Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Prelims Examination 2019
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

18 September 2019
2 hours

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

This question paper consists of **21** printed pages and **1** blank page.

[Turn over

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 $[Co(CN)_6]^{3-}$.

……[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.

……..

……[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.

……[1]

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

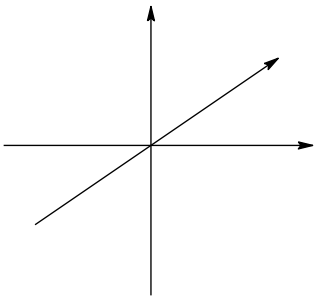
……[1]

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

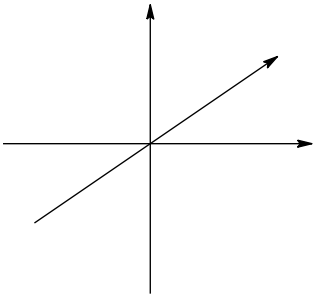
(i) Using the axes below, draw the shape of a 3*d* orbital of cobalt of

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

higher energy level



lower energy level



[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.

……..

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……..

……..

……..[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.

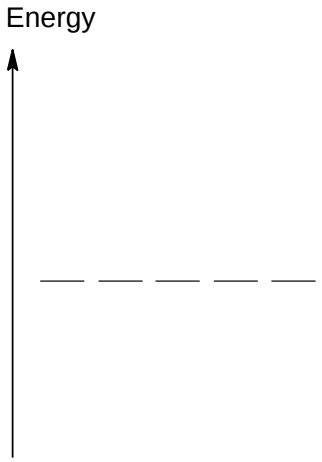

Fig 1.1

[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 in Fig 1.2 .

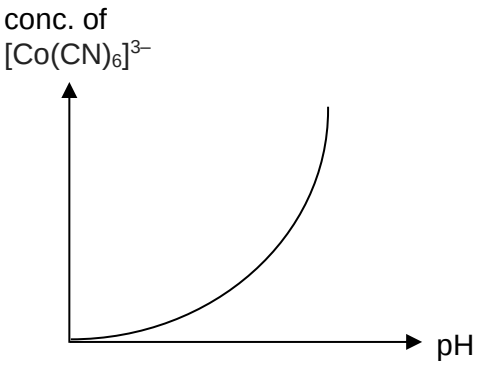

Fig 1.2

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

……[1]

(ii) Hence, using Le Chatelier's Principle, explain the shape of the graph in Fig 1.2.

……..

……..

……..

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……..

…….[2]

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

……..

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……..

…….[1]

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

……..

…….[1]

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

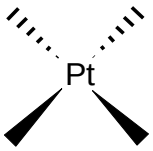
(i) For square planar complexes, *cis-trans* isomerism can be exhibited for **MA_2B_2** type complexes (where **M** is the metal cation, and **A** and **B** are different ligands).

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

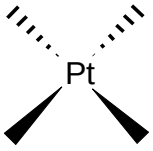
cis:	Both **A** ligands next to one another
trans:	Both **A** ligands are separated by a **B** ligand

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

Cis isomer



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.

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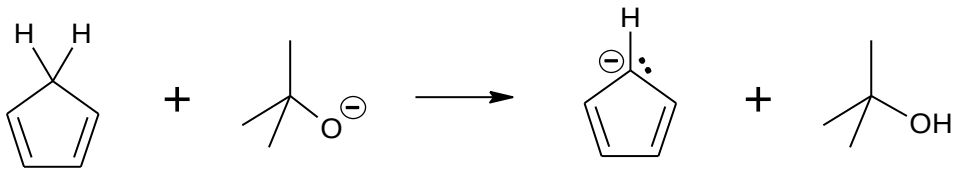
…….[1]

(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.

……..[1]

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

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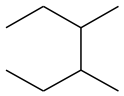
……..[3]

[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 (•).

[3]

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

Number of chiral centre(s) …….. [1]

Number of stereoisomers that are optically active ……..[1]

(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.

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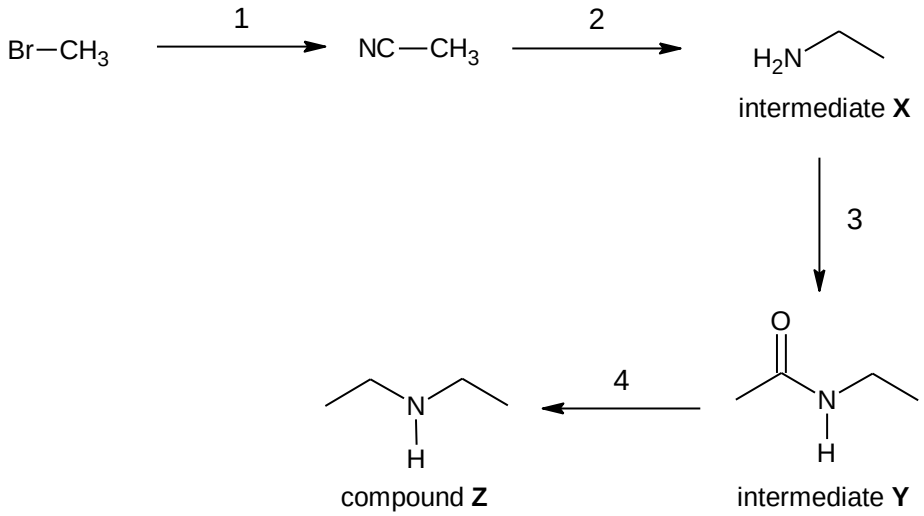
……..[2]

(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.

Types of orbitals used ……

[2]

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

Type of reaction ..…….……...……. [1]

Reagent(s) and condition(s) ….…….. [1]

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

……..

……..

……..[1]

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

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……..[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.

……..

……..[1]

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

……..

……..[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.

[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.

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……..

……..[1]

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

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……..

……..[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.

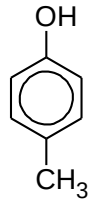
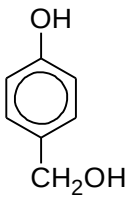
……..[1]

(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.

……..[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.

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……..……..

……..……..

……..…….[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.

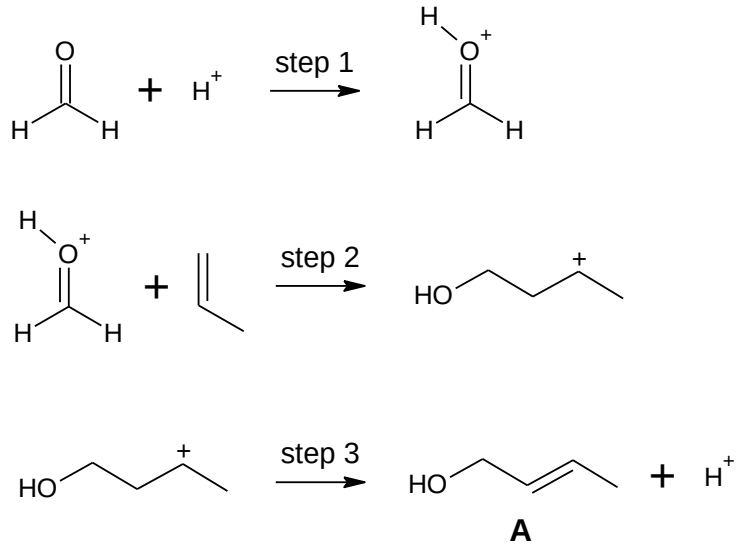

Fig. 4.1

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

……..

……..

……..[1]

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

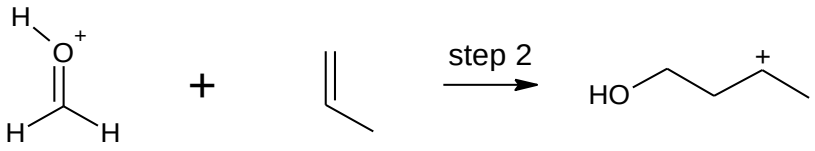

Fig. 4.2

[1]

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

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

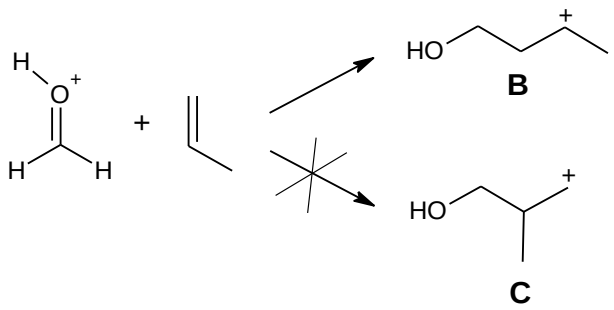

Fig. 4.3

……..

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……..

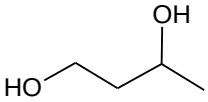
……..

……..[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.

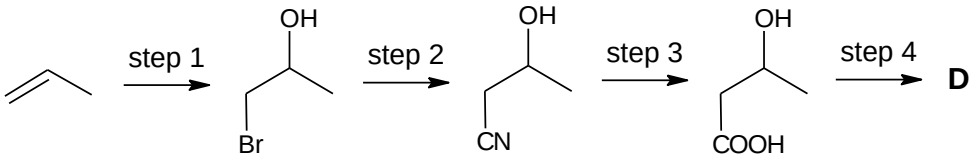


Fig. 4.4

(i) Name the product formed in step 1.

……[1]

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

step 2 ……..[1]

step 3 ……..……[1]

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

[1]

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

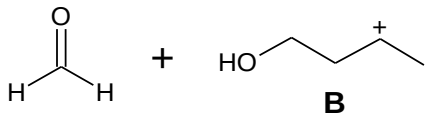
It is an asymmetrical molecule comprising a 6-membered ring. It does not contain any O–O bond and has no reaction with phosphorus pentachloride.

(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.

E

……..

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……..

……..[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**.

……[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.

……

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……[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.

……

……

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……

……

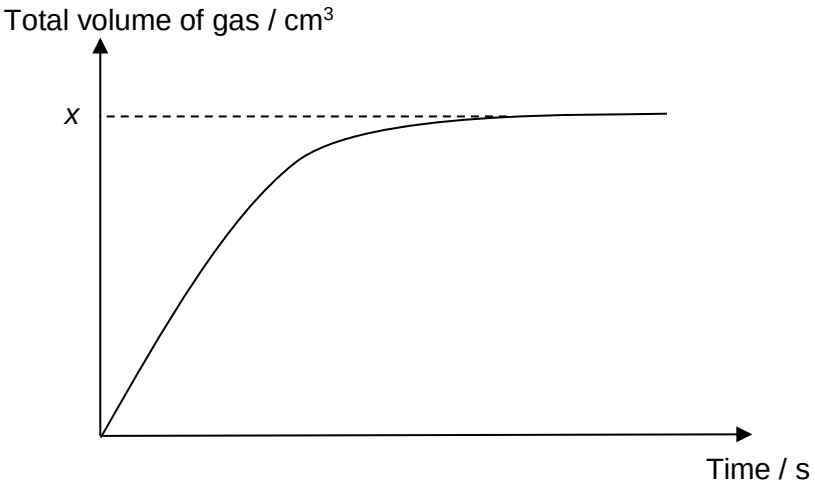
……[2]

(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 $Mg(IO_3)_2$.

……[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.

[1]

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

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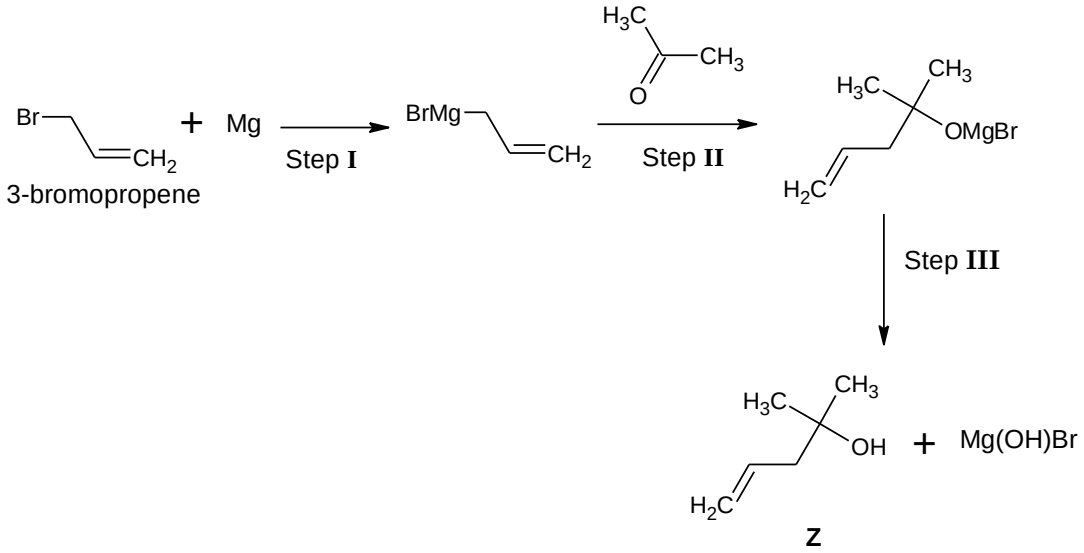
……[3]

(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.

……..……..

……..……..

……..……[1]

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

Step **II** ……..……[1]

Step **III** ……..……..…..[1]

(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.

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……..

…….[2]

[Total: 15]

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