ST ANDREW'S JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME	

CLASS	2	2	S		

CHEMISTRY 9729/03

Paper 3 Free Response **14 September 2023**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that you hand in.

Write in dark blue or black pen.

You may use a 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.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use		
Q1		**21**
Q2		**20**
Q3		**19**
Q4 or Q5		**20**
Total		**80**

This document consists of **36** printed pages (including this cover page).

Section A

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

1 In the manufacture of tinted glass for chapels, a variety of carbonates including calcium carbonate were smelted together to form the needed colourations.

(a) **(i)** Draw a 'dot-and-cross' diagram to show the bonding present within a carbonate ion, CO_3^{2-}. [1]

(ii) State and explain, with reference to the VSEPR theory, the shape of the carbonate ion. [2]

(iii) When sodium carbonate was added to water, a weakly alkaline solution is produced.

Write an equation for this reaction. [1]

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(b) **(i)** Write a balanced equation, with state symbols, for the thermal decomposition of calcium carbonate under standard conditions. [1]

(ii) Construct a fully labelled energy cycle to show that the standard enthalpy change of formation of carbon dioxide is –399 kJ mol^{-1}.

Your cycle should include relevant data from the *Data Booklet* together with the following data.

Standard enthalpy change of atomisation of carbon = +715 kJ mol^{-1} [2]

(iii) The enthalpy changes of formation for these species are shown in the following table.

Species	$CaCO_3$(s)	CaO (s)	CO_2(g)
ΔH_f / kJ mol^{-1}	–1207	–635	–399

Using your answer in **(b)(i)** and **(ii)**, calculate the enthalpy change of decomposition of calcium carbonate. [1]

(iv) By considering the entropy, ΔS, and enthalpy, ΔH, changes in the decomposition of calcium carbonate, predict if the reaction is spontaneous at high or low temperature. [2]

(v) Using relevant data from the *Data Booklet*, suggest how the decomposition temperature of nickel carbonate would compare with calcium carbonate. Explain your reasoning. [2]

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(c) The reaction of propanone with iodine can be catalysed by an acid.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

Sketch a Boltzmann distribution curve for the reaction and use it to explain the effect on the rate of the reaction when the catalyst is removed by adding $CaCO_3$. [3]

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(d) When aqueous Cu^{2+} and Ni are mixed, an equilibrium is set up.

$$Ni + Cu^{2+} \rightleftharpoons Ni^{2+} + Cu$$

(i) Draw a fully labelled diagram of the experimental set-up used to measure the standard cell potential for this equilibrium. [2]

(ii) Calculate the standard cell potential in **(d)(i)** and hence calculate the standard free energy change, $\Delta G^\ominus$, per mole of Cu formed. [2]

(iii) Use the *Data Booklet* to suggest how the position of equilibrium would change when concentrated NH_3 is added to Ni^{2+}/Ni half cell. Explain your answer *a*nd write a balanced equation for this reaction. [2]

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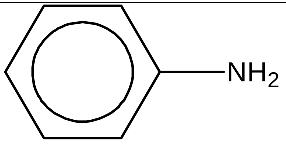
2 **(a)** Methylamine, CH_3NH_2, can function as a *Lewis base*.

(i) Explain what is meant by this statement and illustrate your answer with an equation. [2]

(ii) Describe and explain the relative basicities of the following compounds.

Compound	**formula**
A	CH_3NH_2
B	$CH_3CH_2CH_2CONHCH_3$
C	

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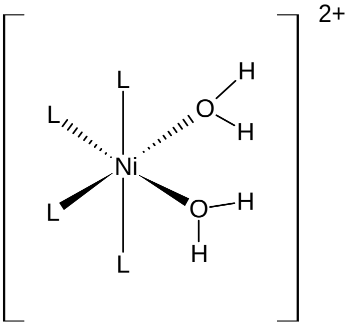
(b) Methylamine can also serve as a *monodentate ligand*.

(i) State what is meant by *monodentate ligand.* [2]

(ii) In the presence of aqueous methylamine, $[Ni(H_2O)_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.

$[Ni(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Ni(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ ---- ***Reaction 2.1***

One of the isomeric octahedral complexes has the *cis* configuration as shown below where L is the CH_3NH_2 ligand.



Draw the **3-dimensional** structure of the *trans* isomer of $[Ni(CH_3NH_2)_4(H_2O)_2]^{2+}$. You may also use L to represent CH_3NH_2. [1]

(iii) Predict the effect of plane-polarised light on the solution containing the *cis* isomer of the $[Ni(CH_3NH_2)_4(H_2O)_2]^{2+}$ complex. Explain your reasoning. [2]

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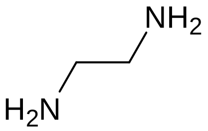
(c) Ethane-1,2-diammine, en, is another ligand that reacts $[Ni(H_2O)_6]^{2+}$ to form octahedral nickel(II) complexes.



ethane-1,2-diammine

When an excess of ethane-1,2-diammine is added to an aqueous solution of $[Ni(H_2O)_6]^{2+}$,the following equilibrium is established.

$[Ni(H_2O)_6]^{2+}(aq) + 3en\ (aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6H_2O\ (l)$ ------ ***Reaction 2.2***

(i) Draw a diagram of the structure of $[Ni(en)_3]^{2+}$, showing the **3-dimensional** arrangement around the Ni(II) ion. [1]

(ii) The K_c value for ***Reaction 2.2*** is 6.76 x 10^{17}. Hence, suggest the sign and magnitude of $\Delta G^\ominus$ for ***Reaction 2.2*** and identify the more stable complex for the reaction. [1]

(iii) With reference to ***Reactions 2.1*** and ***2.2***, suggest why ethane-1,2-diammine forms a more stable nickel(II) complex than with methylamine. [1]

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(d) Nickel complexes often exhibit a range of colours as shown in Table 2.1.

Complex	**Colour**
$[Ni(H_2O)_6]^{2+}$	Green
$[Ni(en)_3]^{2+}$	Blue
$[Ni(H_2O)_6]^{3+}$	Pink

Table 2.1

(i) The five d orbitals in a gas–phase Ni^{2+} ion are degenerate, but are split into two levels when Ni^{2+} ion is in an octahedral complex.

State and explain how the energy of the d subshell of Ni^{2+} ion in an octahedral complex compares with the energy of the d subshell in the gas-phase Ni^{2+} ion. State and explain why the d orbitals split into two levels in an octahedral complex, including which of the d orbitals are in each level. [3]

(ii) Explain the following:

- $[Ni(H_2O)_6]^{2+}$ has a different colour from $[Ni(H_2O)_6]^{3+}$.
- $[Ni(en)_3]^{2+}$ has a different colour from $[Ni(H_2O)_6]^{2+}$. [2]

(iii) When concentrated hydrochloric acid is added to a green solution containing $[Ni(H_2O)_6]^{2+}$, a yellow solution of $[NiCl_4]^{2-}$ is formed and the following equilibrium is established.

$$[Ni(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [NiCl_4]^{2-} + 6H_2O \quad \text{--------} \ \textbf{\textit{Reaction 2.3}}$$

Suggest the expected observation when silver nitrate solution is added dropwise to the yellow solution of $[NiCl_4]^{2-}$. Explain your answer. [2]

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3 1,3-butadiene is a colourless gas at room temperature. It undergoes a reaction with an equimolar amount of HBr to produce a mixture of products as shown in Fig. 3.1

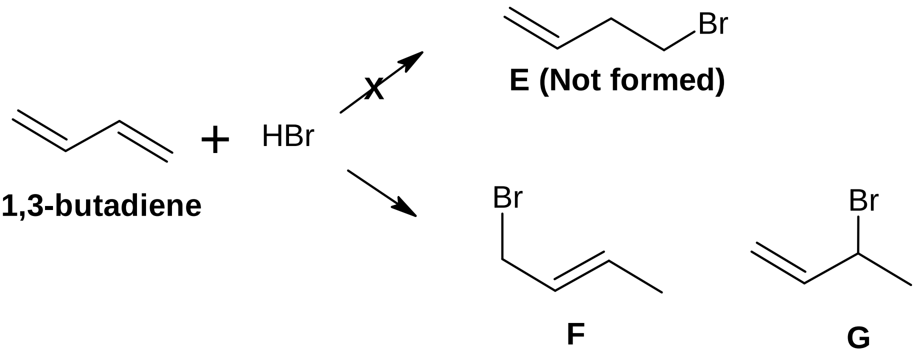
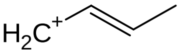


Fig. 3.1

(a) **(i)** Suggest the type of reaction between 1,3-butadiene and HBr. [1]

(ii) The reaction between 1,3-butadiene and HBr to form compound **Y** involves the shifting of the π electrons and the generation of the carbocation,  in the first step.

Complete Fig. 3.2 to suggest the mechanism for this reaction. Draw curly arrows to show the movement of electron pairs, showing relevant lone pairs and dipoles to describe the mechanism.

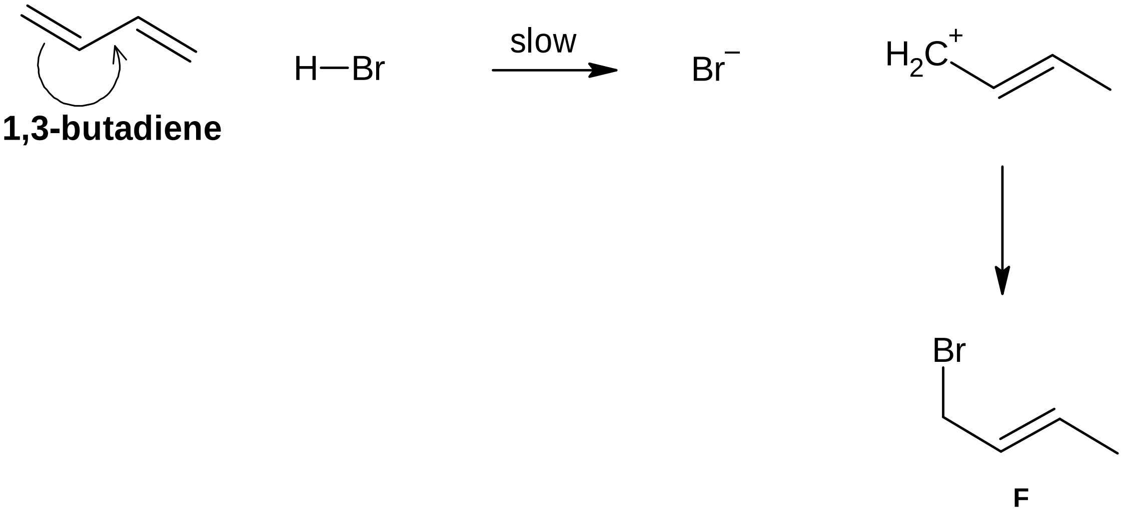


Fig. 3.2

[2]

(iii) Draw the structures of the carbocation intermediates that would result in compound **X** and **Z** respectively. [2]

(iv) Using the structures of the carbocation intermediates of **X**, **Y** and **Z**, suggest reasons to explain Fig. 3.1. Use concepts of electronic effect and delocalisation in your answer. [2]

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(b) 1,3-butadiene can be reduced with hydrogen gas in the presence of a nickel catalyst. Explain why $LiAlH_4$ cannot be used. [1]

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(c) Compound **R** ($C_{13}H_{16}O_3$) contains a 1,4-disubstituted benzene ring and does not contain any chiral centre.

R does not react with 2,4-dinitrophenylhydrazine and PCl_5. When treated with neutral $FeCl_3$, **R** forms a violet solution.

R also reacts with hot aqueous sulfuric acid to form ethanol as one of the products.

When treated with hot acidified $KMnO_4$, **R** forms compounds **S**, $C_8H_8O_2$, **T**, $C_3H_4O_3$ and **U**, $C_2H_4O_2$.

Compound **S** forms a yellow precipitate with alkaline aqueous iodine. **T** and **U** reacts with sodium carbonate to give effervescence.

Suggest possible structures of **R**, **S**, **T** and **U**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [8]

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(d) Copper is one of the oldest transition metals to be used in synthetic organic chemistry. When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with silver and zinc as minor impurities. It contained no other metal. In order to purify it, this alloy was the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

Explain with relevance to relevant $E^\ominus$ values, what happens to the silver and zinc impurities during this purification procedure.

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Section B

Answer **one** question from this section.

4 **(a)** Describe and explain the trend in acidity of the hydrogen halides, HF, HC*l*, HBr and HI. Include equations to illustrate the acidic strength of HF and HI. [3]

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(b) The Koch reaction, as shown in Fig. 4.1, is an organic reaction for the synthesis of tertiary carboxylic acids from alkenes. On treatment with sulfuric acid, the mechanism begins by protonation of the alkene to form a carbocation. This is followed by an attack on the resulting carbocation by carbon monoxide. The subsequent acylium cation is then hydrolysed to the tertiary carboxylic acid.

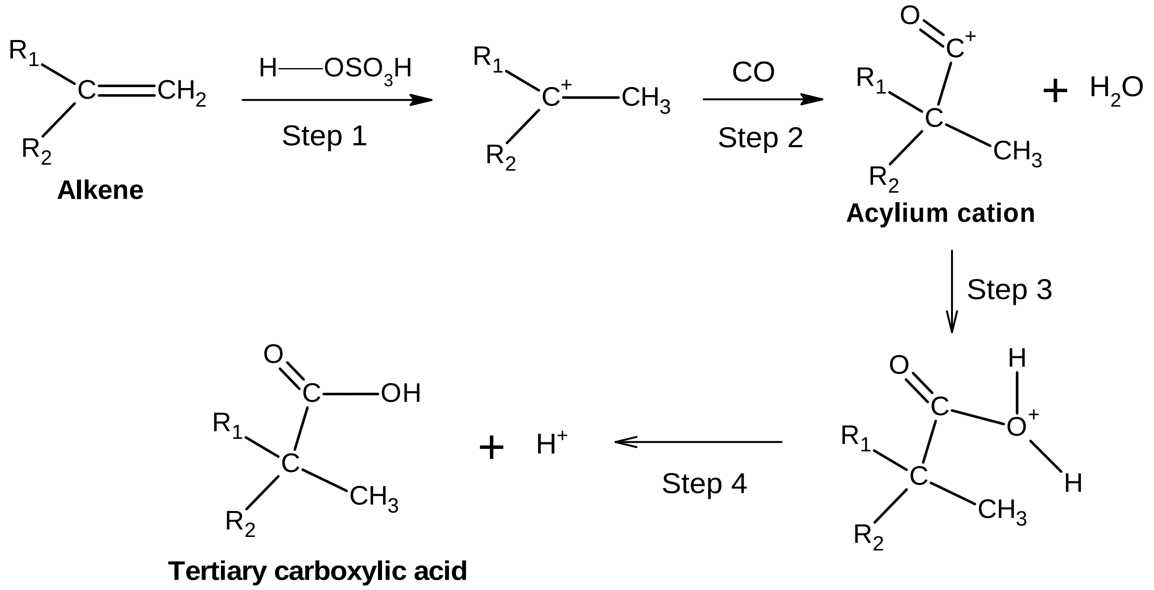
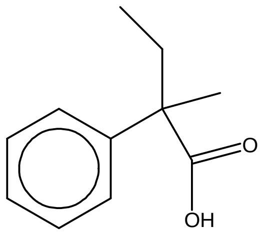


Fig. 4.1

(i) With reference to the hybridisation of the carbon atoms and orbital overlap, describe the covalent bonding in an alkene, C=C. Draw labelled diagram(s) to illustrate your answer. **[2]**

(ii) On Fig. 4.1, draw curly arrows in **Steps 3** and **4**, to show the mechanism for the reaction. Show all relevant lone pairs of electrons in your answer. **[1]**

(iii) Draw the structure of the alkene that produces carboxylic acid **A** from the Koch reaction.



Carboxylic acid A **[1]**

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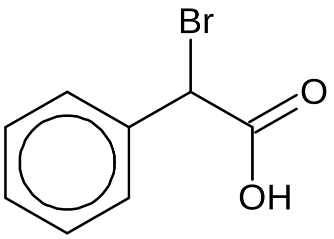
(c) **(i)** Describe the type of stereoisomerism shown by carboxylic acid **A** and draw the structures to illustrate your answer. [2]

(ii) Carboxylic acid **A** and carboxylic acid **B** have different pK_a values. State which compound, **A** or **B**, has a smaller pK_a value. Explain your answer.



Carboxylic acid B

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(d) Alkenes can react with an excess of hydrogen in the presence of a catalyst to form alkanes. Outline the mode of action of the nickel catalyst in the reaction of alkenes with hydrogen. [2]

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(e) 40.00 cm^3 of 0.595 mol dm^{-3} of aqueous sodium hydroxide is added to 25.0 cm^3 of 0.500 mol dm^{-3} of $(CH_3)_3CCOOH$ that was formed from the Koch reaction.

(i) Write an expression for K_a of $(CH_3)_3CCOOH$, giving its units.
Hence, calculate K_a of $(CH_3)_3CCOOH$ given that the initial pH of $(CH_3)_3CCOOH$ is 2.8. [2]

(ii) Write two equations to show how a solution containing $(CH_3)_3CCOO^-(aq)$ and $(CH_3)_3CCOOH(aq)$ behaves as a buffer when small amounts of $OH^-(aq)$ and $H_3O^+(aq)$ are separately added to the solution. [2]

(iii) Calculate the $[(CH_3)_3CCOO^-] / [(CH_3)_3CCOOH]$ ratio when the pH of the solution is 5.6. Hence, comment, with reason, on the effectiveness of the mixture as a buffer in removing H_3O^+ compared to in removing OH^-. [2]

(iv) Write an equation to show that the pH of the equivalence point is more than 7 in this titration. [1]

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5 **(a)** Describe the reactions of Period 3 oxides with water by reference to the reactions of Na_2O, Al_2O_3 and P_4O_{10}.

Write equations for any reactions described. [3]

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(b) Table 5.1 gives the melting points, in °C, of the oxides and chlorides of two elements in the Periodic Table.

	Magnesium	Aluminium
Oxide	2900	2000
Chloride	714	190

Table 5.1

Explain, in terms of structure and bonding, the differences in melting point between

- $MgCl_2$ and $AlCl_3$
- MgO and Al_2O_3 [2]

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(c) Values of two solubility products are given in **Table 5.2**.

Compound	K_{sp}
$Hg_2C_2O_4$	6.5×10^{-7}
$Ag_2C_2O_4$	5.4×10^{-12}

Table 5.2

(i) Write the expression for the solubility product, K_{sp}, of $Hg_2C_2O_4$, stating its units. [2]

(ii) Solid mercury oxalate is shaken with water. The remaining solid is filtered off, leaving a saturated solution, **X**.

Drops of dilute silver nitrate are added to **X** until silver oxalate just precipitates. Using Table 5.2, calculate the concentration of $[C_2O_4^{2-}(aq)]$ in **X** and the concentration of $[Ag^+(aq)]$ when $Ag_2C_2O_4$ just precipitates. [2]

(iii) Suggest and explain how the solubility of $Ag_2C_2O_4$ is affected by adding $NH_3(aq)$. [2]

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(d) Hofmann elimination is an elimination reaction of an amine to form alkenes. The least stable alkene, which contains the fewest substituents on the carbons of the double bond, known as the Hofmann product, is preferentially formed.

The reaction starts with the formation of a quaternary ammonium iodide salt by treatment of the amine with excess methyl iodide, followed by treatment with silver oxide and water to form a quaternary ammonium hydroxide. When this salt undergoes decomposition by heat, the Hofmann product, alkene **Y**, and another alkene, **Z**, are formed.

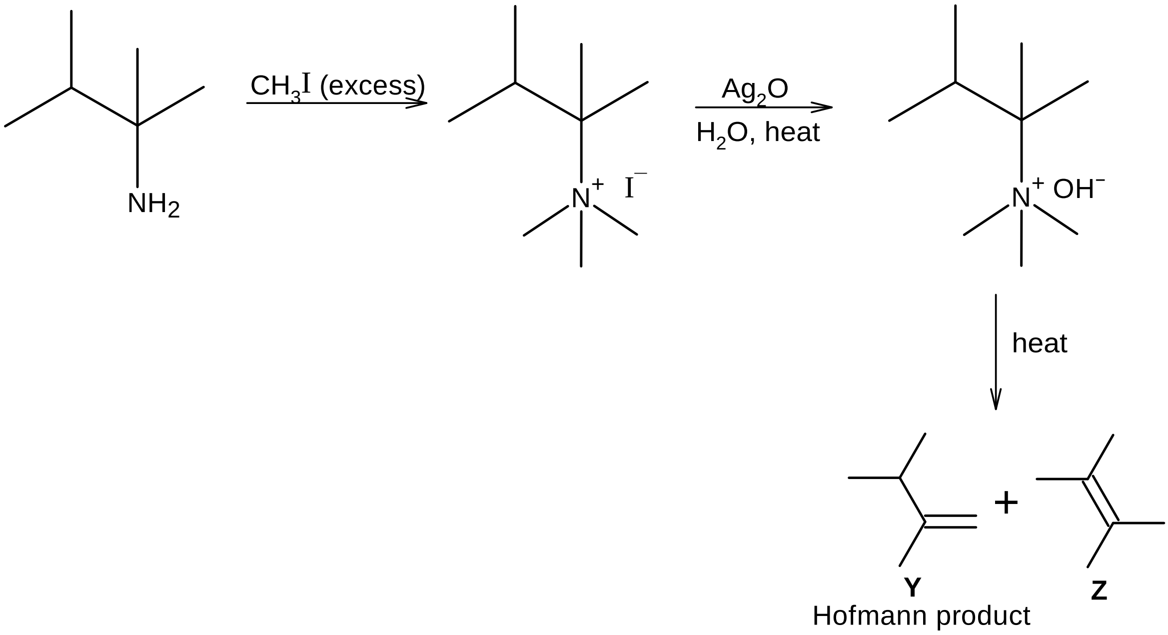
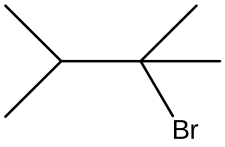


Fig. 5.1

(i) Both alkenes, **Y** and **Z**, are reacted separately with gaseous HBr. In both reactions, 2-bromo-2,3-dimethylbutane is obtained as either the only product or the major product. Explain why.



2-bromo-2,3-dimethylbutane [2]

(ii) The Hofmann product, **Y**, produced in Fig. 5.1 undergoes a reduction reaction, followed by reaction with Br_2 in ultraviolet light to form two mono-brominated products. Draw the structure of these products.

Hence, state the mole ratio in which the products are formed explaining your answer. [3]

(iii) It is found by experiment that during free radical substitution, primary, secondary and tertiary hydrogen atoms are replaced by bromine atoms at different rates, as shown in **Table 5.3**.

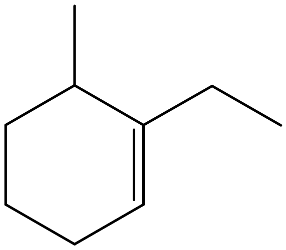
Reaction	relative rate
$RCH_3 \rightarrow RCH_2Br$	1
$R_2CH_2 \rightarrow R_2CHBr$	7
$R_3CH \rightarrow R_3CBr$	21

Table 5.3

Explain why the relative rate of substitution of a tertiary hydrogen atom is faster than that of a primary hydrogen atom. [1]

(iv) Predict the relative ratio of the two possible products from **(ii)** using the information in Table 5.3, together with the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule. [1]

(v) Draw the structure of the amine that produces the following Hofmann product from the Hofmann elimination reaction.



Hofmann product

Hence, suggest another possible alkene that could be formed from the Hofmann elimination reaction. [2]

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