H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY **9729/02**

Paper 2 Structured Questions **01 September 2021**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class 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.
The use of an approved scientific calculator is expected, where appropriate.
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.

For Examiner's Use	
1	**/14**
2	**/16**
3	**/20**
4	**/25**
Total	**/75**

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

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

1 This is a question on the salts of magnesium.

(a) Struvite, $MgNH_4PO_4 \cdot 6H_2O$, is a fertiliser mineral that can be obtained from wastewaters. It is a salt that contains two cations and one anion.

(i) Draw a dot-and-cross diagram of $MgNH_4PO_4$.

[2]

(ii) Explain why $MgNH_4PO_4$ is only slightly soluble in water.

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……

……

…… [1]

(iii) Thermal decomposition of $MgNH_4PO_4$ produces an alkaline gas, water and a white powder of magnesium pyrophosphate, $Mg_2P_2O_7$. Write an equation with state symbols for this reaction.

…… [1]

(b) The value of the solubility products and melting points of some magnesium salts at 298 K are shown in Table 1.1.

Table 1.1

salt	value of solubility product	melting point / °C
magnesium chloride, $MgCl_2$		714
magnesium hydroxide, $Mg(OH)_2$	1.8×10^{-11}	350
magnesium phosphate, $Mg_3(PO_4)_2$	4.0×10^{-25}	1184

In this question, give each of your numerical answers to two significant figures.

Magnesium phosphate is widely used in medication to support the relaxation of muscles. This compound is used to prevent the cramping of muscles and vitamin E deficiency.

(i) With an appropriate equation, define the *lattice energy of magnesium phosphate*.

……

……

…… [2]

(ii) Suggest an explanation, in terms of structure and bonding, for the difference in melting points between magnesium chloride and magnesium phosphate.

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…..

..

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…… [2]

(iii) Write an expression for the solubility product of magnesium phosphate, stating its units.

…… [1]

(iv) Determine the $[Mg^{2+}(aq)]$ of a saturated solution of magnesium phosphate.

[2]

(v) Solid magnesium chloride was slowly added to a solution containing 0.15 mol dm^{-3} of sodium hydroxide and 0.32 mol dm^{-3} of sodium phosphate at 298 K.

Calculate the concentration of hydroxide ions in the solution when the first trace of magnesium phosphate appears.

[3]

[Total: 14]

2 Nitrogen dioxide, NO_2, is a significant air pollutant. It is a precursor for a number of harmful secondary air pollutants such as ozone and particulate matter, and plays a role in the oxidation of atmospheric sulfur dioxide.

PM refers to particulate matter in the atmosphere that are so small they can only be detected using an electron microscope. Most of these particles form in the atmosphere as a result of pollution emitted from power plants, industries and automobiles. PM_{10} is particulate matter 10 μm or less in diameter, $PM_{2.5}$ is particulate matter 2.5 μm or less in diameter. Due to their small size, they can penetrate the deepest parts of the lungs as well as access the gas exchange regions of the lung via diffusion.

To safeguard public health, concentration of NO_2, PM_{10} and $PM_{2.5}$ around Singapore are closely monitored.

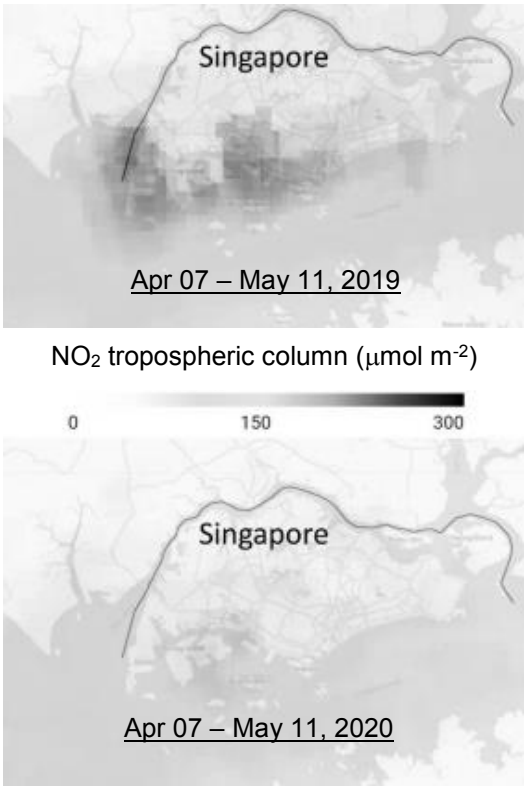

Fig. 2.1 shows mean atmospheric concentrations of NO_2 from 7 April to 11 May 2019 (top) and 2020 (bottom) imaged using data obtained from the ESA Copernicus Sentinel 5P satellite.

Table 2.1 shows change of air quality parameters in Singapore during the Circuit Breaker period of 2020, a stay-at-home order and cordon sanitaire implemented by the Government of Singapore in response to the COVID-19 pandemic in the country on 7 April 2020. During this period, all non-essential workplaces were closed and all schools transitioned to home-based learning.

Fig. 2.1

Table 2.1

	average reading over last 4 years	reading during Circuit Breaker
NO_2 (μg m^{-3})	33.1	15.1
PM_{10} (μg m^{-3})	29.8	23
$PM_{2.5}$ (μg m^{-3})	14.4	10.1

(a) **(i)** Describe and explain, with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide.

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……. [2]

(ii) Using your understanding of the source of NO_2, suggest a reason for the trend shown in Table 2.1.

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……. [1]

(iii) Suggest why the measured PM_{10} and $PM_{2.5}$ did not change as significantly as NO_2.

…..

……. [1]

(b) Haze events have been occurring in China megacities in recent years. These hazes mainly consist of aqueous sulfates, SO_4^{2-}, produced as a result of SO_2 and NO_2 reacting under particularly adverse meteorological conditions. One possible reaction is shown by the following unbalanced equation, where NO_2 undergoes reduction to form NO_2^-.

$$NO_2 + HSO_3^- + H_2O \rightarrow H^+ + NO_2^- + SO_4^{2-}$$

Complete the chemical equation for the reaction.

……NO_2 + ……HSO_3^- + ……H_2O → ……H^+ + ……NO_2^- + ……SO_4^{2-} [1]

(c) NO_2 can be formed from NO, as shown in equation 1.

equation 1 $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Three experiments were carried out to determine order of reaction with respect to NO and O_2, and hence the rate constant for this reaction.

Experiment 1 was carried out with initial concentrations of NO and O_2 at 0.10 mol dm^{-3} and 0.0050 mol dm^{-3} respectively.

Fig. 2.2 shows the concentration of O_2 recorded against time for this experiment.

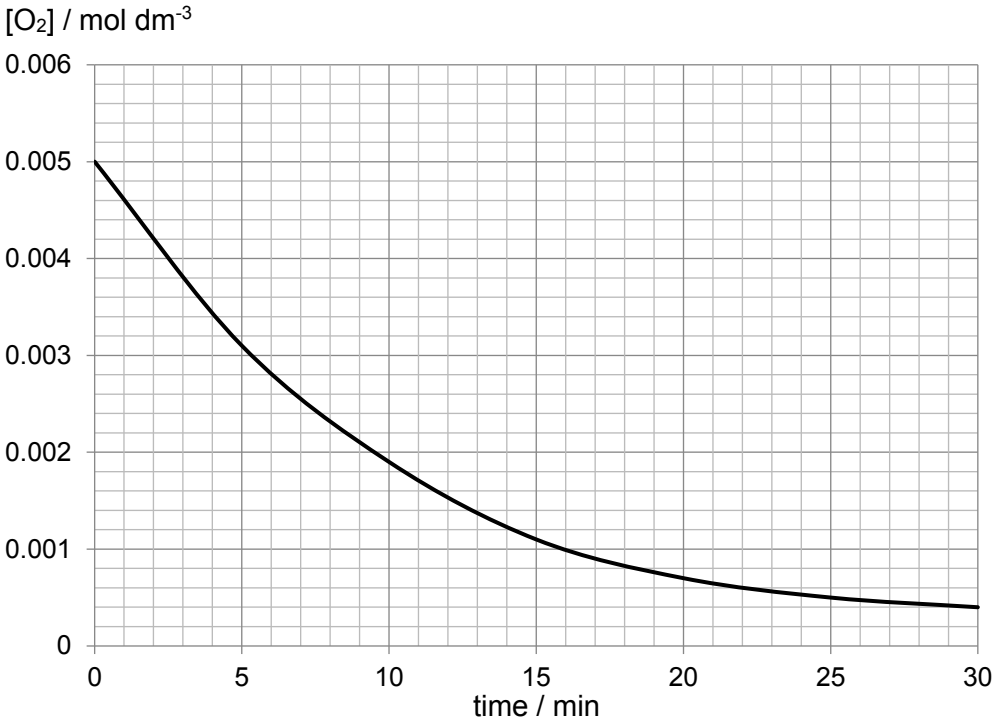

Fig. 2.2

The experiment was repeated to find the initial rate of reaction at different initial concentrations of NO and O_2. The results of these experiments are shown in Table 2.2.

Table 2.2

Experiment	Initial [NO] / mol dm^{-3}	Initial [O_2] / mol dm^{-3}	Initial rate of formation of NO_2 / mol dm^{-3} s^{-1}
2	0.001	0.002	5.55×10^{-10}
3	0.002	0.003	3.33×10^{-9}

(i) Define the terms *order of reaction* and *rate constant*.

…..

…..

…..

…… [2]

(ii) Explain why NO is used in large excess in experiment 1.

…..……

…… [1]

(iii) Using the data given, determine the order of reaction with respect to each of the reactants and hence, calculate the rate constant, stating its units.

[3]

(iv) Determine the initial rate of depletion of O_2 when [NO] = 0.002 mol dm^{-3} and [O_2] = 0.002 mol dm^{-3}.

[2]

(d) The removal of NO_2 is important because of its significant environmental impact. The solution to this problem is to enforce the installation of catalytic converter onto the exhaust pipes of vehicles. With the aid of a Maxwell Boltzmann distribution curve, explain how catalytic converters help to reduce the release of NO_2 into the environment.

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……..... [3]

[Total: 16]

3 **(a)** State and explain the relative Brønsted-Lowry acidity of phenol, nitrophenol and ethanoic acid.

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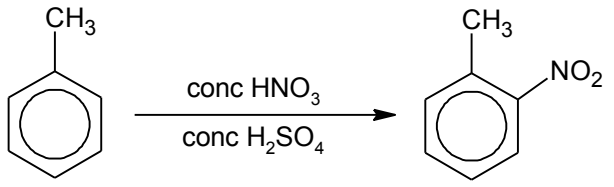
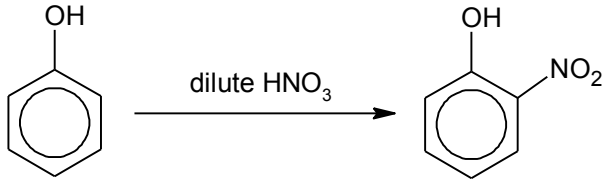
..... [3]

(b) Both methylbenzene and phenol react with nitric acid, but under different conditions.





2-nitrophenol

(i) Describe the mechanism of the reaction between methylbenzene and concentrated nitric acid, showing curly arrows, charges and any relevant lone pairs.

[3]

(ii) Explain why different conditions are needed for these two reactions.

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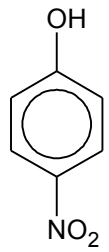
……..

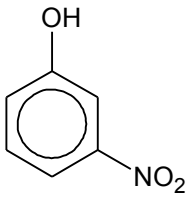
……..

…… [2]

When phenol reacts with dilute nitric acid, two other isomers, 4-nitrophenol and 3-nitrophenol are formed in the reaction mixture.



4-nitrophenol



3-nitrophenol

(iii) Explain why 3-nitrophenol is the isomer least likely to form in this reaction.

……..

……..

…… [1]

(iv) The boiling points of two isomers are shown in Table 3.1.

Table 3.1

compound	boiling point / ^{o}C
2-nitrophenol	216
4-nitrophenol	279

Suggest a reason for the difference in boiling points between 2-nitrophenol and 4-nitrophenol. Include a diagram to illustrate your answer.

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……..

…… [2]

Phenol can be synthesised from nitrobenzene through the following reaction scheme.

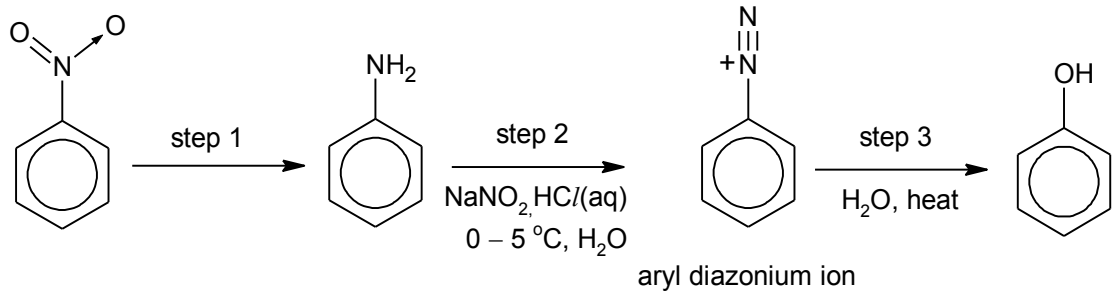


Fig. 3.1

(c) **(i)** Explain, in terms of change in oxidation number of N atom, why step 1 is a reduction reaction.

……..

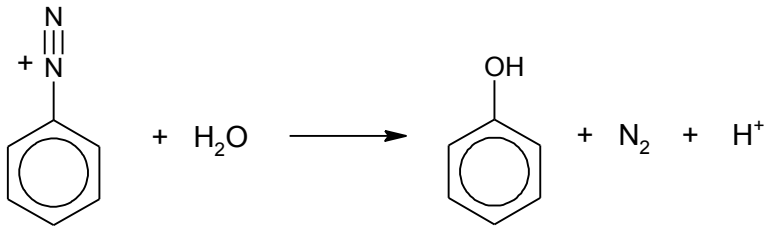
……..

…… [1]

(ii) Write a balanced equation for the reduction of nitrobenzene to phenylamine. Use [H] to represent the reducing agent.

…… [1]

(iii) Aryl diazonium ion reacts with water to form phenol.



aryl diazonium ion

The reaction proceeds via nucleophilic substitution (S_N1) mechanism.

- The first step is the rate determining step. Nitrogen gas is produced.
- This is followed by the water molecule acting as a nucleophile to attack the carbocation formed.
- The third step involves deprotonation to form phenol.

Suggest the mechanism for this reaction, showing curly arrows, charges and any relevant lone pairs.

[2]

(iv) The aryl diazonium ion reacts similarly with ethanol.

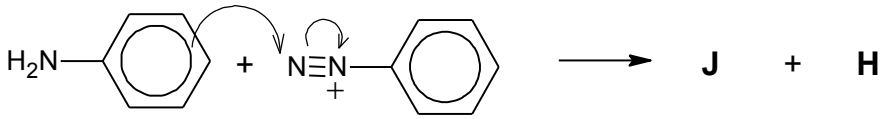
Draw the structure of the organic compound. Suggest how the overall rate of reaction will be affected when ethanol is used in the reaction.

……..

……..

……. [2]

(d) **(i)** In step 3 of Fig. 3.1, a side reaction can occur. The electron deficient aryl diazonium ion can undergo electrophilic substitution with phenylamine to form an azobenzene which contains the diazenyl functional group, - N=N- . Two cis-trans isomeric azobenzene **J** and **H** are formed.



aryl diazonium ion azobenzene

Draw the structures of **J** and **H.**

[2]

(ii) Suggest why cis-azobenzene is less stable than trans-azobenzene.

……

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……. [1]

[Total: 20]

4 NH_3 is produced from N_2 and H_2 in the presence of a catalyst. When NH_3 is heated in a sealed reactor, the following equilibrium is established.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Write an expression for K_p for this equilibrium, stating the units.

[1]

(ii) In an experiment, N_2 and H_2 are placed in a sealed reactor in the molar ratio 1:3. Fig. 4.1 shows the variation in the amounts of N_2 and NH_3 in the system with time. The reactor is maintained at a temperature of 750 K and the total pressure is 197 atm.

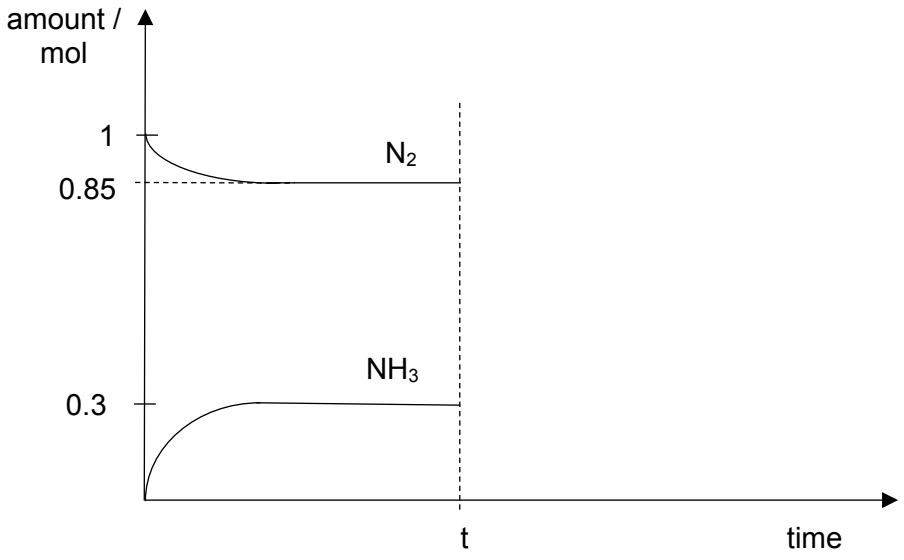

Fig. 4.1

Use the information provided above and data from Fig. 4.1 to calculate the value of K_p for the equilibrium at 750 K.

[2]

(iii) Of the three gases at 750 K, the behaviour of NH_3 deviates the most from ideal gas behaviour and N_2 behaves less ideally than H_2.

Explain the relative deviations from ideal gas behaviour of these gases.

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……..

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……..

……..

…… [2]

(iv) At time t, gases in the sealed reactor were passed into a condenser. NH_3 gas is cooled and removed from the system. The remaining gases were then recycled and passed back into the reactor.

Assuming that the pressure and temperature in the sealed reactor remains unchanged, sketch the changes in amount of N_2 and NH_3 that would be observed from t min in Fig. 4.1. [1]

(v) The reaction to produce NH_3 is repeated with the same amounts of N_2 and H_2 at 750 K in a smaller reactor. State the effects, if any, of this change on the yield of ammonia and on the value of K_p. Explain your answer.

- effect on yield of ammonia

……..

……..

……..

……..

- effect on the value of K_p

……..

……..

……..

…… [2]

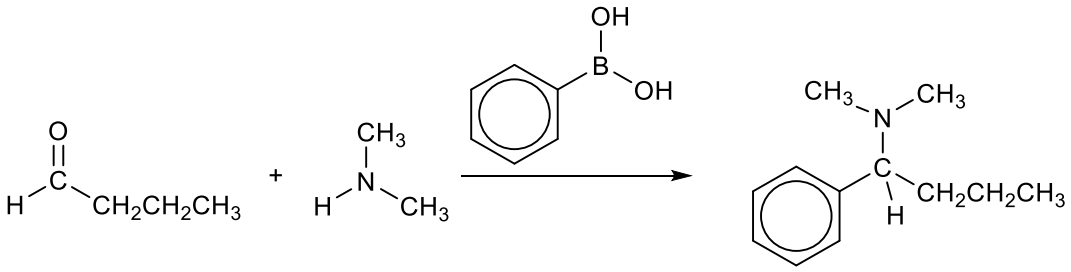
Direct treatment of ammonia and amine with an alkylating agent like alkyl halides, will result in the formation of by-products. With the help of carbonyl compounds, one substituted amine compound rather than a mixture can be obtained. Parts **(b)** and **(c)** introduce two such methods.

(b) Method 1: Petasis reaction

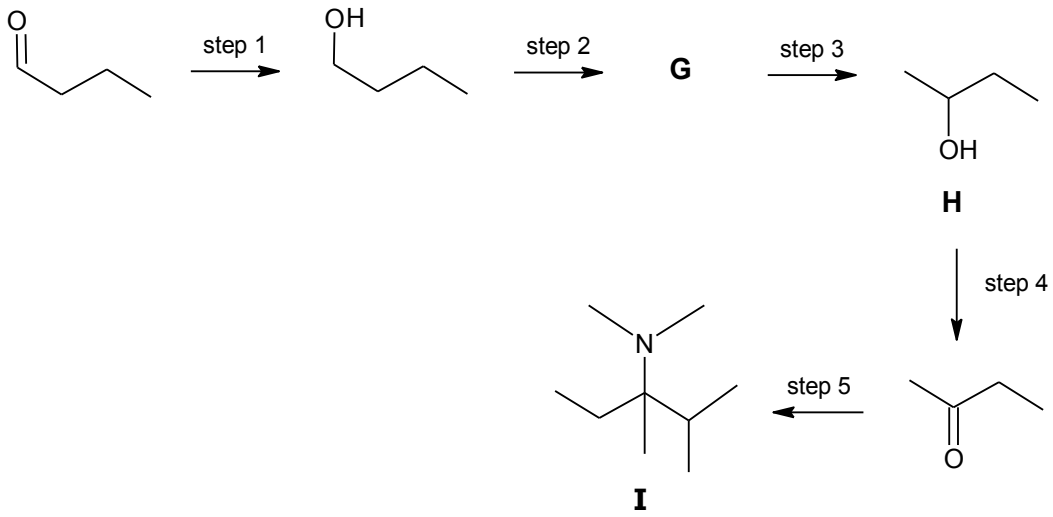
In the Petasis reaction, carbonyl compounds react with amines in the presence of suitable boronic acids to form substituted amines.

The general structure of a boronic acid is $B(OH)_2R$ where R is an alkyl or aryl group.

An example of the Petasis reaction is given below.



The Petasis reaction can be used in step 5 of the following synthesis of compound **I** from butanal.



(i) Suggest the structure of compound **G**.

[1]

(ii) Suggest reagents and conditions for steps 1, 2, 3 and 5.

step 1 ……..

step 2 ……..

step 3 ……..

step 5 ……..

[4]

(iii) State the type of stereoisomerism shown by compound **H** and hence draw the structures of the isomers.

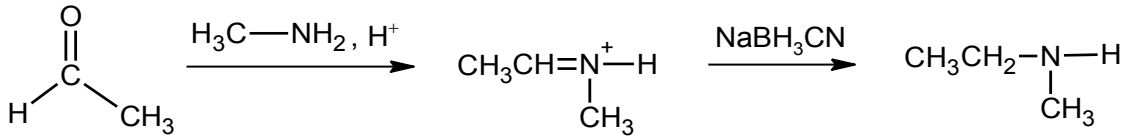
type of stereoisomerism ……

[2]

(c) Method 2: Reductive amination

In the reductive amination of carbonyl compounds, ketones and aldehydes react with primary amine in the presence of an acid catalyst via an iminium ion intermediate. The iminium ion formed is then reduced by $NaBH_3CN$ to form the desired substituted amine.

An example of the reductive amination reaction is given below.



ethanal iminium ion

The mechanism for the above reaction involved a series of five steps as shown in Fig. 4.2.

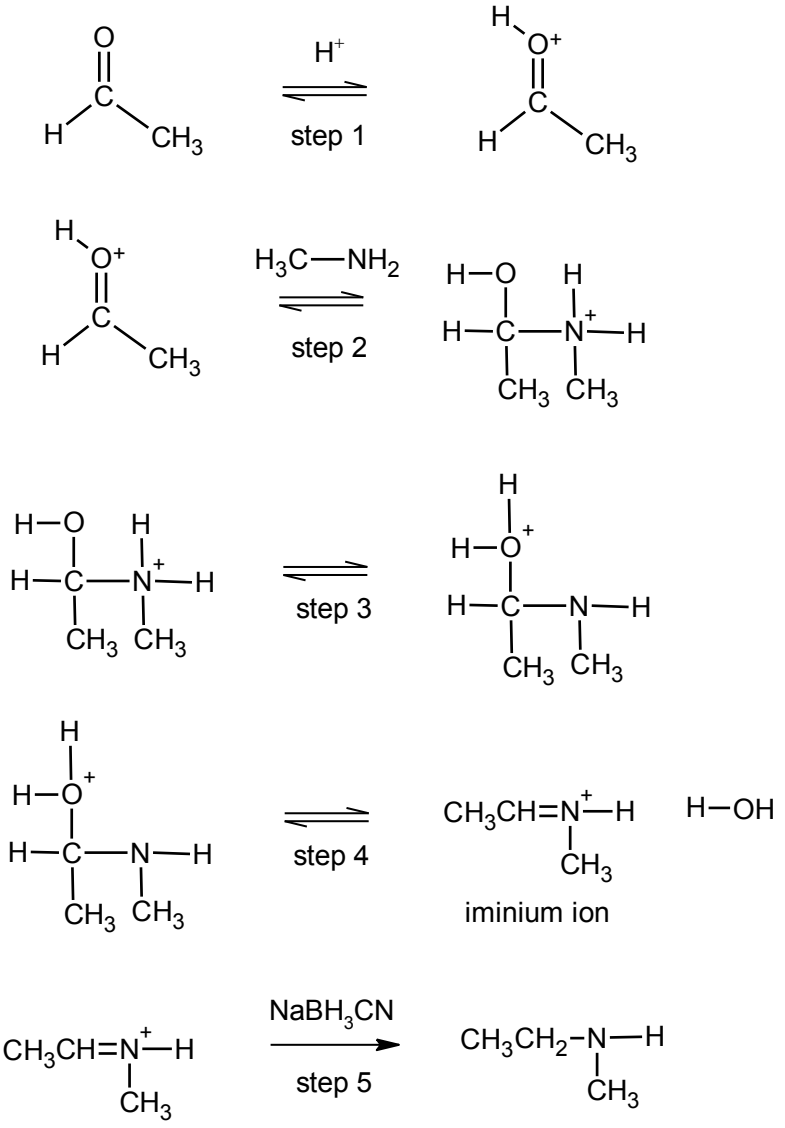


Fig. 4.2

(i) Complete Fig. 4.2 to suggest a mechanism for steps 1 to 4 of the formation of N-ethylmethylamine. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(ii) The iminium ion intermediate formed in step 4 of the reductive amination reaction displays stereoisomerism.

State the type of stereoisomerism. With the aid of a labelled diagram, showing how the orbitals overlap, explain how this stereoisomerism arise.

type of stereoisomerism ……

……..

……..

……..

…… [3]

(iii) Benzaldehyde can also be used in the reductive amination reaction. Other than the use of alkaline aqueous I_2, outline a simple chemical test that you could carry out to distinguish benzaldehyde from ethanal. Hence, write a balanced equation for the reaction that occur.

test ……..

observations ……

……..

……..

balanced equation

[2]

(d) Both N-ethylmethylamine and N-methylethanimine are examples of nitrogen compounds.

Table 4.1

Lewis base	type of hybridisation of N atom
$CH_3CH_2NHCH_3$ N-ethylmethylamine	
$CH_3CH{=}NCH_3$ N-methylethanimine	

(i) Explain how the two nitrogen compounds act as Lewis bases. Illustrate your answer with an equation using one of the Lewis bases stated in Table 4.1.

……..

……. [1]

(ii) Complete Table 4.1 and hence explain why N-ethylmethylamine is more basic than N-methylethanimine.

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……..

……. [2]

[Total: 25]