2020 YIJC Preliminary Examination H2 Chemistry Paper 3 (Suggested Answers)

1 Chlorine is an element in Group 17 of the Periodic Table. It exists as a diatomic gas at room temperature. Chlorine can also be found in many inorganic and organic compounds.

(a) Predict the colour of the final solutions when

- Cl_2(aq) is added to KBr(aq)
- I_2(aq) is added to KC*l*(aq)

Write equations for any reactions that occur. State clearly if no reaction occurs. [2]

- **$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$**
  colour of final solution: orange

- **No reaction**
  colour of final solution: brown

(b) Describe and explain the trend in the thermal stabilities of the hydrogen halides HC*l*, HBr and HI. [2]

The thermal stabilities of the hydrogen halides **decrease** down the Group from HC*l* to HBr to HI.

This is because

- the **size of the halogens increases** from C*l* to I and the valence orbital used for bonding is larger and more diffuse;
- the **effectiveness of the orbitals overlap decreases**;
- this result in the **weaker covalent bond formed between the hydrogen and halogen atoms** or **quoting H-X bond energies**;
- **lesser amount of energy** is required to overcome the covalent bond between the hydrogen and halogen atoms.

(c) Chlorine dioxide, ClO_2 was discovered in 1811 and has been widely used for bleaching purposes in the paper industry and for treatment of drinking water.

(i) ClO_2 can be synthesised from the reaction between $NaClO_3$ and H_2O_2 in an acidic medium.
Construct a balanced equation for the reaction between ClO_3^- and H_2O_2. [2]

reduction: $\mathbf{ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O}$
oxidation: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
$\mathbf{2ClO_3^- + H_2O_2 + 2H^+ \rightarrow 2ClO_2 + 2H_2O + O_2}$

(ii) In the process of handling ClO_2, the concentration of the ClO_2 in aqueous solution must not exceed 45 parts per million by mass, as it will cause irritation to the eyes and nose.

1 part per million can be expressed as 1 mg of the substance in 1 kg of water.

An aqueous solution of ClO_2 was prepared by adding 150 cm^3 of 1.0×10^{-3} mol dm^{-3} $NaClO_3$ to 100 cm^3 of 2.0×10^{-3} mol dm^{-3} H_2O_2.

Using your equation in **(c)(i)**, calculate the concentration of the $ClO_2(aq)$ in **parts per million**, State whether it has exceeded the safety limit.

[Assume the density of the final solution is 1 g cm^{-3}.] [3]

Amount of $NaClO_3$ = $(1.0 \times 10^{-3}) \times 0.15$ = **1.50×10^{-4} mol**
Amount of H_2O_2 = $(2.0 \times 10^{-3}) \times 0.10$ = **2.00×10^{-4} mol**
Limiting reagent: $NaClO_3$

Amount of ClO_2 produced = 1.50×10^{-4} mol
Mass of ClO_2 produced = $(1.50 \times 10^{-4}) \times 67.5 = 0.010125$ g = **10.125 mg**

Total mass of solution = 250 g = 0.250 kg
$[ClO_2]$ in ppm = 10.125 ÷ 0.250 = **40.5 ppm**

It has **not exceeded the safety limit**.

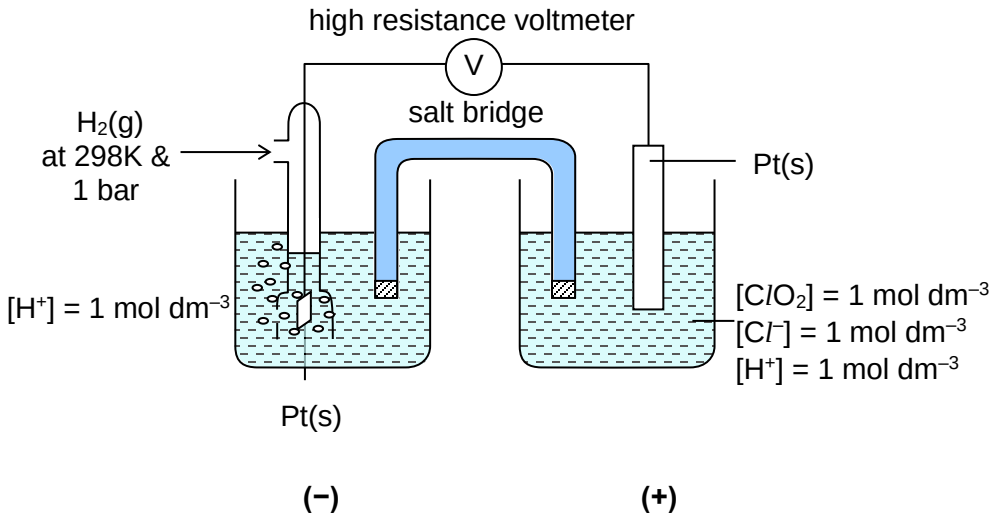
The electrode potential for the reduction of chlorine dioxide is shown.

$$ClO_2(aq) + 4H^+(aq) + 5e^- \rightleftharpoons Cl^-(aq) + 2H_2O(l) \qquad E^\ominus = +1.50V$$

(iii) State what is meant by the term *standard electrode potential*. [1]

The standard electrode potential of an element is the **potential difference between the element and the aqueous solution of its ion at 1 mol dm^{-3} relative to that of the standard hydrogen electrode at 298 K and 1 bar**.

(iv) Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure the standard reduction potential of ClO_2/Cl^- in the laboratory. Indicate clearly the positive and negative electrodes. [3]



Another cell composing of a standard ClO_2/Cl^- half-cell and a standard Fe^{3+}/Fe^{2+} half-cell was set up.

(v) Calculate $\Delta G^\ominus$, in kJ mol^{-1}, for the reaction that occurs [2]

$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$5Fe^{2+} + ClO_2 + 4H^+ \rightarrow 5Fe^{3+} + Cl^- + 2H_2O$
$E^\ominus_{cell} = +1.50 - (+0.77) =$ **+0.73 V**
$\Delta G^\ominus = -nFE^\ominus_{cell} = -5 \times 96500 \times 0.73 = -352225$ J mol^{-1} = **–352 kJ mol^{-1}**

(vi) State and explain what happens to the standard cell potential, $E^{\ominus}_{cell}$, when chlorine gas is bubbled into the Fe^{3+}/Fe^{2+} half-cell. [2]

When chlorine is bubbled into into the Fe^{3+}/Fe^{2+} half-cell, **Fe^{2+} will be oxidised to Fe^{3+} causing $[Fe^{2+}]$ to decrease** (or $[Fe^{3+}]$ to increase).

As such the $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ equilibrium shifts to the right and $E^{\ominus}_{reduction}(Fe^{3+}/Fe^{2+})$ to become more positive and **$E^{\ominus}_{cell}$ less positive**.

(d) Describe and explain the relative ease of hydrolysis of chloroethane, chlorobenzene and ethanoyl chloride. [3]

reactivities: **ethanoyl chloride > chloroethane > chlorobenzene**

Ethanoyl chloride is more reactive than chloroethane towards nucleophilic substitution reactions because **the δ+ charge on the carbonyl carbon is higher due to the additional electron withdrawing O atom bonded to it** or **the reactive carbon of ethanoyl chloride is sp^2 hybridised and is trigonal planar which has less steric hindrance than the tetrahedral carbon in chloroethane**.

Chlorobenzene is less reactive than chloroethane because the **C–C*l* bond in chlorobenzene is stronger** than that in chloroethane as it has a partial double bond character due to the **delocalisation of the lone pair of electrons on the C*l* atom into the benzene** or the **rear side of the carbon–halogen bond is blocked by the benzene ring and the π electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile**, rendering approach of the nucleophile difficult.

[Total: 20]

2 **(a)** Propanone reacts with iodine in acidic conditions as shown below.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

The rate of the reaction may be followed by measuring the concentration of the iodine at regular time intervals.

Four separate sets of experiments were carried out in which the initial concentrations of the reactants were varied as shown in Table 2.1.

Table 2.1

experiment	initial concentration × 10^{-2} / mol dm^{-3}		
	propanone	hydrochloric acid	iodine
1	5	5	5
2	5	5	10
3	2	5	5
4	5	10	5

The results of experiment 1 and 2 are shown in Figure 2.1.

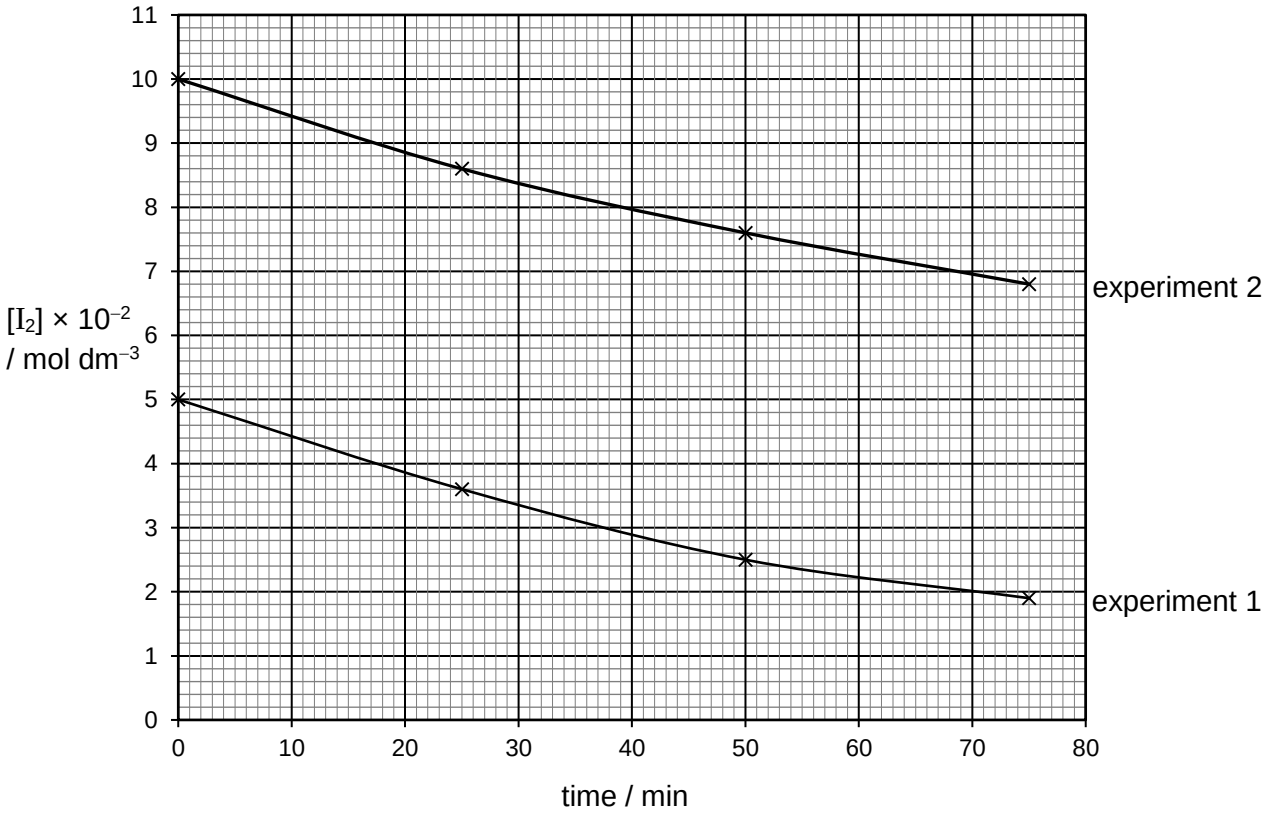


Fig. 2.1

The results shown in Table 2.2 were obtained for experiment 3 and 4.

Table 2.2

experiment	initial rate / mol dm^{-3} min^{-1}
3	2.70×10^{-4}
4	1.25×10^{-3}

(i) Using Fig. 2.1, determine the order of reaction with respect to $[I_2]$. Draw clearly any construction lines on Fig. 2.1 and show all your working. [1]

- To determine the order of reaction with respect to iodine,

  initial rate of experiment 1 $= -\dfrac{(5-2) \times 10^{-2}}{0-48} = 6.25 \times 10^{-4}$ mol dm^{-3} min^{-1}

  initial rate of experiment 2 $= -\dfrac{(10-7) \times 10^{-2}}{0-49} = 6.1224 \times 10^{-4}$ mol dm^{-3} min^{-1}

  When the concentration of iodine increases by 2 times, the rate of the reaction remains constant.

  Hence the **order of reaction with respect to iodine is 0 order**.

(ii) Determine the orders with respect to $[H^+]$ and $[CH_3COCH_3]$ [2]

- To determine the order of reaction with respect to hydrochloric acid,

  initial rate of experiment 1 $= 6.250 \times 10^{-4}$ mol dm^{-3} min^{-1}
  initial rate of experiment 4 $= 1.25 \times 10^{-3}$ mol dm^{-3} min^{-1}

  When the concentration of iodine increases by 2 times from experiment 1 to experiment 4, the rate of the reaction increases by $\dfrac{1.25 \times 10^{-3}}{6.25 \times 10^{-4}} = 2.0$ times.

  Hence the **order of reaction with respect to hydrochloric acid is first order**.

- To determine the order of reaction with respect to propanone,

  initial rate of experiment 1 = 6.250×10^{-4} mol dm^{-3} min^{-1}
  initial rate of experiment 3 = 2.70×10^{-4} mol dm^{-3} min^{-1}

  When the concentration of propanone increases by 2.5 times from experiment 3 to experiment 1, the rate of the reaction increases by $\frac{6.25 \times 10^{-4}}{2.7027 \times 10^{-4}} = 2.31 \approx 2.5$ times.

Hence the **order of reaction with respect to propanone is first order**.

(iii) Hence write the rate equation for the reaction, and calculate a value of the rate constant. Include units in your answer. [3]

rate = k[CH_3COCH_3][HC*l*]

Using experiment 1, $6.25 \times 10^{-4} = k(5 \times 10^{-2})(5 \times 10^{-2})$ k = **0.250**	Using experiment 2, $6.1224 \times 10^{-4} = k(5 \times 10^{-2})(5 \times 10^{-2})$ k = **0.250**
Using experiment 3, $2.70 \times 10^{-4} = k(2 \times 10^{-2})(5 \times 10^{-2})$ k = **0.270**	Using experiment 4, $1.25 \times 10^{-3} = k(5 \times 10^{-2})(10 \times 10^{-2})$ k = **0.250**

units of k = **mol^{-1} dm^3 min^{-1}**

(iii) The reaction of propanone with iodine proceeds via a three-step mechanism.

The first step is the protonation of propanone, which is a fast step. The second step is the deprotonation of the intermediate formed in the first step to produce another intermediate, CH_2=C(OH)CH_3.

Suggest a mechanism, which is consistent to your rate equation in **(a)(ii)** and indicate the rate determining step.

The use of curly arrows is **not** required. [3]

Step 1: $CH_3COCH_3 + H^+ \rightarrow CH_3C(OH)CH_3^+$
Step 2: $CH_3C(OH)CH_3^+ \rightarrow CH_2{=}C(OH)CH_3 + H^+$ (rate-determining step)
Step 3: $CH_2{=}C(OH)CH_3 + I_2 \rightarrow CH_3COCH_2I + HI$

(b) The boiling points of propanone, propan-1-ol and ethanoic acid increase, as shown in Table 2.2.

Table 2.2

compound	formula	M_r	boiling point / ^oC
propanone	CH_3COCH_3	58	56
propan-1-ol	$CH_3CH_2CH_2OH$	60	97
ethanoic acid	CH_3CO_2H	60	118

Suggest explanations for these differences. [2]

All three compounds have **simple molecular structure** and are polar.

Propanone has **permanent dipole – permanent dipole** interactions between the molecules while propan-1-ol and ethanoic acid have **intermolecular hydrogen bonds**.

Propanone has a lower boiling point than propan-1-ol and ethanoic acid because **less amount of energy** is required to overcome the **weaker permanent dipole – permanent dipole interactions** between the molecules in propanone.

Ethanoic acid has a higher boiling point than propan-1-ol because **the dipole moment of the O–H bond in carboxylic acid is greater than that in alcohol due to the electron-withdrawing carbonyl functional group**. Hence more energy is required to overcome the **stronger hydrogen bonds** between the ethanoic acid than that in propan-1-ol.

(c) Lithium aluminium hydride, $LiAlH_4$, sodium boron hydride, $NaBH_4$, and di-isobutyl aluminium hydride, DIBAL, are commonly used reducing agents in organic synthesis.

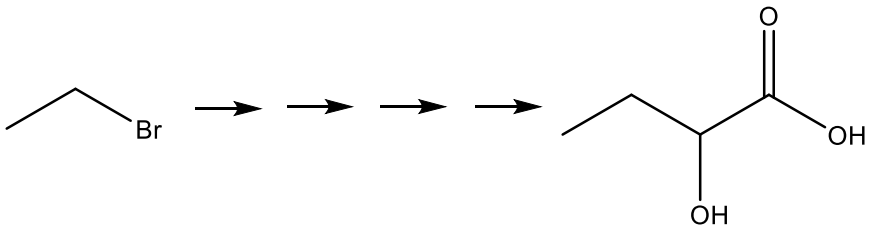
Carboxylic acids can be reduced to primary alcohols by $LiAlH_4$, but not by $NaBH_4$ because it is a stronger reducing agent.

Nitriles, –CN, are reduced to primary amines by $LiAlH_4$, but are reduced to aldehyde by DIBAL.

(i) Suggest why $LiAlH_4$ is a stronger reducing agent than $NaBH_4$. [1]

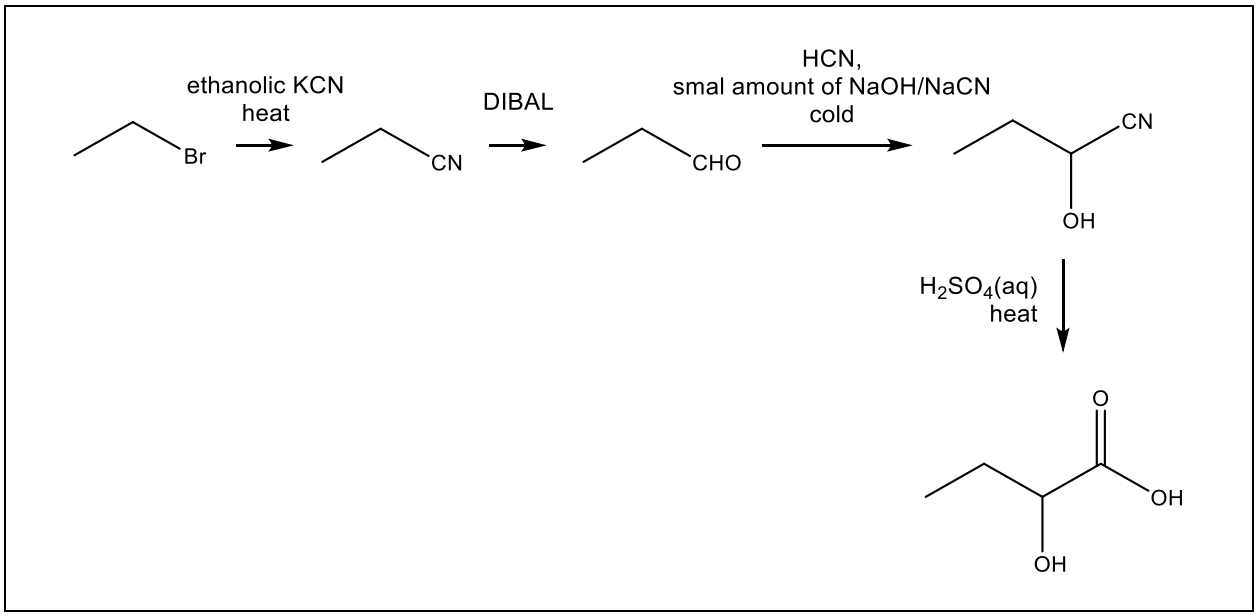
The **Al–H bond has a larger electronegativity difference than the B–H** resulting the H atoms in AlH_4^- carrying more of the negative charges as compared to those in BH_4^-.
or
$LiAlH_4$ produces H^- more readily as the **Al–H bond is weaker than the B–H bond**.

(ii) 2-hydroxybutanoic acid can be synthesised in 4 steps from bromoethane.



bromoethane 2-hydroxybutanoic acid

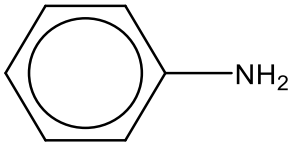
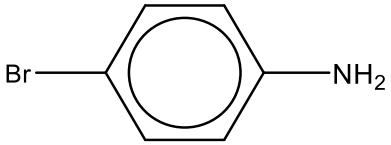
Suggest a synthesis of 2-hydroxybutanoic acid starting from bromoethane using DIBAL in one of the steps. Include reagents and conditions for all reactions, and the structures of all intermediate compounds in your answer. [4]


ethanolic KCN
heat
DIBAL
HCN,
smal amount of NaOH/NaCN
cold
Br
CN
CHO
CN
OH
H_2SO_4(aq)
heat
O
OH
OH

[Total: 16]

3 **(a)** The K_b values of 3 bases, at 25°C, are shown in Table 3.1.

Table 3.1

base	formula	K_b / mol dm^{-3}
ethylamine	$CH_3CH_2NH_2$	4.5×10^{-4}
phenylamine		7.4×10^{-10}
4-bromophenylamine		5.3×10^{-11}

(i) Ethylamine can behave as a *Brønsted-Lowry* base in aqueous medium.

Explain what is meant by this statement. [1]

Ethylamine is a **proton acceptor** since it has a lone pair of electrons on the N atom.

(ii) Write the K_b expression for ethylamine. [1]

$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$$

(iii) Calculate the pH of 0.50 mol dm^{-3} solution of ethylamine. [2]

$pOH = -\log\sqrt{K_b \times c}$

$= -\log\sqrt{4.47 \times 10^{-4} \times 0.50}$

$= \mathbf{1.83}$

$pH = 14 - 1.83 = \mathbf{12.2}$

(iv) Explain the relative magnitudes of the K_b values in Table 3.1. [3]

Decreasing order of base strength: **ethylamine > phenylamine > 4-bromophenylamine**

Ethylamine has the largest K_b value and is the strongest base as the **lone pair on N is more available to accept a proton,** as **the electron donating $-CH_2CH_3$ group increases the electron density at the N atom.**

Phenylamine has a smaller K_b value and is a weaker base than ethylamine as the **lone pair of electrons on the N atom is delocalised into the benzene ring**. This **decreases the electron density on nitrogen atom**, making the **lone pair of electrons on N atom less available to accept a proton.**

4-bromophenylamine has a smaller K_b value than phenylamine and is the weakest base as the **additional electron-withdrawing bromo group** further **decreases electron density on nitrogen atom**, making the **lone pair of electrons on N atom less available to accept a proton.**

(b) Compound **A**, $C_8H_{11}NO$ is weakly basic. It dissolves in dilute hydrochloric acid to give a solution from which a crystalline solid **B** is isolated.

A decolourises aqueous bromine and a white precipitate **C**, $C_8H_9NOBr_2$, is formed.

When **A** is heated with alkaline aqueous iodine and then followed by careful acidification, some yellow crystals are produced together with **D**, $C_7H_7NO_2$. However, no orange crystals are observed when 2,4–dinitrophenylhydrazine is added to **A**.

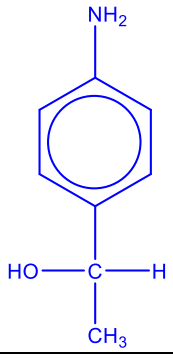
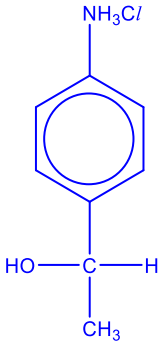
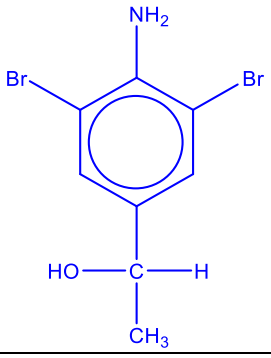
D can be produced from 4–nitromethylbenzene in a two–step reaction via an intermediate **E**. 4–nitromethylbenzene is first heated with tin in the presence of concentrated hydrochloric acid, followed by aqueous sodium hydroxide to form **E**, and then followed by adding hot acidified potassium manganate(VII) to produce **D**.

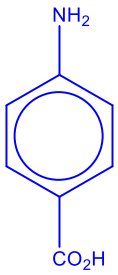
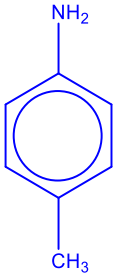
Deduce the structures of the compounds **A, B, C, D** and **E**, explaining the reactions described. [11]

Explanation of reactions:

information	type of reaction	functional group
• A has comparable C:H ratio		• A has **benzene ring**
• **A** is weakly basic		• **A** has an **amine group**
• **A** dissolves in dilute hydrochloric acid to give a solution from which a crystalline solid **B** is isolated	• **acid-base reaction / neutralisation**	• **B** is an **ammonium salt**
• **A** decolourises $Br_2(aq)$ and a white precipitate **C**, $C_8H_9NOBr_2$, is formed.	• **electrophilic substitution**	• **A** is a **phenylamine**
• When **A** is heated with alkaline aqueous iodine and then followed by careful acidification, some yellow crystals are produced together with **D**, $C_7H_7NO_2$.	• **oxidation**	• **A** has **$-CH(CH_3)OH$ or $-COCH_3$** • **D** has a **RCO_2H** • **Yellow crystals are CHI_3.**
• **A** has no reaction with 2,4-DNPH	-	• **A** has **$-CH(CH_3)OH$** or **A** is not a **carbonyl compound**
• 4–nitromethylbenzene is first heated with tin in the presence of concentrated hydrochloric acid, followed by aqueous sodium hydroxide to form **E**	• **reduction**	• **E** is a **phenylamine**
• **E** reacts with hot acidified $KMnO_4$ to produce **D**	• **oxidation**	• **D** is **benzoic acid**

Structures of unknowns

A	B	C
		

D	E
	

(c) **(i)** During electrophoresis, a potential difference is applied across the solution containing the four amino acids and the results are obtained as shown in Figure 3.1.

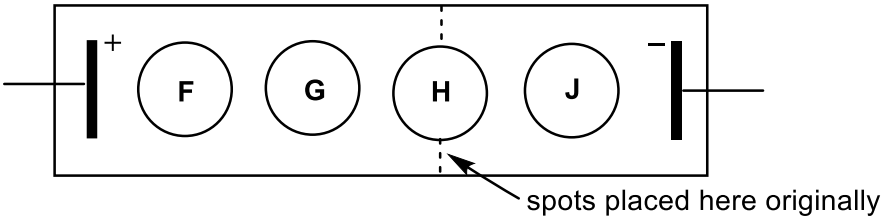
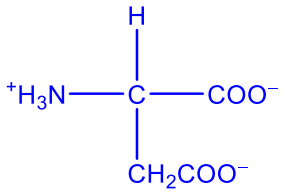
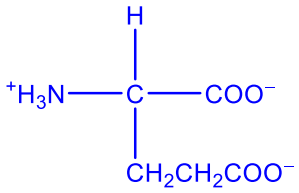
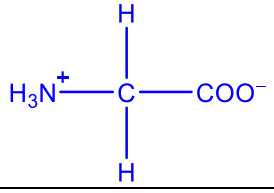
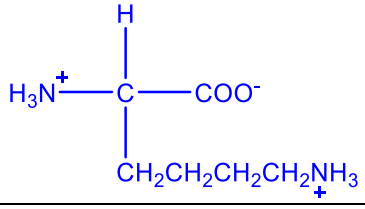


Figure 3.1

With reference to the isoelectronic point p*I* data provided in Table 3.2, draw the corresponding structure of the four amino acids present in the buffer solution of pH 6.07 and hence, deduce the identities of the amino acids **F**, **G**, **H** and **J**.

[4]

F	aspartic acid	
G	glutamic acid	
H	glycine	
J	lysine	

(ii) Amino acids can act as buffer in solutions. By means of equations, show how glycine can act as a buffer when

- dilute hydrochloric acid and
- dilute sodium hydroxide

is added separately into its solution. [2]

- $NH_2CH_2CO_2H + H^+ \rightarrow {}^+NH_3CH_2CO_2H$
  or
  ${}^+NH_3CH_2COO^- + H^+ \rightarrow {}^+NH_3CH_2CO_2H$
- $NH_2CH_2CO_2H + OH^- \rightarrow NH_2CH_2CO_2^-$
  or
  ${}^+NH_3CH_2COO^- + OH^- \rightarrow NH_2CH_2CO_2^-$

[Total: 24]

4 The modern Periodic Table in use today was developed by Henry Moseley in 1913 in which the elements are arranged in order of increasing atomic number.

The position of an element in the Periodic Table is defined by its period number and group number. Elements with similar chemical properties are grouped into specific columns and also blocks such as *s*-, *p*- and *d*-blocks, with each block denoting the type of valence subshell.

(a) Describe and explain the trend of first ionisation energy down a group. [2]

Going down a group, the first ionisation energy **decreases**.

This is because

- the **nuclear charge increases** due to an increase in the number of protons the elements have,
- the **shielding effect also increases** because of the **increase in the number of electronic shells**.
- the **increase in the shielding effect outweighs the increase in the nuclear charge** resulting in **a decrease in the effective nuclear charge** of the elements.
- the amount of energy to remove the outmost electron decreases

(b) The elements in Period 3 of the Periodic Table reacts with oxygen to form oxides that have different acid-base behaviour.

The acid-base behaviour of aluminium oxide, Al_2O_3 is similar to that of sodium oxide, Na_2O, on the one hand, and phosphorus(V) oxide, P_4O_{10}, on the other.

Describe what these similarities are.
Write equations for all the reactions you choose to illustrate your answer. [4]

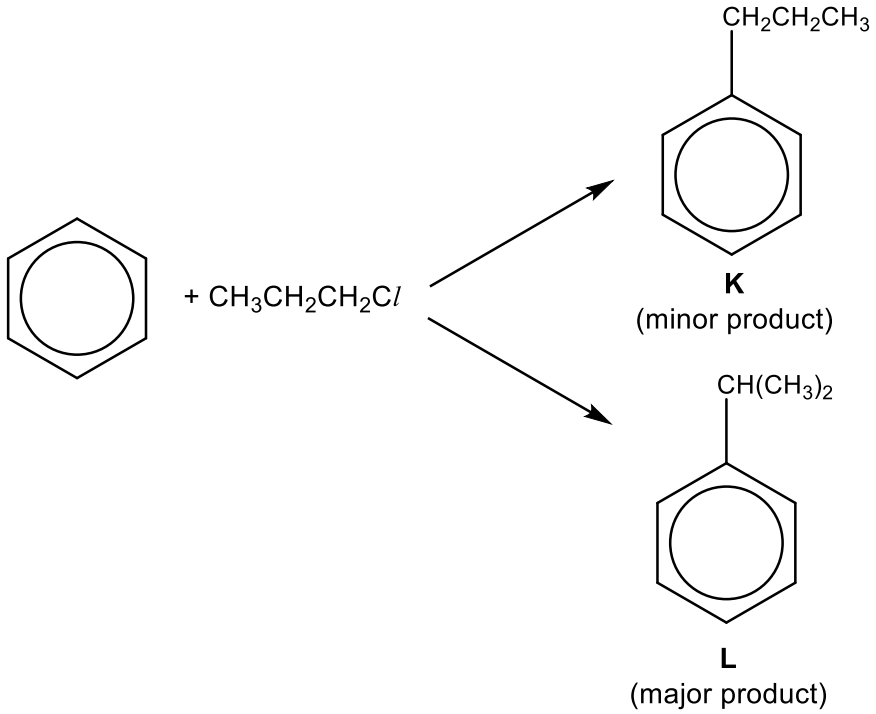
Like Na_2O which is ionic thus basic, Al_2O_3 is also ionic oxide, and thus behaves as a basic oxide in the reaction with acids to give salt and water.

$$\mathbf{Na_2O(s) + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2O(l)}$$
$$\mathbf{Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)}$$

Like P_4O_{10} which is covalent thus acidic, Al_2O_3 can also behave as an acidic oxide in the reaction with alkalis to give salt and water since it has covalent character

$$\mathbf{P_4O_{10}(s) + 12OH^-(aq) \rightarrow 4PO_4^{3-}(aq) + 6H_2O(l)}$$
$$\mathbf{Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)}$$

(c) Aluminium chloride, $AlCl_3$, is often used as a catalyst in the Friedel-Craft alkylation. When benzene is added to 1-chloropropane in the presence of $AlCl_3$, a mixture of two isomers, **K** and **L**, with different quantities are formed.



(i) The aluminium chloride used to react with 1-chloropropane must be anhydrous.

With the aid of equations, explain why anhydrous condition must be used in the reaction. [1]

If water is present, $AlCl_3$ will dissolve in water and undergoes hydrolysis and hence no longer available to react with $CH_3CH_2CH_2Cl$.

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O_6)]^{3+} + 3Cl^-$
$[Al(H_2O_6)]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+$

(ii) The reaction between aluminium chloride and 1-chloropropane can be described as an *acid-base* reaction.

Explain why this is so. Write an equation for the reaction. [2]

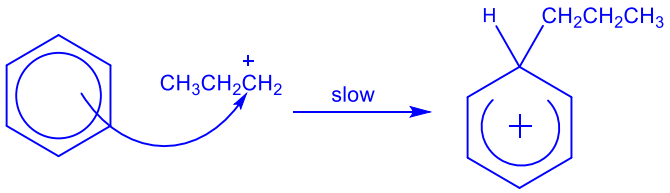
In this reaction **$AlCl_3$ is acting as a Lewis acid, which is an electron-pair acceptor** while **$CH_3CH_2CH_2Cl$ is acting as a Lewis base, which is an electron-pair donator**. Hence the reaction can be describe as an acid-base reaction.

$AlCl_3 + CH_3CH_2CH_2Cl \rightarrow AlCl_4^- + CH_3CH_2CH_2^+$

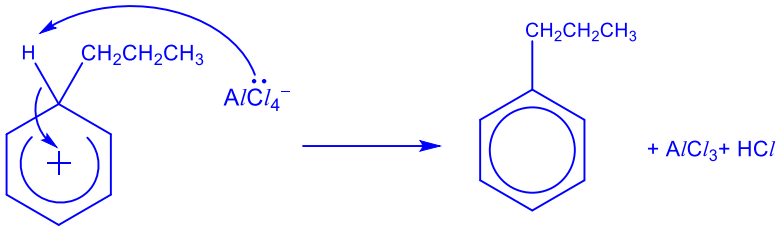
(iii) Suggest a mechanism for the formation of isomer **K** from benzene, showing all charges and using curly arrows to show the movements of electron pairs. [2]

Electrophilic Substitution

Step 1:

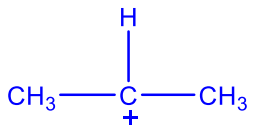


Step 2:



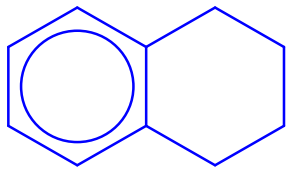
(iv) Another organic intermediate is also formed in the reaction between aluminium chloride and 1-chloropropane. This organic intermediate led to the formation of isomer **L**.

Draw the structure of the organic intermediate in the formation of isomer **L** and hence explain why isomer **L** is formed in greater proportion. [2]



Compound **L** was obtained in larger quantity than Compound **K** because **the carbocation intermediate is a secondary carbocation, which is more stable it has more electron-donating alkyl groups.** Hence, a higher proportion of this secondary carbocation is formed and this leads to a higher percentage of Compound **L** obtained.

(v) In a similar reaction, 1 mole of benzene reacts with 1 mole of $BrCH_2CH_2CH_2CH_2Br$ to form two moles of HBr. Predict the structure of the product formed. [1]



(d) Copper is a *d*-block element and can be found in period 4 of the Periodic Table.

(i) State the electronic configuration of Cu. [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

(ii) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with silver and tin as minor impurities. It contained no other metal. In order to purify it, this alloy was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

Explain, with reference to relevant $E^{\ominus}$ values, what happened to the silver and tin impurities during this purification procedure. [3]

	$E^{\ominus}_{red}$ / V
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80

When the current runs through the circuit, **Sn will be oxidised to Sn^{2+} at the anode** (Cu will also be oxidised to Cu^{2+}) since it has a **more negative reduction potential as compared to Cu**.

Ag will not be oxidised due to its **more positive $E^{\ominus}$ reduction potential** compared to Cu, and will drop to the bottom as sludge.

Subsequently both Cu^{2+} and Sn^{2+} will migrate to the cathode. However, **Sn^{2+} will not be reduced** to **Sn as it has a more negative reduction potential than Cu** (only Cu^{2+} will be reduced to Cu). Hence, Sn^{2+} remains in solution.

(iii) A current of 1.5 A was passed through the cell described in **(d)(ii)** for 48.0 minutes, and the cathode electrode removed, washed, dried and weighed.

Calculate the expected increase in mass of the cathode. [2]

At the cathode, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

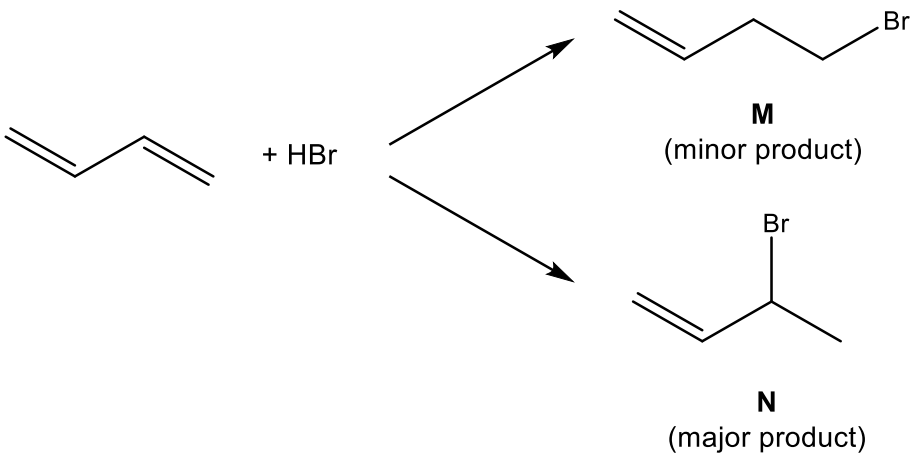
$Q = 1.5 \times 48.0 \times 60 = 4320$ C
Amount of electrons passed through = $4320 \div 96500$ = **0.044766 mol**

Amount of Cu deposited = $0.044766 \div 2 = 0.022383$ mol
Expected mass increase = 0.022383×63.5 = **1.42 g**

[Total: 20]

5 **(a)** Buta-1,3-diene reacts with HBr to form different isomers under different conditions as shown in Fig 5.1.

At low temperatures,



At high temperatures,

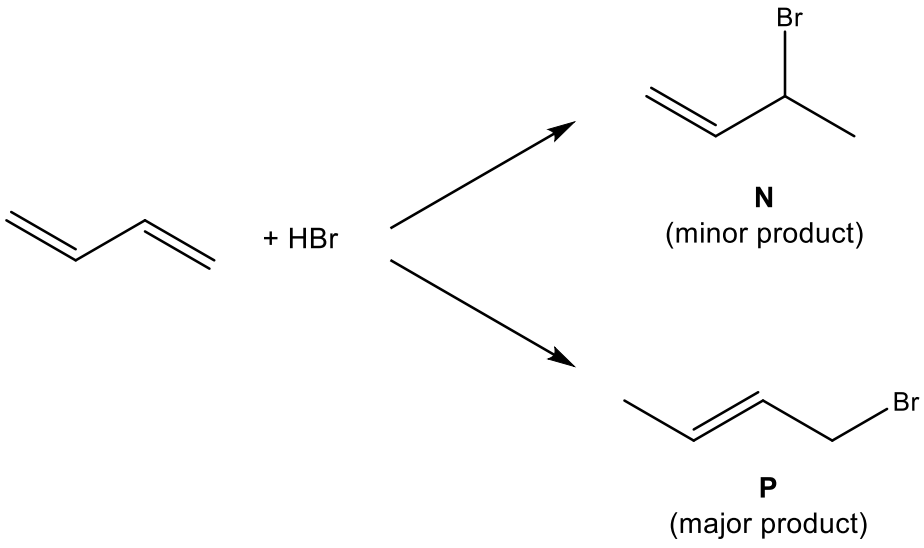


Fig 5.1

(i) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms involved in the C=C bond of buta-1,3-diene. [3]

- **sp^2** which is formed by the mixing of 1 2s orbital and 2 2p orbitals

The bonds between the carbon atoms of buta-1,3-diene are

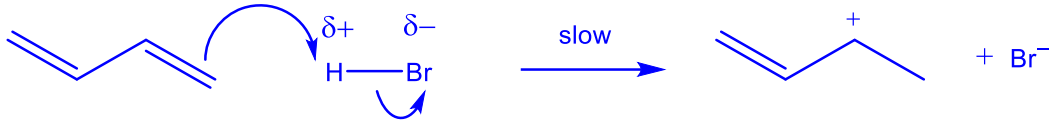
- **sigma, σ, bonds which are formed by the head-on overlap of the sp^2 hybridised orbitals of the 2 carbon atoms** , and
- **pi, π, bonds which are formed by the side-way overlap of the unhybridised 2p orbitals of the 2 carbon atoms**.

(ii) At low temperatures, isomer **N** is formed in a greater proportion than isomer **M**.

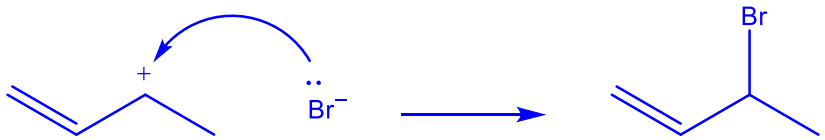
Suggest a mechanism for this reaction and use it to explain the preferential production of isomer **N**. [3]

Electrophilic Addition

Step 1:



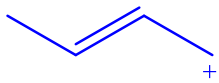
Step 2:



Isomer **N** is preferentially formed over **M** as the carbocation intermediate formed is a secondary carbocation as compared to the formation of a primary carbocation for **M**. There are **more electron-donating alkyl groups in the secondary carbocation intermediate for N to disperse the positive charge on the carbocation intermediate, making it more stable** as compared to the carbocation intermediate in **M**.

(iii) At higher temperatures, isomer **P** is more likely to be formed as the organic intermediate formed is more stable than that formed in isomer **N**.

Draw the structure of the organic intermediate in the formation of isomer **P** and suggest a reason why it is more stable than the intermediate formed in isomer **N**. [2]



This organic intermediate is more stable because it is a **more substituted alkene**.

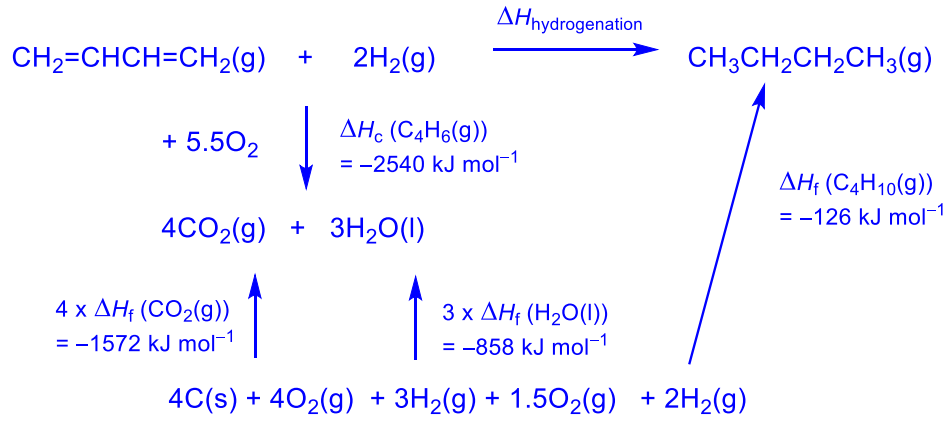
(iv) Buta-1,3-diene can also undergo hydrogenation to form butane.

$$CH_2{=}CH\text{-}CH{=}CH_2(g) + 2H_2(g) \rightarrow CH_3CH_2CH_2CH_3(g)$$

Construct a suitable energy cycle using this equation and use the data from Table 5.1 and your cycle to calculate the standard enthalpy change of hydrogenation of buta-1,3,diene. [3]

Table 5.1

Standard enthalpy change of formation of $CH_3CH_2CH_2CH_3(g)$	−126 kJ mol^{-1}
Standard enthalpy change of formation of $CO_2(g)$	−393 kJ mol^{-1}
Standard enthalpy change of formation of $H_2O(l)$	−286 kJ mol^{-1}
Standard enthalpy change of combustion of $CH_2{=}CH\text{-}CH{=}CH_2(g)$	−2540 kJ mol^{-1}



$\Delta H_{hydrogenation} = -2540 + 1572 + 858 - 126 =$ **-236 kJ mol^{-1}**

(v) A beaker containing 150 cm^3 of water was heated up by burning 1.2 g of buta-1,3-diene in excess oxygen. The process was known to be 70% efficient.

Calculate the expected increase in the temperature of water. [3]

Amount of buta-1,3-diene burnt = 1.2 ÷ 54.0 = 0.0222 mol
Heat evolved by combustion = 2540 × 0.0222 mol = **56.44 kJ**

Heat absorbed by water = 0.7 × 56.44 = **39.51 kJ**

39511 = 150 × 4.18 × ΔT

ΔT = **63.0 °C**

(b) A mixture contains equal quantities of two isomers, **Q** and **R**. These isomers have the molecular formula C_4H_7BrO.

Both isomers form orange precipitate and pale yellow precipitate with 2,4–dinitrophenylhydrazine and alkaline aqueous iodine respectively, but does not form any precipitate with Tollens' reagent. When heated with ethanolic silver nitrate, a pale cream precipitate is formed.

(i) Suggest what these observations indicate about the functional groups in both the isomers. [1]

Both isomers contains

- a **ketone with CH_3CO-** structure, and
- a **bromoalkane**

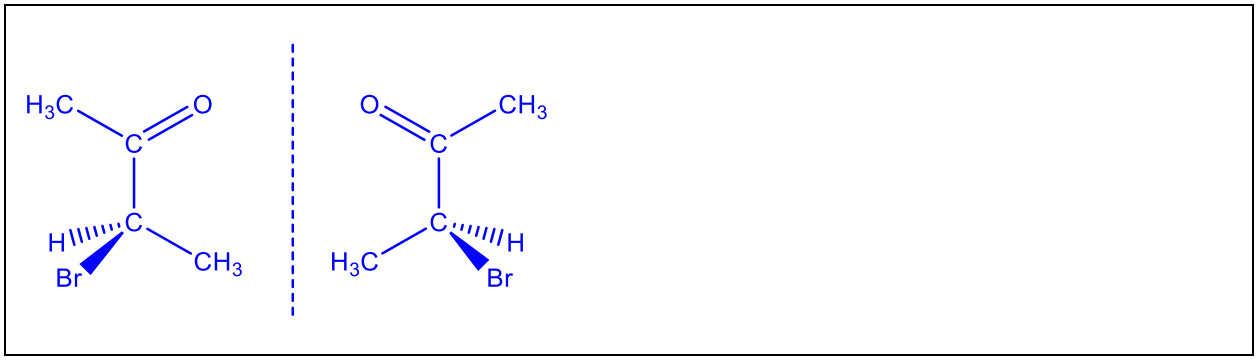
(ii) When plane-polarised light is passed through this mixture there is no effect, but pure **Q** rotates plane-polarised light.

Explain these observations. [3]

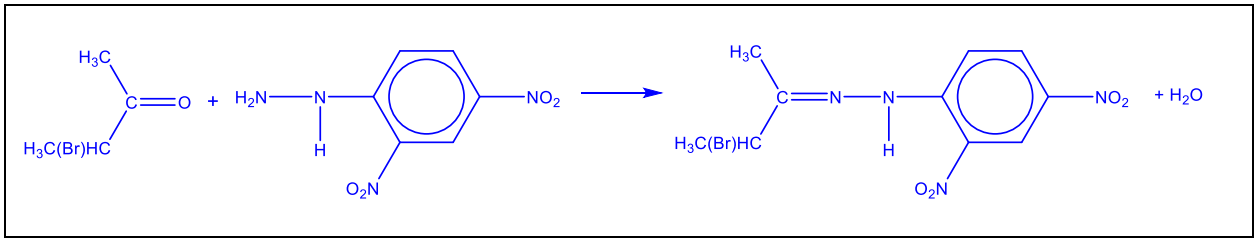
Q and **R** are **enantiomers and are optically active**. Hence pure **G** rotates plane-polarised light.

Q and **R rotates the plane of polarised light by the same angle but in opposite directions**. Since there is an equal quantities of **Q** and **R**, the optical activity of **Q** is **exactly cancelled out** by **R**. Hence, the mixture has no net optical activity and does not rotate plane-polarised light.

(iii) Draw the three-dimensional structures of **Q** and **R**. [1]



(iv) Write an equation for the reaction between **Q** and 2,4-dinitrophenylhydrazine. [1]



[Total: 20]