Name:		**Centre/Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response Questions

18 September 2024
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. 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	
Section A	
1	**20**
2	**20**
3	**20**
Section B	
4 / 5	**20**
Total	**80**

This document consists of **32** printed pages.

Section A

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

1 **(a)** A bomb calorimeter and a Styrofoam cup calorimeter are both tools used in thermodynamics to measure heat changes during a chemical reaction. However, they differ significantly in their design, operation, and the type of reaction they measure.

Fig. 1.1 shows a simplified diagram of a bomb calorimeter which can be used for the accurate determination of heat changes during the combustion of alkanes.

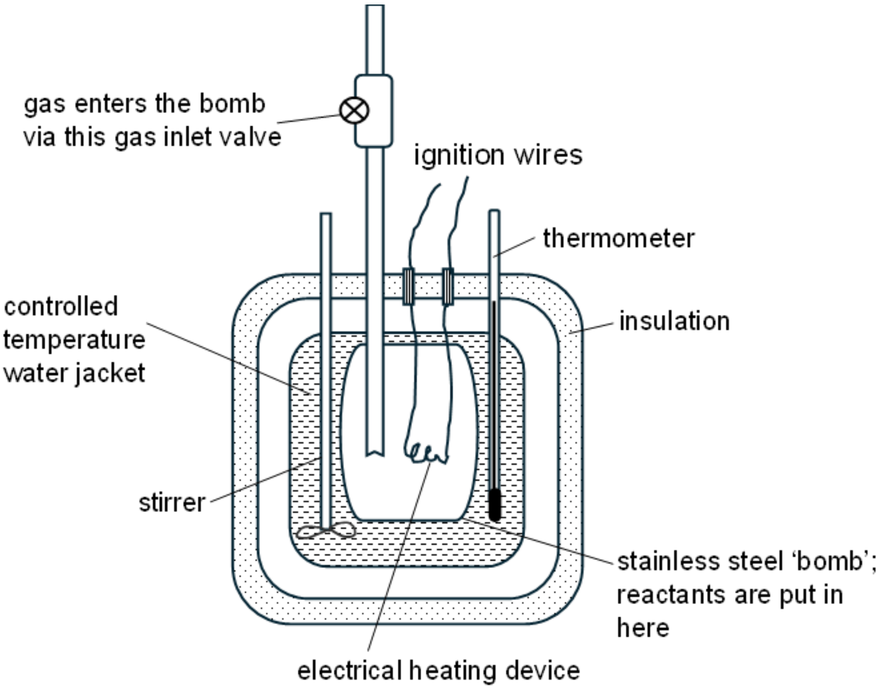

Fig. 1.1

The combustion process takes place at constant volume and the reaction is initiated via the electrical heating device which ignites the mixture.

(i) State one reason why the conditions inside the bomb calorimeter are considered non-standard. [1]

(ii) Suggest a reason why the Styrofoam cup calorimeter would be unsuitable to be used to measure heat changes during the combustion of alkanes. [1]

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(b) The heat capacity of a bomb calorimeter, C_{cal}, is the amount of heat required to raise the temperature of the calorimeter by 1 °C, and it can be calculated using a fuel which the heat change is known.

In an experiment to calculate C_{cal}, 2.00 g of liquid hexane is ignited with oxygen gas which is required to be in 20% excess.

A temperature change of 12.6 °C is recorded.

Under the conditions of the experiment, 1.00 mol of hexane releases 4254 kJ of energy when combusted.

(i) Write an equation for the complete combustion of hexane. [1]

(ii) Calculate the number of moles of oxygen gas needed to ensure the excess and hence, the volume occupied by this same amount of oxygen gas at a temperature of 298 K and a pressure of 1.00 atm, assuming ideal gas behaviour. [2]

(iii) Calculate the heat capacity of the bomb calorimeter, C_{cal}, in kJ K^{-1}. [2]

(iv) When the experiment is repeated with 2.00 g of butane, the temperature change recorded is 12.3 °C. Calculate the heat change per mole of butane combusted.

If you were unable to calculate a value for C_{cal} in **(b)(iii)**, use 6.50 kJ K^{-1}.

[2]

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(c) **(i)** Halogenoalkanes, R−X, undergo substitution reactions with *nucleophiles*.

Define what a *nucleophile* is. [1]

Table 1.1 shows the melting points of two metal nitrites which have different structure and bonding.

Table 1.1

metal nitrite	melting point/ °C
$AgNO_2$	140
KNO_2	441

Fig. 1.2 shows a general structure of $AgNO_2$.

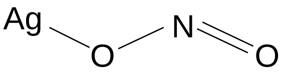

Fig. 1.2

(ii) Draw a 'dot-and-cross' diagram to show the type of bonding present in KNO_2. [1]

(iii) With consideration of the difference in bonding between KNO_2 and $AgNO_2$, explain why R−X react with KNO_2 to form alkyl nitrites, R−ONO, while R−X react with $AgNO_2$ to form nitroalkanes, $R{-}NO_2$, as the major product.

[R = alkyl group] [2]

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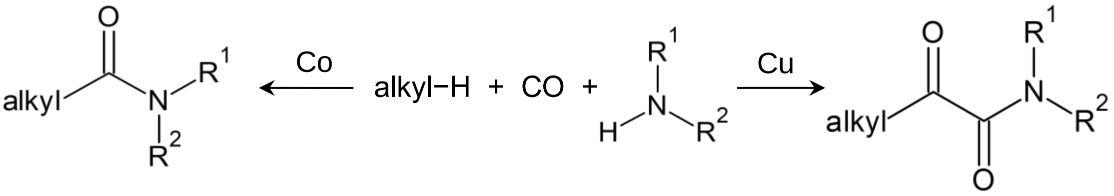
(d) Carbonylation reactions are chemical reactions in which a carbon monoxide (CO) molecule is incorporated into an organic molecule.

Fig. 1.3 shows metal-controlled mono- and double-carbonylation reactions of alkanes with amines to prepare alkyl amides and alkyl α-ketoamides respectively. The choice of the Co or Cu catalyst precursor was the key to producing a switch in the reaction selectivity.



mono-carbonylation

double-carbonylation

[R = alkyl group or H atom]

Fig. 1.3

(i) State the type of reaction common to both carbonylation reactions seen in Fig. 1.3. [1]

Fig. 1.4 shows a reaction scheme which includes the carbonylation reactions shown in Fig. 1.3.

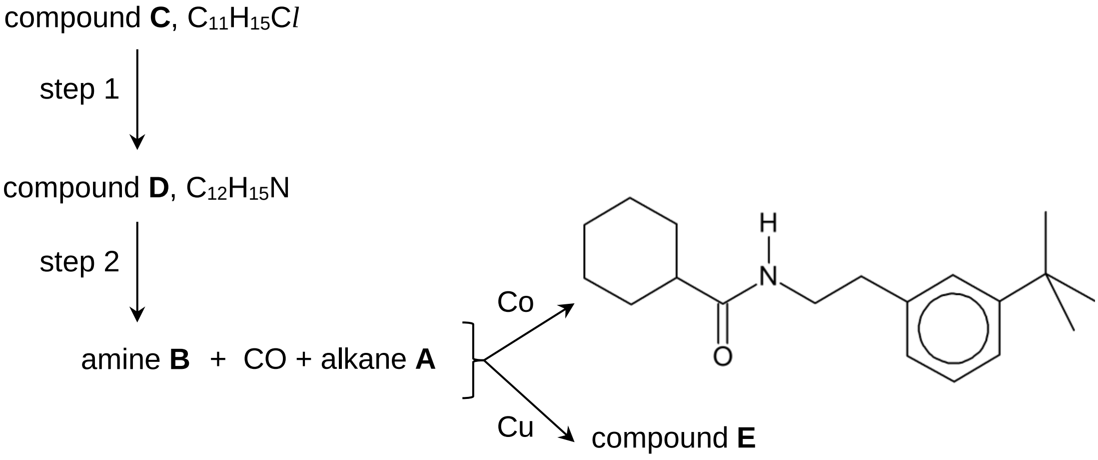


Fig. 1.4

(ii) With reference to Fig. 1.4, draw the structures of
- alkane **A**,
- amine **B**,
- compounds **C** and **E**. [4]

(iii) With reference to Fig. 1.4, identify the reagents and conditions for steps 1 and 2. [2]

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[Total: 20]

2 **(a)** Describe the reactions, if any, of the chlorides $NaCl$, $AlCl_3$ and PCl_5 with water. Write an equation for any reaction and state the pH of the resultant mixtures. [3]

(b) In 1849, the German chemist Adolf Kolbe reported his investigations into the electrolysis of aqueous solutions of sodium salts of carboxylic acids, using inert platinum electrodes. The reaction occurring at the anode is described by the equation shown below.

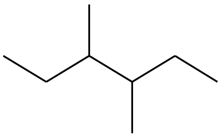
$$2RCO_2^- \rightarrow R{-}R + 2CO_2 + 2e^-$$

R can be any alkyl group.

(i) Identify the substances liberated at the cathode during the electrolysis. [1]

(ii) Calculate the volume of CO_2 gas produced at the anode at room temperature and pressure when a current of 0.100 A is passed through the electrolytic cell for 45.0 minutes. [2]

3,4-dimethylhexane is produced from the Kolbe electrolysis of the aqueous solution of the sodium salt of a carboxylic acid.



3,4-dimethylhexane

(iii) Draw the structure of the salt used to produce 3,4-dimethylhexane. Give the systematic name of the salt. [2]

There are three different types of 3,4-dimethylhexane molecule.

- molecule **X** rotates plane polarised light to the right.
- molecule **Y** rotates plane polarised light to the left.
- molecule **Z** has no effect on plane polarised light.

(iv) Deduce the isomeric relationship between molecules **X** and **Y**. Explain your reasoning. [1]

(v) Draw the 3-dimensional structure of molecule **Z**, showing its stereochemical formula. Hence, explain why **Z** has no effect on plane polarised light. [2]

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(c) The carbon atom in CO_2 is sp hybridised.

(i) Explain what is meant by sp hybridisation with reference to the carbon atom in CO_2. [1]

(ii) Draw a labelled diagram to show how orbitals overlap to form one of the carbon–oxygen sigma bonds in CO_2.
Assume that the oxygen atoms in CO_2 are sp^2 hybridised. [1]

(iii) Explain the overall polarity of a CO_2 molecule by reference to its shape. [1]

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(d) The half-life of a second-order reaction with respect to a reactant A can be calculated using the formula in Fig. 2.1.

$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_t}$$

k is the rate constant at a specific temperature.
$[\mathrm{A}]_t$ is the concentration of reactant A at time t.

Fig. 2.1

(i) State how **successive** half-lives vary for a second-order reaction as the concentration of reactant A decreases over time.

Hence, sketch a concentration of reactant A versus time graph for a second-order reaction. Label clearly two **successive** half-lives on the graph. [2]

The decomposition of nitrogen dioxide to nitric oxide and oxygen is known to follow second-order kinetics.

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

The rate constant, k, for the decomposition at 300 °C is 0.54 $mol^{-1}\ dm^3\ s^{-1}$.

(ii) At 300 °C, a sample of NO_2 in a closed container took 46.3 s for its concentration to decrease to one-fourth of its original value.

Use the formula in Fig. 2.1 to determine the original concentration, in mol dm^{-3}, of NO_2 in the container. [2]

(iii) Nitrogen dioxide has significant environmental consequences if emitted into the atmosphere.

Describe and explain with the aid of suitable equations, the role of NO_2 in the oxidation of atmospheric sulfur dioxide. [2]

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3 **(a)** **(i)** Describe the distribution of mass and charges within an atom with reference to its structure. [1]

(ii) In two separate experiments a beam of electrons and a beam of protons, travelling at the same velocity, passed through an electric field.

State two ways in which the behaviour of electrons would differ from that of protons. [1]

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(b) When dinitrogen tetroxide, N_2O_4, and nitrogen monoxide, NO, are mixed in a 1:2 ratio in a 1 dm^3 sealed container, the two gases react slowly to form dinitrogen trioxide, N_2O_3.

$$N_2O_4(g) + 2NO(g) \rightleftharpoons 2N_2O_3(g) \qquad \Delta H^\ominus = -26\ \text{kJ mol}^{-1}$$

(i) Sketch a graph showing how the rates of the forward and reverse reactions change from the time the two gases are mixed (t = 0) to the time **after** the reaction reaches equilibrium ($t = t_{eqm}$). Label your two lines clearly. [2]

(ii) State and explain how the position of equilibrium might change when
- temperature is increased,
- the container is compressed. [2]

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(c) Describe and explain the relative ease of hydrolysis of the following three organochlorine compounds.

C_6H_5Cl $C_6H_5CH_2Cl$ CH_3COCl

[3]

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(d) Compounds **Q** and **R** are chiral compounds with molecular formula $C_9H_{10}O_3$. **Q** effervesces with aqueous sodium carbonate but not **R**.

Q can react with PCl_5(s) to form compound **S**, $C_9H_8OCl_2$. **Q** does not react when heated with acidified $KMnO_4$. When **Q** is reacted with limited Cl_2(g) under ultraviolet light, compound **T**, $C_9H_9O_3Cl$, is the only product formed.

When concentrated HNO_3 is added to **R**, compound **U**, $C_9H_8O_7N_2$, is formed. **R** forms a yellow precipitate with alkaline aqueous iodine but does not react with Tollens' reagent. When **R** is heated with concentrated H_2SO_4, compound **V** is formed.

Suggest possible structures for **Q**, **R**, **S**, **T**, **U** and **V**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [11]

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Section B

Answer **one** question from this section.

4 This question explores the chemistry of magnesium and nickel compounds.

(a) The Grignard reagent is an organometallic reagent containing magnesium attached to an alkyl group and a halogen. CH_3MgBr is an example of a Grignard reagent.

Fig. 4.1 shows the reaction of CH_3MgBr with propanal to produce compound **X** which forms butan-2-ol when treated with a dilute acid.

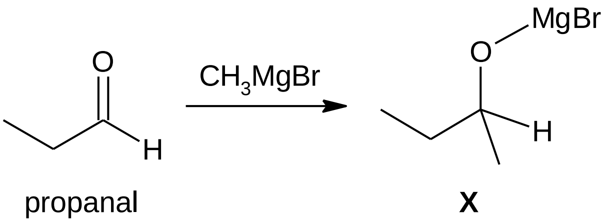


Fig. 4.1

(i) Explain why propanal cannot be converted to butan-2-ol using lithium aluminium hydride or sodium borohydride. [1]

(ii) The reaction between propanal and CH_3MgBr is a nucleophilic addition reaction which proceeds via the following two steps.

- In the slow step, the nucleophile $:CH_3^-$ attacks the electrophilic carbon in propanal, forming a reactive intermediate.
- This reactive intermediate then reacts with ^+MgBr to form **X**.

Use the information provided to draw the mechanism for this reaction.

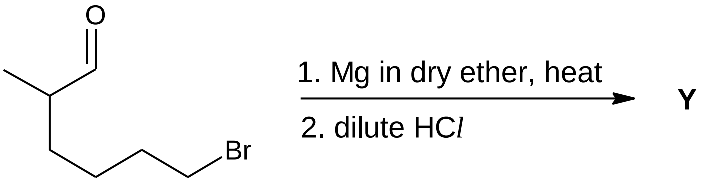
In your answer, indicate the movement of electron pairs with curly arrows, and show any relevant lone pairs and partial charges. [3]

(iii) With reference to your answer in **(a)(ii)**, explain why the resultant product mixture is optically inactive. [2]

(iv) The synthesis of Grignard reagents involves heating a bromoalkane with magnesium metal in dry ether. An example is shown below.

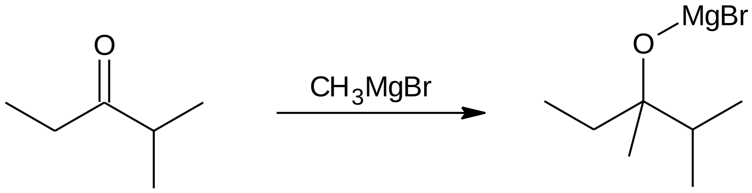
$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

Using this information and Fig. 4.1, draw the structure of the organic product **Y** of the following reaction.



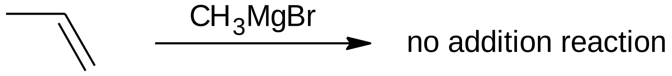
[1]

(v) The reaction between CH_3MgBr and 2-methylpentan-3-one occurs at a slower rate as compared to the reaction of CH_3MgBr in Fig. 4.1.



2-methylpentan-3-one

In contrast, CH_3MgBr does not undergo addition reaction with propene.



propene

By comparing to the reaction of CH_3MgBr in Fig. 4.1, suggest reasons to explain each observation above. Use the concepts of electronegativity, electronic and steric effects in your answer. [3]

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(b) Nickel is widely used in the production of stainless steel and many other metal alloys.

(i) ^{78}Ni is a known isotope of nickel with a *relative isotopic mass* of 78.

A sample of nickel contains 3 isotopes of nickel. Table 4.1 shows the identity of these isotopes and their relative abundance in the sample.

Table 4.1

isotope	relative abundance / %
^{58}Ni	75.4
^{60}Ni	22.5
^{78}Ni	2.1

Define the term *relative isotopic mass* and calculate the relative atomic mass of nickel in the sample. Leave your answer to 2 decimal places. [2]

(ii) Elemental nickel can be oxidised by nitric acid, HNO_3. Nitrous oxide, NO, is produced as one of the products of this reaction.

In an experiment, 5 g of nickel was reacted with excess nitric acid. At the end of the reaction, 1.36 dm^3 of NO gas was collected at room temperature and pressure.

Using appropriate calculations, determine the final oxidation state of nickel at the end of the reaction. [2]

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(c) Magnesium carbonate and nickel(II) hydroxide are sparingly soluble salts. Table 4.2 shows their K_{sp} values at 25 °C.

Table 4.2

salt	solubility product, K_{sp}
$MgCO_3$	6.82×10^{-6}
$Ni(OH)_2$	5.84×10^{-16}

(i) 1 dm^3 saturated solutions of $MgCO_3$ and $Ni(OH)_2$ are evaporated to dryness. Using appropriate calculations, show that the saturated solution containing $MgCO_3$ will produce a larger mass of solid after being evaporated to dryness. [2]

(ii) State and explain how the solubility of $Ni(OH)_2$ in water would compare with its solubility in solutions of higher pH. [1]

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(d) When heated to a sufficiently high temperature, nickel(II) carbonate decomposes to give nickel(II) oxide.

Using appropriate data from the *Data Booklet*, suggest with reasoning, how the decomposition temperature of nickel(II) carbonate will compare to that of barium carbonate. [3]

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[Total: 20]

5 **(a)** The nickel−iron battery is a rechargeable battery which uses Fe(s) and NiO(OH)(s) as its electrodes, and aqueous potassium hydroxide as its electrolyte.

During a typical discharge, Fe forms $Fe(OH)_2$ while NiO(OH) forms solid $Ni(OH)_2$ respectively. The standard cell potential measured during this discharging process is +1.40 V.

(i) Define *standard cell potential*. [1]

(ii) Write half–equations for the reactions taking place, in an alkaline medium, at the anode and cathode during the discharging process.
Include state symbols. [2]

(iii) Using the information from **(a)** and your answer in **(a)(ii)**, calculate $\Delta G^{\ominus}_{\text{cell}}$ and comment on its significance in the discharging process. [2]

(iv) The standard electrode potential of the $Fe(OH)_2$/Fe half−cell is measured against a standard hydrogen electrode. A reading of −0.88 V is obtained from the voltmeter.

Calculate the standard electrode potential, $E^{\ominus}$, for the NiO(OH)/$Ni(OH)_2$ half−cell. [1]

(v) State and explain the effect on the electrode potential, *E*, for the NiO(OH)/$Ni(OH)_2$ half−cell when a higher concentration of aqueous potassium hydroxide is used as the electrolyte. [1]

(vi) The electrolyte, KOH, is known to slowly degrade over the years and must be replaced to ensure the functionality of the rechargeable battery.

Explain, with the aid of equation(s), how the electrolyte can be degraded with the absorption of atmospheric carbon dioxide gas. [2]

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(b) **(i)** Describe and explain the trend in atomic radius of transition elements. [2]

(ii) Nickel and iron are both transition elements.

With reference to your answer in **(b)(i)**, suggest why nickel and iron are suitable to be mixed as an alloy. [1]

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(c) Nickel can also be used as a catalyst to convert alkenes into alkanes.

State the type of reaction in this conversion. [1]

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(d) An especially valuable organoboron intermediate can be prepared by the addition of a dialkylborane, R_2BH, to a carbon−carbon double bond in an alkene. An example of the reaction involving propene is shown in Fig. 5.1.

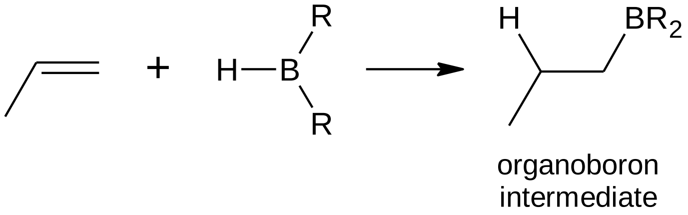


Fig. 5.1

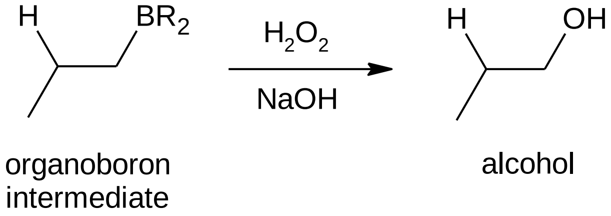
(i) Suggest a reason why the boron is added to the less substituted carbon atom of the C=C bond in Fig. 5.1. [1]

The formation of the organoboron intermediate in Fig. 5.1 occurs via a one-step mechanism. The electron deficient boron and partial negative hydrogen are both **simultaneously** added to the same side of a carbon−carbon double bond. The bond pair of electrons between B and H is used to form the new C−H bond.

(ii) Propose a mechanism for the reaction between but-1-ene and dialkylborane, R_2BH.

Show all relevant dipoles, curly arrows and structure of the organoboron intermediate. [2]

(iii) The organoboron intermediate shown in Fig. 5.1 can be further converted into an alcohol.



With reference to the information in **(d)** and Fig. 5.2, suggest a structure of compound **Z**.

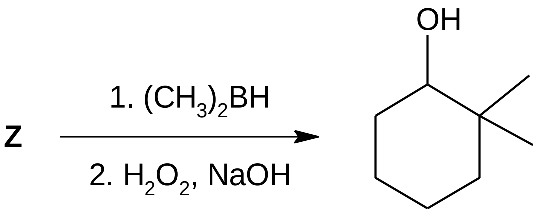


Fig. 5.2

[1]

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(e) Propene also undergoes electrophilic addition with hydrogen halides in the form of HCl, HBr and HI.

The hydrogen halides behave differently when heated as shown by the observations given in Table 5.1.

Table 5.1

hydrogen halide	observations
HCl	No visible change even with strong heating
HBr	Strong heating produces brown vapour
HI	Heating produces violet vapour

Explain fully the observations in Table 5.1. [3]

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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