.

[2]

(iv) Solution **D** is formed when *Rochelle salt* (an aqueous solution of potassium sodium tartrate $KNaC_4H_4O_6$) is mixed with a solution of $CuSO_4$ in basic medium.

Use the following data to determine the chemical formula of the copper tartrate anion complex.

- The composition by mass of the elements is

  Cu: 17.76 % C: 26.85% H: 1.68% O: 53.71%

- The chemical formula takes the form of $[\boldsymbol{ML_2}]^{n-}$.

[2]

(b) Copper(II) ions are commonly used as *homogeneous catalysts* in the removal of harmful cyanide ions, CN^- from wastewater by hydrogen peroxide to form the less harmful cyanate CNO^- ions as illustrated in the following reaction.

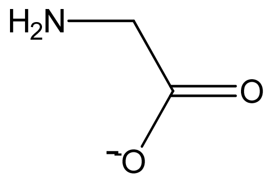
$$CN^-(aq) + H_2O_2(aq) \longrightarrow CNO^-(aq) + H_2O(l)$$

By considering relevant E^θ values from the *Data Booklet*, explain how copper(II) ions act as *homogeneous catalyst* in this reaction, writing balanced equations where appropriate.

[3]

Given: $CNO^- + H_2O + 2e \rightleftharpoons CN^- + 2OH^-$ $\quad E^\theta = -0.97$ V

(c) When aqueous glycine solution is added to a heated ethanolic solution of copper(II) ethanoate, light blue needles of a planar, neutral copper–glycinate complex is obtained upon cooling.



glycinate ion

(i) Draw the three–dimensional structure of the copper–glycinate complex ion.

[1]

(ii) State the type of isomerism exhibited by the copper–glycinate complex ion.

[1]

[Total: 12]

END OF PAPER