Name:	Answers	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Prelims Examination 2019
Year 6

H2 CHEMISTRY 9729/02

Paper 2 Structured Questions

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Write in dark blue or black pen.

3 You may use an HB pencil for any diagrams or graphs.

4 Do not use staples, paper clips, glue or correction fluid.

5 Write your answers in the spaces provided on this question paper.

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

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
Question No.	Section A Marks
1	/21
2	/14
3	/12
4	/13
5	/15
Total	/75

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

1 This question explores the chemistry of transition metal complexes.

(a) Cobalt cations readily form complexes with ligands. Some of the cobalt complexes with their absorption frequencies are shown in Table 1.1. The absorption frequency is the frequency of light absorbed for each complex, and is proportional to the energy of light absorbed.

Table 1.1

Complex	Absorption Frequency / cm^{-1}
$[Co(CN)_6]^{4-}$	15300
$[Co(CN)_6]^{3-}$	33500
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200
$[Co(NH_3)_6]^{3+}$	22870

(i) State the electronic configuration of the cobalt cation in $[Co(CN)_6]^{3-}$.

Electronic configuration: **$\underline{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6}$**

[1]

(ii) Using the information in Table 1.1, state the relationship between the oxidation state of the metal cation and the absorption frequency of its complex.

A **$\underline{\text{higher oxidation state}}$** of the metal cation will result in a **$\underline{\text{higher absorption frequency}}$** of the complex.

[1]

(iii) Stronger field ligands generate a *d* orbital splitting pattern with a larger energy gap when bonded to transition metal cations.

Using the information in Table 1.1, rank CN^-, H_2O and NH_3 in order of increasing ligand field strength.

Ligand field strength: **$\underline{H_2O < NH_3 < CN^-}$**

[1]

(iv) Hence, predict a value for the absorption frequency of $[Co(NH_3)_6]^{2+}$.

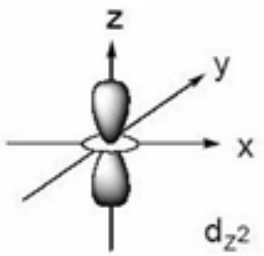
Any value between 9300 and 15300 (excluding boundaries)

[1]

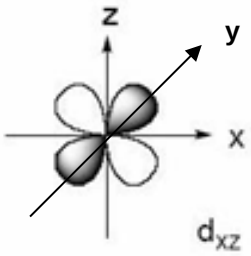
(b) In the presence of an octahedral ligand field, the 3*d* orbitals of cobalt are split into two energy levels.

(i) Using the axes below, draw the shape of a 3*d* orbital of cobalt of

- a higher energy level,
- a lower energy level, in the presence of an octahedral ligand field.



Higher energy level
(accept $d_{x^2-y^2}$)



Lower energy level
(accept d_{xy}, d_{yz})

[2]

(ii) Hence, explain why the 3*d* orbitals of cobalt are split into two energy levels in the presence of an octahedral ligand field.

The d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that **<u>are in the region of the lone pairs of the ligands</u>**. There is **<u>greater repulsion between these orbitals and the incoming ligands</u>**. As a result, these orbitals are **<u>more destabilised</u>** and higher in energy.

The d_{xy}, d_{yz} and d_{xz} orbitals have lobes that project **<u>between the lone pairs of the ligands</u>**. There is **<u>less repulsion</u>** between these orbitals and the negative charges (lone pairs of the ligands). As a result, these orbitals are **<u>less destabilised</u>** and lower in energy.

[2]

(iii) In the presence of a tetrahedral ligand field, the ligands approach in between the axes.

Complete Fig 1.1 to show how the degenerate 3*d* orbitals of cobalt will split in a tetrahedral ligand field. Label all the orbitals in your diagram.

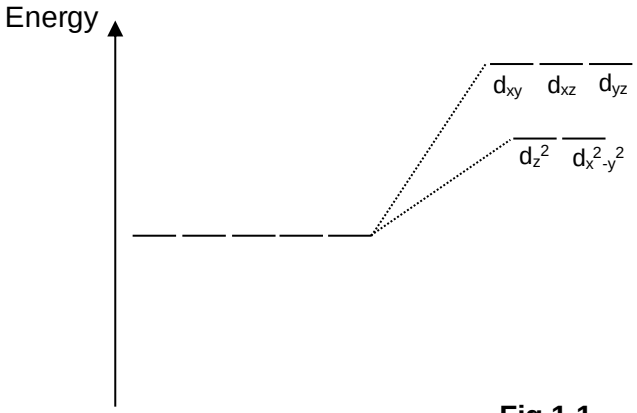


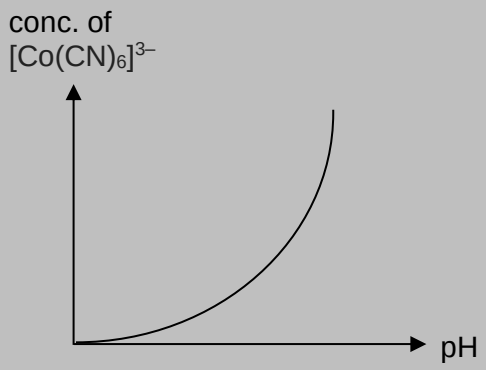
Fig 1.1

[2]

(c) Another cobalt complex, $[CoCl_6]^{3-}$ undergoes ligand exchange with CN^- ligands to form $[Co(CN)_6]^{3-}$ according to the following equilibrium.

$$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$$

The effect of pH on the concentration of $[Co(CN)_6]^{3-}$ formed is shown in the graph below.



(i) Write an equation that describes the dissociation of the weak acid, HCN, in water.

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

[1]

(ii) Hence, using Le Chatelier's Principle, explain the shape of the graph above.

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ -----(1)
$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$ ------(2)

When pH increases, the **$[H^+]$ decreases. This shifts the position of equilibrium (1) to the right to produce more H^+**. This also increases the concentration of CN^-.

The **increase in CN^- causes the position of equilibrium (2) to shift to the right to decrease the concentration of CN^-**. This results in an **increase in concentration of $[Co(CN)_6]^{3-}$ as pH increases**.

[2]

(iii) Explain why the Gibbs free energy change and enthalpy change for the forward reaction are approximately equal.

Since **there is no change of state or number of moles of particles from reactants to products**, the **entropy change is approximately zero**. Hence, $\Delta G \approx \Delta H$.

[1]

(iv) Hence deduce the sign of the enthalpy change of the forward reaction given that it is spontaneous.

Since reaction is spontaneous, ***ΔG* is negative**. Hence, given $\Delta G \approx \Delta H$, ***$\Delta H$* must be negative**.

[1]

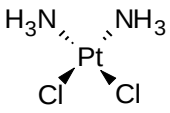
(d) Similar to organic compounds, transition metal complexes may exhibit stereoisomerism.

(i) For square planar complexes, *cis-trans* isomerism can be exhibited for **MA_2B_2** type complexes (where **M** is the metal cation, and **A** and **B** are different ligands).

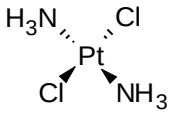
cis and *trans* isomers are differentiated in the following way:

cis:	Both **A** ligands next to one another
trans:	Both **A** ligands are separated by a **B** ligand

$[Pt(Cl)_2(NH_3)_2]$ is a square planar complex. Complete the diagrams below to show the structures of its *cis* and *trans* isomers.



Cisplatin



trans isomer

[1]

(ii) For any transition metal complex, enantiomerism is exhibited if it has:

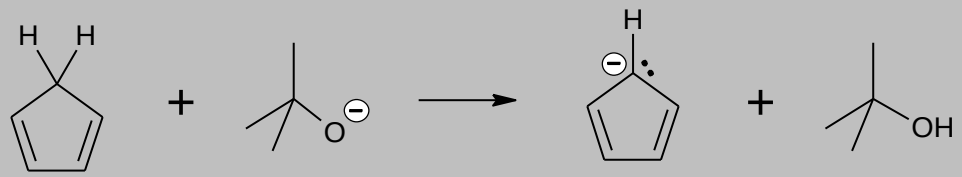
- Mirror images that are non-superimposable and
- No internal plane of symmetry

Deduce if the *trans* isomer of $[Pt(Cl)_2(NH_3)_2]$ can exhibit enantiomerism.

It **cannot exhibit enantiomerism** as it has an **internal plane of symmetry** and / or has **mirror images** that are **superimposable**.

[1]

(e) The cyclopentadienyl anion is a common ligand in transition metal complexes. This anion can be generated via the following reaction between tert–butoxide anion and cyclopentadiene.



Cyclopentadiene tert-butoxide cyclopentadienyl anion

An organic compound is considered aromatic if all of the following three criteria are met:

- it is a cyclic planar compound,
- it has a delocalised π electron system, and
- it has $(4n + 2)$ π electrons, where n is an integer.

One such example is benzene.

(i) State the type of reaction that generates the cyclopentadienyl anion from cyclopentadiene.

Acid–Base

[1]

(ii) Given that the cyclopentadienyl anion is aromatic, explain fully how it meets the three criteria stated above.

All the carbon atoms in the anion are **sp^2 hybridised and have trigonal planar geometry**. Hence, the anion is a cyclic planar anion.

The **lone pair of electrons** on the carbon is **in a *p*-orbital which is overlapping with the π bonds of the 2 C=C bonds**.

Hence, there is a delocalised π electron system with **6 π electrons**.

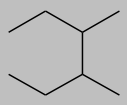
[3]

[Total: 21]

2 Halogenoalkanes are widely used commercially as they are important precursors for many organic synthesis.

(a) One method of synthesising halogenoalkanes is the free radical substitution of alkanes. For example, butane can be chlorinated in the presence of UV light.

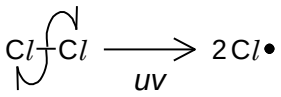
However, this is not a preferred method of synthesising halogenoalkanes as there are multiple by–products. For example, one by–product of the monochlorination of butane is shown below.



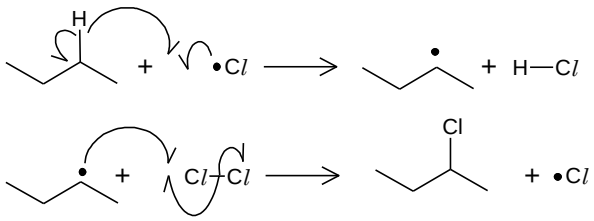
3,4–dimethylhexane

(i) Draw the mechanism of the reaction between butane and chlorine that would result in the formation of 3,4–dimethylhexane. Show the movement of electrons by using suitable curly arrows and indicate any unpaired electron using a dot (•).

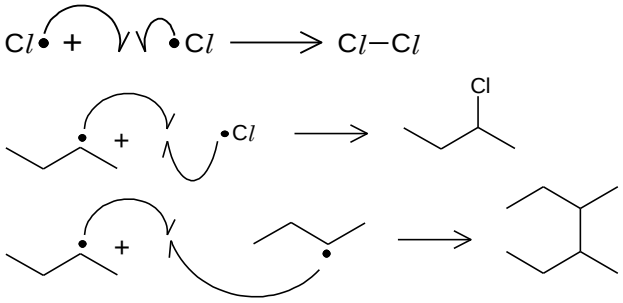
Initiation:



Propagation:



Termination:



[3]

(ii) State the number of chiral centre(s) present on 3,4–dimethylhexane and the number of stereoisomers that are optically active.

No. of chiral centres: **2**

No. of stereoisomers that are optically active: **2**

[2]

(b) One application of halogenoalkanes was the use of chlorofluorocarbons (CFCs) as refrigerants in the 20th century. However, CFCs have been replaced with hydrofluorocarbons (HFCs) due to their detrimental impact on the ozone.

CFCs produce radicals in the presence of UV light. For example, chlorodifluoromethane, $CHCl F_2$, readily produces chlorine radicals in the stratosphere. These radicals speed up the depletion of the ozone layer.

HFCs, such as fluoroform, CHF_3, do not produce radicals in the presence of UV light.

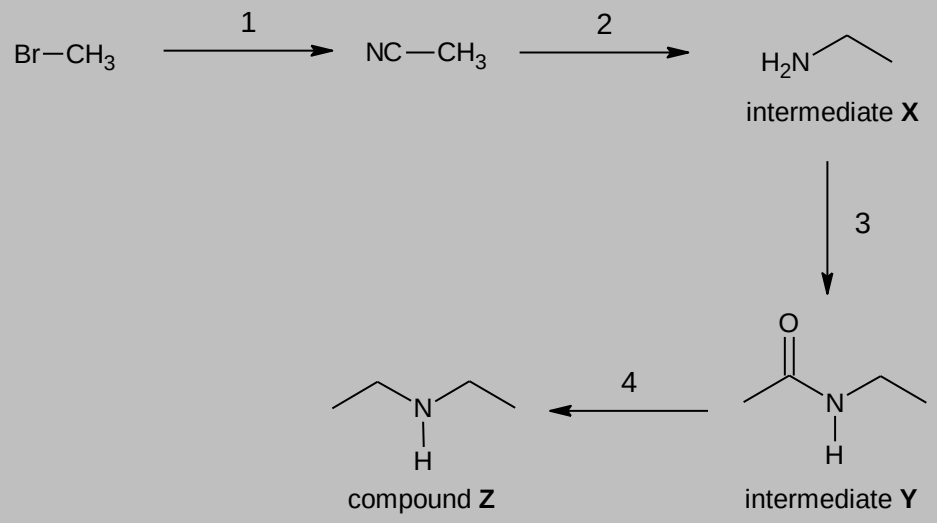
With reference to the *Data Booklet*, explain why CHF_3 does not deplete the ozone layer whereas $CHCl F_2$ does.

B.E.(C–F) = 485 kJ mol^{-1}
B.E.(C–C*l*) = 340 kJ mol^{-1}

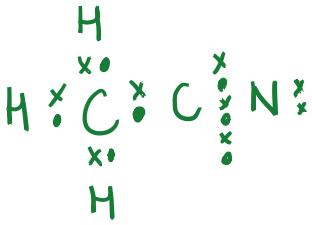
Since the bond energy of the C–F bond is higher than that of the C–C*l* bond, the **C–F bond is stronger than the C–C*l* bond**. Hence, the UV light **does not provide sufficient energy to break the C–F bond** to produce fluorine radicals.

[2]

(c) Halogenoalkanes also find their application as precursors in the synthesis of nitrogen–containing organic compounds. One such synthesis involving bromomethane is shown below.



(i) Draw a dot–and–cross diagram to show the bonding in CH_3CN and state the types of orbitals used to form the carbon–carbon bond in the molecule.



Orbitals used: **2sp and 2sp^3**

[2]

(ii) State the type of reaction occurring in step 4 and the reagent(s) and condition(s) needed.

Type of reaction: **Reduction**
Reagent(s) and condition(s): **$LiAlH_4$ in dry ether**

[2]

(iii) Explain why ethanoic acid **cannot** be used in step 3 to form intermediate **Y**.

Ethanoic acid will undergo an **acid-base / neutralisation reaction** with the amine in intermediate **X** instead.

[1]

(iv) Compare and explain the basicity of intermediate **X** and compound **Z**.

Compound **Z is more basic than intermediate X**.

The N atom of **Z** has **2 (or more) electron-donating alkyl groups** attached to it, while that in **X** only has 1. Hence, there is a greater electron density of

the N atom of Z and the **lone pair of electrons on N is more available for donation** to form a dative bond with H^+.

[2]

[Total: 14]

3 Brown iodine water is decolourised when warmed with ethanol in an alkaline medium. A series of 'clock' experiments were conducted to study the kinetics of this reaction. The time taken for the decolourisation of iodine in each experiment is found in Table 3.1.

Table 3.1

Expt	Volume of I_2(aq) / cm^3	Volume of ethanol / cm^3	Volume of NaOH (aq) / cm^3	Volume of deionised water / cm^3	Time taken, *t* / s
1	5	20	20	10	42
2	5	30	20	0	28
3	10	20	20	5	42

(a) (i) Describe another observable change that occurs as the reaction proceeds.

Yellow ppt of CHI_3 forms

[1]

(ii) Explain why the total volume of reaction mixture is kept constant.

So that the initial **concentration of each reactant** (in the reaction mixture) is **directly proportional to the volume used**.

[1]

(iii) Given relative rate $\propto \frac{\text{volume of } I_2}{t}$, use this relationship to deduce the order of reaction with respect to [ethanol] and [iodine]. Explain your answer.

Comparing experiments 1 and 2, when [iodine] is constant and [ethanol] $\times \frac{3}{2}$, time required $\times \frac{2}{3}$ OR relative rate $\times \frac{3}{2}$.
∴ first-order wrt [ethanol]

Comparing experiments 1 and 3, when [ethanol] is constant and [iodine] doubles, relative rate doubles.
∴ first-order wrt [iodine]

[2]

(b) The clock method can also be used to study the comproportionation reaction between bromate(V) and bromide ions in acidic medium.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

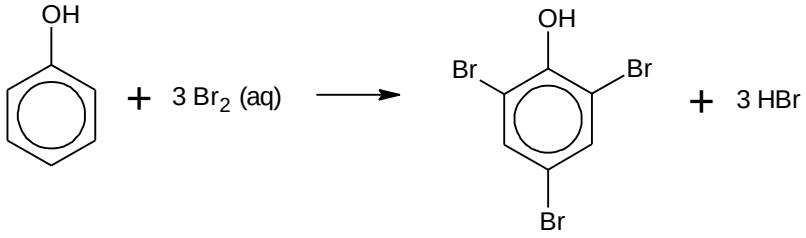
A small, fixed amount of phenol and a few drops of litmus are used in every experiment. The time taken for the disappearance of the pink colouration is measured.

(i) Comment if the reaction is expected to occur via an elementary step.

No, it is extremely **unlikely for so many (12) reactant species to collide at the appropriate geometry**.

[1]

(ii) Using a suitable equation, explain the purpose of adding a small, fixed amount of phenol in every experiment.



It ensures that the extent of reaction for every experiment is kept constant / A fixed amount of Br_2 will react with phenol before the colour change occurs.

[2]

(c) The pH of a reaction mixture can be kept constant in a kinetics experiment using a suitable buffer. Phosphoric acid, H_3PO_4, can be used to prepare buffers of varying pH values as it has three pK_a values of 2.14, 7.20 and 12.37.

(i) State the components present in a phosphate buffer of pH 7.50.

$H_2PO_4^-$ and HPO_4^{2-}

[1]

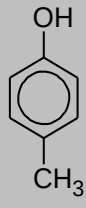
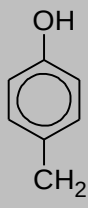
(ii) Write a suitable equation to show how the buffer system outlined in **(c)(i)** can resist change in pH when a small amount of OH^- is added.

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

[1]

(d) Two physical properties of two substituted phenols are shown in Table 3.2.

Table 3.2

	p–cresol	4–hydroxybenzyl alcohol
Structure		
pK_a	10.3	9.82
Boiling point / °C	202	252

Suggest a reason for the difference in each property.

- pK_a

The **electronegative O atom / the additional electron withdrawing –OH group** on 4–hydroxylbenzyl alcohol **disperses the negative charge on the phenoxide ion.**

This **stabilises the conjugate base**. Hence, 4–hydroxylbenzyl alcohol dissociates to a larger extent and is a **stronger acid** than p–cresol.

- Boiling point

4–hydroxylbenzyl alcohol forms **more extensive hydrogen bonds** with other 4–hydroxylbenzyl alcohol molecules (due to the presence of the additional –OH group). Hence, **more energy** is require to overcome these bonds in boiling.

[3]

[Total: 12]

4 Methanal reacts with propene to form an organic product **A**.

(a) The mechanism for the formation of **A** is shown in Fig 4.1.

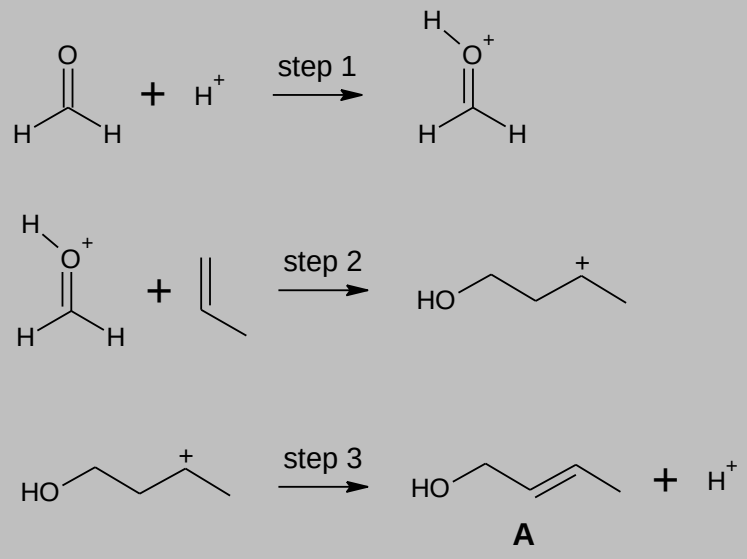


Fig. 4.1

(i) Deduce whether propene is acting as an electrophile or a nucleophile in step 2. Explain your answer.

Propene acts as a **nucleophile** because it **donates an electron pair** to the electron deficient carbon of the protonated carbonyl group.

[1]

(ii) Complete Fig 4.2 using curly arrow(s) to show the movement of electron pair(s) for step 2.

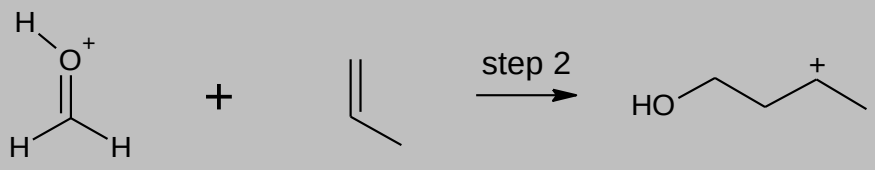
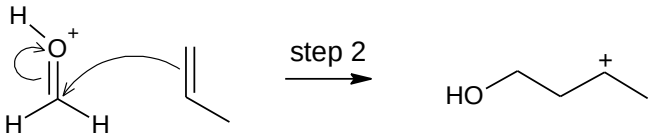


Fig. 4.2

Mechanism



[1]

(iii) In step 2, intermediate **B** is produced rather than **C**.

Suggest an explanation for the preferential production of intermediate **B**.

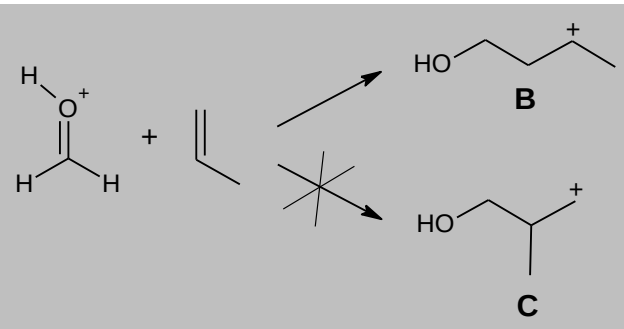
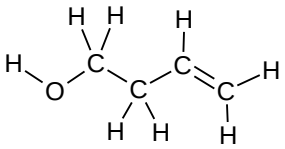


Fig. 4.3

Intermediate **B** is a **secondary carbocation** which is **more stable** than **C**, a **primary carbocation**, as there are **more electron-donating alkyl groups** to **disperse its positive charge**.

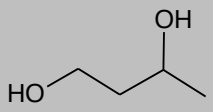
[2]

(iv) Step 3 may result in three isomeric organic products. Draw the displayed formula of the organic product which is a constitutional isomer of **A**.



[1]

(b) The reaction between methanal and propene under a different set of conditions gives molecule **D** with the following structure.



It can also be made from propene in the 4-step process shown in Fig 4.4.

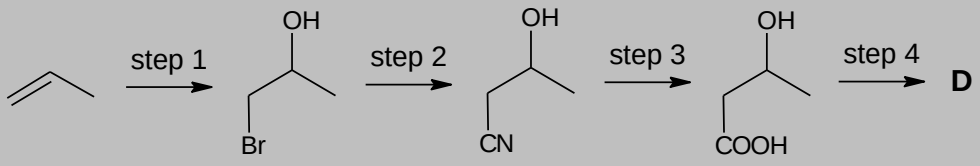


Fig. 4.4

(i) Name the product formed in step 1.

1-bromopropan-2-ol

[1]

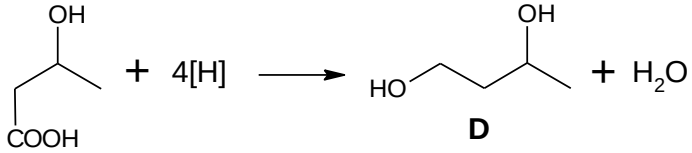
(ii) State the reagents and conditions needed for steps 2 and 3.

step 2: **KCN in ethanol, heat** under reflux

step 3: **dilute HC*l*, heat** under reflux

[2]

(iii) Step 4 is a reduction reaction. Write an equation for step 4 using [H] to represent the reducing agent.



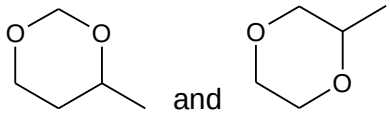
D

[1]

(c) Molecule **E** has molecular formula $C_5H_{10}O_2$.

It is an asymmetrical molecule comprising a 6-membered ring. It does not contain any O–O bond and has no reaction with phosphorus pentachloride.

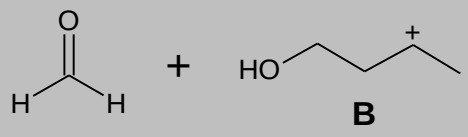
(i) Suggest **two** structures of **E** that are consistent with the information provided.



[2]

(ii) The formation of **E** involves the nucleophilic attack of methanal on intermediate **B**.

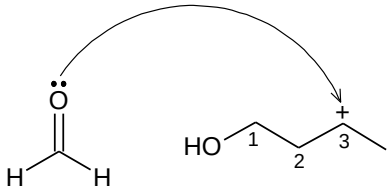
Complete Fig 4.5 using curly arrow(s) to show the movement of electron pair(s) for this nucleophilic attack.



B

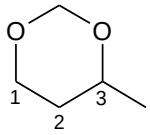
Fig. 4.5

Hence deduce the likely structure of **E** from your answer in **(c)(i)**. Explain your reasoning.



B

The nucleophilic attack using the lone pair of electrons on O atom of methanal on the positively charged carbon atom in intermediate **B** will result in the **<u>two O atoms</u>** in the product **E** being **<u>3 carbon atoms apart</u>**. Hence the likely structure of **E** is as follows.



[2]

[Total: 13]

5 (a) **R**, **T**, **U** and **V** are consecutive elements in the third period of the Periodic Table. Among these four elements, **T** has the highest melting point and **U** has the highest first ionisation energy.

(i) Identify element **T**.

Silicon

[1]

(ii) The oxides of elements **T** and **U** can be obtained when the elements are burned in excess oxygen. The oxides of **T** and **U** have melting points of 1710 °C and 340 °C respectively.

Explain briefly the difference in melting points between these oxides.

The oxide of **T** (SiO_2) has a <u>giant molecular structure</u>. <u>Large amount of energy</u> is required to break the <u>strong and extensive covalent bonds</u> between Si and O atoms and hence oxide of **T** has a higher melting point. [1]

The oxide of **U** (P_4O_{10}) has a <u>simple molecular structure</u>. Less energy is required to break the <u>weak intermolecular forces of attraction</u> between the molecules and hence oxide of **U** has a lower melting point.

[2]

(iii) Describe the reactions, if any, of the oxides of elements **R** and **V** with water. Include the approximate pH value of any resulting solution formed.

The oxide of **R** (Al_2O_3) is <u>insoluble in water</u>. Hence, the <u>pH</u> of the resulting solution is <u>7</u>.

The oxide of **V** (SO_3) <u>reacts readily with water</u> to produce a strongly acidic solution of <u>pH 2</u>.

[2]

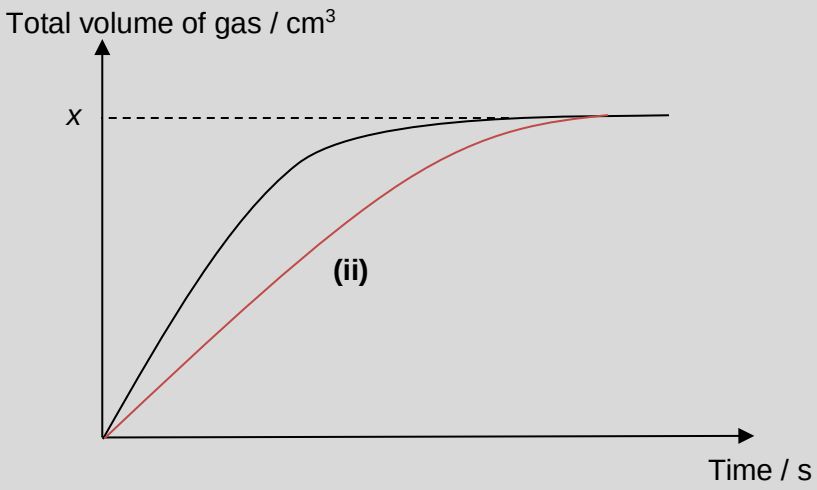
(b) Barium and magnesium form iodate(V) compounds, $Ba(IO_3)_2$ and $Mg(IO_3)_2$. Upon heating, each of the iodates decomposes to give a solid residue. Purple fumes and a gas that relights a glowing splint are also observed.

(i) Write a balanced equation, with state symbols, for the thermal decomposition of $Mg(IO_3)_2$.

$Mg(IO_3)_2(s) \rightarrow MgO(s) + I_2(g) + \frac{5}{2}O_2(g)$ [1]

[1]

The graph below shows the total volume of gas collected over time when 0.1 mol of $Mg(IO_3)_2$ is heated.



(ii) Sketch, on the same axes above, the graph that would be obtained when 0.1 mol of $Ba(IO_3)_2$ was heated at the same temperature till no further change was observed.

Gentler gradient with **same total volume**

[1]

(iii) Explain the shape of the graph that you have drawn for **(b)(ii)**.

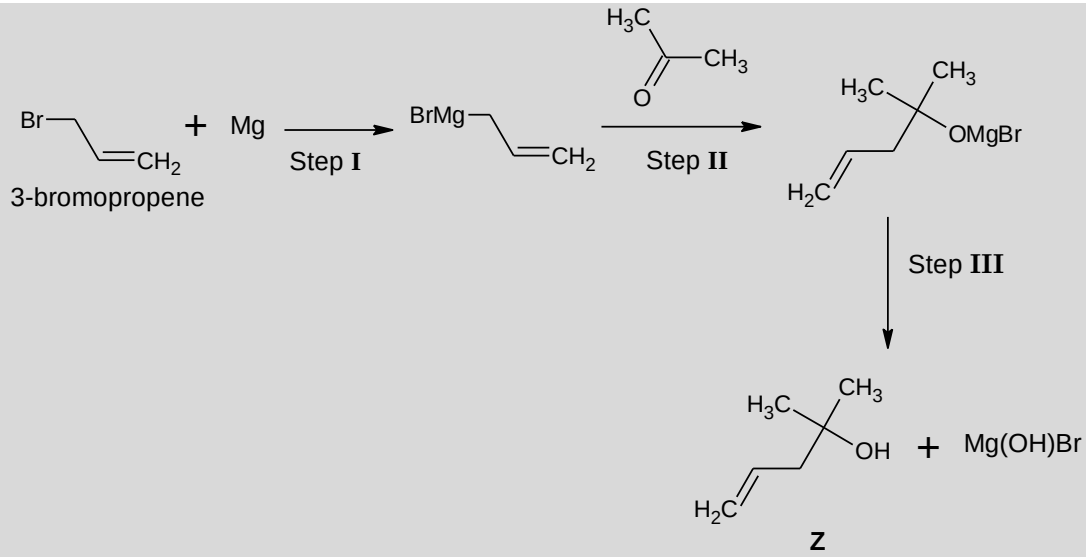
Ba^{2+} has a larger ionic radius and hence a smaller charge density. The polarising power of Ba^{2+} is smaller and the electron cloud of iodate ion is being polarised to a smaller extent. $Ba(IO_3)_2$ is hence more thermally stable and requires a longer time to decompose.

Since the initial number of moles of iodates remains the same and the number of moles of gas produced are the same, the total volume of gas collected remains unchanged for $Ba(IO_3)_2$.

[3]

(c) Grignard reagents, RMgX, are organo-magnesium halides derived from an alkyl halide, RX, and magnesium.

The use of a Grignard reagent in the conversion of 3-bromopropene to compound **Z** is given below.



(i) The alkyl group in RMgX behaves like an anion, R^-, and is a strong Lewis base.

Explain why propene is formed as a side product in both steps **I** and **II** if both reactions are **not** carried out under anhydrous conditions.

The nucleophilic carbon from $CH_2{=}CHCH_2^-$ will **accept a H^+ from water /** undergoes **acid-base reaction with water**.

[1]

(ii) Suggest the type of reaction occurring in steps **II** and **III**.

Step **II:** Nucleophilic Addition
Step **III:** Hydrolysis

[2]

(iii) A small amount of 3-bromopropene, propanone and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish 3-bromopropene from the other two compounds. State what you would observe.

Add NaOH(aq) and heat, followed by excess HNO_3(aq) and then $AgNO_3$(aq).

Cream ppt is seen in the test tube containing 3-bromopropene.
No ppt seen for the other two test-tubes.

[2]

[Total: 15]