RAFFLES INSTITUTION
2021 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	
CLASS	INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

17 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

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

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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 Examiner's Use						
Section A			**Section B**			**Total**
1	**/ 23**		(Circle the question you have answered)			**/ 80**
2	**/ 20**		**4**	**/ 20**		
3	**/ 17**		**5**	**/ 20**		

Section A

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

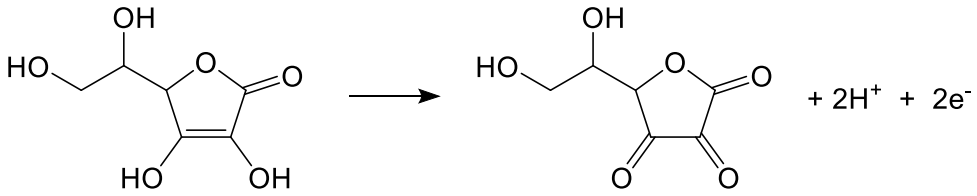
1 Alcohols, carbonyl compounds and esters are commonly found in both natural and artificial flavourings.

(a) **(i)** When iodine dissolves in hexane, the solution is purple.

Describe a reaction that uses this observation to illustrate the relative oxidising abilities of iodine and chlorine. [1]

(ii) Explain the above reaction using relevant $E^{\ominus}$ values from the *Data Booklet*. [1]

(iii) Ascorbic acid (M_r = 176.0) is a food additive commonly added to candy to give a sour flavour. Iodine can be used to determine the amount of ascorbic acid in food by oxidising the ascorbic acid to dehydroascorbic acid.



ascorbic acid dehydroascorbic acid

A 100.0 g sample of a candy was dissolved in hot water. The resulting solution was filtered and diluted to 100 cm^3 in a volumetric flask.

A 10.0 cm^3 aliquot of the solution was pipetted into a conical flask and a few drops of starch solution was added. The sample was then titrated with 0.005 mol dm^{-3} of iodine solution. The titre volume was 22.05 cm^3.

Calculate the percentage by mass of ascorbic acid in the candy. [3]

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(b) Alcohols can be prepared from halogenoalkanes.

Three different halogenoalkanes, bromopropane, chloropropane and iodopropane, were hydrolysed to form propanol. Outline how you would determine the difference in the rate of hydrolysis of the three compounds. You should include the expected observations of the experiment.

You are provided with 0.10 mol dm^{-3} silver nitrate solution in ethanol and the pure halogenoalkanes in liquid state. Details regarding use of specific glassware are not required. [3]

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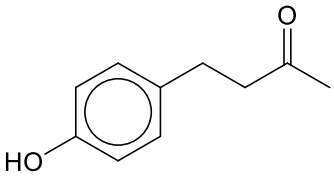
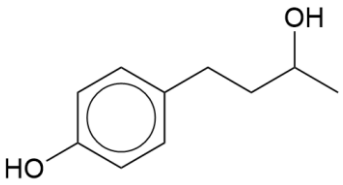
(c) The characteristic berry flavour found in red raspberries is due to the phenolic compound known as raspberry ketone (RK).



raspberry ketone (RK)

(i) Draw the structure of the organic product formed when RK is reacted with an excess of $Br_2(aq)$. [1]

(ii) RK can be converted to rhododendrol.



rhododendrol

State the reagents and conditions required to convert RK to rhododendrol and name the type of reaction which occurred. [1]

(iii) By comparing the relative acidities of the relevant functional groups, explain the reaction when sodium hydroxide is added to rhododendrol. [2]

(iv) Describe a chemical test, with appropriate observations, which would distinguish between RK and rhododendrol. [2]

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(d) Another additive commonly used in perfumes is gardenol which imparts a floral scent.

When gardenol, $C_{10}H_{12}O_2$, is heated with dilute H_2SO_4, two compounds **B** and **C** are formed. Compound **B** liberates CO_2 from Na_2CO_3.

$$\text{gardenol} \xrightarrow[\text{heat}]{H_2SO_4} \underset{(C_2H_4O_2)}{\mathbf{B}} + \mathbf{C}$$

(i) Name the type of reaction shown and suggest the functional groups present in gardenol, **B** and **C**. [2]

When heated with acidified $KMnO_4$, gardenol forms compounds **B** and **D**. Compound **C** also forms compound **D** when heated with acidified $KMnO_4$. Compound **C** contains a chiral centre, while compound **B** does not.

(ii) Deduce the structures of compounds **B**, **C**, **D** and gardenol, explaining the reactions described. [5]

(iii) Based on your structure of compound **C**, explain which carbon is chiral, and draw the pair of enantiomers. [2]

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2 Iron is the most abundant element (by mass) on Earth, constituting about 80% of the inner and outer cores of Earth. Iron exists in a wide range of oxidation states, although the +2 and +3 states are the most common.

(a) Use the information below and data from the *Data Booklet* to construct an energy cycle to determine the enthalpy change for the following reaction.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

enthalpy change of formation of CO(g)	= –110 kJ mol^{-1}
enthalpy change of atomisation of Fe(s)	= +414 kJ mol^{-1}
sum of first and second electron affinities of O	= +703 kJ mol^{-1}
lattice energy of $Fe_2O_3(s)$	= –15067 kJ mol^{-1}

[4]

(b) Nanochemistry is an emerging field of chemistry which employs the use of extremely small particles that have nanometer-sized dimensions.

Nanoparticles of metal compounds such as $Fe(OH)_2$ are used in water treatment to remove toxic substances like selenite(IV) ions, SeO_3^{2-}, which adsorb onto the surfaces of the nanoparticles.

(i) Explain how the use of nanoparticles will improve the removal of toxic substances in water treatment. [1]

(ii) Suggest why water samples with high alkaline pH will hinder the adsorption of SeO_3^{2-}. [1]

Once adsorbed, the selenite(IV) ions, SeO_3^{2-}, may be reduced to selenium, Se.

(iii) Write a half-equation for the reduction of SeO_3^{2-} to Se in an alkaline medium. [1]

(iv) Suggest a reason to explain why the surfaces of $Fe(OH)_2$ nanoparticles with SeO_3^{2-} adsorbed appear red-brown after some time. [1]

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(c) Nanoparticles have been synthesised through electrolysis. For instance, anodising of aluminium can be carried out to produce nanoparticles of aluminium oxide.

Draw a labelled diagram showing the set-up for the anodising of aluminium and write equations for the two reactions occurring at the anode. [3]

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Iron and nickel are the most abundant metals in metallic meteorites.

(d) When 2.00 g of solid K_xNiF_6 was reacted with water, 0.004 moles of oxygen was evolved and an acidic solution **E** was formed. Solution **E** consists of KF, HF and NiF_2.

Solution **E** was divided into **two equal parts**.

Titration of one part with 0.40 mol dm^{-3} NaOH required 19.90 cm^3 for neutralisation.

The other part was electrolysed using a current of 0.40 A and it took 32 minutes to completely deposit the nickel metal at the cathode.

(i) Calculate the number of moles of HF and NiF_2 in solution **E**. [2]

(ii) Hence, deduce the value of x in K_xNiF_6. [1]

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(e) The Mond process produces pure nickel metal via the decomposition of nickel tetracarbonyl, $Ni(CO)_4$.

The two key steps of the Mond process are shown below.

Step 1 Impure nickel reacts with carbon monoxide to form nickel tetracarbonyl, which is then channeled into another chamber. The other solid impurities remain.

$$Ni(s) + 4CO(g) \xrightarrow{70\ °C} Ni(CO)_4(g) \qquad \Delta H_r^{\ominus} = -160.9\ kJ\ mol^{-1}$$

Step 2 Nickel tetracarbonyl undergoes decomposition to yield the pure nickel metal.

$$Ni(CO)_4(g) \xrightarrow{170\ °C} Ni(s) + 4CO(g) \qquad \Delta S_r^{\ominus} = +410\ J\ K^{-1}\ mol^{-1}$$

(i) Calculate the volume of CO(g), in m^3, formed from the complete decomposition of 300 g of $Ni(CO)_4$ at 100 kPa and 170 °C.
M_r of $Ni(CO)_4$ = 170.7 [1]

(ii) Comment on the sign of $\Delta S_r^{\ominus}$ in Step 2. [1]

(iii) The boiling point of $Ni(CO)_4$ is 42 °C. Suggest two reasons why Step 1 is carried out at 70 °C rather than at room temperature. [2]

(iv) Explain why the temperature is increased from 70 °C to 170 °C for Step 2 of the Mond process. Show relevant calculations to support your answer.

You may assume that $\Delta H_r^{\ominus}$ and $\Delta S_r^{\ominus}$ do not vary with temperature. [2]

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3 Nitrogen plays an important role in the chemical industry. It is used to manufacture explosives, catalysts and organic compounds.

(a) There are over 20 binary compounds containing the elements hydrogen and nitrogen. One example is N_4H_4.

Draw the structures of the two straight-chain constitutional isomers of N_4H_4. For one of the constitutional isomers, draw its two stereoisomers. [2]

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(b) NH_3 is commonly used as a nucleophile in organic synthesis. In some circumstances, NH_3 adds to C=C bonds.

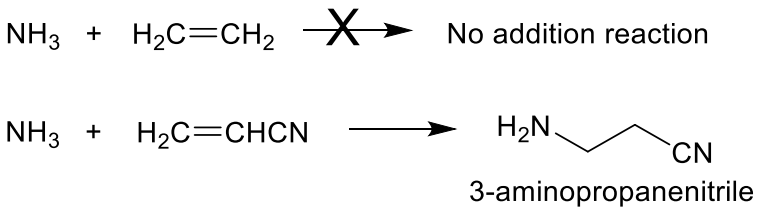

Fig. 3.1

(i) Use concepts of electronegativity and electronic effects to suggest reasons to explain Fig. 3.1. [2]

(ii) Draw the structural formula of the organic product obtained when 3-aminopropanenitrile was heated with excess dilute hydrochloric acid. [1]

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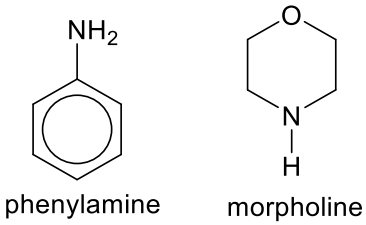
(iii) Reactions between amines and CH_2=CHCN proceed like that between NH_3 and CH_2=CHCN.

When CH_2=CHCN was added to an equimolar mixture of phenylamine and morpholine, only one of the amines reacted to form one product.



phenylamine morpholine

Suggest with reasoning, which amine has reacted and hence, draw the structure of the product. [2]

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(c) In the presence of $NaBH_3CN$, an amine can react with a carbonyl compound, such as methanal, as shown below.

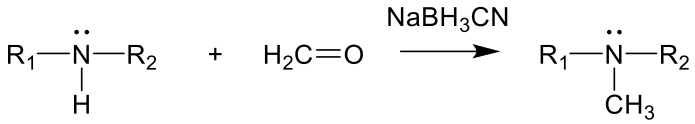
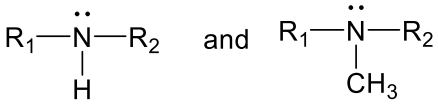


Fig. 3.2

R_1 and R_2 = H, alkyl or aryl group

(i) Briefly explain which of the two gaseous amines is more basic. [1]



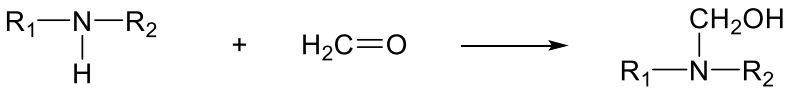
(ii) Both $NaBH_4$ and $NaBH_3CN$ are reducing agents.

① Compare their reducing power, given that both reducing agents produce hydride ions as the reacting species.

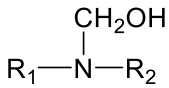
② Explain why $NaBH_4$ cannot be used for the reaction in Fig. 3.2.

[2]

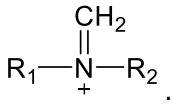
(iii) In the first stage of the reaction, an amine reacts with methanal as shown in the following equation.



The second stage of the reaction involves the following mechanistic steps.

1. The –OH in  reacts with H^+.

2. Heterolytic fission of the C–O bond occurs. This causes the loss of a water molecule and the formation of a carbocation.

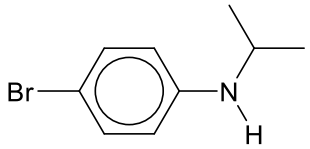
3. Subsequently, the carbocation forms the ion,  .

For steps 1, 2 and 3, draw curly arrows to show the movement of electrons and charges on the intermediates. [3]

(iv) Phenylamine reacts with bromine to form 2,4,6-tribromophenylamine. In order to produce a mono-brominated product, additional steps are required.

Starting with phenylamine, propose a 4-step reaction sequence to produce compound **B**. You should include a suitable carbonyl compound in one of the steps and consider the information given in Fig. 3.2.

Include the structures of all intermediates of the reaction sequence in your answer. [4]



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Section B

Answer **one** question from this section.

4 **(a)** In aqueous solution, benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes above 10 °C.

$$C_6H_5N_2Cl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

The rate of this reaction can be followed by measuring the volume of nitrogen evolved at different times. The following results were obtained.

time, t / min	V_t / cm^3	$(V_\infty - V_t)$ / cm^3
0.0	0.0	197.5
3.5	19.5	178.0
6.0	36.5	161.0
10.0	60.0	137.5
14.0	83.0	114.5
18.0	99.5	98.0
22.0	115.5	82.0

V_t is the volume of N_2 after t minutes.
V_∞ is the volume of N_2 evolved at the end of the reaction.

(i) Define the *order of reaction with respect to a reactant*. [1]

(ii) State the significance of the term $(V_\infty - V_t)$. [1]

(iii) The graph of $(V_\infty - V_t)$ against t was plotted and given in Fig. 4.1.

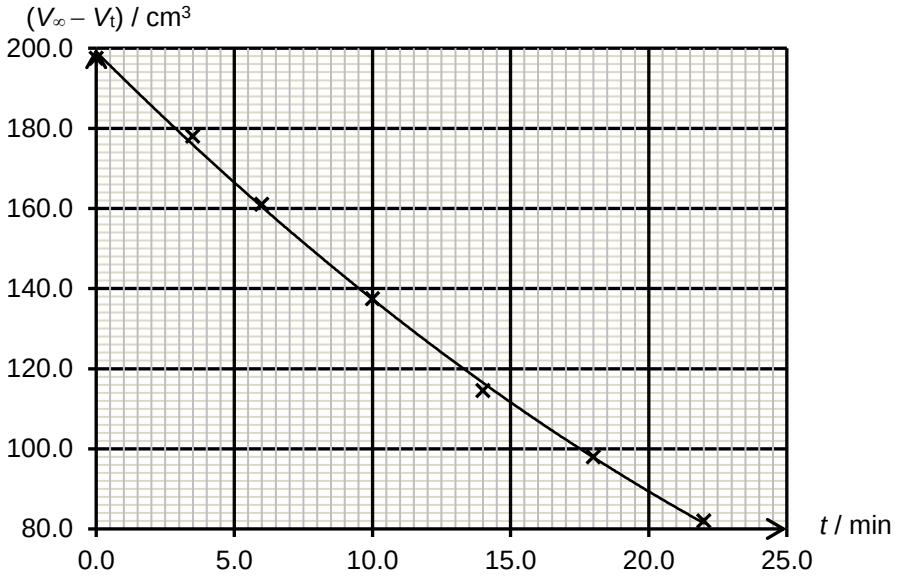


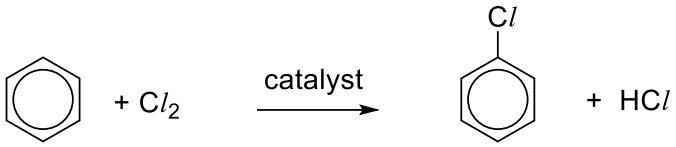
Fig. 4.1

Using this graph, show that the reaction is first order with respect to $C_6H_5N_2Cl$. [1]

(iv) Explain why the order of this reaction with respect to H_2O is zero.

Hence, write the rate equation for the decomposition of $C_6H_5N_2Cl$ in aqueous solution. [2]

(b) Benzene undergoes chlorination via an electrophilic substitution reaction, in the presence of a suitable Lewis acid catalyst.



(i) Suggest a suitable catalyst for the chlorination reaction and draw the mechanism. [3]

(ii) Iodine reacts with benzene in a similar way to chlorine.

Use relevant bond energy values given in the *Data Booklet* to calculate the enthalpy change of iodination of benzene and comment on the spontaneity of the reaction.

You may assume that all reactants and products are in the gaseous state during the reaction. [2]

(iii) For the iodination of benzene, nitric acid is used to oxidise I_2 to the electrophile I^+.

Write an equation for the generation of I^+ in acidic medium using HNO_3, given that NO_2 is produced in the reaction. [1]

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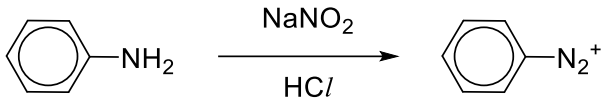
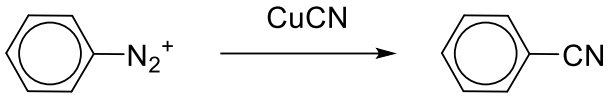
(c) Phenylamine can be converted into the benzenediazonium ion according to the following reaction.



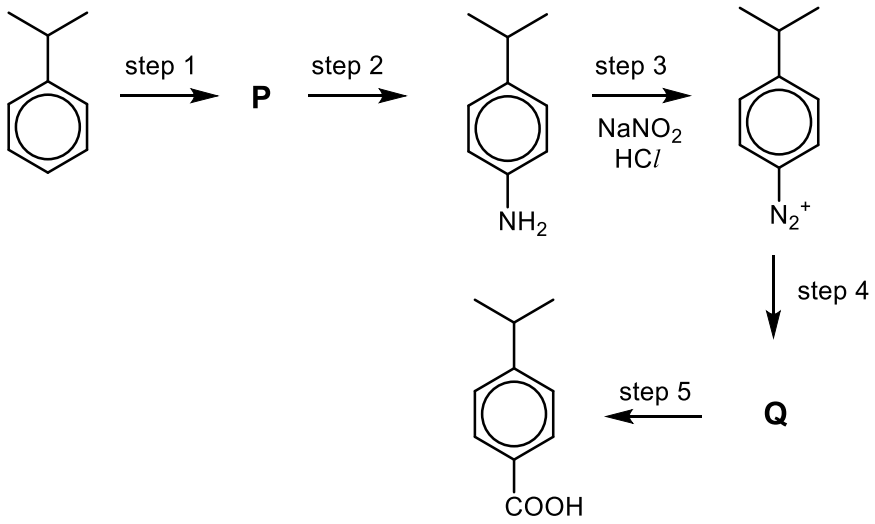
benzenediazonium ion

The benzenediazonium ion can be used to synthesise benzonitrile, in a reaction known as the Sandmeyer reaction.



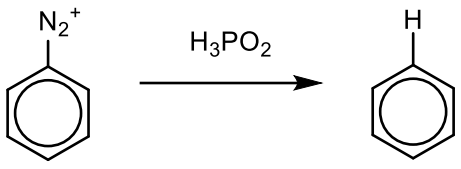
benzonitrile

(i) In the following reaction scheme involving the Sandmeyer reaction, state the reagents and conditions required for steps 1, 2, 4 and 5, and suggest structures for the organic compounds **P** and **Q**.



[6]

(ii) When treated with hypophosphorus acid, H_3PO_2, the diazo group of $C_6H_5N_2^+$ is replaced with a hydrogen atom.



By making use of this reaction, suggest a 3–step synthesis of 1,3,5-tribromobenzene starting from phenylamine. [3]

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[Total: 20]

5 Mixtures of concentrated acids are often used in inorganic and organic reactions.

When concentrated hydrochloric acid, HC*l*, and concentrated nitric acid, HNO_3, are mixed, volatile products such as nitrosyl chloride, NOC*l*, and chlorine gas, Cl_2, are produced.

(a) **(i)** Given that N is the central atom, draw a dot-and-cross diagram of NOC*l*. [1]

(ii) State the shape of NOC*l* and suggest a bond angle for the molecule. [2]

(iii) The nitrogen-chlorine bond in NOC*l* has a bond length of 198 pm.

With reference to your answer in **(i)**, explain how the nitrogen-oxygen bond length in NOC*l* would compare to this value. [1]

(iv) The boiling points of NOC*l* and Cl_2 are –5.6 °C and –34.0 °C respectively.

Explain why NOC*l* has a higher boiling point. [2]

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(b) NOC*l* can decompose into NO and Cl_2 gases as shown.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

(i) Write the expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) Gaseous NOC*l* was placed in a sealed container at a pressure of 0.50 atm. When the system reached equilibrium, 4% of the NOC*l* had decomposed.

Calculate the value of K_p, giving its units. [2]

(iii) At time *t*, the volume of the sealed container in **(ii)** was instantaneously increased to twice its original at constant temperature, and the system allowed to reach equilibrium.

Sketch a graph to show how the total pressure of the system changed with time as the processes in **(ii)** and **(iii)** were carried out.

You should label your axes clearly and indicate any relevant values. [2]

(iv) Explain how the partial pressures of the individual gases will change when the volume of the sealed container was doubled from time *t* in **(iii)**. [2]

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A mixture of concentrated nitric acid, HNO_3, and concentrated sulfuric acid, H_2SO_4, is needed for the nitration of benzene.

(c) Describe the mechanism for the nitration of benzene. [3]

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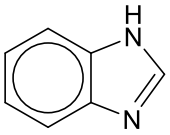
Question 5 continues on the next page.

(d) Benzimidazole derivatives are frequently used in ring systems for small molecule pharmaceutical drugs.



benzimidazole

The following scheme shows a proposed synthesis route for benzimidazole. Study Fig 5.1 and answer the questions that follow.

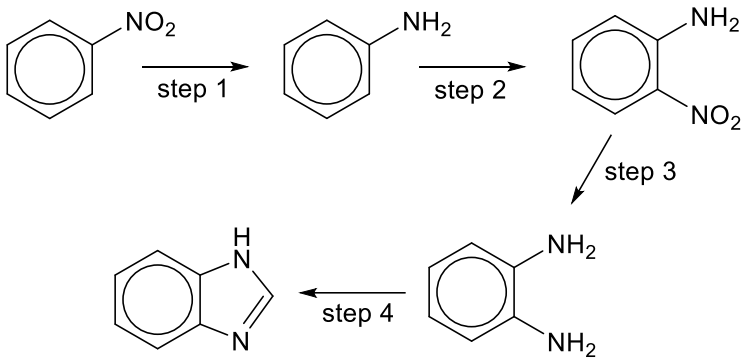
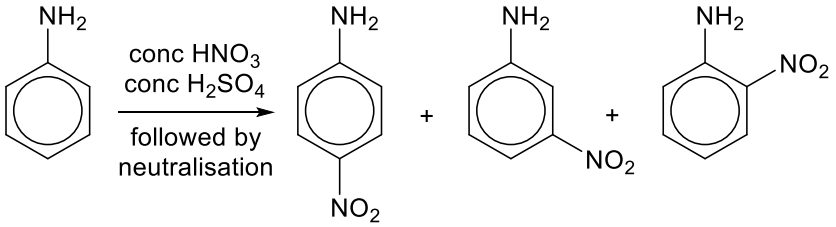


Fig 5.1

(i) Write a balanced equation for step 1 using [H] to represent the reducing agent. [1]

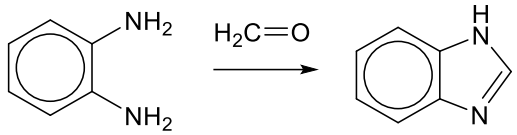
(ii) As a trial experiment for step 2, when phenylamine was reacted with concentrated HNO_3 and concentrated H_2SO_4, the proportion of 3-nitrophenylamine was found to be unexpectedly high.



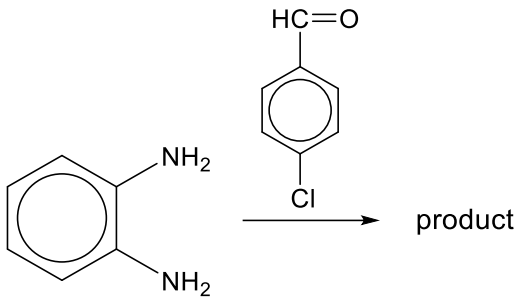
(35%) (63%) (2%)

Explain why 3-nitrophenylamine was the major product. [2]

Step 4 can be carried out as shown below.



(iii) Suggest the structure of the product for the following reaction.



[1]

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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.

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