13 Extension Topic – Organic Chemistry Halogen Derivatives

GUIDING QUESTIONS

Halogenoalkanes

- How are halogenoalkanes synthesised?
- Which classes of reagents do halogenoalkanes react with and why? What types of reactions does halogenoalkanes undergo and why?
- How do halogenoalkanes react with nucleophiles? What are the factors which determine the mechanism of nucleophilic substitution?
- How does the reactivity compare between different halogenoalkanes?

Halogenoarenes

- How are halogenoarenes synthesised?
- How does the reactivity of a halogenoarene compare with that of a halogenoalkane towards nucleophilic reagents?

LEARNING OUTCOMES

Students should be able to:

11.4(a) recall the chemistry of halogenoalkanes as exemplified by
  (i) the following nucleophilic substitution reactions of bromoethane: hydrolysis; formation of nitriles; formation of primary amines by reaction with ammonia
  (ii) the elimination of hydrogen bromide from 2-bromopropane

11.4(b) describe and explain the mechanism of nucleophilic in halogenoalkanes
  (i) S_N1 in terms of stability of the carbocation intermediate
  (ii) S_N2 in terms of steric hindrance of the halogenoalkanes

11.4(c) explain the stereochemical outcome in nucleophlic substitution involving optically active substrates:
  (i) inversion of configuration in S_N2 mechanism
  (ii) racemisation in S_N1 mechanism

11.4(d) interpret the different reactivities of halogenoalkanes and chlorobenzene with particular reference to hydrolysis and to the relative strengths of the C–Hal bonds

11.4(e) explain the unreactivity of chlorobenzene compared to halogenoalkanes towards nucleophilic substitution in terms of the delocalisation of the lone pair of electrons on the halogen and steric hindrance

11.4(f) suggest characteristic reactions to differentiate between
  (i) different halogenoalkanes
  (ii) halogenoalkanes and halogenoarenes

11.4(g) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness

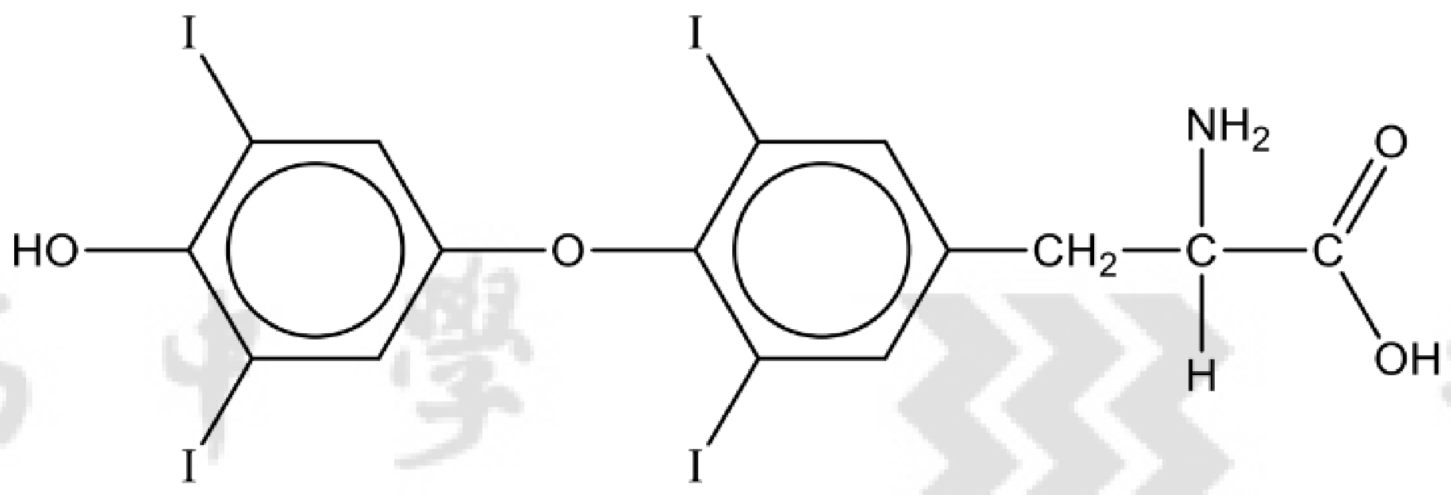
11.4(h) recognise the concern about the effect of chlorofluoroalkanes (CFCs) on the ozone layer [the mechanistic details of how CFCs deplete the ozone layer are <u>not</u> required]

REFERENCES

1. Peter Cann and Peter Hughes. Chemistry for Advanced Level. John Murray (Publishers) Ltd. Chapter 25.
2. John McMurry. Organic Chemistry. Brooks/Cole. Chapters 10-11.

1 INTRODUCTION

There are only a few naturally-occurring organic halogen compounds. One example is thyroxine, a hormone secreted by the thyroid gland.



thyroxine

Synthetic halogen compounds have a variety of commercial applications such as insecticides, herbicides, dry-cleaning agents and degreasers, fire-extinguishing chemicals, and polymers. However, many chlorinated hydrocarbons are suspected to be carcinogenic and are being replaced by other compounds.

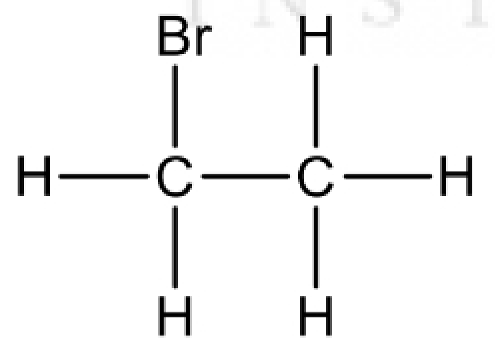
Organic halogen compounds are often used as intermediates in organic synthesis; they are readily formed from common materials and can easily be transformed into many different functional groups.

Two main types of halogen compounds will be discussed: **halogenoalkanes** and **halogenoarenes**.

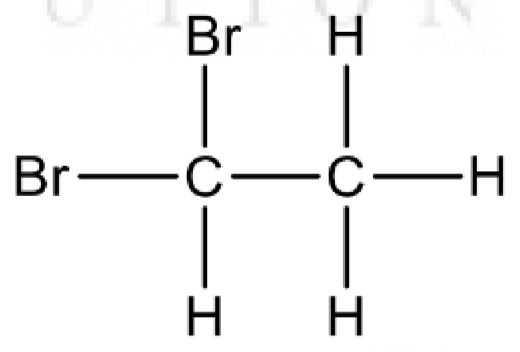
1.1 Halogenoalkanes (alkyl halides)

They are alkanes with one or more H atoms replaced by the halogen atom, F, C*l*, Br or I.

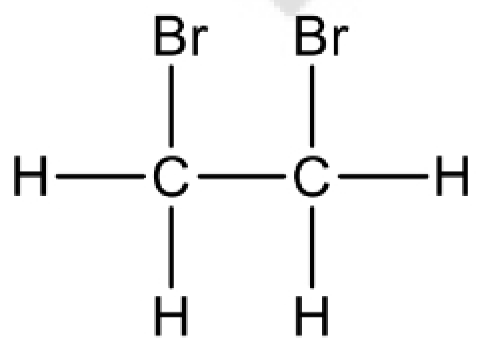
In IUPAC nomenclature, the halogen is considered as a substituent of the hydrocarbon. These compounds are therefore named using the prefixes, fluoro-, chloro-, bromo- and iodo-. Some examples are given below.



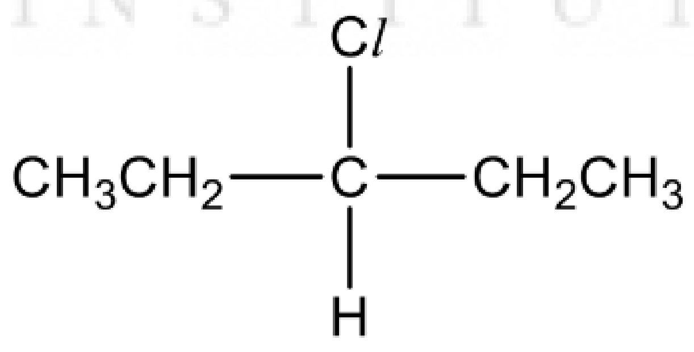
Bromoethane



1,1-dibromoethane



1,2-dibromoethane



3-chloropentane

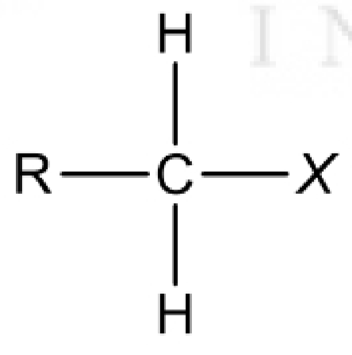
Halogenoalkanes may show constitutional isomerism and enantiomerism. For example, there are five isomers with the molecular formula, C_4H_9Br.

Self-practice 1.1

(a) Draw the five isomers (constitutional and enantiomers) with the molecular formula, C_4H_9Br.

(b) Give the IUPAC names of the four constitutional isomers.

Halogenoalkanes are classified as **primary (1°)**, **secondary (2°)** or **tertiary (3°)**, depending on how many alkyl groups are attached to the halogenated carbon (the carbon atom that is joined to the halogen atom, *X*).

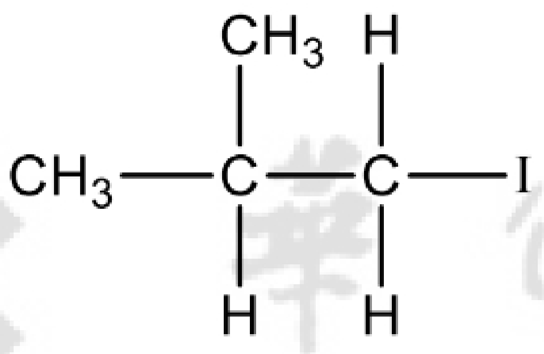


$$\mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-}X$$

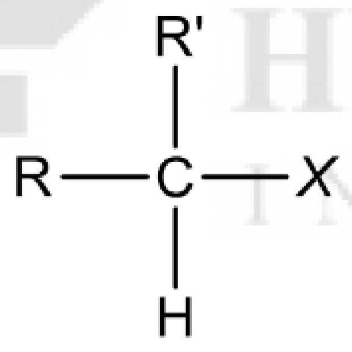
Primary halogenoalkanes

In a primary halogenoalkane, the carbon, which carries the halogen atom, is only attached to **one** alkyl group or one other carbon atom.

e.g. CH_3CH_2Br $CH_3CH_2CH_2Cl$



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-I}$$

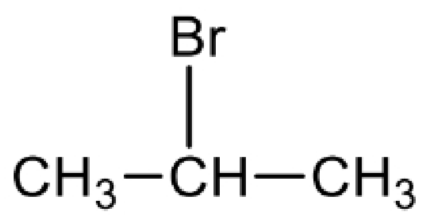


$R-\overset{R'}{\underset{H}{C}}-X$

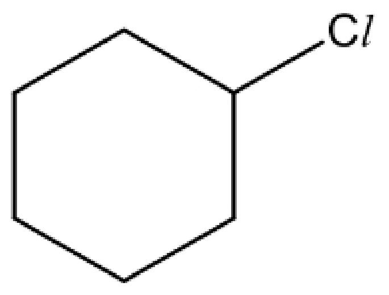
Secondary halogenoalkanes

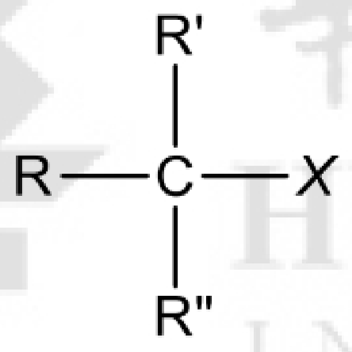
In a secondary halogenoalkane, the carbon, which carries the halogen atom, is attached to **two** alkyl groups or two other carbon atoms.

e.g.



$CH_3-\overset{Br}{CH}-CH_3$



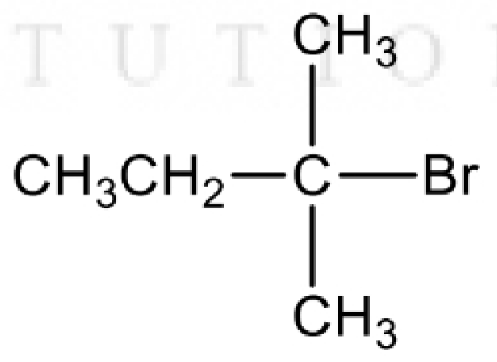


$R-\overset{R'}{\underset{R''}{C}}-X$

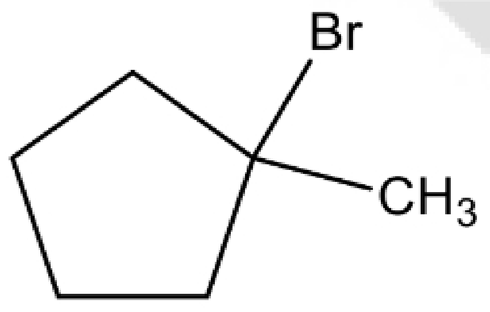
Tertiary halogenoalkanes

In a tertiary halogenoalkane, the carbon, which carries the halogen atom, is attached to **three** alkyl groups or three other carbon atoms.

e.g.



$CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Br$



Self-practice 1.2

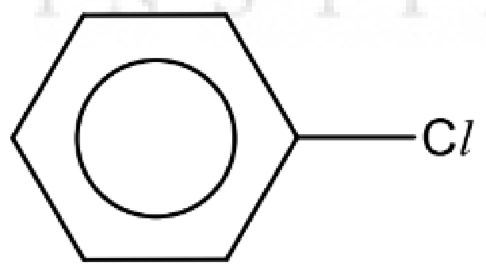
Draw the structural formulae of the halogenoalkanes in the table and classify them as primary, secondary or tertiary.

Name	Structural formula	Classification (primary, secondary or tertiary)
3-chloropropene		
chlorocyclopentane		
1-bromo-1-methylcyclohexane		

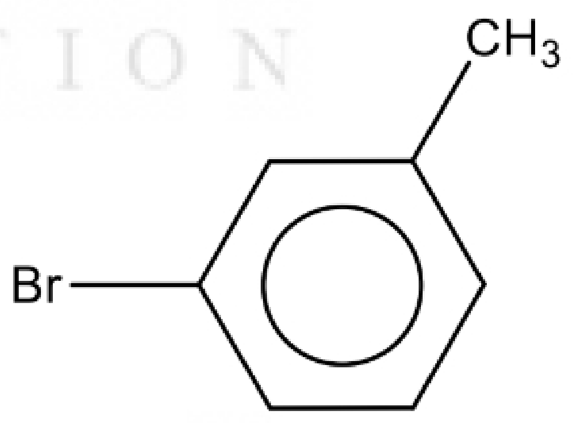
1.2 Halogenoarenes (aryl halides)

These compounds have a halogen atom attached directly to an aromatic carbon ring.

e.g.



chlorobenzene



1-bromo-3-methylbenzene

1.3 Physical properties of halogenoalkanes

Halogenoalkanes are generally colourless liquids with sweetish smells. They are immiscible with and denser than water. Boiling points of halogenoalkanes are higher than those of their corresponding alkanes (alkanes with the same number of carbon atoms). For the same alkyl group, the boiling point increases in the order: chloroalkane < bromoalkane < iodoalkane.

Self-practice 1.3

The boiling points of some organic compounds are given below.

Compound	Structural formula	Name	Boiling point /°C
A	$CH_3CH_2CH_3$	propane	−42
B	$CH_3CH_2CH_2Cl$	1-chloropropane	47
C	$CH_3CH_2CH_2Br$	1-bromopropane	71
D	$CH_3CH_2CH_2I$	1-iodopropane	102

Explain each of the following.

(a) The boiling point of compound *B* is higher than that of *A*.

(b) The boiling point increases in the order, $B < C < D$.

Note that the main intermolecular forces in halogenoalkanes are dispersion forces (also called instantaneous dipole-induced dipole attractions). The difference in permanent dipole-permanent dipole attractions is not as significant as dispersion forces and does not explain the observed boiling point trend. There is a small amount of permanent dipole-permanent dipole attractions between molecules and this will be important for the chloroalkanes, becoming less so with bromo- and iodoalkanes since they are less polar.

2 PREPARATION OF HALOGENOALKANES AND HALOGENOARENES

Halogenoalkanes can be prepared from:

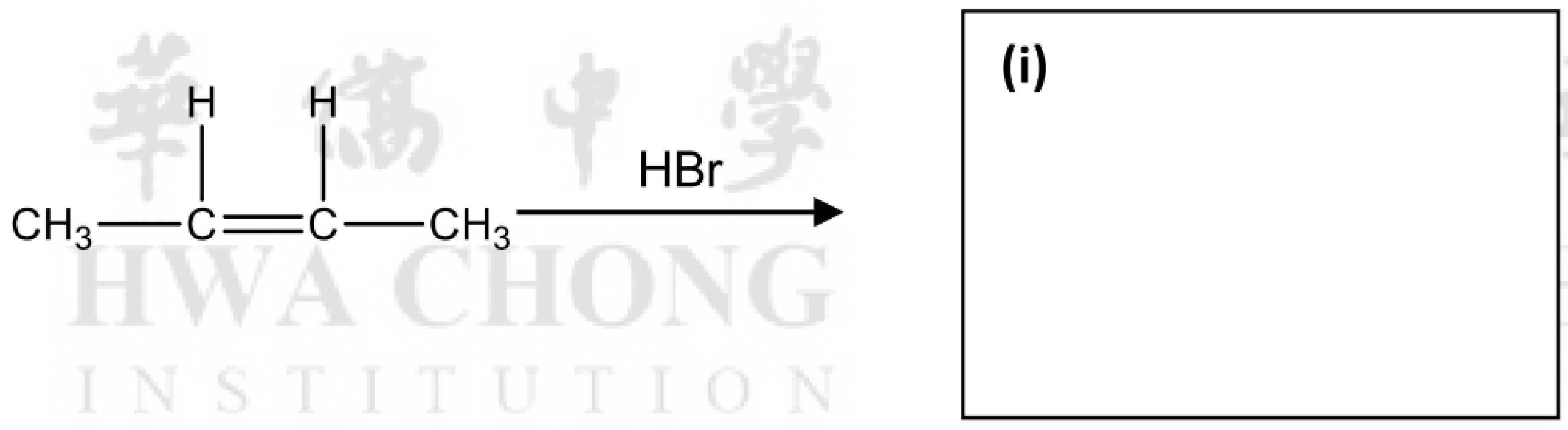
- Free radical substitution of alkanes (Topic 10 Alkanes)
- Electrophilic addition on alkenes (Topic 11 Alkenes)
- Nucleophilic substitution of alcohols (to be covered in Topic 16 Hydroxy Compounds)

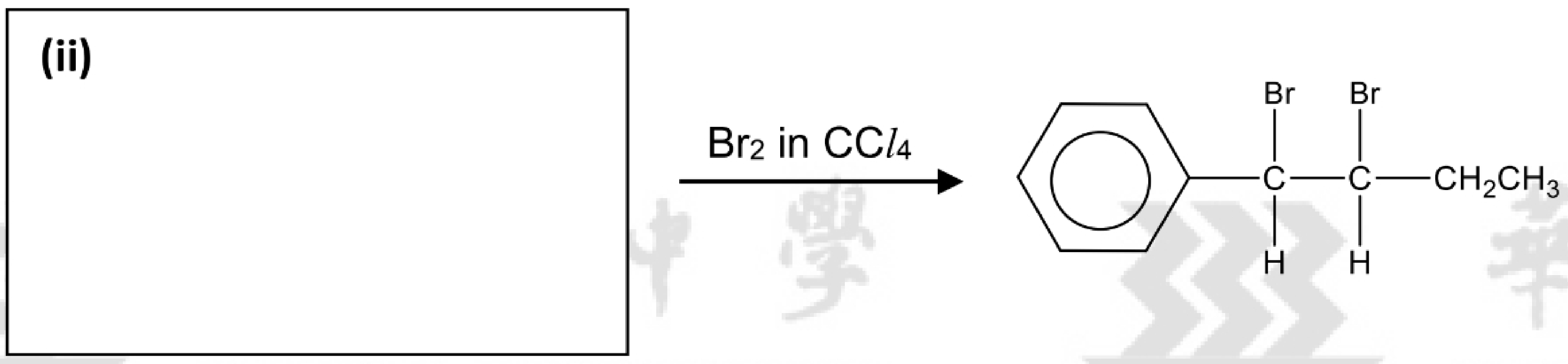
Halogenoarenes can be prepared from:

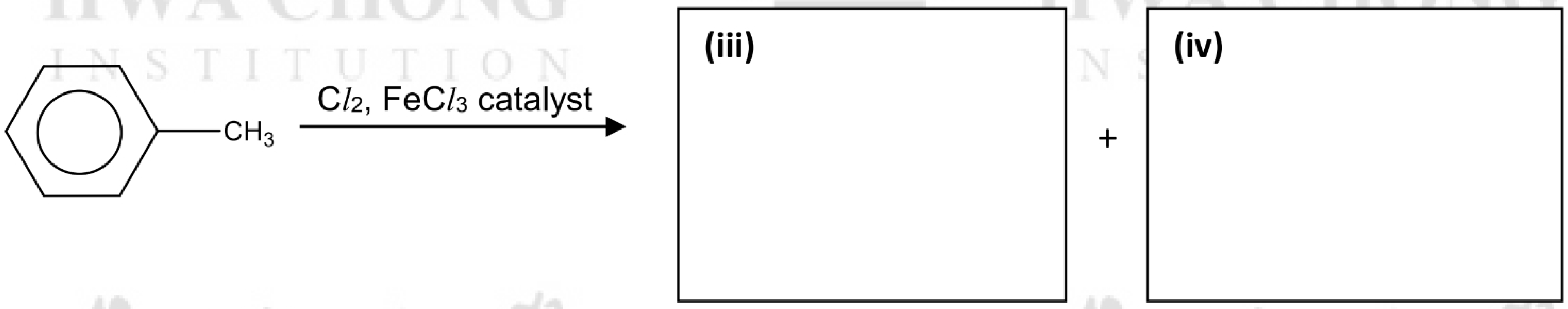
- Electrophilic substitution of arenes (Topic 12 Arenes)

Self-practice 2.1

Draw the structure of the organic compound in each of the following boxes.







3 REACTIONS OF HALOGENOALKANES

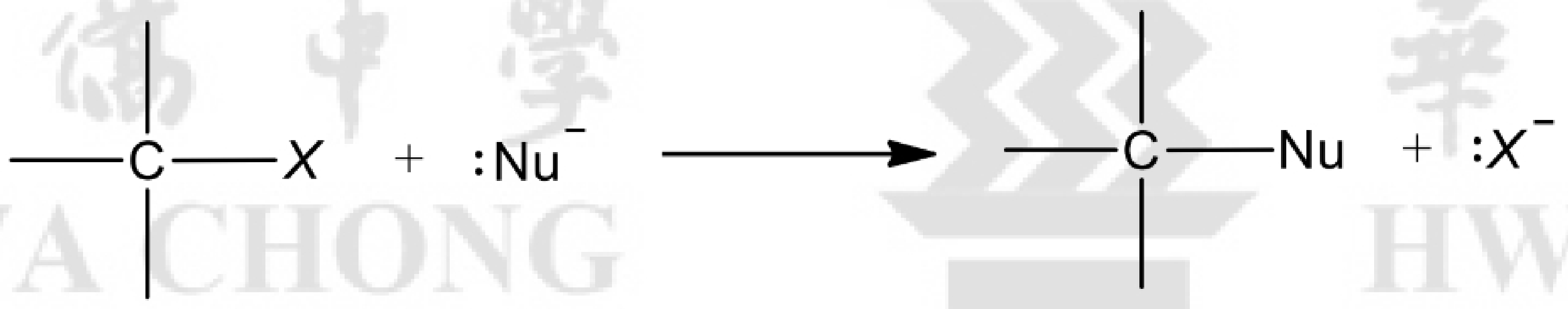
Halogenoalkanes undergo two types of reactions: **nucleophilic substitution** and **elimination**.

3.1 Nucleophilic substitution reactions

Halogenoalkanes are fairly reactive compounds, owing largely to the polarity of the C–X bond. Halogens are more electronegative than carbon, so the carbon-halogen bond is polar. The electron-deficient carbon atom has a partial positive charge which causes it to be attractive to **nucleophiles**.

During reaction, the halogen atom in the halogenoalkane can be substituted by a nucleophile e.g. OH^-, CN^- and NH_3. This reaction typical of halogenoalkanes is called **nucleophilic substitution**.

The overall reaction for nucleophilic substitution can be represented as:

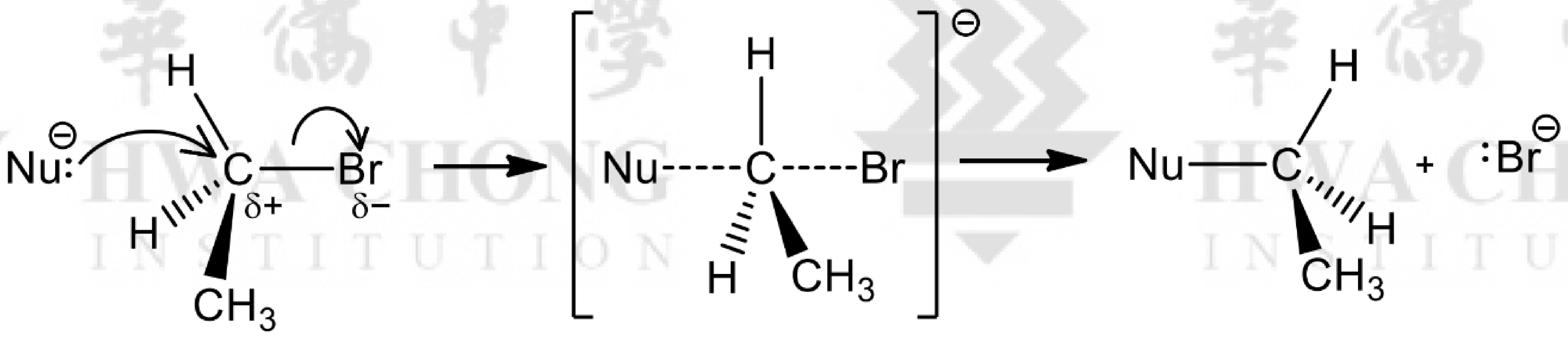


In this reaction, the halogen atom leaves as the halide ion, X^-. We refer to the halide ion as the leaving group. A leaving group is an anion or molecule that departs with a pair of electrons in a heterolytic bond cleavage.

3.1.1 General mechanisms of nucleophilic substitution mechanisms

Nucleophilic substitution reactions can proceed by either an $\mathbf{S_N1}$ or $\mathbf{S_N2}$ mechanism. Generally, primary halogenoalkanes undergo nucleophilic substitution via the one-step mechanism $\mathbf{S_N2}$ while tertiary halogenoalkanes undergo reactions via the two-step mechanism $\mathbf{S_N1}$. Secondary halogenoalkanes may react via either mechanism.

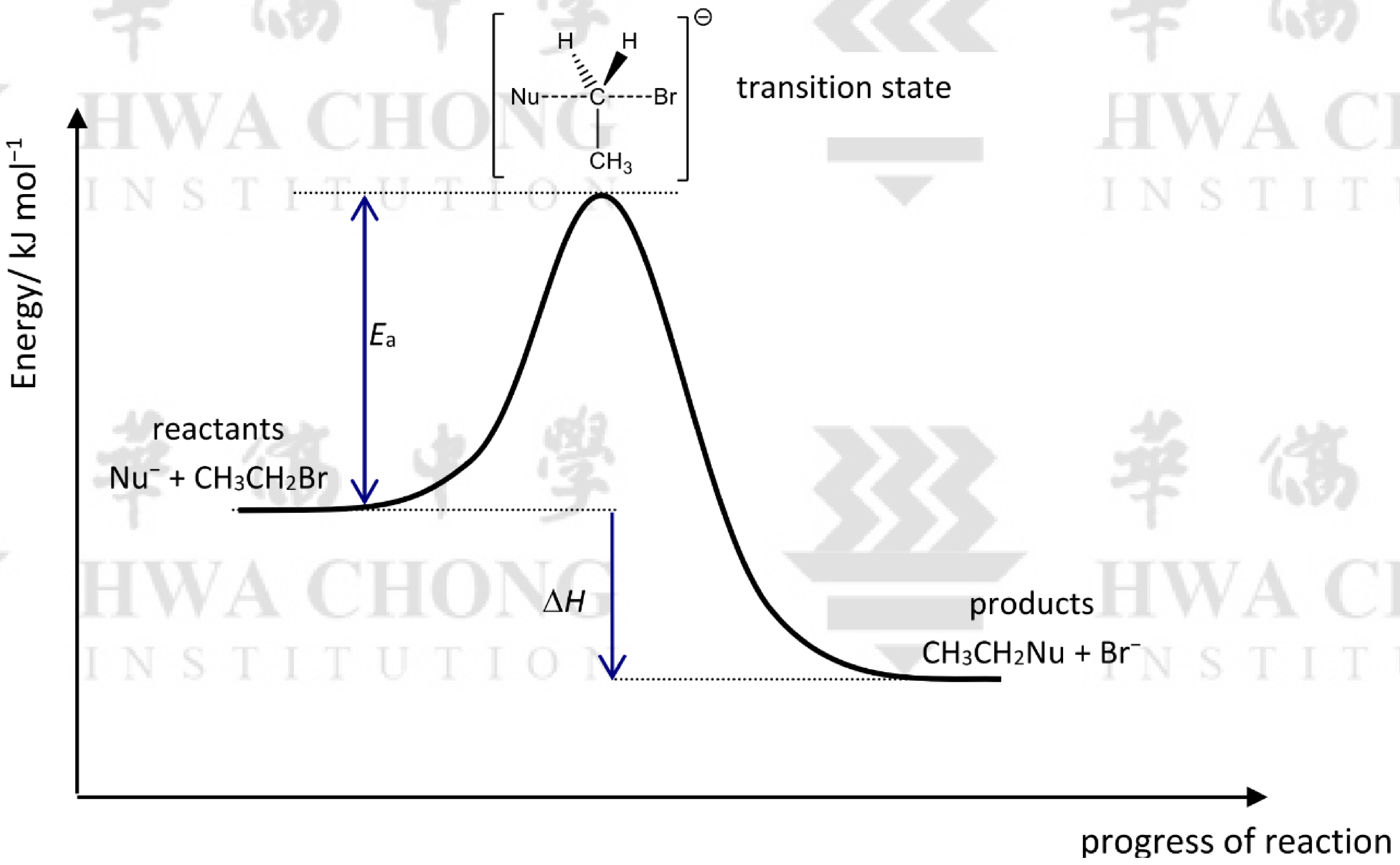
- **S_N2 mechanism (bimolecular nucleophilic substitution)**



transition state

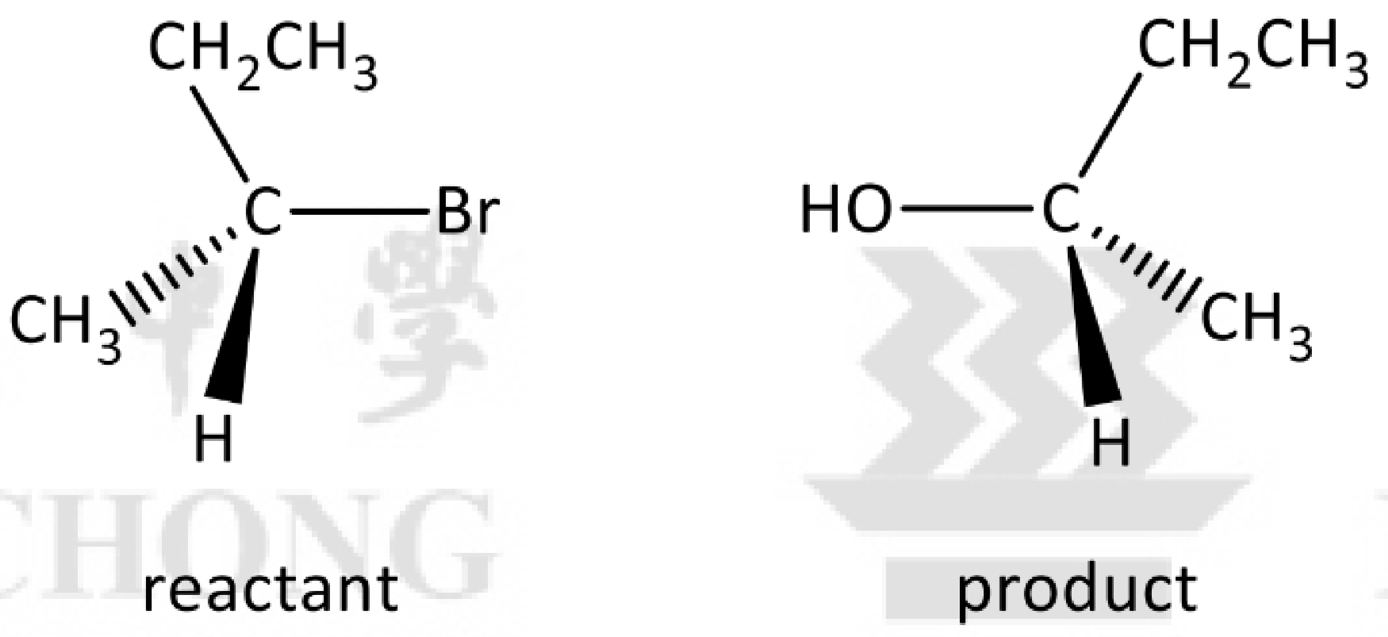
  - The C–Br bond in bromoethane is **polar** due to the difference in electronegativity between the carbon and bromine atoms.

- The **nucleophile** attacks the partially positively charged carbon atom from the side opposite to the bromine atom. The nucleophile donates its lone pair to the electron-deficient carbon so that a bond begins to form between the nucleophile and the carbon atom.
- At the same time, the C–Br bond is simultaneously weakened and begins to break. Both the bonding electrons in the C–Br bond are donated to the Br atom to form Br^-.
- An unstable, activated complex called a **transition state** is formed where the entering nucleophile and the leaving Br^- ion are partially bonded to the same carbon atom. Bond breaking and bond forming occur simultaneously. This is a **one-step mechanism**.
- Rate = $k[RBr][Nu^-]$
- The mechanism is known as S_N2 (**bimolecular** nucleophilic substitution), because two species are involved in the rate determining step of the mechanism.
- The energy profile or reaction pathway diagram for the S_N2 mechanism is given below.



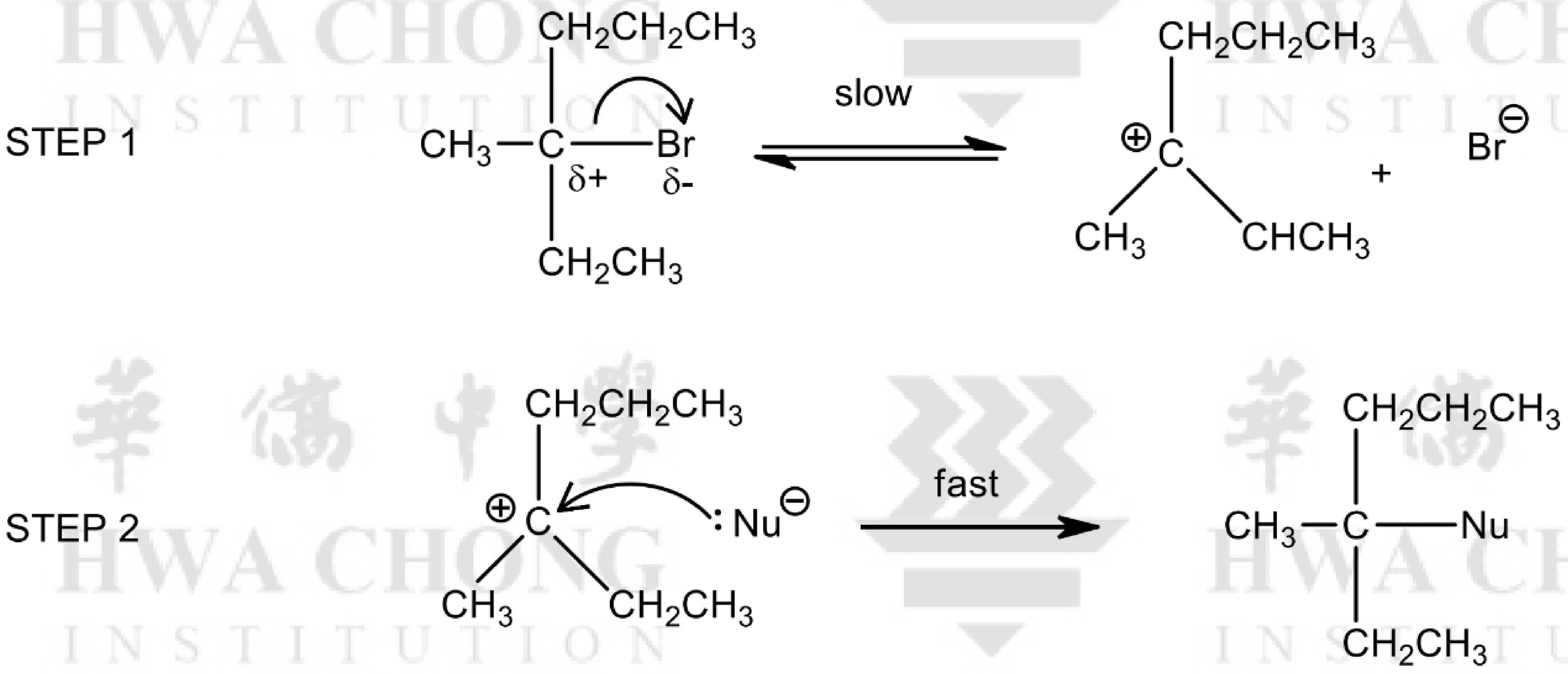
Stereochemistry

If the original R*X* molecule is chiral, the stereochemistry at the electron-deficient carbon will be **inverted** after the substitution reaction (see below).



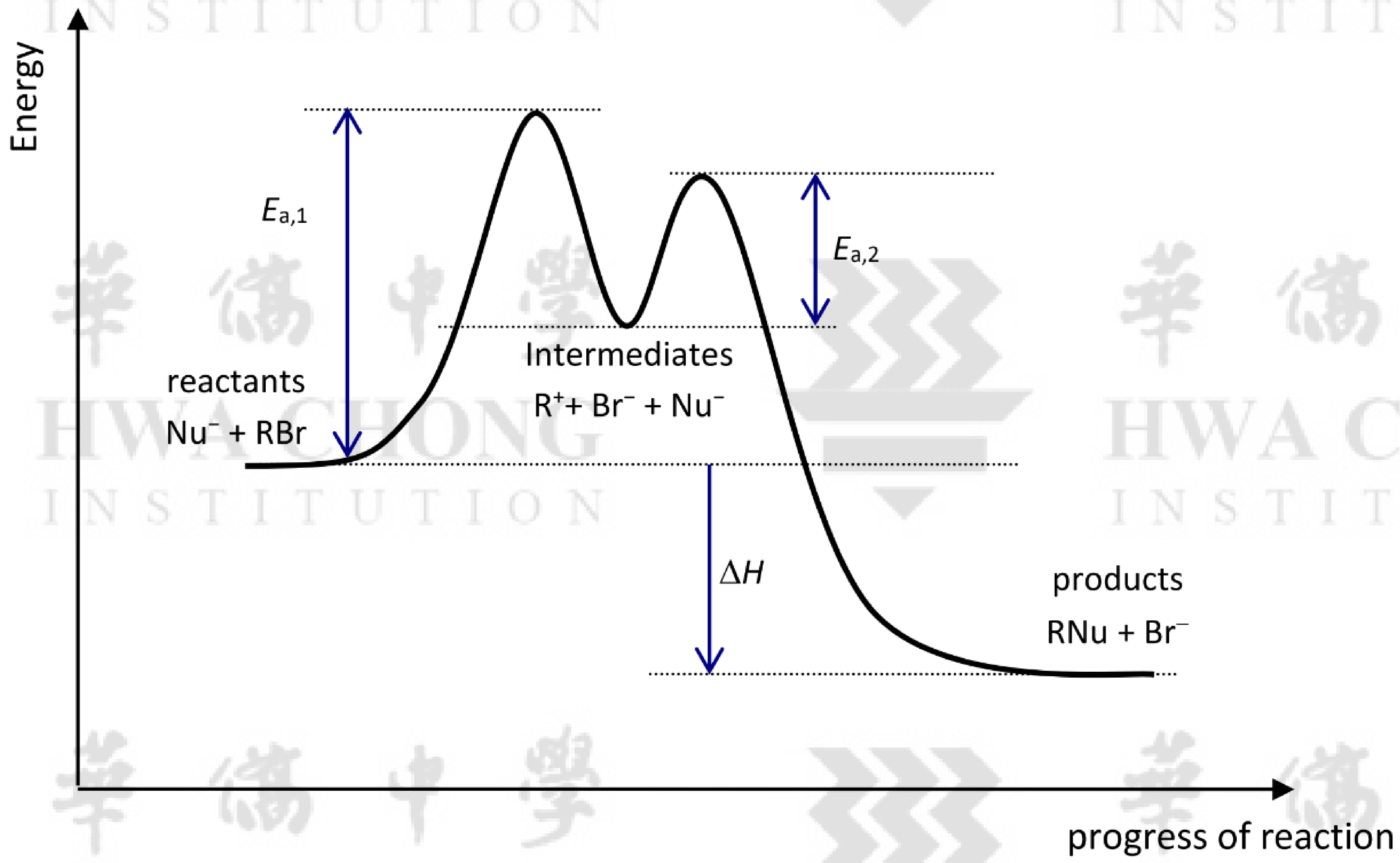
If the reaction occurs purely through the S_N2 mechanism, only one of the enantiomers will be formed as the product. There will not be a mixture of two enantiomers. As a result, the product obtained through the S_N2 mechanism will be optically active, if there is a chiral carbon present.

- **S_N1 mechanism (unimolecular nucleophilic substitution)**



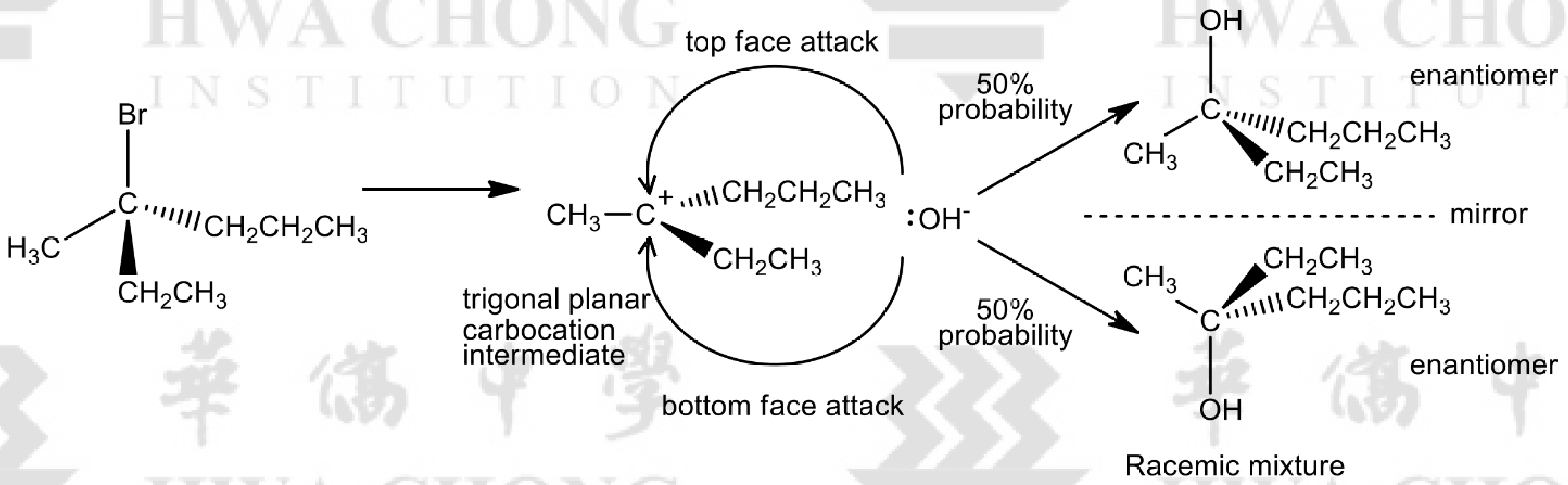
- The C–Br bond in 3-bromo-3-methylhexane is **polar** due to the difference in electronegativity between the carbon and bromine atom.
- In the first step, heterolytic fission of the C–Br bond occurs, giving a **carbocation intermediate** and a bromide ion. The electron-donating alkyl groups help to stabilise the carbocation intermediate.
- In the second step, the highly reactive carbocation is readily attacked by the **nucleophile** to form the product.
- This is a **two-step mechanism**.
- Rate = k[RBr]
- The mechanism is known as S_N1 (**unimolecular** nucleophilic substitution) because only one species is involved in the rate determining step of the mechanism.

- The energy profile or reaction pathway diagram for the S_N1 mechanism is given below.



Stereochemistry

Since the carbocation is **trigonal planar** with respect to the electron-deficient carbon, the nucleophile is able to attack from the top and bottom face of the carbocation with **equal probability**. If the addition of the nucleophile results in a chiral product, a **racemic mixture** is formed in this mechanism as both mirror image enantiomers are formed in equal quantities.



Self-practice 3.1

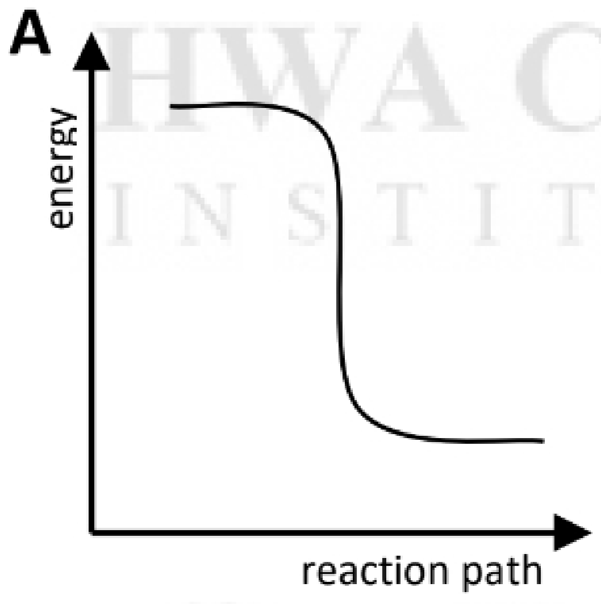
A possible reaction of hydrolysis of 2-chloro-2-methylpropane is as shown.

$$(CH_3)_3C\text{–}Cl \xrightarrow{slow} (CH_3)_3C^+ + Cl^-$$

$$(CH_3)_3C^+ + OH^- \xrightarrow{fast} (CH_3)_3C\text{–}OH$$

Which diagram represents the reaction profile for this mechanism? Hint: Consider the bond energies.

A



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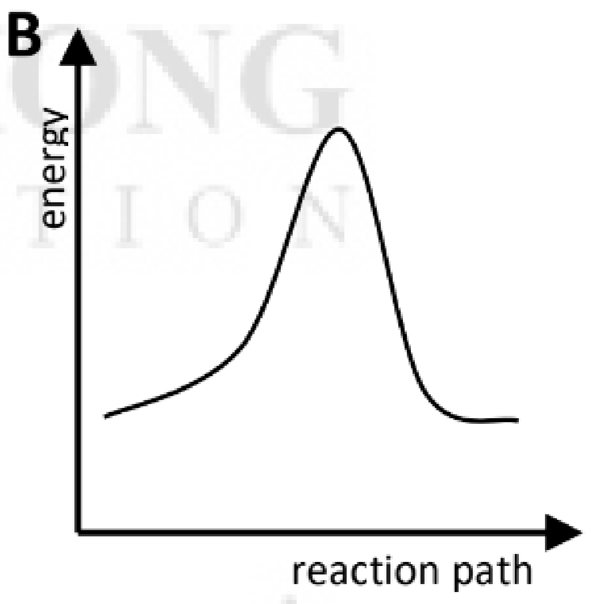

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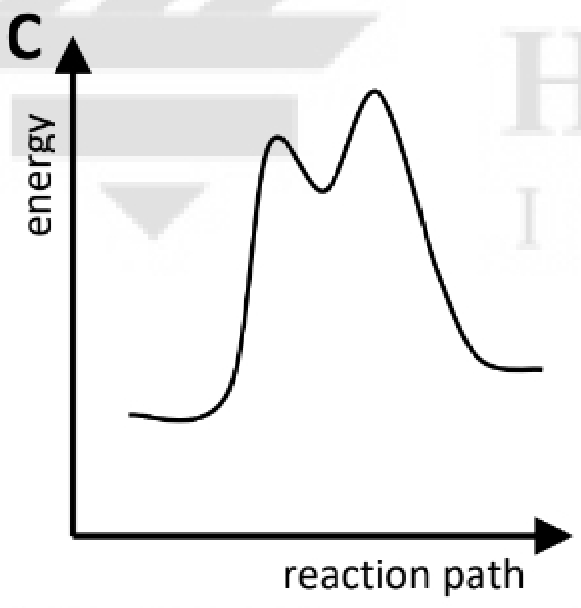

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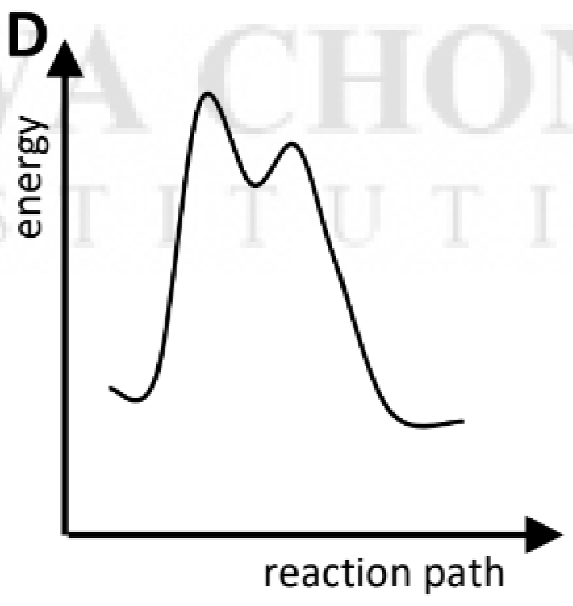
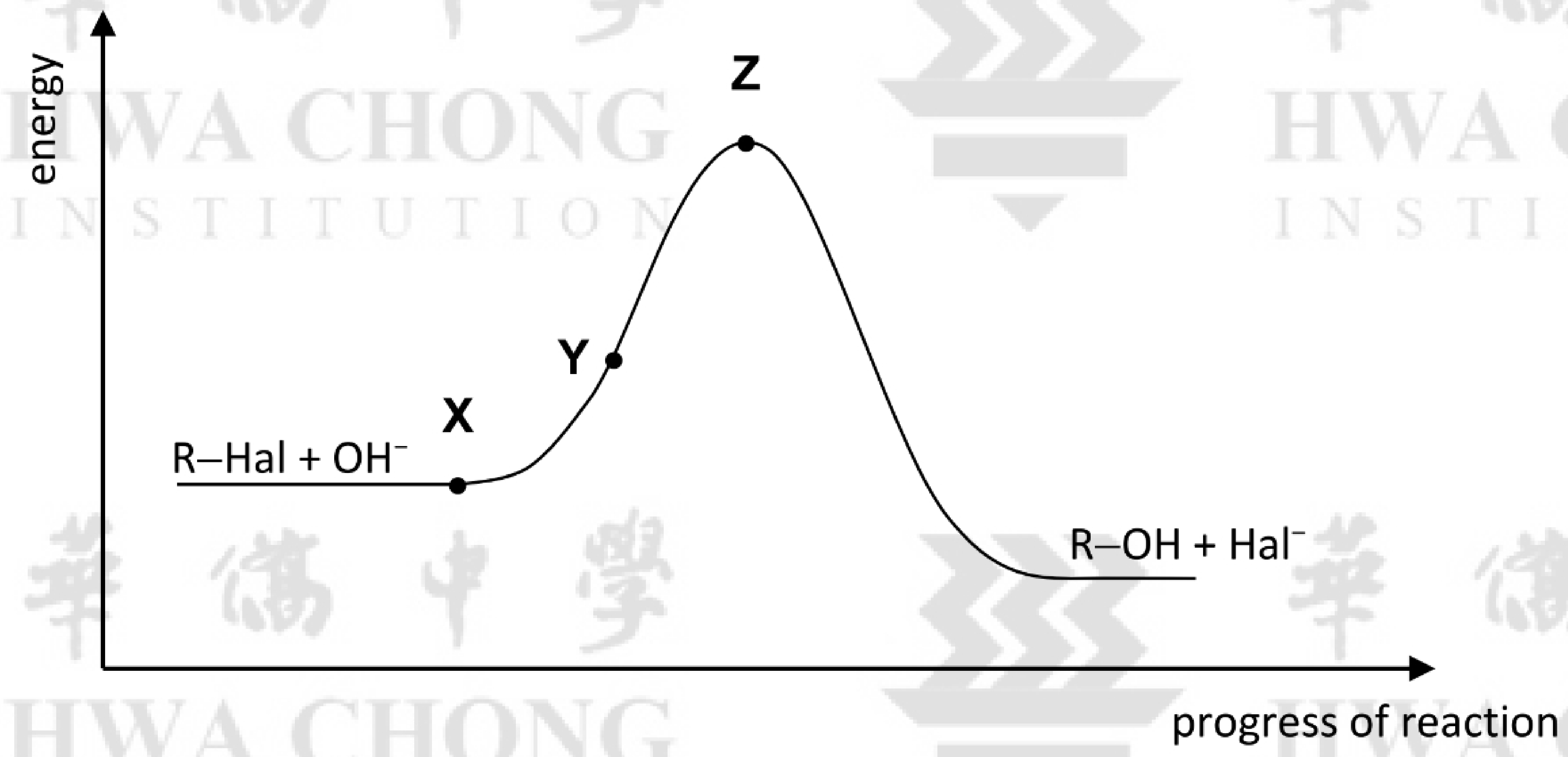


Self-practice 3.2

Halogenoalkanes react with aqueous alkali. One mechanism has the energy profile shown below.



Which of the statements are correct?

1 The reaction is an example of nucleophilic substitution.

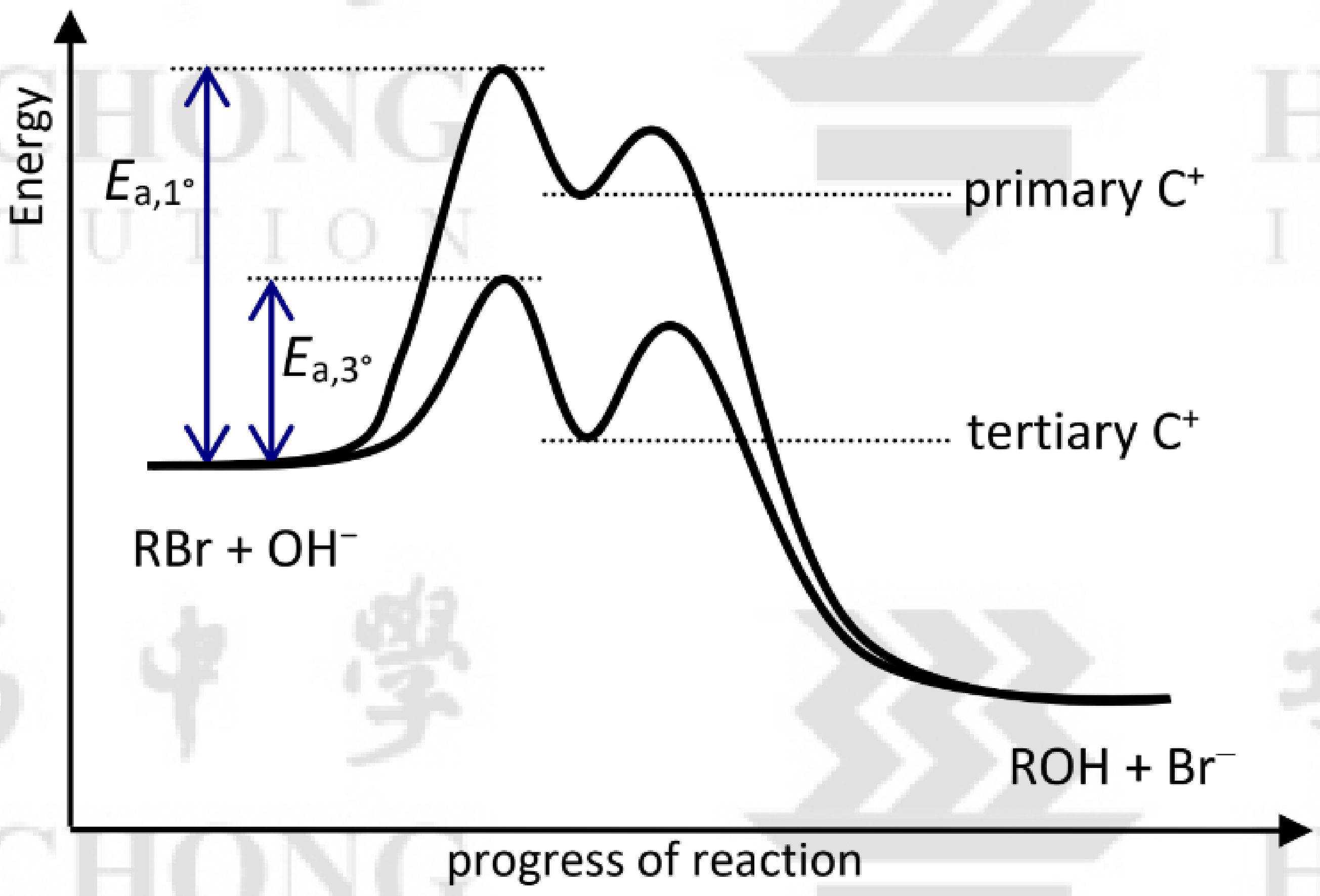
2 Between **X** and **Z** the C–Hal bond will be lengthening.

3 The energy difference between **X** and **Y** represents the activation energy.

Effect of structure of the halogenoalkane on the relative rates of S_N1 and S_N2

- **S_N1 in terms of stability of the carbocation intermediates**

  Alkyl groups donate electrons to the carbocations and help to stabilise them. As such, the stability of carbocations increases in the order primary < secondary < tertiary. As the carbocation becomes more stable, the activation energy for the reaction leading to it decreases. See the figure below for the reaction profiles for the S_N1 hydrolysis of a primary and a tertiary bromoalkane:



  We therefore expect that the **rate of S_N1 will increase in the order primary < secondary < tertiary**.

- **S_N2 in terms of the steric hindrance of the halogenoalkane**

  The transition state in S_N2 has five groups arranged around the central carbon atom. It is therefore more crowded than either the starting halogenoalkane or the final product, each of which has only four groups around the central atom.

  The more alkyl groups there are around the central atom, the more crowded will be the transition state and the higher the activation energy. This will thus slow down the S_N2 reaction. **The rate of S_N2 will increase in the order tertiary < secondary < primary.**

- These two effects reinforce each other — the S_N1 reaction is faster with tertiary halogenoalkanes, while the S_N2 reaction is faster with primary halogenoalkanes.

  Overall, we expect primary halogenoalkanes to react predominantly by the S_N2 mechanism, tertiary halogenoalkanes to react predominantly by the S_N1 mechanism, and secondary halogenoalkanes to react by a mixture of the two.

- There are exceptions to the preference in mechanism due to the same electronic and steric considerations.

  E.g. 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, despite being a primary halogenoalkane, is practically inert to substitution by the S_N2 mechanism because of steric hindrance.

  On the other hand, (chloromethyl)benzene, despite being a primary halogenoalkane, favours substitution by the S_N1 mechanism due to stabilisation of the carbocation intermediate by delocalisation of the positive charge into the benzene ring.

Lecture exercise 3.1

Bromoethane, CH_3CH_2Br, reacts with sodium methoxide , $CH_3O^-Na^+$, to form $CH_3CH_2OCH_3$.
Name and describe the mechanism for the reaction.

Relative rates of nucleophilic substitution

In comparing the reactivity between different halogenoalkanes, there is one main factor at work:

Strength of the C–*X* bond

The ease of nucleophilic substitution in halogenoalkanes depends on the ease of breaking the C–*X* bond. As the size of the halogen atom increases, the **C–*X* bond length increases** and the **bond strength decreases**, and hence nucleophilic substitution takes place more readily. The C–F bond is very strong and fluoroalkanes are extremely unreactive and do not undergo nucleophilic substitution.

Compound	C–*X* bond length /nm	Bond energy /kJ mol^{-1}
CH_3F	13.9	+485
CH_3Cl	17.8	+340
CH_3Br	19.3	+280
CH_3I	21.4	+240

3.1.2 Nucleophilic substitution with OH$^-$ to form alcohols

$$R–X + OH^-(aq) \rightarrow R–OH + X^- \qquad X = Cl, Br \text{ or } I$$

Reagents and conditions: dilute NaOH, heat

This reaction is also known as alkaline hydrolysis.

3.1.3 Nucleophilic substitution with CN^- to form nitriles

$$R\text{–}X + CN^- \rightarrow R\text{–}CN + X^-$$

Reagents and conditions: ethanolic KCN, heat

The lone pair of electrons is donated by the C atom of CN^-.
This reaction serves to increase the length of the carbon chain by one C atom, and is known as a step-up reaction.

The nitrile formed can be used in the synthesis of carboxylic acids (via hydrolysis) and amines (via reduction) as shown below.

Acidic hydrolysis of nitriles

$$R\text{–}CN + H^+ + 2H_2O \rightarrow RCO_2H + NH_4^+$$

Reagents and conditions: dilute H_2SO_4, heat

Alkaline hydrolysis of nitriles

$$R\text{–}CN + OH^- + H_2O \rightarrow RCO_2^- + NH_3$$

Reagents and conditions: dilute NaOH, heat

Reduction of nitriles

$$R\text{–}CN + 4[H] \rightarrow RCH_2NH_2$$

Reagents and conditions: $LiAlH_4$ in dry ether or
$H_2(g)$, Ni catalyst, high P

3.1.4 Nucleophilic substitution with NH_3 to form amines

$$R{-}X + NH_3 \rightarrow R{-}NH_2 + HX$$

Reagents and conditions: ethanolic concentrated NH_3, heat in sealed tube

Comments: the sealed tube is to prevent the ammonia from escaping

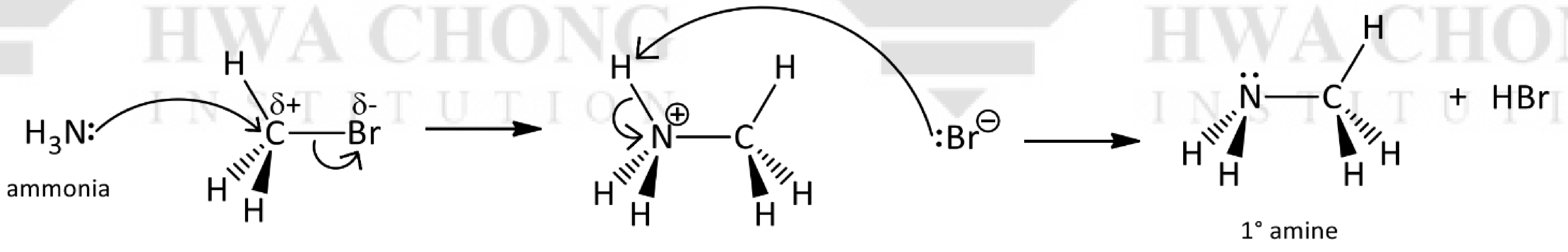
("ethanolic concentrated NH_3" means a concentrated solution of NH_3 in ethanol.)

A primary amine is formed in the above reaction. Like ammonia, this primary amine possesses a lone pair of electrons on the N atom. The electron-donating alkyl group makes the amine more nucleophilic than ammonia. If an excess of halogenoalkane is present, the amine can readily react with the halogenoalkane to form a secondary amine. Further reactions can then occur to form more substituted amines:

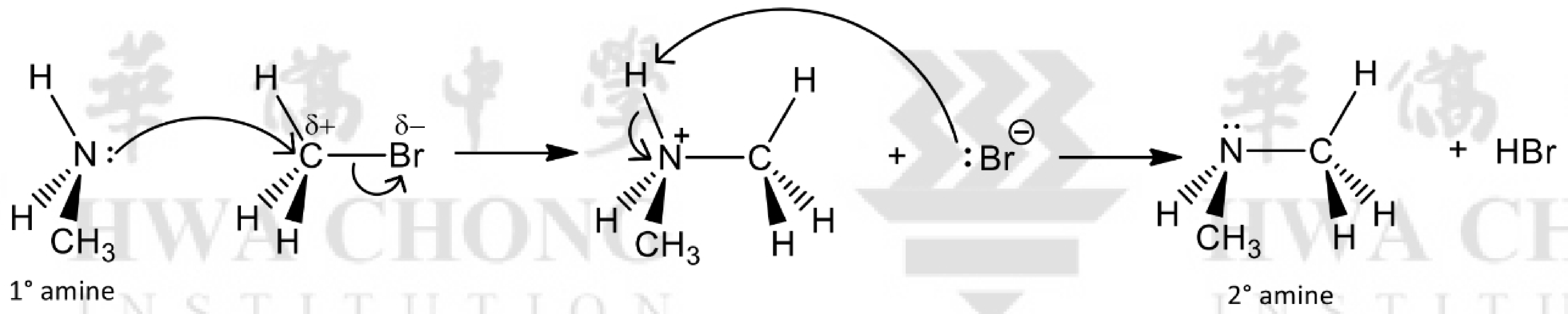
$RX + RNH_2 \rightarrow R_2NH + HX$ (secondary amine formed)
$RX + R_2NH \rightarrow R_3N + HX$ (tertiary amine formed)
$RX + R_3N \rightarrow R_4N^+ X^-$ (quaternary ammonium salt formed)

The following mechanism shows how primary and secondary amines may be formed from the nucleophilic substitution of a halogenoalkane, using ammonia and bromomethane as an example:

Ammonia as the nucleophile can react with bromomethane to form methylamine (primary amine):



If excess bromomethane is present, the 1° amine reacts with the bromomethane:



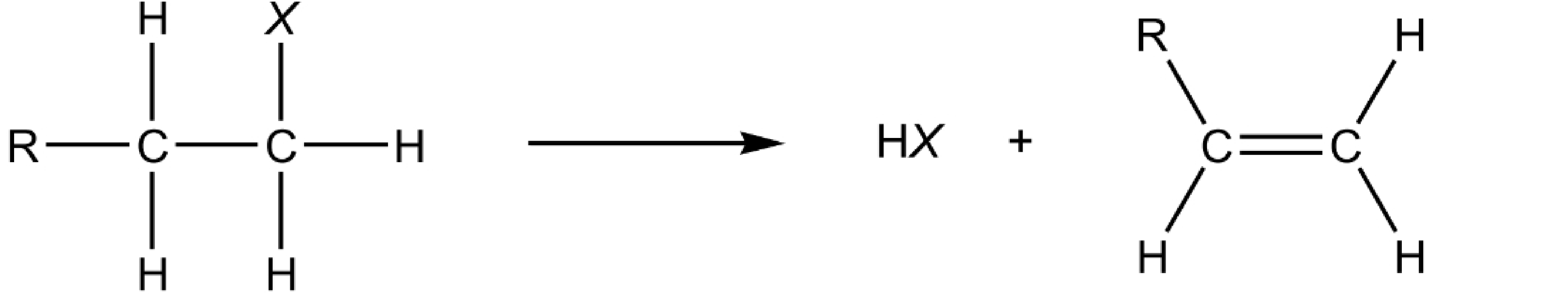
Note: The formation of the different amines when excess halogenoalkane is used causes the yield of the primary amine to decrease, and also makes the separation of products difficult. As such to obtain the primary amine as the main product and avoid the further reactions described above, **excess ammonia** should be used.

Self-practice 3.3

The previous mechanisms showed how a side product, the secondary amine, can be formed from the reaction between ammonia and excess bromomethane. Suggest mechanisms to show how the tertiary amine $(CH_3)_3N$ and quarternary ammonium salt $(CH_3)_4N^+Br^-$ may be formed in further reactions with excess bromomethane.

3.2 Elimination

Halogenoalkanes take part in elimination reactions resulting in the formation of alkenes.

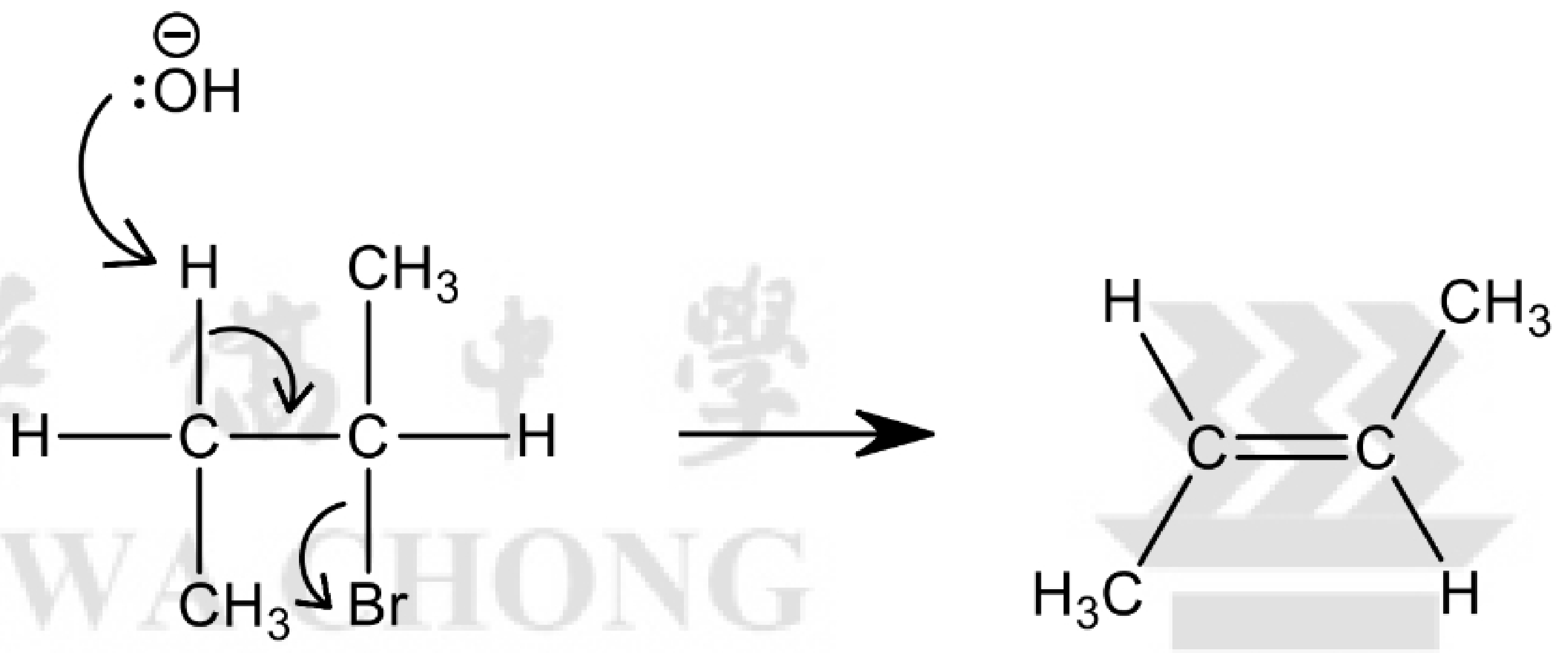


Reagents and conditions: ethanolic KOH, heat

When KOH is dissolved in ethanol, the OH^- behaves more as a base than a nucleophile. It is able to remove a hydrogen ion from the **carbon atom adjacent to the C–*X***, causing the C–*X* to break, forming an alkene.

The same reagent (hydroxide ion) can therefore carry out two different types of reaction (nucleophilic substitution or elimination) when reacted with the same halogenoalkane. Both reactions do in fact occur at the same time, but the significance of substitution versus elimination varies, depending on the solvent, the nucleophile and the halogenoalkane used.

<u>Elimination (E2) mechanism</u> (For your information)



The ease of elimination reactions depends on the strength of the C–*X* bond. The weaker the C–*X* bond, the more readily the halogenoalkane undergoes elimination.

More than one alkene can be formed when the carbon bonded to the halogen has more than one adjacent carbon atom with hydrogen atom(s) bonded to it. Both constitutional and *cis-trans* isomers may be formed.

Lecture exercise 3.2

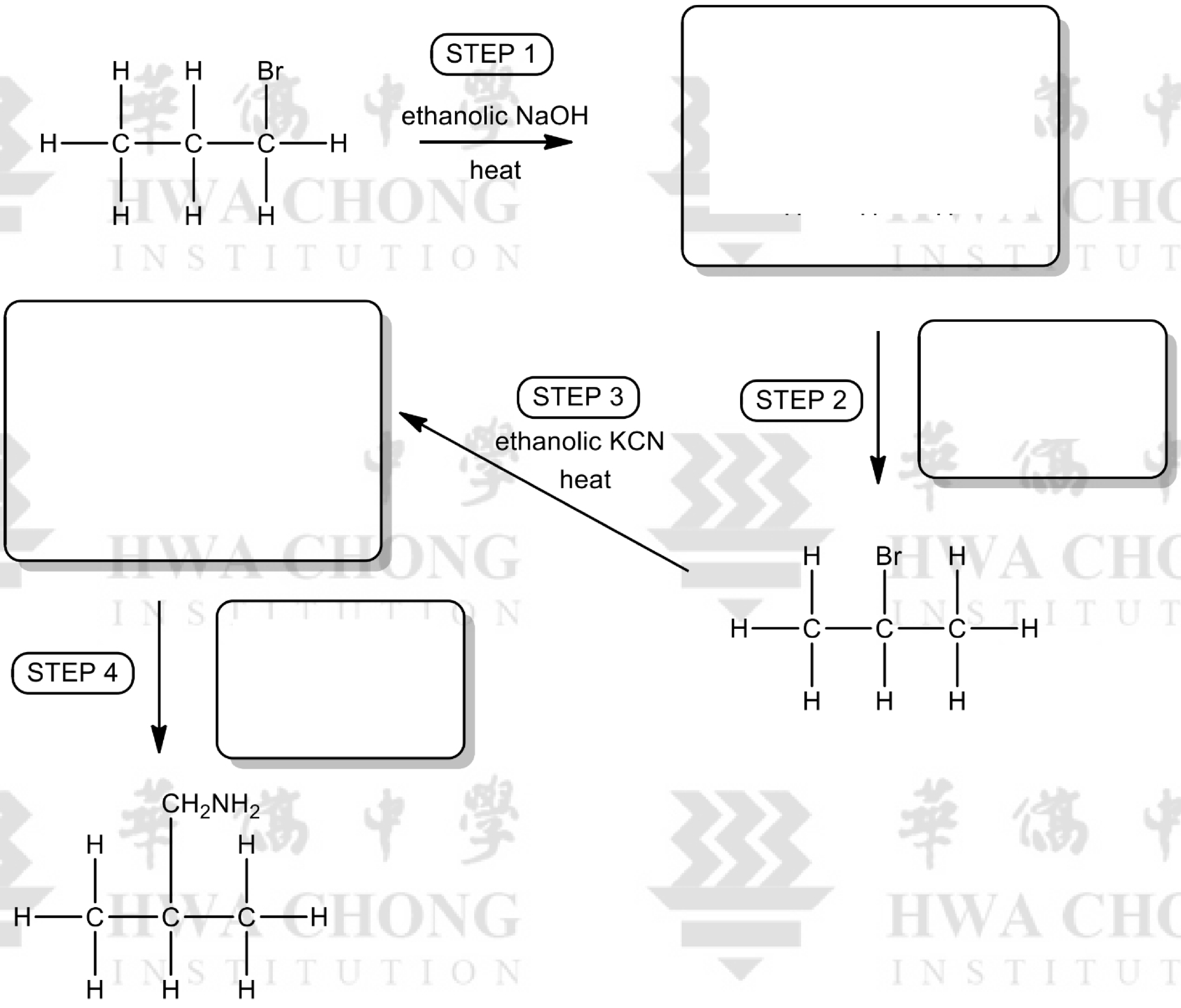
Draw the structural formulae of the three alkenes formed when 2-bromobutane undergoes elimination with hot ethanolic NaOH.

For your information:

The major product is the alkene with the largest number of alkyl groups attached to the double-bonded carbon atoms. This is known as *Saytzeff's* rule. (Also spelt *Zaitsev* in some books.) Based on *Saytzeff's* rule, the major product for the above reaction is but-2-ene.

Lecture exercise 3.3

Fill in the boxes with the correct reagents and structures of compounds in the reaction scheme.



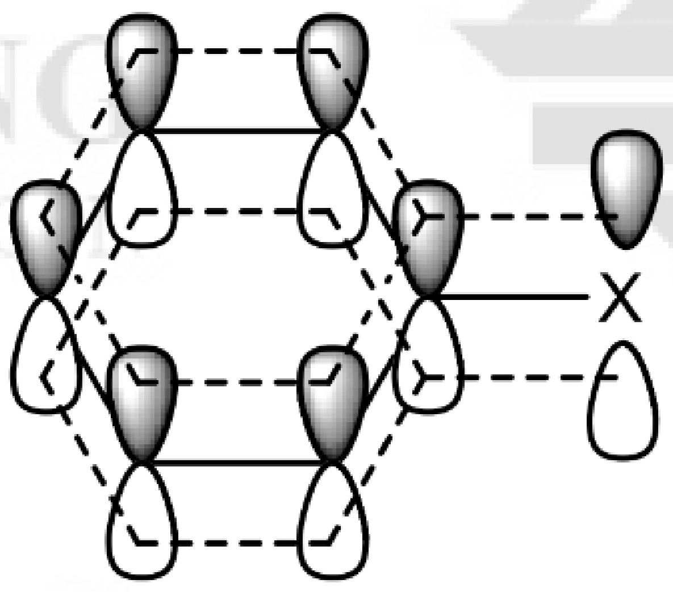
4 REACTIONS OF HALOGENOARENES

4.1 Reactivity of halogenoarenes

Halogenoarenes are very much less susceptible to nucleophilic substitution than halogenoalkanes.

Reasons:

1. The lone pair of electrons on the halogen atom delocalises into the benzene ring.



As a result, there is **partial double bond character** in the C–*X* bond, so its bond length is shorter and bond strength is stronger than that in the corresponding halogenoalkane. The C–*X* bond in halogenoarenes is very difficult to break.

2. Sterically, the rear side of the C–X bond in halogenoarenes is blocked by the benzene ring. Also, the π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

For your information:

Intrinsically, the C–X bonds in halogenoarenes are shorter and stronger compared to those in halogenoalkanes. The carbon atom in halogenoarenes is sp^2 hybridised, while the carbon atom in halogenoalkanes is sp^3 hybridised. The sp^2 hybrid orbital is known to have a higher *s* character than the sp^3 hybrid orbital.

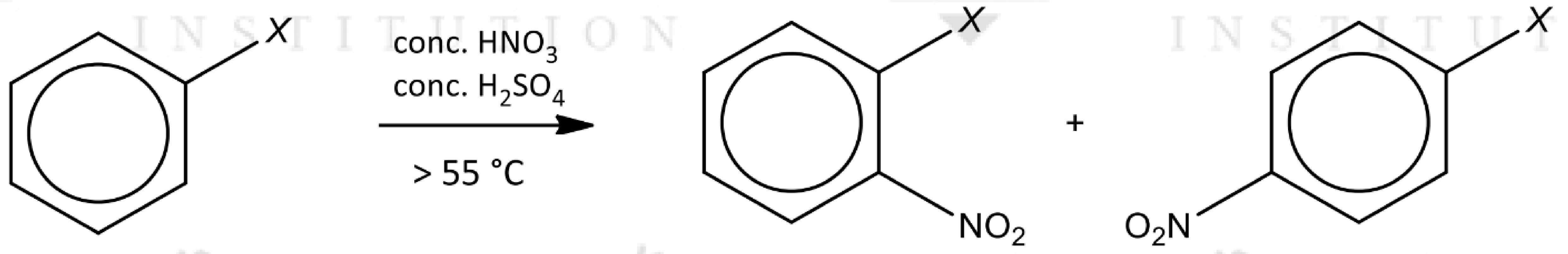
As the percentage of *s* character in a hybrid orbital increases, the orbital becomes more like an *s* orbital and hence the electrons are held more tightly by the nucleus than those in an orbital with less *s* character. Hence making the sp^2 C–X bond in the halogenoarenes stronger.

For the reasons stated above, nucleophilic substitution of halogenoarenes cannot be achieved by the same reagents and conditions used for halogenoalkanes, and is only possible under very vigorous conditions.

4.2 Electrophilic substitution on the benzene ring of halogenoarenes

The halogenoarenes undergo electrophilic substitution on the benzene ring similar to other arenes. [See Topic 12 Arenes]

However, halogenoarenes are much less susceptible to electrophilic substitution as the halogen substituent is deactivating. The halogen substituent is also 2,4-directing. The deactivating and directing effects are seen in the nitration of chlorobenzene where a higher temperature is required and two isomers are formed.

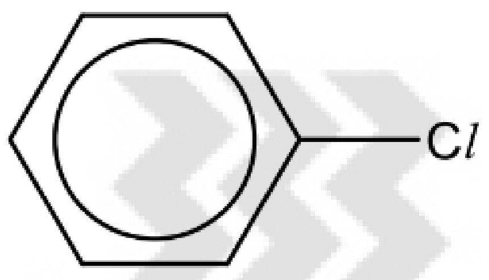
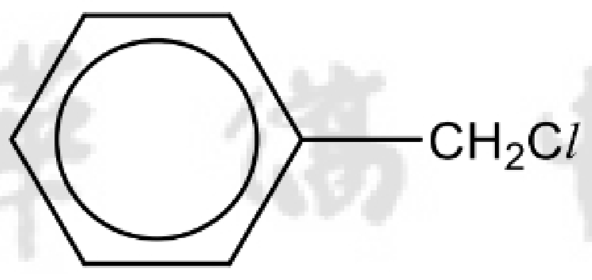


X = C*l*, Br & I

X is deactivating and 2,4-directing

Lecture exercise 4.1

State whether the following reactions take place in the respective halogen-containing compounds.

Compound	CH_3CH_2Cl		
Delocalisation of electrons	No	In the benzene ring as well as over to the chlorine atom	Within benzene ring only
Nucleophilic substitution			
Elimination			
Electrophilic substitution			

5 DISTINGUISHING TESTS FOR HALOGENOALKANES

5.1 Comparing colour of AgX precipitate

The general method for distinguishing between the type of halogen substituents present in halogenoalkanes is to compare the colour of the silver halide precipitates that are formed after the compound undergoes nucleophilic substitution by hydroxide ion. The test involves 3 steps.

Step 1: Add **NaOH(aq)** and heat. [Reaction: $RX + OH^- \rightarrow ROH + X^-$]
Step 2: Add **excess dilute HNO_3**. [Removes unreacted OH^- so that brown Ag_2O ppt will not be formed in the next step]
Step 3: Add **$AgNO_3$(aq)** and observe the colour of precipitate formed. [$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$]

The expected observations (for the positive tests) are given in the table below. Sometimes, the colours of AgCl and AgBr are difficult to differentiate. We can follow up by adding NH_3(aq); AgCl dissolves in dilute aqueous NH_3 while AgBr does not.

	Chloroalkane, RCl	Bromoalkane, RBr	Iodoalkane, RI
Colour of precipitate formed	white	cream	yellow
Identity of precipitate	AgCl	AgBr	AgI
Solubility of precipitate in NH_3 solution	dissolves in dilute aqueous NH_3	dissolves in concentrated NH_3	insoluble even in concentrated NH_3
	$AgX + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + X^-$ Colourless complex ion [Reasons for the solubility will be discussed in Topic 14 Solubility Equilibria]		

5.2 Comparing rate of formation of AgX precipitate

The three different halogenoalkanes can also be distinguished using ethanolic $AgNO_3$. In this method, the rates of the formation of the silver halide precipitates will be different. The identity of the halogenoalkane can also be determined from the colour of the AgX precipitate formed.

	Chloroalkane, RCl	Bromoalkane, RBr	Iodoalkane, RI
Add 1 cm^3 of the organic compound in a test tube. Add 1 cm^3 of ethanolic $AgNO_3$ and place the test tube in a hot water bath.	white ppt (AgCl) formed in 5 – 8 minutes	cream ppt (AgBr) formed in 3 – 5 minutes	yellow ppt (AgI) formed almost immediately

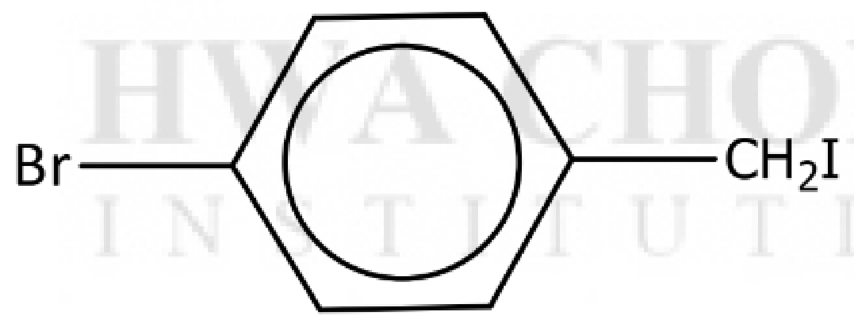
Explanation of the difference in the rate of formation of Ag*X* precipitate:
The C–*X* bond must break in a nucleophilic substitution reaction to give the halide ion. In this reaction, the nucleophile is ethanol. Bond strength decreases in the order C–C*l* > C–Br > C–I, as shown by the bond energies, +340, +280 and +240 kJ mol^{-1} obtained from the *Data Booklet*.

In this mechanism, the C–*X* is broken in the rate-determining step. Hence the stronger the C–*X* bond, the higher the activation energy of the rate-determining step, and hence a slower rate. The weaker the C–*X* bond, the easier and more readily it breaks to give the halide ion and the Ag*X* precipitate forms more quickly.

Lecture exercise 5.1

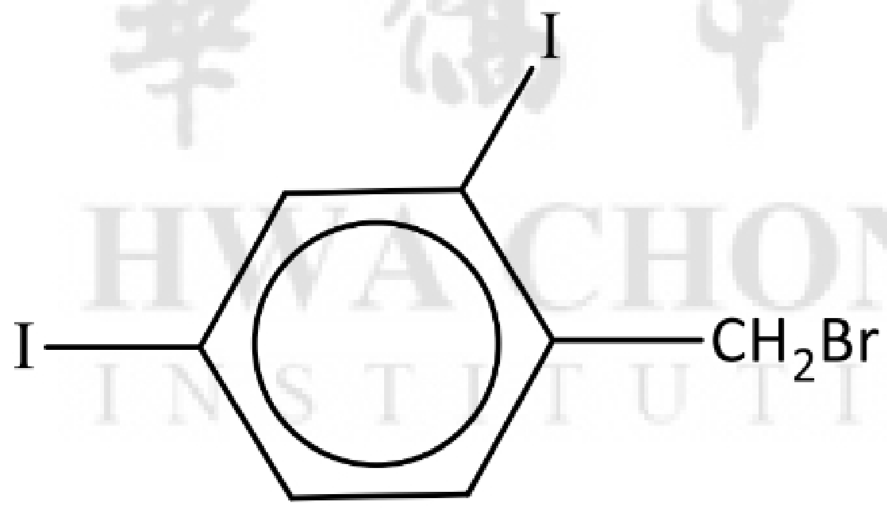
A liquid *L* gave a pale yellow precipitate when shaken for some time with cold ethanolic silver nitrate. Which of the following could *L* be?

1



2 $CH_3CH_2CH_2I$

3



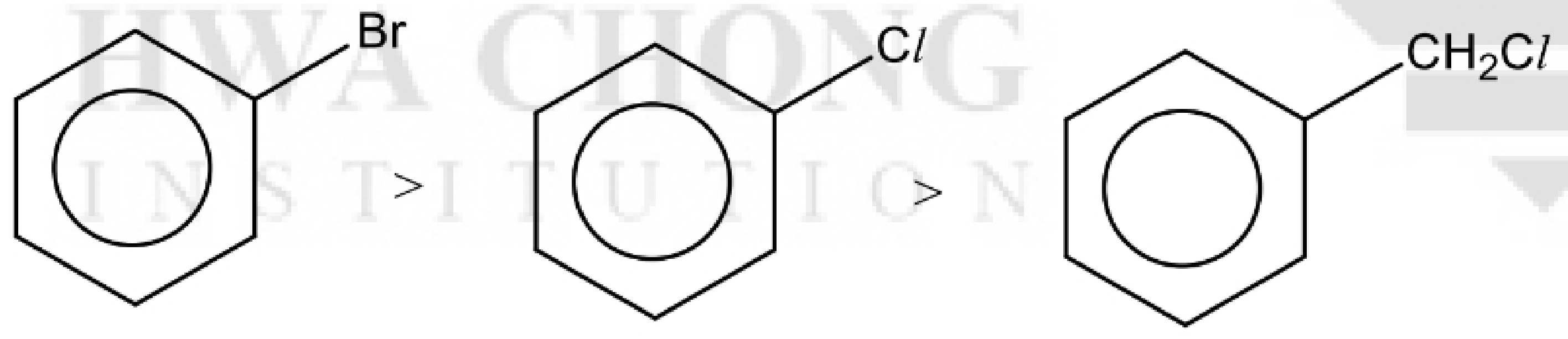
Lecture exercise 5.2

Which sequence shows the correct order of **decreasing** ease of hydrolysis?

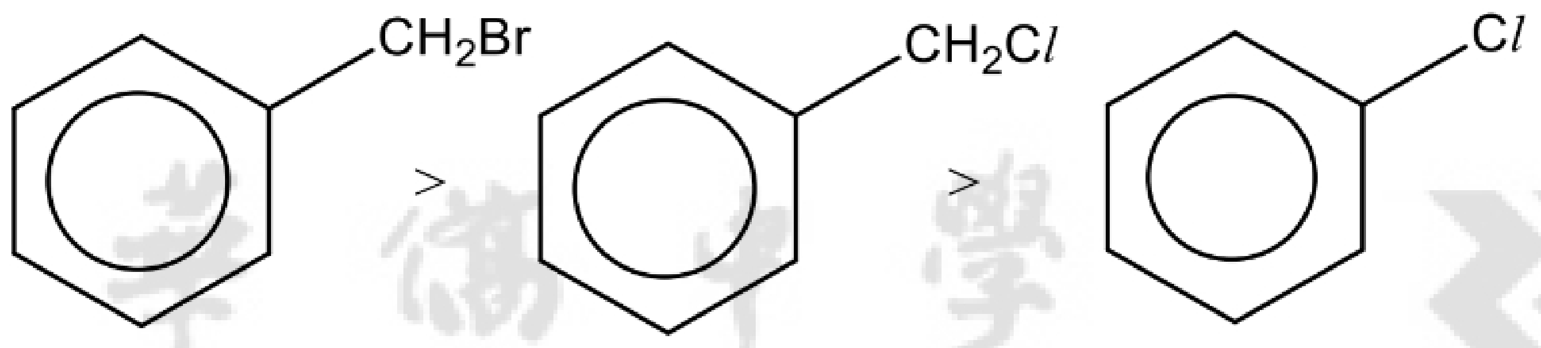
A $CH_3CH_2Cl > CH_3CH_2Br > CH_3CH_2I$

B $(CH_3)_2CHCl > (CH_3)_2CHI > (CH_3)_2CHBr$

C



D



6 HALOGENOALKANES AND THE ENVIRONMENT

6.1 Uses of halogenoalkanes

Halogenoalkanes are used as refrigerants, aerosol propellants and fire extinguishers.

Fluoroalkanes are less reactive than chloroalkanes due to the high bond energy of the C–F bond. They are more useful in certain applications where their inertness are required, such as non-stick coating on pots and pans and as taps and stoppers in laboratory glassware like burettes and standard flasks. The commercial name for polytetrafluoroethene is Teflon®.

Chlorofluorocarbons (CFCs), often known by the trade name 'Freons', are used as refrigerants, aerosol propellants and in fire extinguishers.

These compounds have some useful properties:
(1) they are inert and non-flammable
(2) they are non-toxic
(3) they are compounds that liquefy under pressure and therefore vapourise readily when that pressure is released
(4) they are odourless

6.2 Effect of CFCs on the ozone layer

Depletion of the ozone layer

Chlorofluorocarbons (CFCs) in aerosol sprays deplete the ozone (O_3) layer and expose us to ultraviolet radiation from the sun. The O_3 layer absorbs ultraviolet rays and is vital in screening the earth from excess ultraviolet radiation. Too much exposure to ultraviolet radiation causes skin cancer and widespread crop failure.

Due to the strength of C–F and C–C*l* bonds, fluoroalkanes and CFCs are stable molecular entities under ambient conditions, which exhibit low toxicity, low reactivity, and low flammability. However, this lack of reactivity also provides CFCs a lifespan that can exceed 100 years, giving them time to diffuse into the upper stratosphere, where the strong UV radiation will cleave the weaker C–C*l* bond (bond energies: C–C*l* = +340 vs. C–F = +485 kJ mol^{-1}) homolytically to generate reactive C*l*• radicals, which will catalyse the decomposition of ozone into oxygen, leading to depletion of the ozone layer.

$$CF_3Cl \quad + \quad uv \quad \rightarrow \quad Cl\bullet \quad + \quad \bullet CF_3$$

In the stratosphere, oxygen atoms are produced when O_2 absorbs UV light at 250 nm wavelength.

$$O_2 \rightarrow 2O$$

Once oxygen atoms form, they can react with oxygen molecules to produce ozone, which by absorption of ultraviolet light, decompose to re-form oxygen atoms and oxygen molecules. An equilibrium is set up between the two processes.

Natural ozone formation : $O + O_2 \rightarrow O_3$
Natural ozone depletion : $O_3 \rightarrow O + O_2$
Chlorine atoms (radicals) disrupt the equilibrium by acting as a homogeneous catalyst for the destruction of ozone:

$$Cl\bullet \quad + \quad O_3 \quad \rightarrow \quad ClO\bullet \quad + \quad O_2 \quad \text{-----------}\mathbf{(1)}$$
$$ClO\bullet \quad + \quad O \quad \rightarrow \quad Cl\bullet \quad + \quad O_2 \quad \text{-----------}\mathbf{(2)}$$

As shown by equations **(1)** and **(2)**, the chlorine atoms are regenerated, and in the process remove the oxygen atoms needed to make more ozone by the natural ozone formation reaction. (The above mechanistic details of how CFCs deplete the ozone layer are not required)

Measures to protect the ozone layer

- Reduce use of CFCs in industrial and household applications. Since 1987, at the Montreal Protocol, the use of CFCs has been increasingly banned in an increasing number of countries.
- Substitutes such as hydrocarbons, hydrofluorocarbons or fluorocarbons have been used in place of CFCs. For example, some aerosols use propane or butane as propellant instead of CFCs. However, alkanes are highly flammable and pose a fire hazard.

Self-practice 6.1

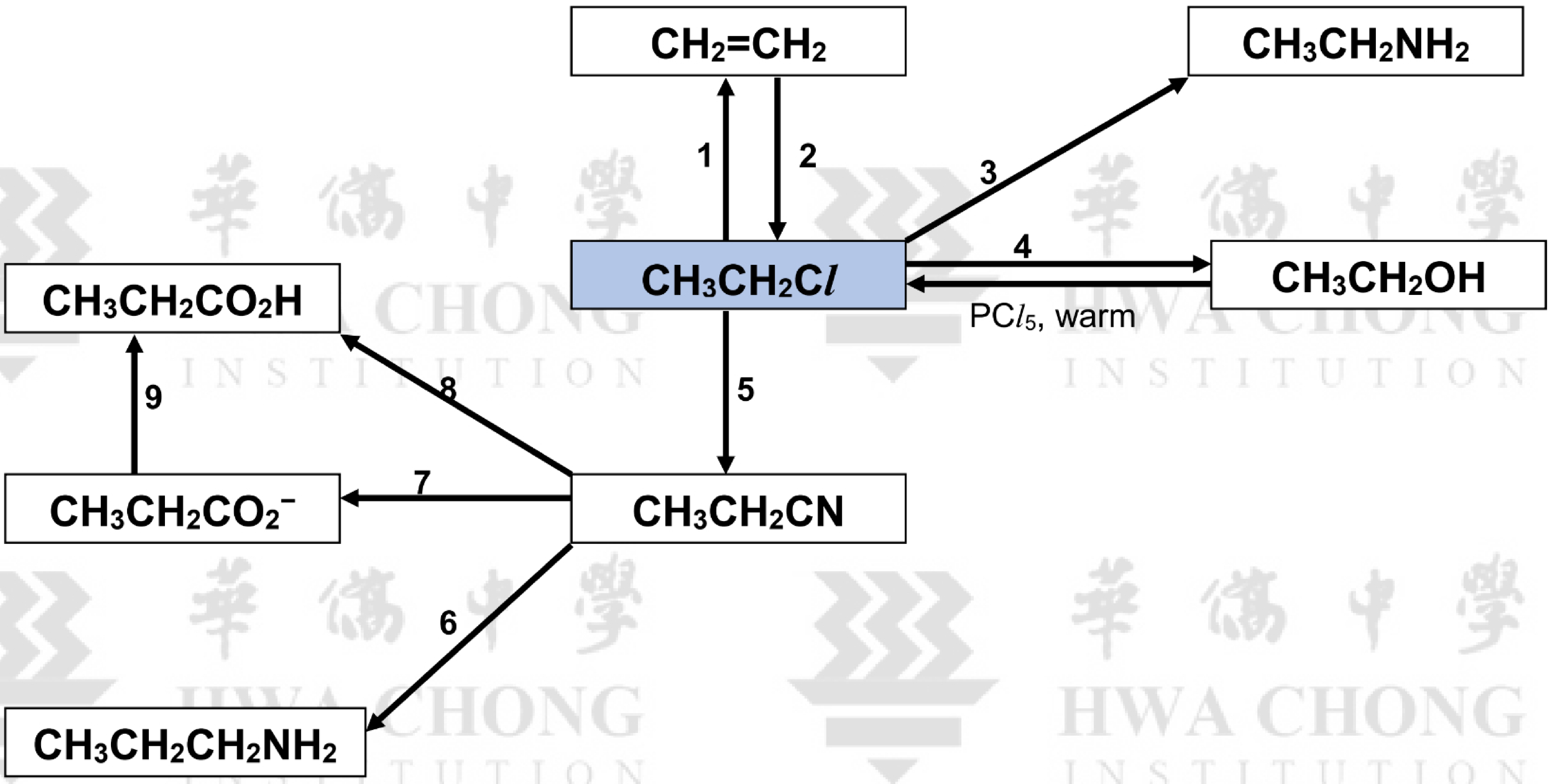
Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerators and in making foamed plastics, but are now known to destroy ozone in the upper atmosphere.

Which of the following compounds will **not** destroy ozone, and therefore can be used as a replacement for CFCs?

A $CHBr_3$
B CCl_3CBr_3
C $CHClFCClF_2$
D $CH_3CH_2CH_2CH_3$

Summary of reaction of halogenoalkanes

State the reagents and conditions needed for the conversions on the arrows below:



Summary of reaction of halogenoarenes