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**CHEMISTRY**

**9701/43**

Paper 4 A Level Structured Questions

**October/November 2019**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your centre number, candidate 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.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

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.

This document consists of **20** printed pages.

Answer **all** the questions in the spaces provided.

1 An electrochemical cell is constructed using two half-cells.

- an  $\text{Sn}^{4+}/\text{Sn}^{2+}$  half-cell
- an  $\text{Al}^{3+}/\text{Al}$  half-cell

(a) State the material used for the electrode in each half-cell.

- $\text{Sn}^{4+}/\text{Sn}^{2+}$  half-cell .....
- $\text{Al}^{3+}/\text{Al}$  half-cell .....

[1]

(b) The cell is operated at 298 K.

The  $\text{Al}^{3+}/\text{Al}$  half-cell has standard concentrations.

The  $\text{Sn}^{4+}/\text{Sn}^{2+}$  half-cell has  $[\text{Sn}^{4+}] = 0.300 \text{ mol dm}^{-3}$  and  $[\text{Sn}^{2+}] = 0.150 \text{ mol dm}^{-3}$ .

(i) Use the Nernst equation to calculate the electrode potential,  $E$ , of the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  half-cell under these conditions.

$$E = \dots\dots\dots \text{ V [2]}$$

(ii) Calculate the  $E_{\text{cell}}$  under these conditions.

$$E_{\text{cell}} = \dots\dots\dots \text{ V [1]}$$

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

- (c) Aluminium is produced industrially by electrolysis of a melt containing large amounts of  $Al^{3+}$  ions.

Calculate the mass of aluminium that is obtained when a current of 300 000 A is passed for 24 hours. Give your answer to **three** significant figures.

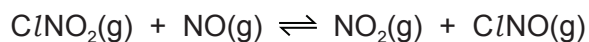
mass = ..... units = ..... [4]

- (d) Explain why chromium metal cannot be obtained by the electrolysis of dilute aqueous chromium(II) sulfate. Your answer should include data from the *Data Booklet*.

.....  
.....  
.....  
..... [2]

[Total: 12]

- 2 When  $\text{ClNO}_2$  reacts with  $\text{NO}$  an equilibrium is established.



In each  $\text{ClNO}_2$  molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

- (a) Draw a 'dot-and-cross' diagram for the  $\text{ClNO}_2$  molecule.

[2]

- (b) The reaction between  $\text{ClNO}_2$  and  $\text{NO}$  is first order with respect to each reactant.

- (i) Write the rate equation for this reaction.

rate = ..... [1]

- (ii) Deduce the units of the rate constant,  $k$ , when the concentrations of both gases are measured in  $\text{mol dm}^{-3}$  and the rate is measured in  $\text{mol dm}^{-3} \text{s}^{-1}$ .

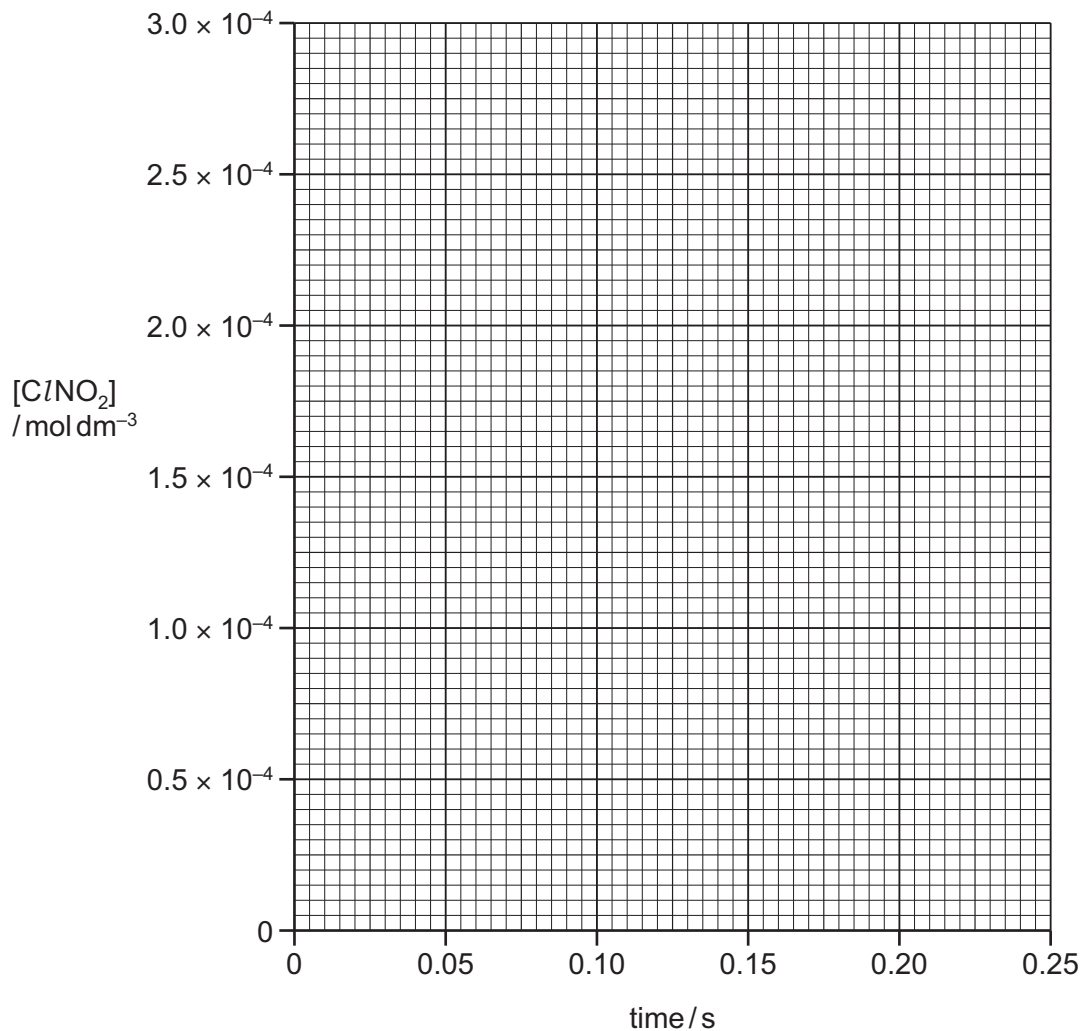
..... [1]

- (iii) State and explain whether or not the reaction **could** take place in a single step.

.....  
 .....  
 ..... [1]

(c) An experiment is carried out in which the initial  $[ClNO_2]$  is  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ . A large excess of NO is used. The initial rate of reaction is  $1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$ . The rate of the reaction is assumed to be constant for the first 0.20 seconds.

(i) Draw a graph on the grid to show how the concentration of  $ClNO_2$  varies for the first 0.20 seconds.



[2]

(ii) Deduce the concentration of the  $NO_2$  product at 0.20 seconds.

..... [1]

(iii) After 20 seconds the concentration of  $ClNO_2$  remains constant.

Explain this observation.

..... [1]

[Total: 9]

3 (a) Explain what is meant by the term *entropy of a system*.

.....  
 ..... [1]

(b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is ..... because .....

.....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is ..... because .....

.....

- the change corresponding to the lattice energy of calcium chloride,  $\Delta H_{\text{latt}} \text{CaCl}_2(\text{s})$ , takes place

The entropy change is ..... because .....

.....

[3]

(c) The reaction  $\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$  is not spontaneous at room temperature.

(i) Give the full name for the term  $\Delta G^\ominus$ .

..... [1]

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation .....

.....

.....

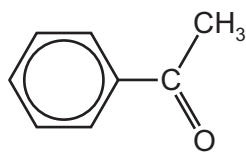
.....

[2]

[Total: 7]

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

Identify the other reagents used and describe any essential reaction conditions.

.....  
 ..... [2]

(b) Phenylethanone is treated separately with three reagents.

Complete the table, for each reagent, to give the structural formula of one organic product formed and the name of the mechanism involved. If there is no reaction you should write 'no reaction'.

reagent	organic product	name of mechanism
chlorine gas at 10 °C in the presence of ultra-violet light		
a mixture of concentrated nitric and sulfuric acids at 50 °C		
bromine water		

[5]

(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

(i) Name the mechanism of this reaction.

..... [1]

(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of  $\text{CN}^-$  ions.

phenylethanone

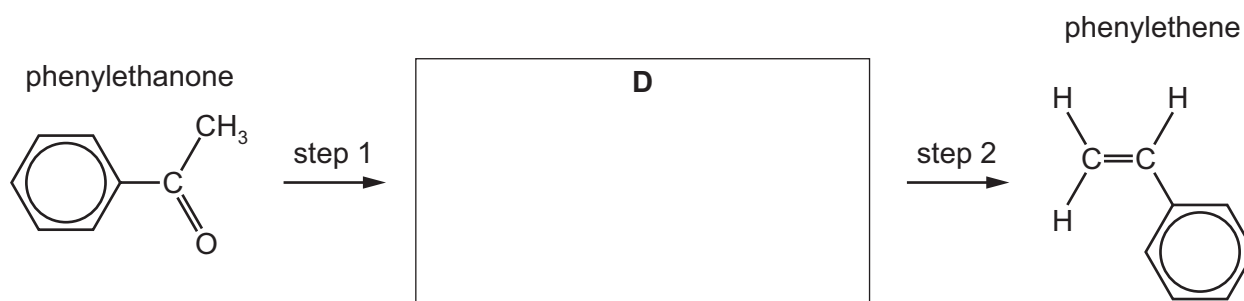
intermediate

product



[4]

(d) Phenylethanone can be used as a starting material to make phenylethene in a two-step synthesis.



(i) Draw the structure of compound **D** in the box. [1]

(ii) Identify a suitable reagent for step 1.

..... [1]

(iii) Identify a suitable reagent for step 2.

..... [1]



(iv) State the number of peaks in the C-13 NMR spectrum of **phenylethene**.

..... [1]

(v) Suggest C-13 chemical shift ranges expected for the different types of carbon environment in **phenylethanone**.

.....

.....

..... [2]

[Total: 18]

5 Silver sulfide,  $\text{Ag}_2\text{S}$ , is very insoluble in water.

(a) (i) Write an expression for the solubility product,  $K_{\text{sp}}$ , of  $\text{Ag}_2\text{S}(\text{s})$ .

$$K_{\text{sp}} =$$

[1]

(ii) The solubility of  $\text{Ag}_2\text{S}(\text{s})$  in water at 298 K is  $1.16 \times 10^{-17} \text{ mol dm}^{-3}$ .

Calculate the numerical value of the solubility product,  $K_{\text{sp}}$ , of  $\text{Ag}_2\text{S}(\text{s})$  at 298 K.

$$K_{\text{sp}} = \dots\dots\dots [2]$$

(iii) Calculate the minimum volume of water needed to dissolve 1.00 g of  $\text{Ag}_2\text{S}(\text{s})$  under standard conditions.

$$\text{volume} = \dots\dots\dots \text{ dm}^3 [2]$$

(b) Bromic(I) acid,  $\text{HOBr(aq)}$ , is a weak acid. Its  $K_a$  is  $2.0 \times 10^{-9} \text{ mol dm}^{-3}$ .

(i) Calculate the pH of  $0.20 \text{ mol dm}^{-3}$   $\text{HOBr(aq)}$ .

pH = ..... [2]

(ii)  $5.0 \text{ cm}^3$  of  $0.20 \text{ mol dm}^{-3}$  potassium hydroxide,  $\text{KOH}$ , are added to  $20.0 \text{ cm}^3$  of  $0.20 \text{ mol dm}^{-3}$   $\text{HOBr(aq)}$ .

Calculate the pH of the buffer solution produced.

pH = ..... [2]

[Total: 9]

6 The elements in Group 2 include magnesium, calcium, strontium and barium.

(a) (i) Write an equation for the change representing the first ionisation energy of magnesium. Include state symbols.

..... [1]

(ii) Write an equation for the reaction of strontium with cold water. Include state symbols.

..... [1]

(iii) Describe and explain the trend in reactivity observed in the reactions of these Group 2 metals with cold water.

.....

.....

..... [1]

(b) The Group 2 metal nitrates decompose when heated.

(i) Describe fully what is seen when anhydrous calcium nitrate is heated in a test-tube and decomposition occurs.

.....

..... [1]

(ii) Write an equation for the decomposition of calcium nitrate.

..... [1]

(iii) Describe and explain the variation in thermal stability of the Group 2 metal nitrates down the group.

.....

.....

..... [3]

(c) Describe and explain the variation in the solubility of the Group 2 metal sulfates down the group.

.....

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 12]

7 Manganese, chromium and ruthenium are all transition elements.

(a) Explain what is meant by a *transition element*.

.....  
 .....  
 ..... [1]

(b)  $\text{MnO}_4^-$ (aq) and  $\text{Cr}_2\text{O}_7^{2-}$ (aq) act as oxidising agents in acidic solution. Both these oxidising agents will oxidise a solution of  $\text{Sn}^{2+}$  to give a solution of  $\text{Sn}^{4+}$ . Solutions containing  $\text{Sn}^{2+}$  and solutions containing  $\text{Sn}^{4+}$  are colourless.

(i) Describe the colour change seen when an excess of  $\text{Sn}^{2+}$ (aq) is added separately to

- dilute acidified  $\text{MnO}_4^-$ (aq)

from ..... to .....

- dilute acidified  $\text{Cr}_2\text{O}_7^{2-}$ (aq).

from ..... to .....

[1]

(ii) Write an equation for the reaction between  $\text{Sn}^{2+}$ (aq) and acidified  $\text{Cr}_2\text{O}_7^{2-}$ (aq).

..... [1]

(c) Ruthenium, Ru, forms complex ions. In one such complex ion, **X**, the ruthenium ion has a co-ordination number of six. Each complex ion **X** contains one  $\text{Ru}^{2+}$  ion, one  $\text{Cl}^-$  ion, one  $\text{SO}_2$  molecule and the remaining ligands are  $\text{NH}_3$  molecules.

The  $\text{SO}_2$  molecule acts as a monodentate ligand and is attached to the  $\text{Ru}^{2+}$  ion via the sulfur atom. **X** exists in two isomeric forms.

(i) State what is meant by a *co-ordination number of six*.

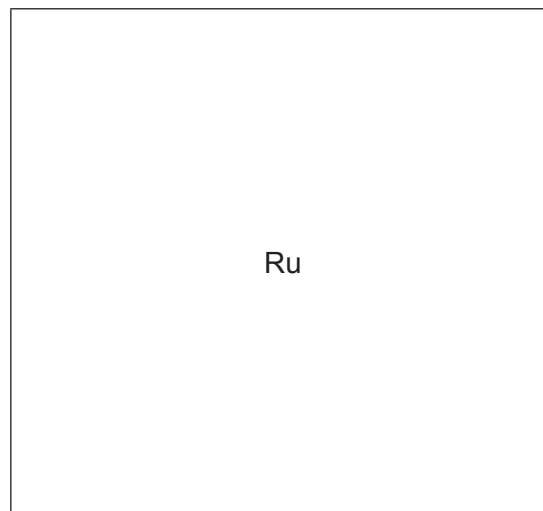
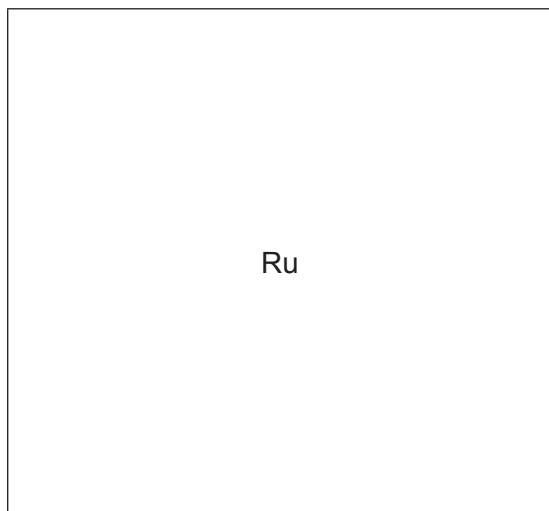
..... [1]

(ii) State the formula of **X**. Include its charge.

..... [1]

(iii) Draw the two isomeric forms of **X** in the boxes below. Your diagrams should show

- the three-dimensional shapes of the two isomers
- how each ligand is attached to the central ruthenium ion.



[3]

(iv) Suggest the type of isomerism shown by **X**.

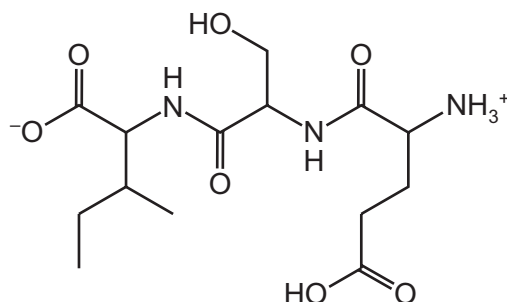
..... [1]

(v) Explain the origin of colour in a transition element complex such as **X**.

.....  
.....  
.....  
.....  
.....  
.....  
.....  
..... [3]

[Total: 12]

- 8 Proteins are natural polymers. When one particular protein is partially hydrolysed the product mixture includes tripeptide **E**.

tripeptide **E**

- (a) (i) Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

..... [1]

- (ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

The three amino acids should be shown in the correct form for the conditions you have chosen in (a)(i).

--	--	--

[2]

- (b) If a pure sample of **E** is obtained in aqueous solution, several different types of intermolecular forces are possible between pairs of **E** molecules.

Name three different types of intermolecular force that exist between pairs of **E** molecules, stating the groups on the molecules where the forces are acting.

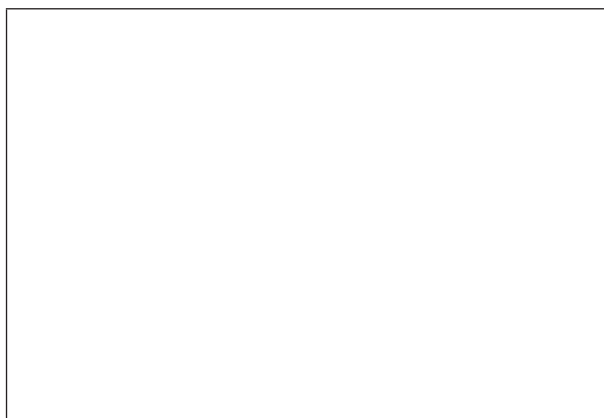
type of force/bond	pair of groups responsible

[3]



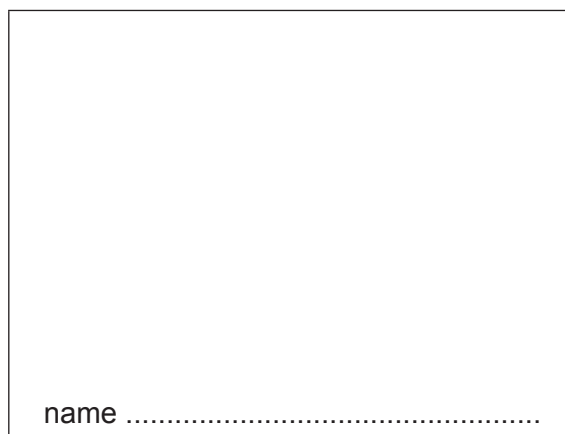
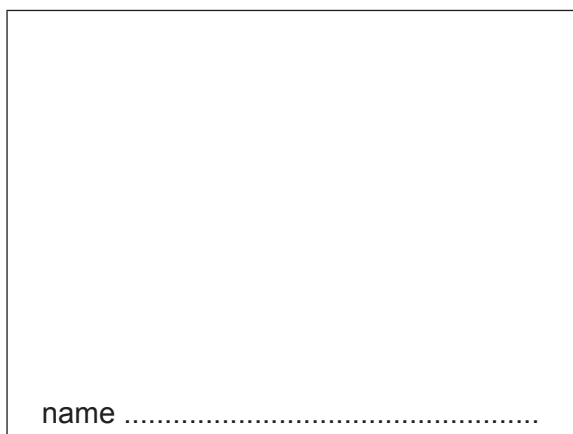
(c) Polyesters and polyamides are two important types of condensation polymer.

- (i) Draw the structure of a compound that can polymerise to produce a polyamide, without the need for a second monomer.



[1]

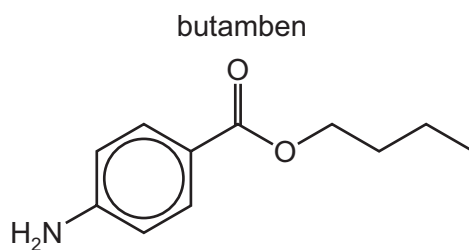
- (ii) Draw the structures of two different compounds that can polymerise together to produce a polyester with **four** carbon atoms per repeat unit. Name the two compounds.



[4]

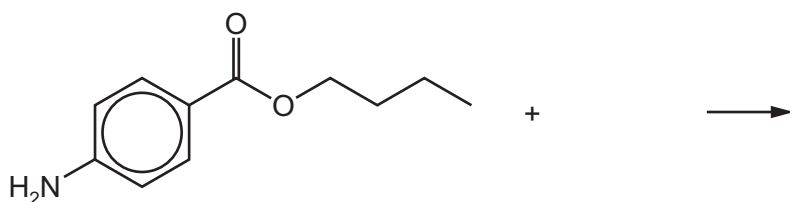
[Total: 11]

9 The structure of butamben is shown.



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.

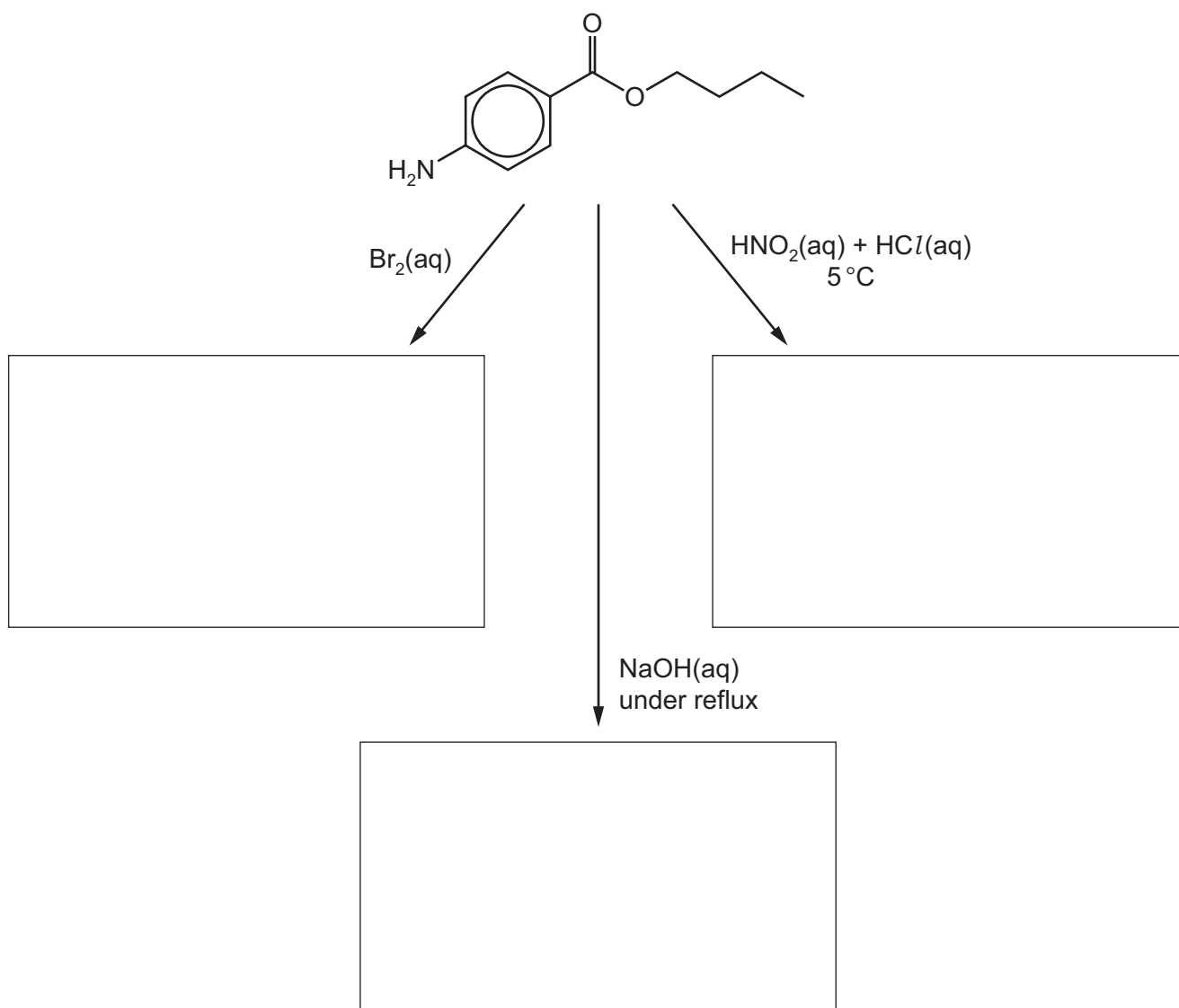


[1]

(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

.....  
.....  
..... [1]

- (b) Complete the reaction scheme below to show the structural formulae of the products formed when butamben is treated separately with the stated reagent.



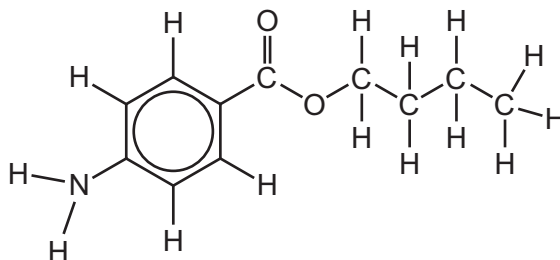
[3]

(c) The proton NMR spectrum of butamben in  $\text{CDCl}_3$  contains one or more peaks that show a triplet splitting pattern.

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

..... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in (c)(i).



[1]

(iii) Describe and explain how the proton NMR spectrum of butamben in  $\text{D}_2\text{O}$  would differ from the proton NMR spectrum of butamben in  $\text{CDCl}_3$ .

.....  
 ..... [2]

(d) The mass spectrum of butamben includes peaks at  $m/e$  92 and 57.

Identify the fragments responsible for these peaks.

$m/e$  92 = .....

$m/e$  57 = .....

[1]

[Total: 10]

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