

11 Extension Topic – Organic Chemistry

Alkenes

GUIDING QUESTIONS

- Which classes of reagents does alkenes react with and why? What types of reactions do alkenes undergo and why?
- How do alkenes react with electrophiles?
- What is the major product obtained when an unsymmetrical alkene reacts with hydrogen halide and why?

LEARNING OUTCOMES

Students should be able to:

- 11.3(d)** explain the general reactivity of alkenes towards electrophilic reagents/electrophile
- 11.3(e)** describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
- (i) electrophilic addition of water/steam, hydrogen halides and halogens
 - (ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen)
 - (iii) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol
 - (iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules
- 11.3(f)** describe the mechanism of electrophilic addition in alkenes, using bromine/ethene as an example
- 11.3(g)** apply Markonikov's rule to the addition of hydrogen halides to unsymmetrical alkenes and explain the composition of products in terms of the stability of carbocation intermediates

REFERENCES

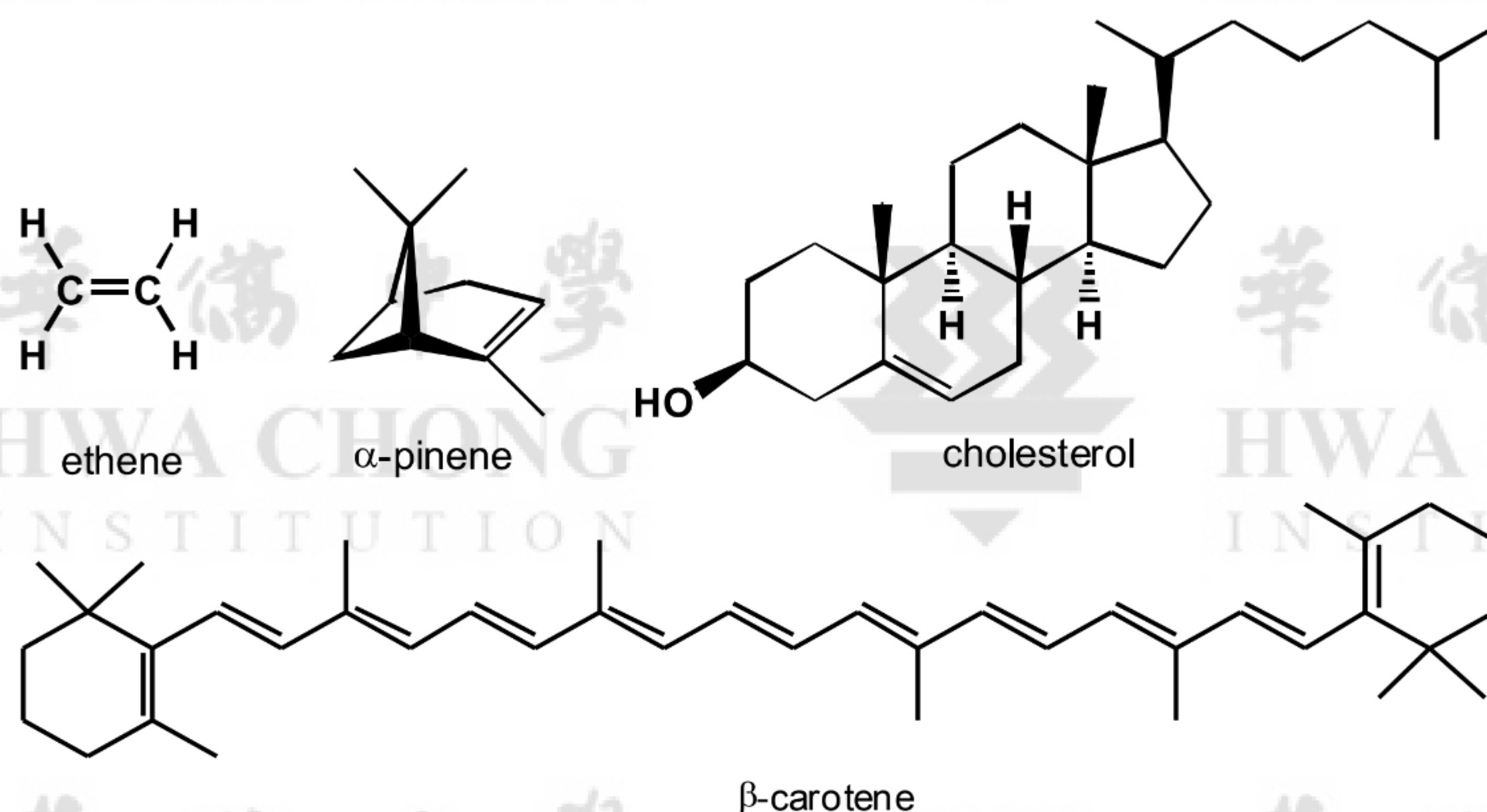
1. L. G. Wade, Jr, *Organic Chemistry*, 8th Ed., Chapters 7 and 8.
2. Cann & Hughes, *Chemistry for Advanced Level*, Chapter 24.
3. J. McMurry, *Organic Chemistry*, 7th Ed., Chapter 6 and 7.

1 INTRODUCTION

Alkenes are unsaturated hydrocarbons that contain at least one **carbon-carbon double bond**, C=C. Alkenes are said to be unsaturated because they have fewer than the maximum possible number of hydrogen atoms.

Alkenes occur abundantly in nature. Examples include:

- ethene, a gas responsible for the ripening of fruits;
- α -pinene, a major component of turpentine which is commonly used as paint solvent;
- cholesterol, a precursor for the synthesis of steroid hormones and vitamin D;
- β -carotene, the orange pigment responsible for the colour of carrots.



1.1 Nomenclature

Aliphatic alkenes containing only one carbon-carbon double bond have the general formula C_nH_{2n} , where n is the number of carbon atoms in the molecule. Do note that this general formula is not applicable for aliphatic alkenes containing more than one carbon-carbon double bond and alicyclic alkenes.

n	Name	Molecular Formula	Structural Formula
2	Ethene	C_2H_4	
3	Propene	C_3H_6	
4	But-1-ene	C_4H_8	

Table 1. Table showing some examples of alkenes

The number “1” in but-1-ene is used because the carbon-carbon double bond is on C1 and C2. What do you think is the structure of but-2-ene?

The IUPAC rules for naming alkenes are similar to those for alkanes.

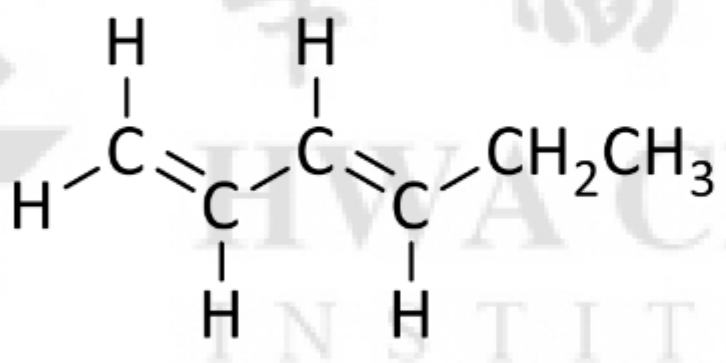
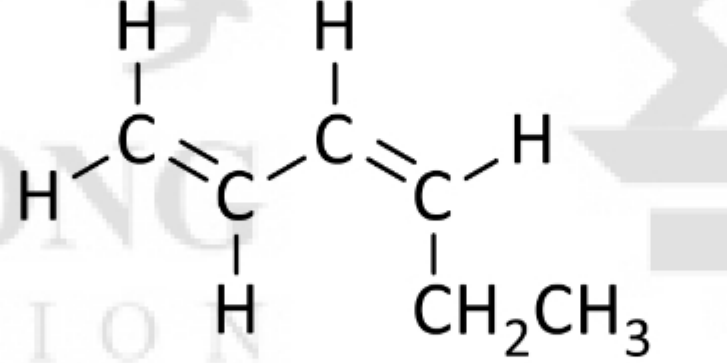
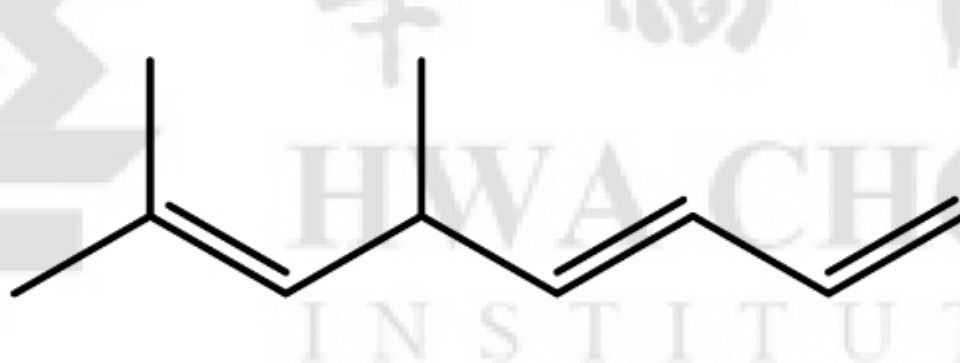
1. Find the **longest parent chain containing the double bond** and name the compound accordingly using the suffix -ene.
2. **Number the double bond from the end of the chain nearest to the double bond.** If the double bond is equidistant from the two ends, begin at the end nearer the first branch point. The number, followed by a hyphen, precedes the name of the parent chain.

$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{CH}_3$
but-1-ene	hex-2-ene	2-methylhex-3-ene

3. **Number the substituents** according to their position in the chain **and list them alphabetically.**
4. If **more than one double bond is present**, indicate the position of each and use the suffixes -diene, -triene, -tetraene, and so on.

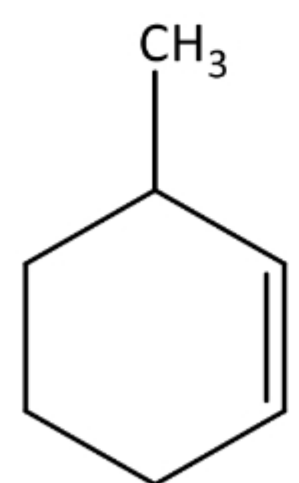
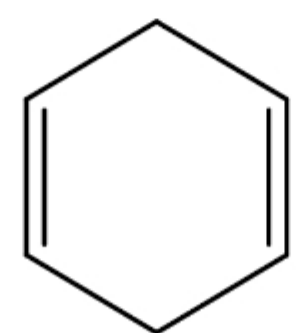
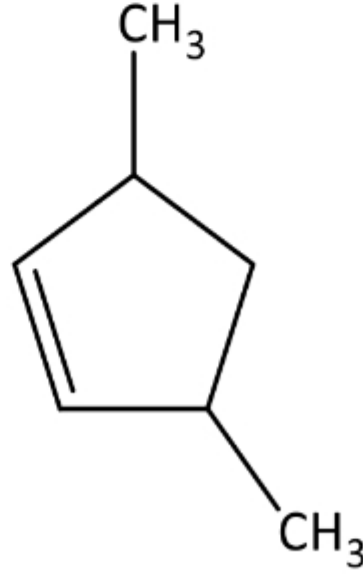
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}=\text{CH}_2$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CHCH}_3$	$(\text{CH}_3)_2\text{C}=\text{CHCH}(\text{CH}_3)\text{CH}=\text{CHCH}=\text{CH}_2$
hexa-1,3-diene	2-methylpenta-1,3-diene	5,7-dimethylocta-1,3,6-triene

5. Stereochemical descriptors, such as *cis* and *trans*, are placed in front of the prefix, followed by a hyphen.

		
<i>trans</i> -hexa-1,3-diene	<i>cis</i> -hexa-1,3-diene	<i>trans</i> -5,7-dimethylocta-1,3,6-triene

Note: When drawing the stereochemical formula of *cis-trans* isomers, the geometry around each carbon of the C=C bond should be shown to be trigonal planar.

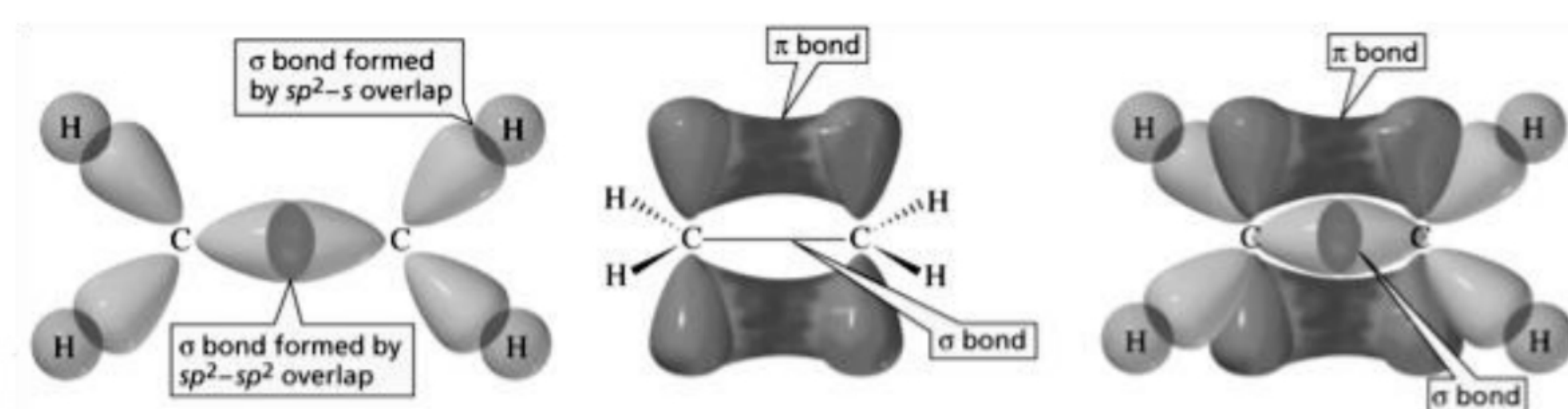
6. Cycloalkenes are named in a similar way. Number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible.

		
3-methylcyclohexene	cyclohexa-1,4-diene	3,5-dimethylcyclopentene

Self-Practice 1.1

Draw the structural formulae of

- (a) 2,3-dimethylocta-1,4,6-triene
(b) 2-ethyl-3-methylcyclohepta-1,4-diene.

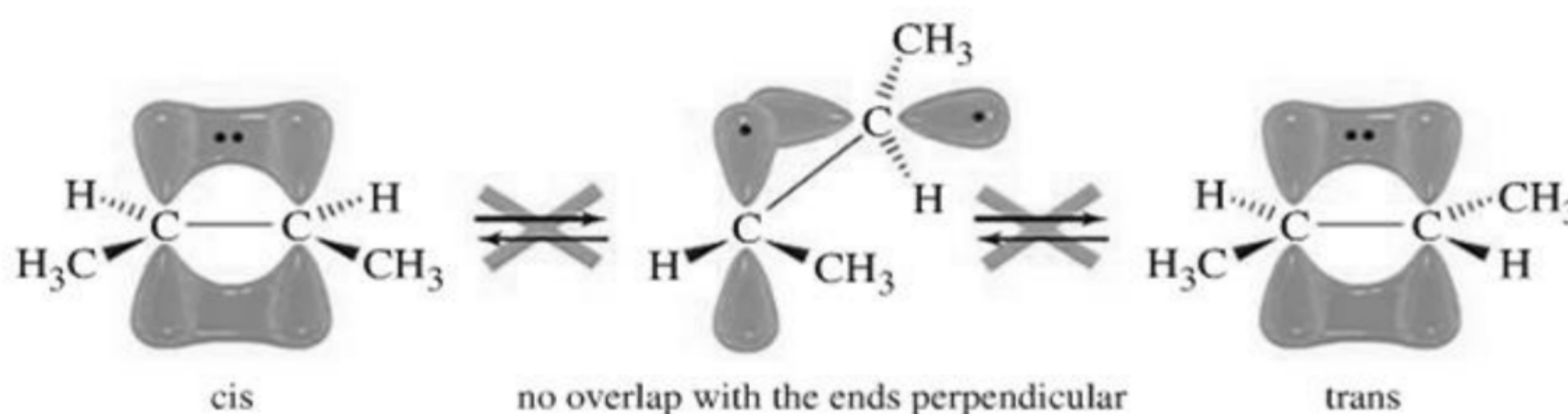
1.2 Electronic structure of ethene

In Topic 2 Chemical Bonding, you have learnt the hybridisation, shape and bonding of ethene.

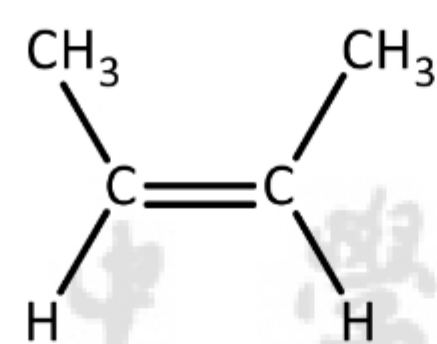
- The ethene molecule is trigonal planar with respect to each carbon atom.
- The carbon-carbon double bond in ethene is made up of one σ bond and one π bond. The carbons are sp^2 -hybridised and have three equivalent sp^2 hybrid orbitals that lie in a plane at angles of 120° to one another. The carbons form a σ bond with each other by head-on overlap of sp^2 orbitals, as well as a π bond by side-on overlap of unhybridised p orbitals orientated perpendicular to the sp^2 plane. The π -electron cloud lies above and below the plane of the atoms.
- The C-H bonds are σ bonds formed by head-on overlap of sp^2 orbital of C and s orbital of H.

1.3 *Cis-trans* isomerism in alkenes

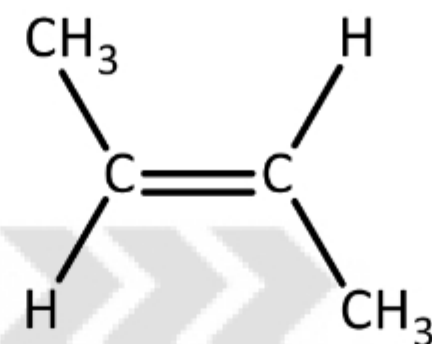
In Topic 9 Isomerism, you have learnt that *cis-trans* isomerism arises in alkenes due to **restricted rotation about the C=C bond** and **2 different groups attached to each C=C carbon atom**.



But-2-ene can exist as *cis*-but-2-ene and *trans*-but-2-ene as shown below. *Cis*-but-2-ene has the same groups on the **same side of the double bond**, whereas *trans*-but-2-ene has the same groups on the **opposite sides of the double bond**.



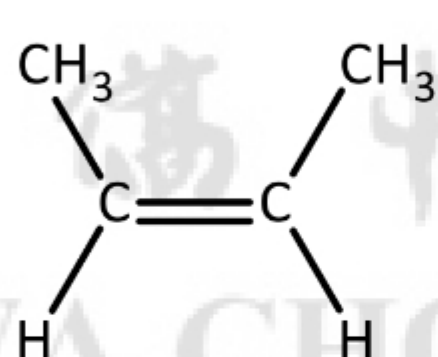
cis-but-2-ene
(*cis* isomer)



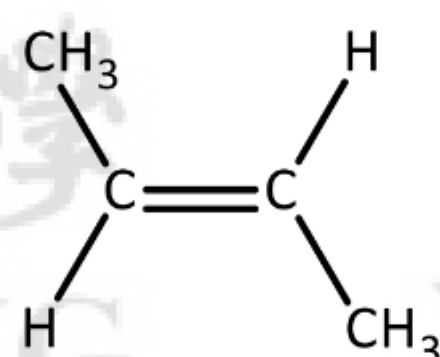
trans-but-2-ene
(*trans* isomer)

***Cis-trans* isomerism cannot exist if any one of the C=C carbons carries two identical groups.**

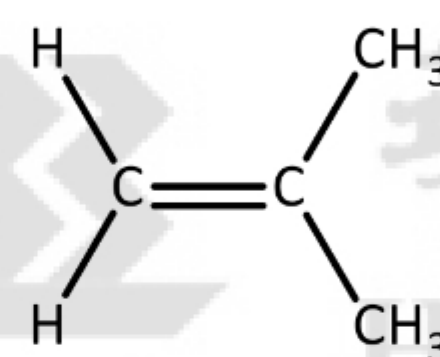
2-methylpropene is an example of a constitutional isomer of *cis*-but-2-ene and *trans*-but-2-ene.



cis-but-2-ene



trans-but-2-ene



2-methylpropene

(constitutional isomer of
the *cis* and *trans* isomers)

Cycloalkenes with **up to 7 carbon atoms** exist only as the “*cis* isomers”. Cycloalkenes with **8 or more carbon atoms** can exist as *cis-trans* isomers.

Self-Practice 1.2

Draw the *cis-trans* isomers of $(Cl)CH=C(CH_3)Br$.

2 PHYSICAL PROPERTIES OF ALKENES

2.1 Boiling and melting points within the homologous series

The trend in the boiling and melting points within the homologous series indicate that as the number of carbon atoms increases, the boiling points increase correspondingly. This is due to the increase in number of electrons and hence the size of the electron cloud, leading to stronger dispersion forces between the molecules.

The trend in melting points is not as clear as the trend in boiling points as melting point also depends on how the molecules are packed in the solid lattice.

	Boiling point (°C)	Melting point (°C)
Ethene	−104	−169
Propene	−47	−185
But-1-ene	−6	−138
Pent-1-ene	30	−165

Table 2. Boiling and melting points of a few alkenes.

2.2 Physical properties of *cis-trans* isomers

Boiling point of *cis-trans* isomers

There can be differences in the boiling and melting points between the *cis* and *trans* isomers of alkenes e.g. 1,2-dichloroethene

Isomer	Boiling point (°C)	Melting point (°C)
<i>cis</i> -1,2-dichloroethene	60.3	−81
<i>trans</i> -1,2-dichloroethene	47.5	−50

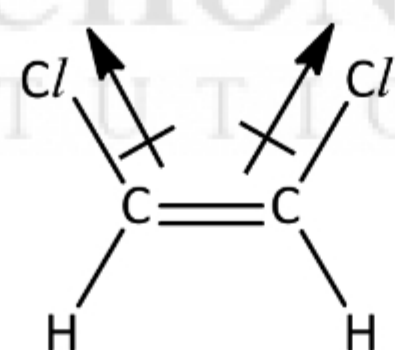
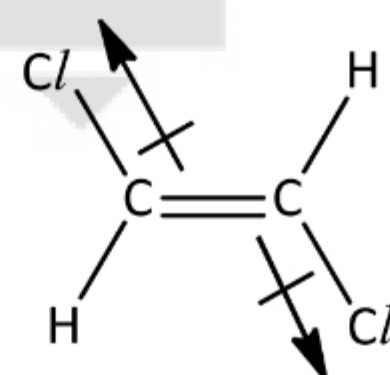
Table 3. Boiling and melting points of *cis*- and *trans*- isomers of 1,2-dichloroethene

You will notice that:

- the *cis*-isomer has the higher boiling point;
- the *trans*-isomer has the higher melting point.

Between the *cis* and the *trans* isomer of disubstituted alkenes, **the *cis* isomer tend to have higher boiling points**. The reason for this is that *cis* isomers tend to be more polar. We shall use 1,2-dichloroethene as an example below:

- In the *cis* isomer, the polar C–Cl bonds result in dipole moments that do not cancel out, hence producing an overall dipole moment for the molecule. Thus, the *cis* isomer is polar and permanent dipole-permanent dipole interactions (on top of dispersion forces) exist between molecules.

*cis*-1,2-dichloroethenedipole moment $\neq 0$ *trans*-1,2-dichloroethene

dipole moment = 0

- In the *trans* isomer, the two dipole moments cancel out such that the overall dipole moment for the molecule is zero. Hence, the *trans* isomer is non-polar and only dispersion forces exist between molecules.
- Hence, more energy is required to overcome the stronger forces of attraction between *cis* isomers, leading to a higher boiling point.

This effect is less noticeable for some alkenes, for example:

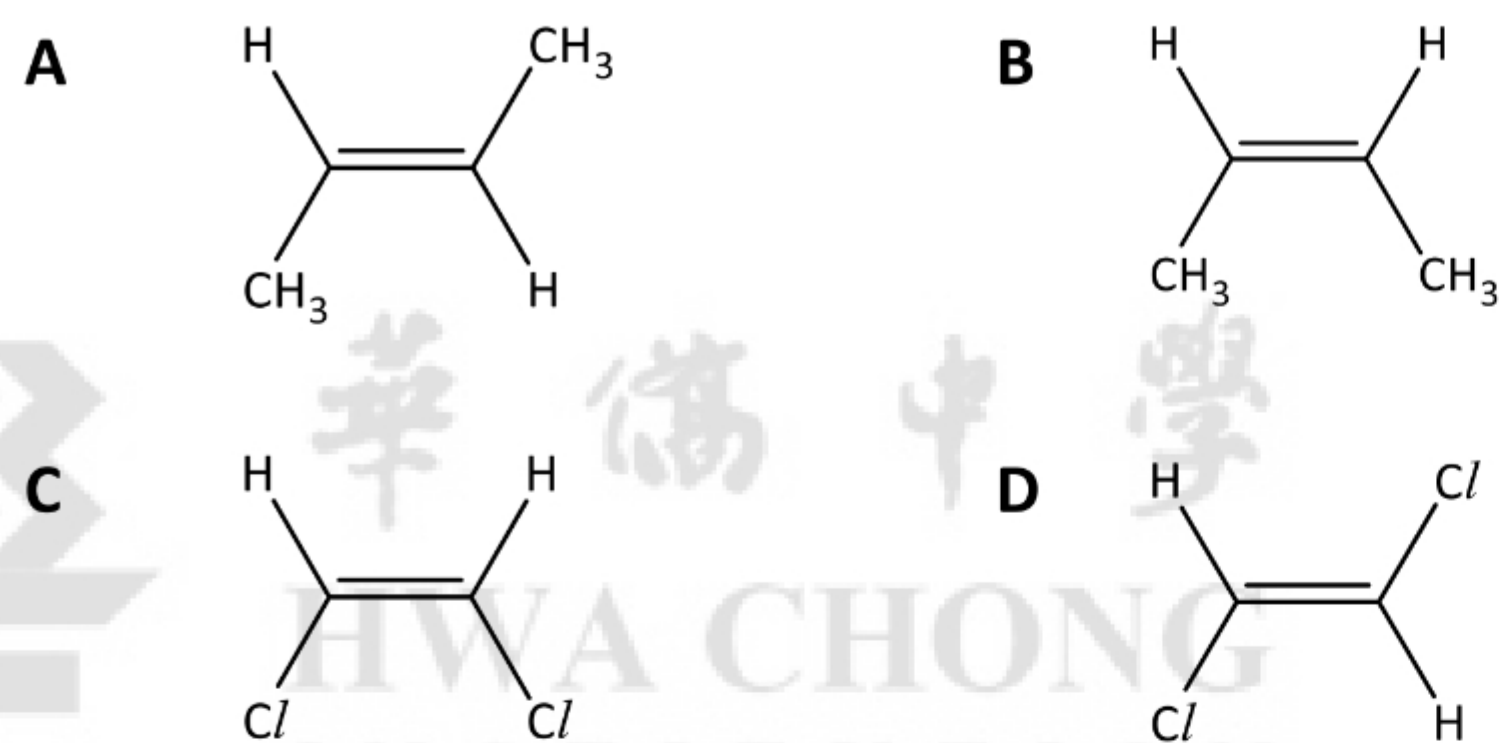
Isomer	Boiling Point (°C)
<i>cis</i> -but-2-ene	4
<i>trans</i> -but-2-ene	1
<i>cis</i> -pent-2-ene	37
<i>trans</i> -pent-2-ene	36

Table 4. Table showing the boiling points of some *cis-trans* isomers

Their similar boiling points can be understood from the fact that both isomers (in the case of *cis*-but-2-ene and *trans*-but-2-ene) contain the methyl group as a substituent and this is a relatively non-polar group such that the *cis* isomer is not much more polar than the *trans* isomer. The same reasoning can be applied to *cis*-pent-2-ene and *trans*-pent-2-ene.

Self-Practice 2.1

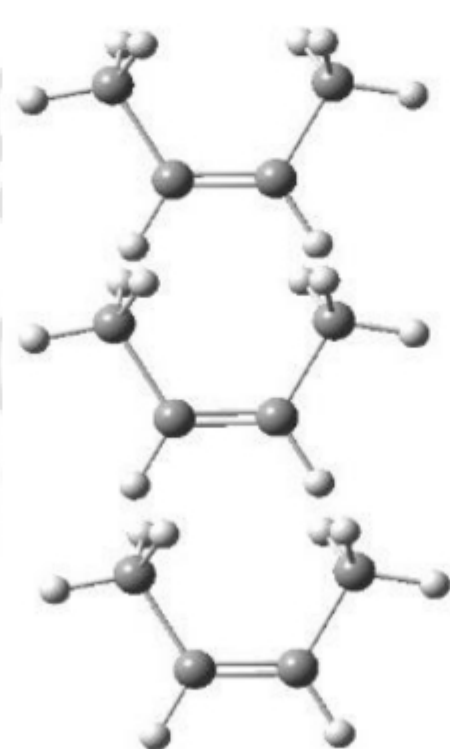
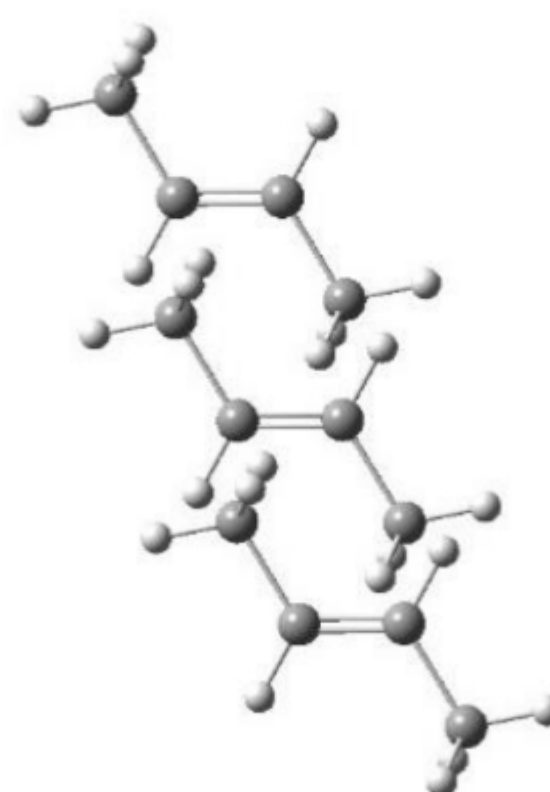
Which of the following compounds has the highest boiling point?

**Melting point of *cis-trans* isomers**

Between the *cis* and the *trans* isomer of alkenes, the ***trans* isomer tend to have higher melting point.**

In order for the intermolecular forces of attraction to work well in a solid, the molecules must be able to pack together efficiently in the solid state.

- The *trans* isomer pack better than the *cis* isomer due to the higher symmetry of the *trans* isomer. The “U” shape of the *cis* isomer does not pack well compared to the straighter shape of the *trans* isomer.
- The better packing of the *trans* isomer in the solid state means that the dispersion forces work more effectively in holding the molecules together when compared to the *cis* isomer.
- Hence more energy is required to overcome the forces of attraction between *trans* isomer, leading to a higher melting point.

*cis**trans*

2.3 Solubility

In order for dissolution to occur, the solute molecules and the solvent molecules should have favourable intermolecular forces of attraction.

Non-substituted alkenes can form favourable dispersion forces with non-polar solvents such as benzene and tetrachloromethane. Hence they are soluble in non-polar solvents.

Non-substituted alkenes can only form permanent dipole-induced dipole intermolecular forces with water, which are much weaker than the hydrogen bonding between water molecules themselves (as well as the dispersion forces between non-substituted alkene molecules). Hence they are insoluble in water.

2.4 Density

Liquid alkenes are less dense than water and form an immiscible layer above water.

Their densities increase slightly with increasing number of carbon atoms present. This is because the increase in the strength of intermolecular dispersion forces causes the alkene molecules to attract more closely together, resulting in a slightly smaller volume of the liquid. Since $\rho = m/V$, with a larger relative molecular mass, the density of the liquid increases.

2.5 Viscosity

The viscosity of liquid alkenes increases with increasing number of carbon atoms present as the strength of dispersion forces between the molecules increases. In addition, straight-chain alkenes have higher viscosity as compared to branched alkenes.

3 PREPARATION OF ALKENES

Alkenes can be prepared by the following reactions:

- Elimination of hydrogen halide from halogenoalkanes (to be covered in Topic 13 Halogen Derivatives)
- Dehydration of alcohol (to be covered in Topic 16 Hydroxy Compounds)

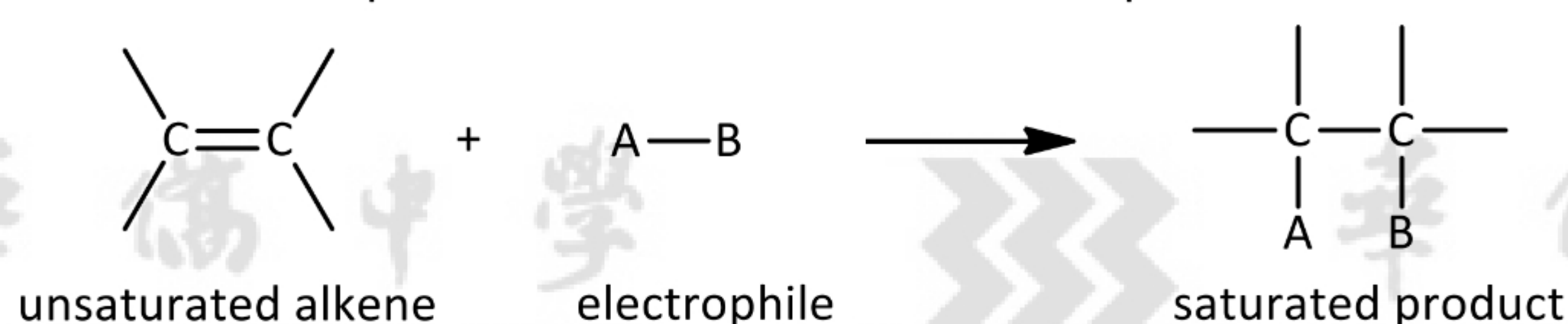
4 REACTIONS OF ALKENES

Reactivity of alkenes in terms of electrophilic reagents

Even though C=C bond is stronger than C–C bond, alkenes are more reactive than alkanes. This is due to the electron-rich C=C. The π bond (electron cloud), which lies on the surface of the molecules, attracts **electrophiles**.

During reaction, the weaker π bond is broken instead of the σ bond in the C=C bond. In place, two strong bonds (C–A and C–B) are formed in the product, leaving the carbon atoms joined by a single bond. This typical reaction of alkenes is known as **electrophilic addition**.

The overall reaction for electrophilic addition of alkenes can be represented as:

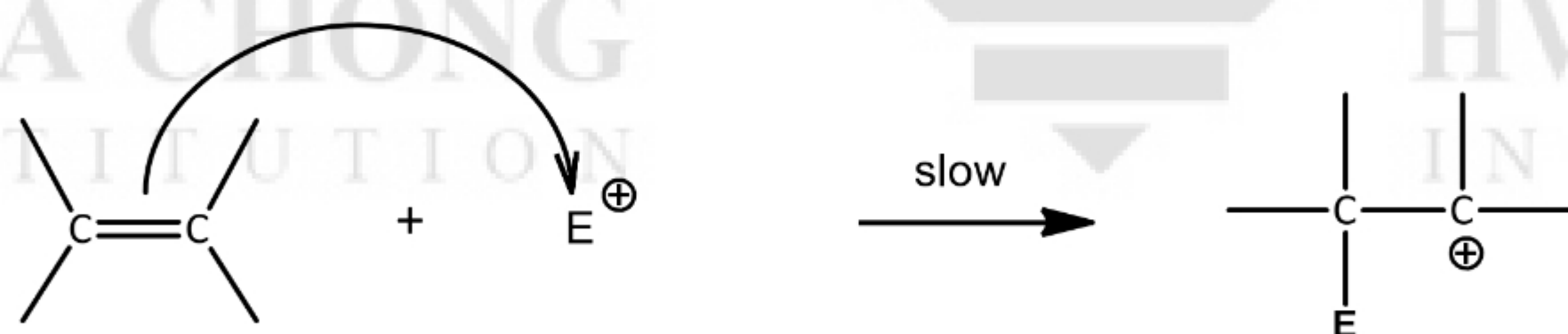


Examples of electrophiles that react with alkenes include hydrogen halides and halogens.

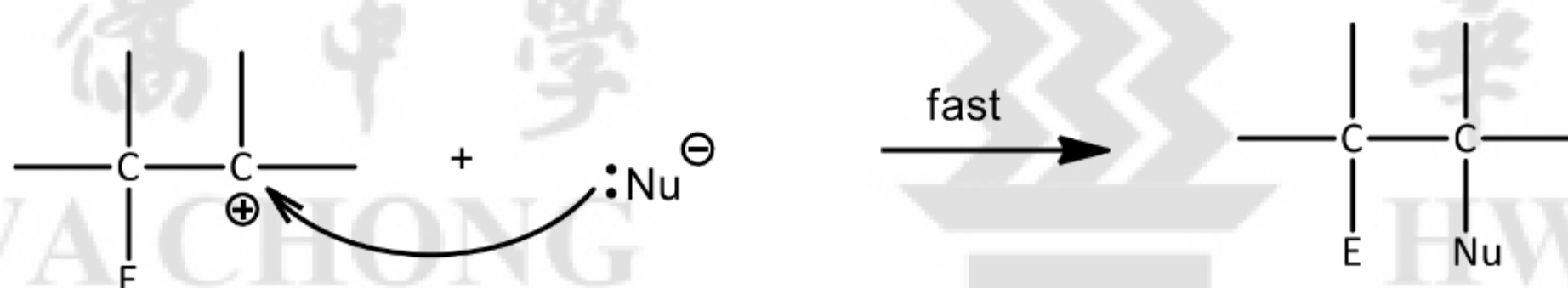
4.1 Electrophilic addition

4.1.1 General mechanism of electrophilic addition

Step 1: Initial attack by the π electrons of the C=C bond on the electrophile, forming a positively-charged carbocation intermediate.

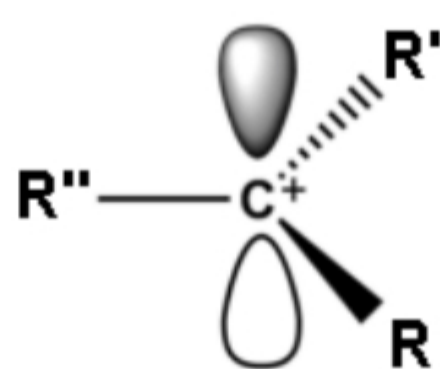


Step 2: Subsequent attack of the unstable carbocation intermediate by nucleophile to generate a stable product.



4.1.2 Carbocation intermediate

In electrophilic addition to alkenes, the carbocation is an important intermediate. Before studying the reactions of alkenes, we need to learn more about the structure and factors affecting the stability of carbocations.

Structure

The central carbon atom is positively charged and sp^2 hybridised. The 3 substituents are arranged in a trigonal planar geometry around the central carbon atom. As the carbon atom has lost an electron, the unhybridised p orbital is empty.

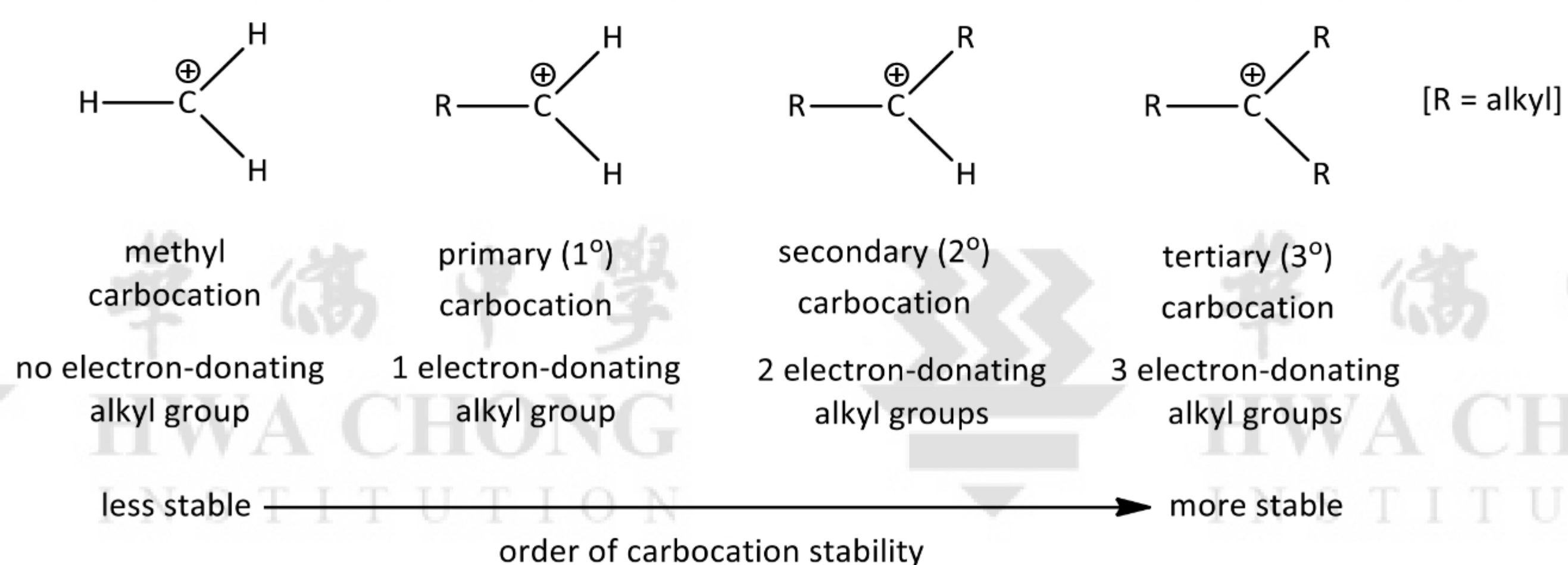
Due to the positive charge on the carbon atom, the carbon atom is electron-deficient and strongly attracts any **nucleophile** towards it. And because the geometry around the carbon atom is **planar**, the nucleophiles may **attack from either side of the plane**.

Stability

In general, organic species with a charge on it are less stable. Therefore, anything that disperses the charge would stabilise the species as a whole. Conversely, anything that intensifies the charge on it would destabilise it.

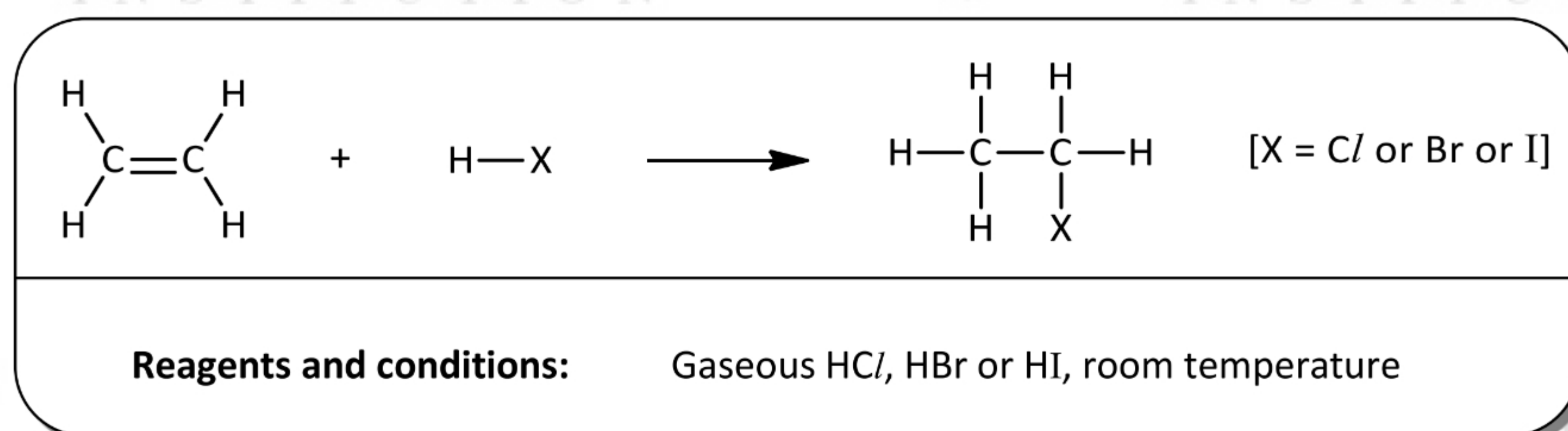
As mentioned earlier, the central carbon atom of the carbocation is positively charged. The 3 substituents bonded to it can affect the stability of the carbocation as a whole depending on whether they are electron donating or electron withdrawing.

Alkyl groups e.g. methyl ($-CH_3$) are considered **electron donating groups**. Therefore, the **more alkyl substituents the carbocation has, the more stable it would be**, as the **electron donating groups disperse the positive charge on the central carbon atom**.

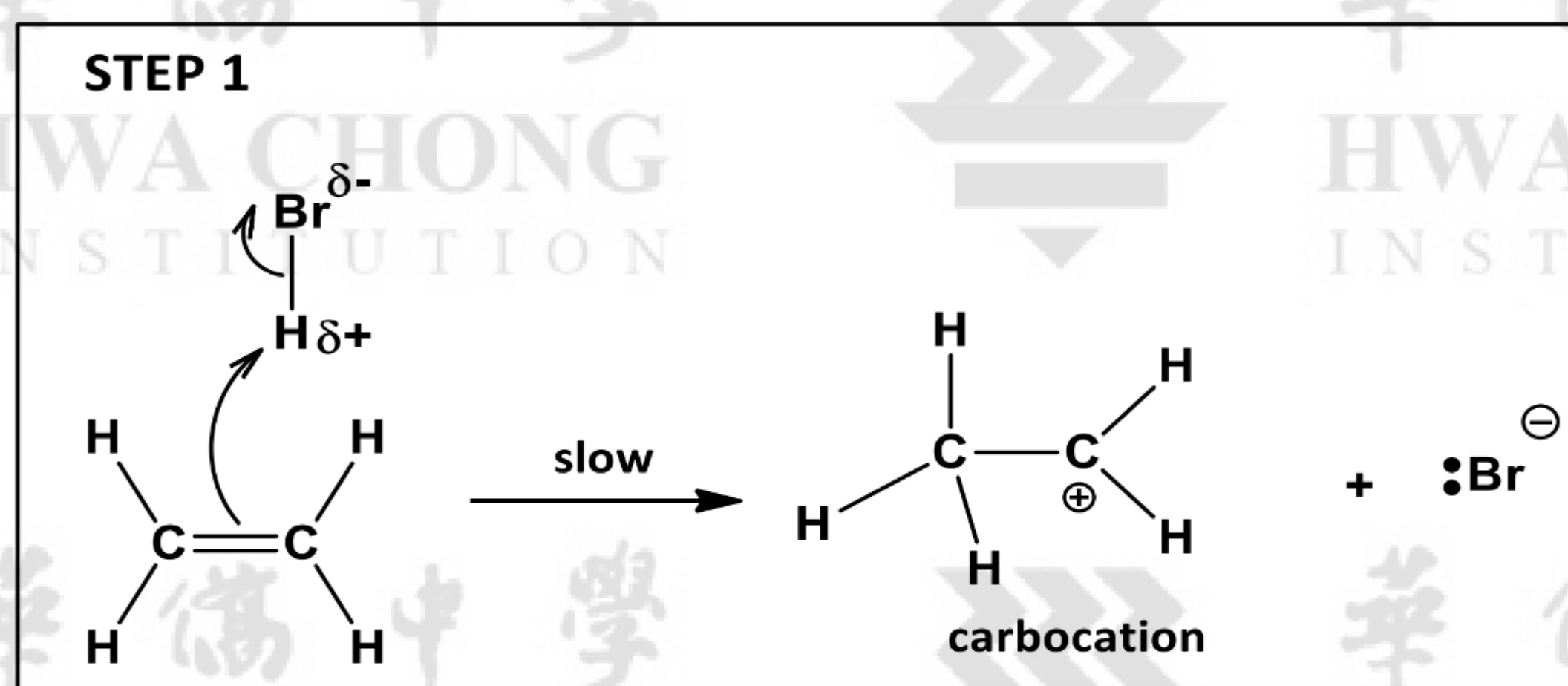


Conversely, **electron withdrawing substituents** like halogens would destabilise the carbocation as they **intensify** the positive charge on the central carbon atom.

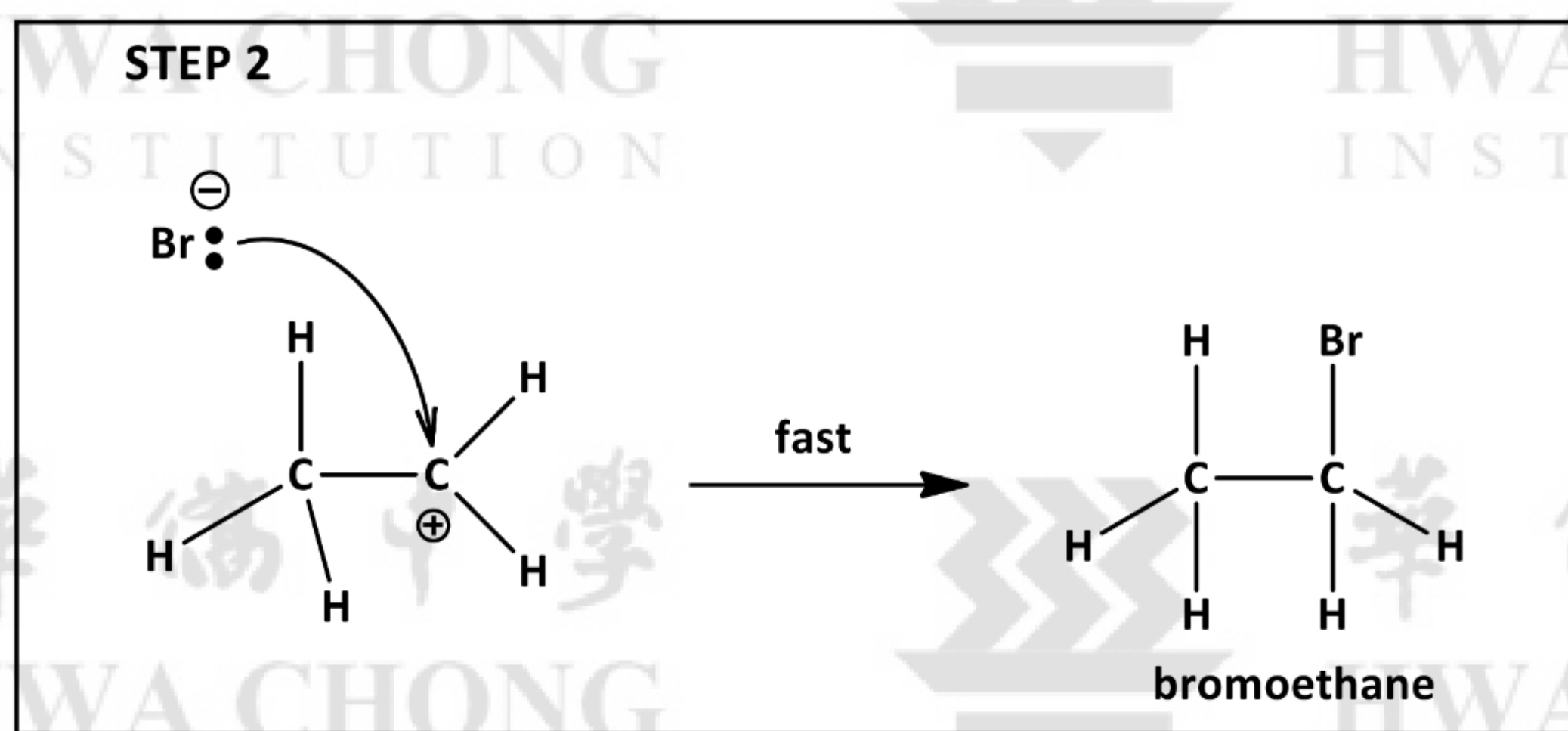
4.1.3 Electrophilic addition of hydrogen halides (H-X)



The general reaction mechanism of electrophilic addition applied to the reaction between ethene and HBr is illustrated as follows:

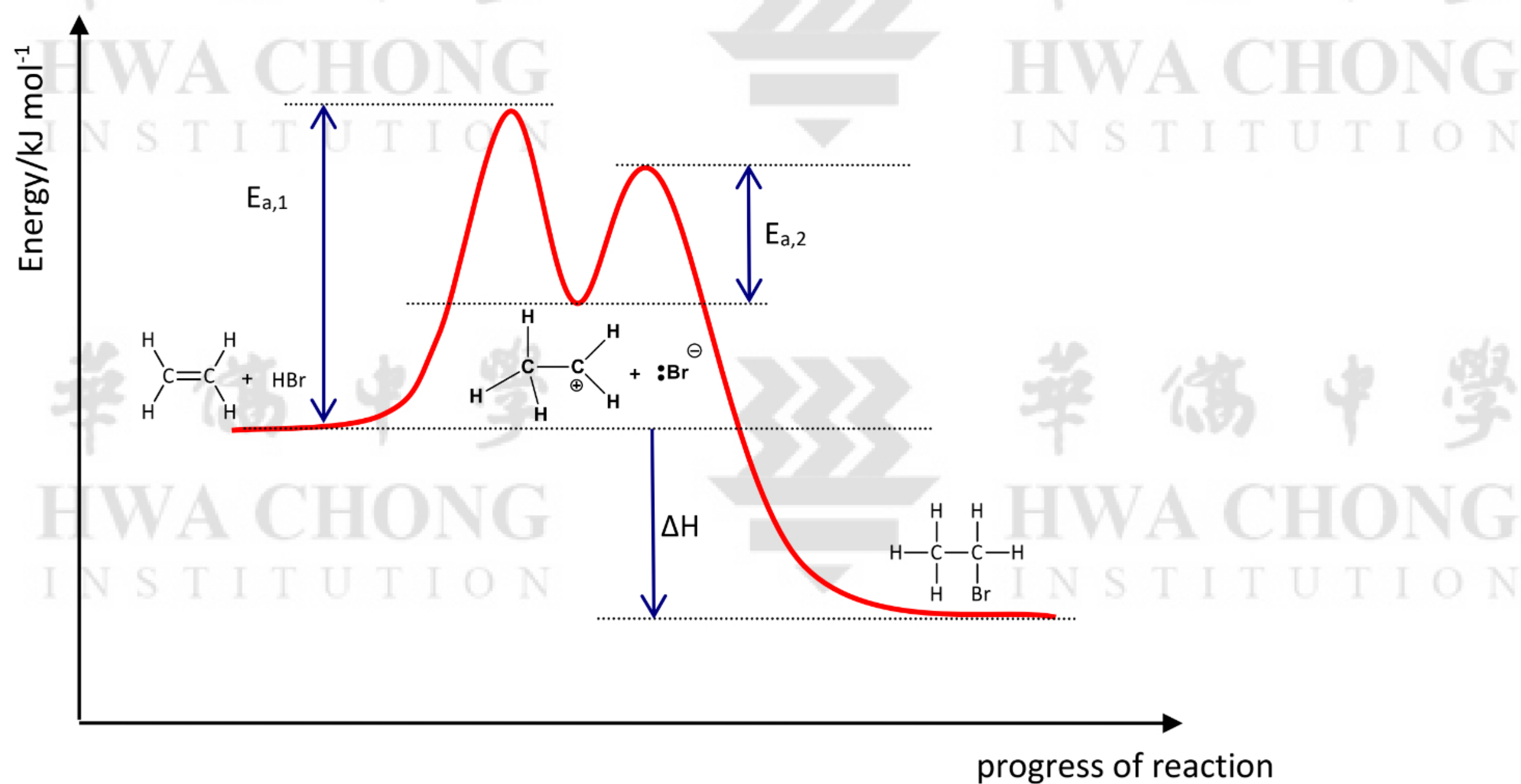


- This is the **rate-determining step** (involves breaking of the π bond).
- As the polar HBr molecule approaches the π electron cloud of ethene in the correct orientation, the high electron density of the π electron cloud “attacks” the electron deficient H atom on the HBr molecule. (*Note: arrow must show the direction of electron movement.)
- The π bond in the C=C bond breaks, forming a new C-H bond. The H-Br bond undergoes heterolytic fission producing a **carbocation intermediate** and a bromide ion.



- In the next step, the bromide anion acts as a nucleophile and attacks the unstable carbocation intermediate quickly as the negatively charged bromide ion is attracted to the positively charged carbon, forming a new C–Br bond. A stable product, bromoethane is formed.

The energy profile diagram of the electrophilic addition of hydrogen halide to ethene is as follows:



Self-Practice 4.1

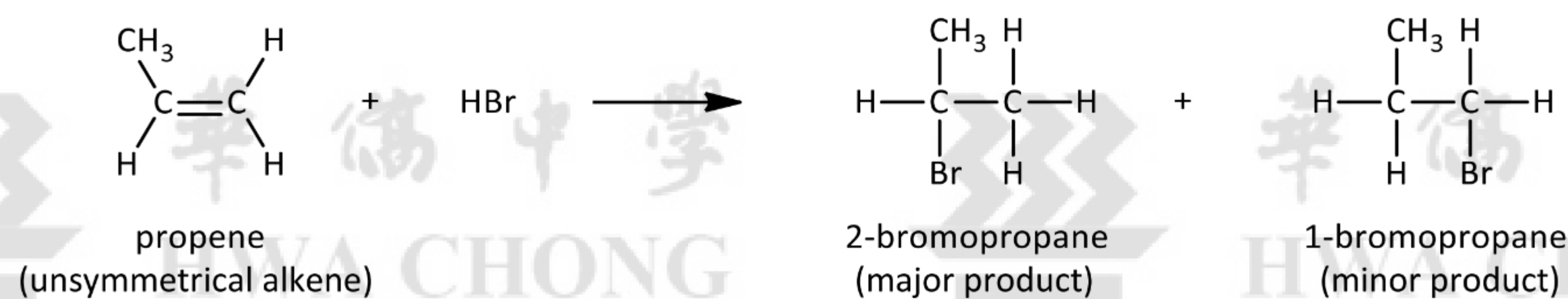
Hydrogen bromide reacts with ethene to form bromoethane. What is the best description of the organic intermediate in this reaction?

- A** It contains carbon, hydrogen and bromine.
- B** It has a negative charge.
- C** It is an electrophile.
- D** It is a free radical.

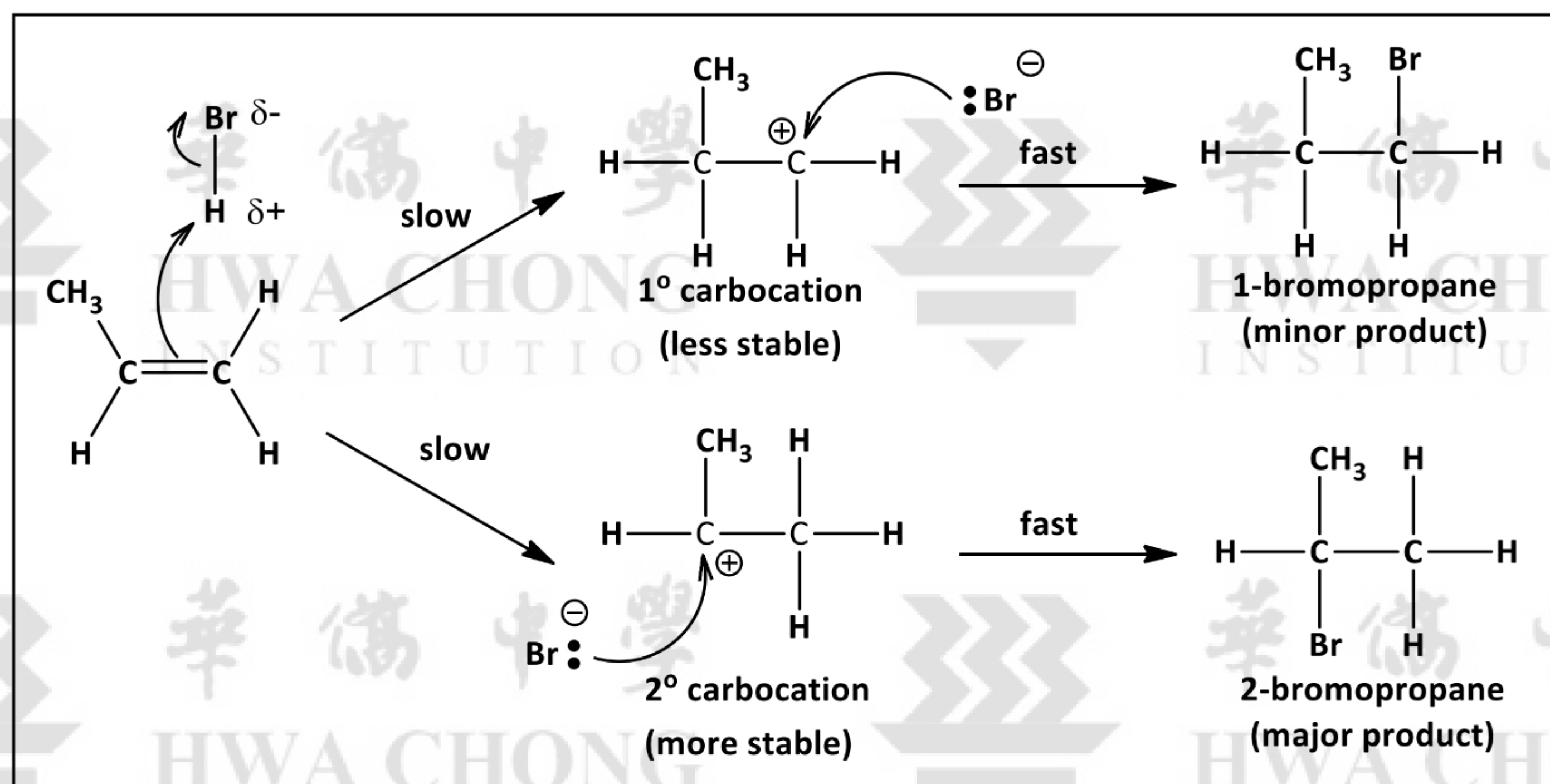
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Addition to an unsymmetrical alkene

When a hydrogen halide adds across the double bond of an **unsymmetrical alkene**, there are two possible products. One of them is preferred over the other. Why is this so?

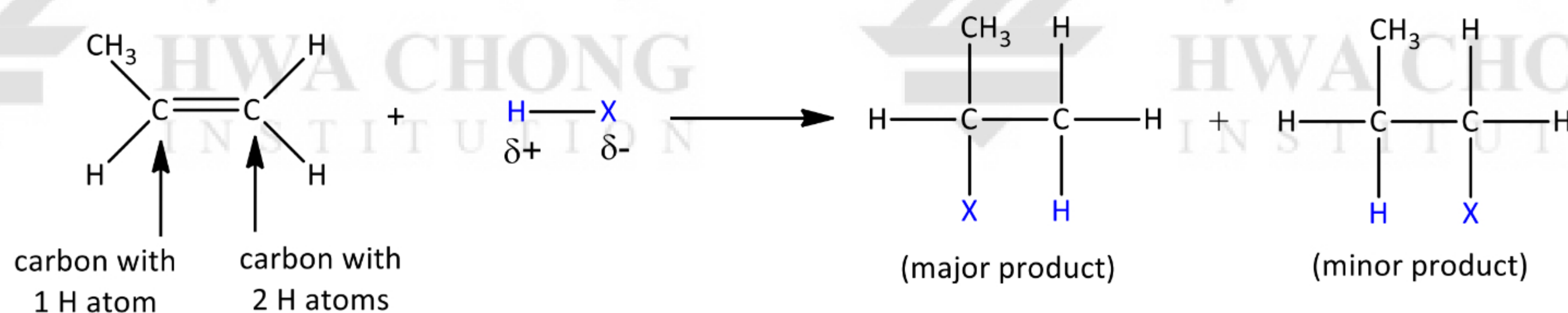


To explain this observation, we need to look at the 2 possible intermediates that generate each product.



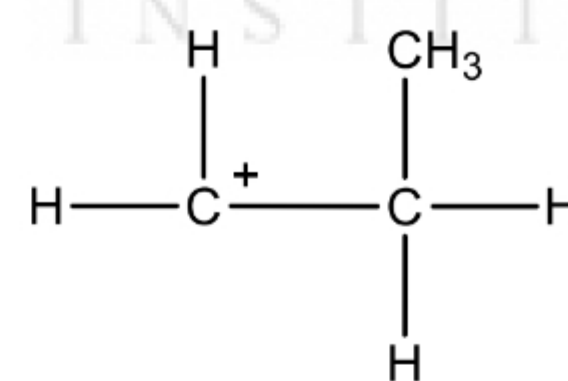
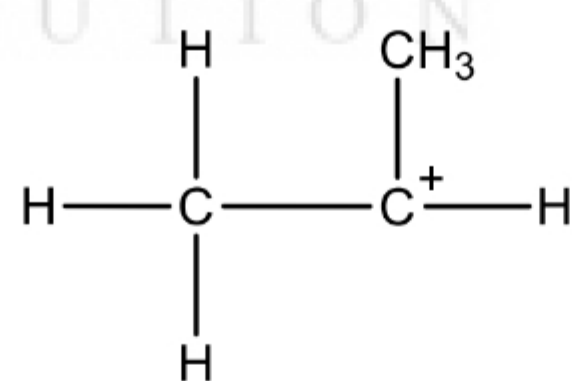
Markovnikov's rule

The Markovnikov's rule states that in the addition of HX to an alkene, the H atom adds to the C atom of the double bond that holds the greater number of H atoms. Reactions that follow this rule are said to follow Markovnikov orientation and give the Markovnikov product.



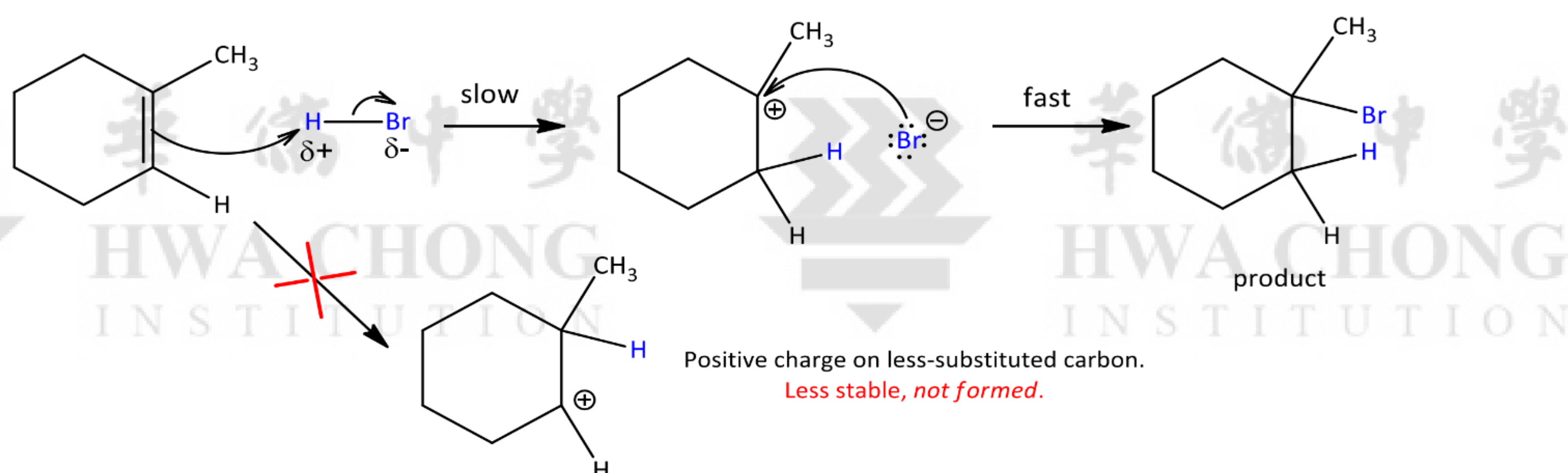
[X = Cl, Br or I]

This observation is due to the stability of the carbocation intermediate formed. Since alkyl groups are electron-donating, they tend to disperse the positive charge on a cation, and thus stabilise it. The



secondary carbocation is more stable than as the secondary carbocation has 2 electron-donating groups while the primary carbocation only has one. The more stable the carbocation, the lower the energy of the transition state that precedes it.

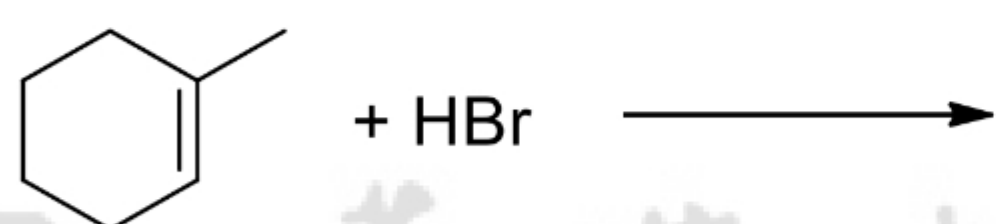
In an electrophilic addition to an alkene, the electrophile adds in such a way so as to generate the most stable carbocation intermediate. In short, in an electrophilic addition to an alkene, the electrophile adds to the less-substituted end of the double bond to give the more substituted (and therefore more stable) carbocation.



However, we are often interested in adding electrophiles other than H to the double bonds of alkenes. Markovnikov's rule can be extended to include a variety of other additions, based on the addition of the electrophile in such a way as to produce the most stable carbocation.

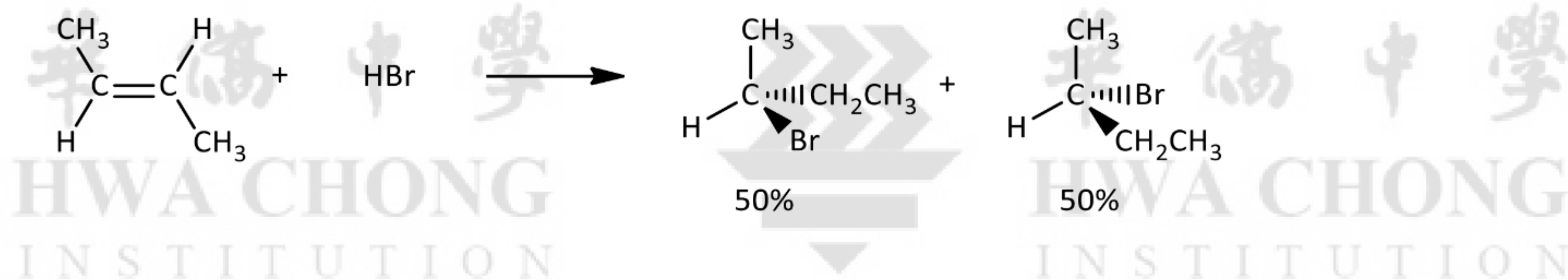
Self-Practice 4.2

Identify the major product of the following reaction:

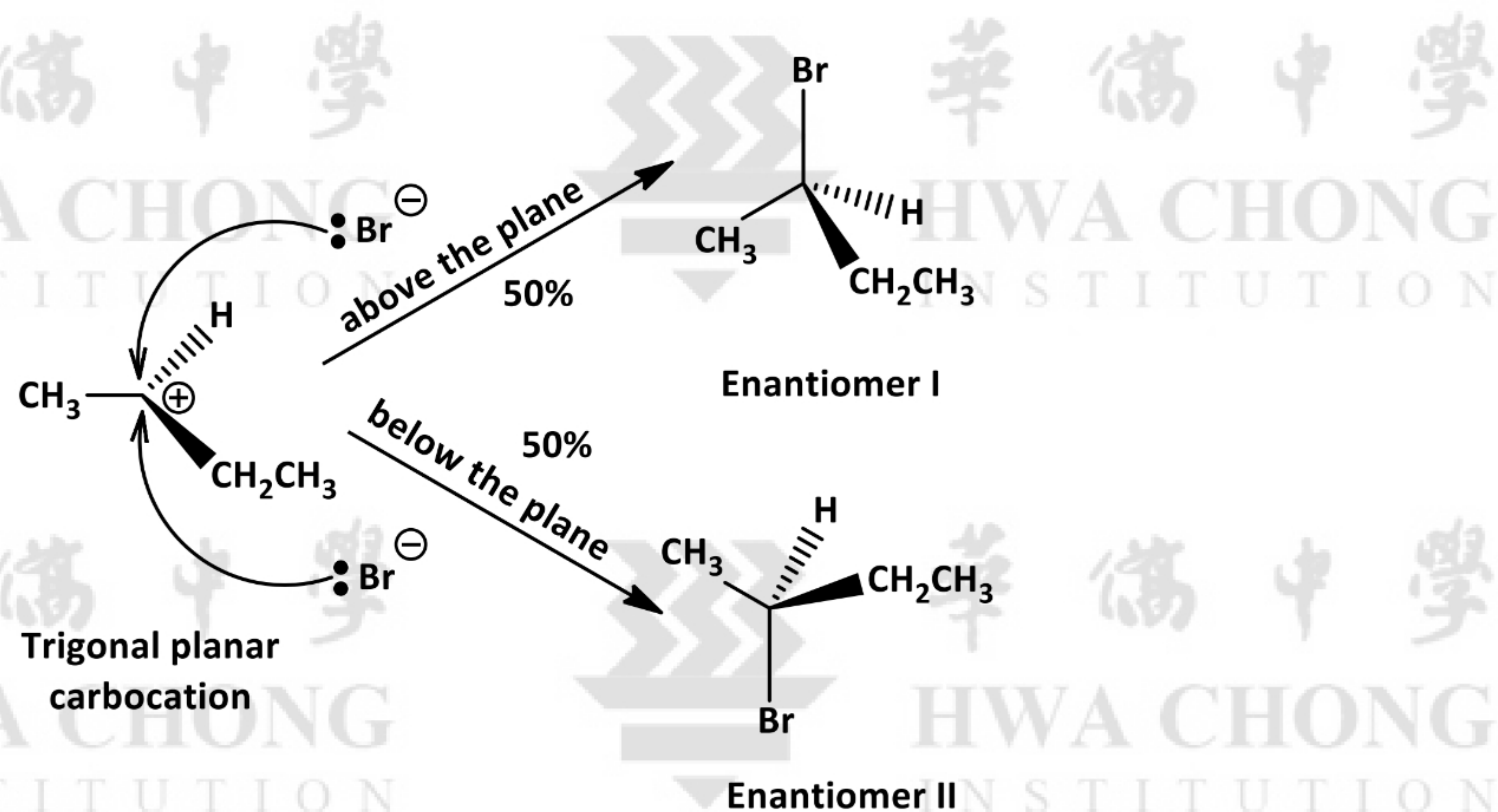


Formation of a racemic mixture

When a hydrogen halide adds across the double bond of an alkene that produces an intermediate carbocation with 3 different groups attached to it, it produces **equal** amounts of 2 enantiomers, forming a **racemic mixture**.

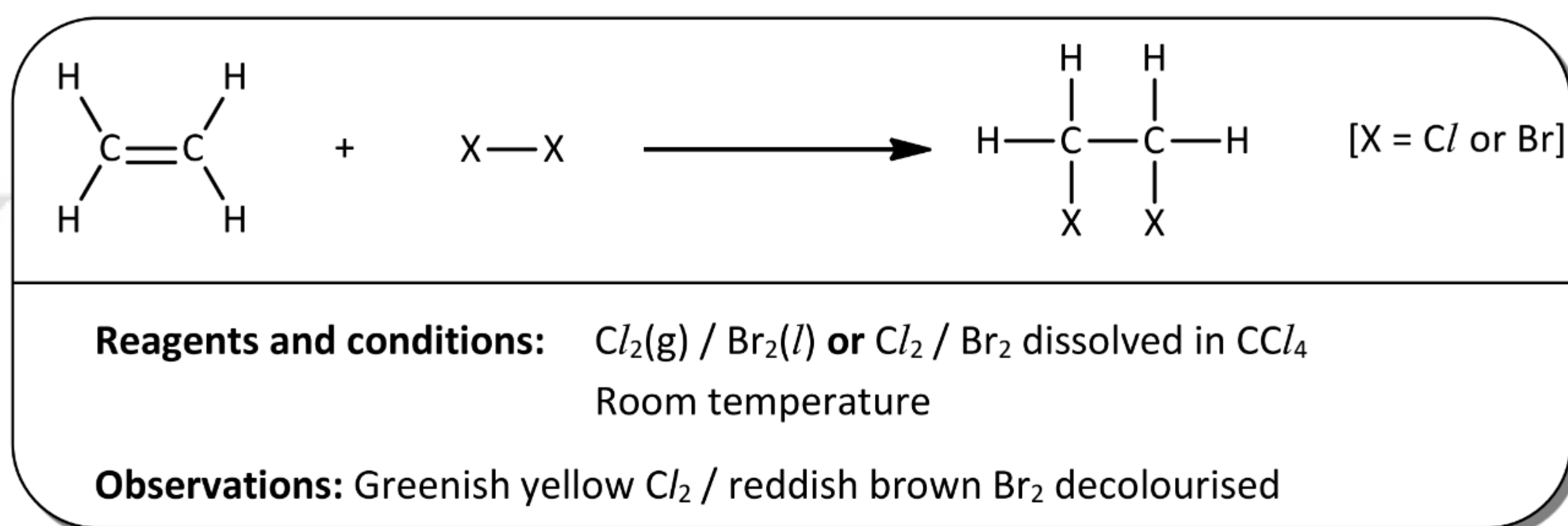


This occurs because the geometry about the positively charged carbon is planar, hence it has equal chances of being attacked from the top or bottom by the bromide ion in the second step, thereby producing the two enantiomers in equimolar ratio.



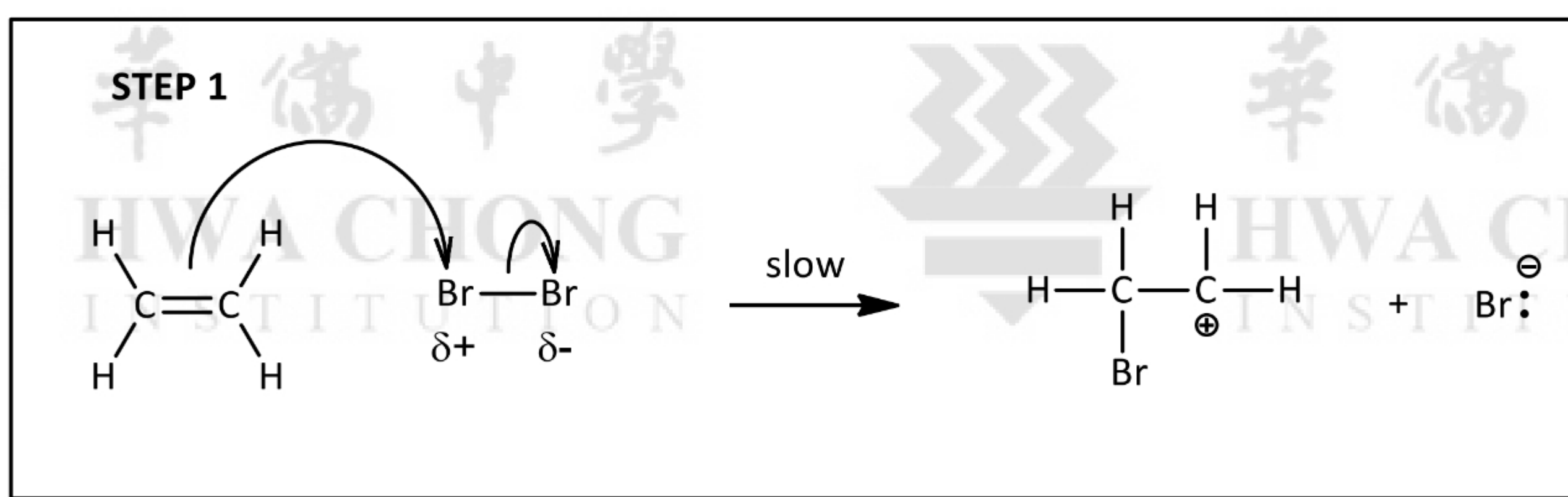
4.1.4 Electrophilic addition of halogens (X₂)

Alkenes also readily react with chlorine or bromine to form halogenoalkanes with two atoms of halogens attached to adjacent carbon atoms. The reaction with fluorine is very violent while iodine does not react with most alkenes.

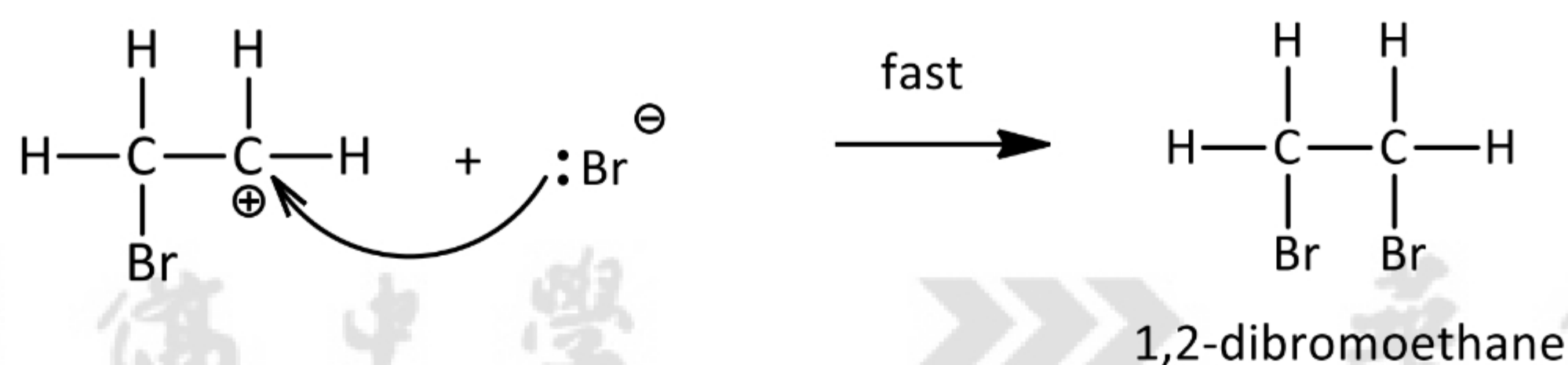


Electrophilic addition of halogens can occur in the presence of UV light but the reaction is usually carried out in the absence of UV light to prevent free radical substitution of the alkyl substituents on the alkene or of the product.

For the mechanism, we will use the electrophilic addition of Br₂ to ethene as an example. The mechanism takes place in two steps.



- As the non-polar Br₂ molecule approaches the π electron cloud of ethene, the high electron density of the π electron cloud polarises the electron cloud of the Br₂ molecule.
- The Br-Br bond undergoes heterolytic fission resulting in a bromide anion with the other bromine atom bonded to the alkene to form a positively charged carbocation intermediate.
- This is the rate-determining step as it involves breaking the π bond in ethene and Br-Br bond.

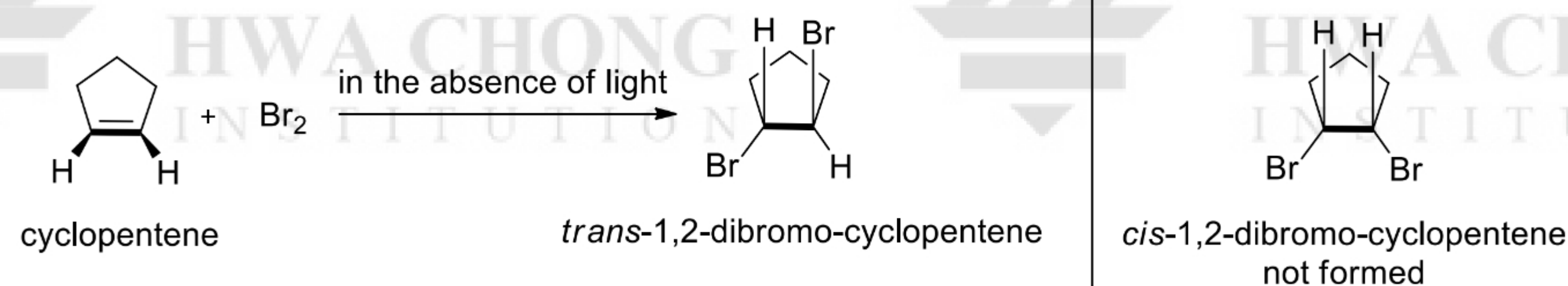
STEP 2

- In this step, the bromide anion acts as a nucleophile to attack the carbocation intermediate to form the product, 1,2-dibromoethane.
- This step is fast as it involves the reaction between oppositely charged species. The mutual electrostatic attraction results in the easy formation of the stable 1,2-dibromoethane.

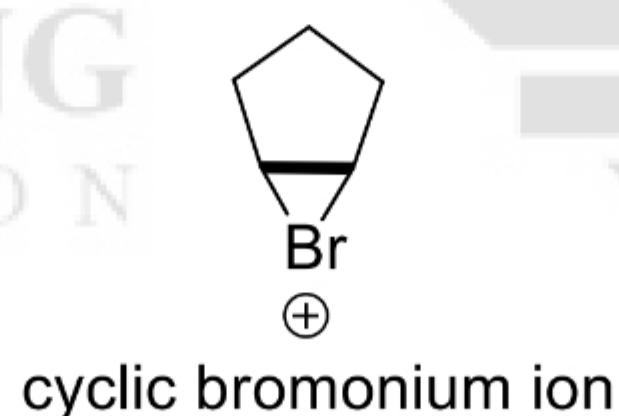
For your information

Although the mechanism Section 4.1.4 is reasonable and follows that of the alkene reaction with hydrogen halides, studies have shown that it is not completely consistent with some observations.

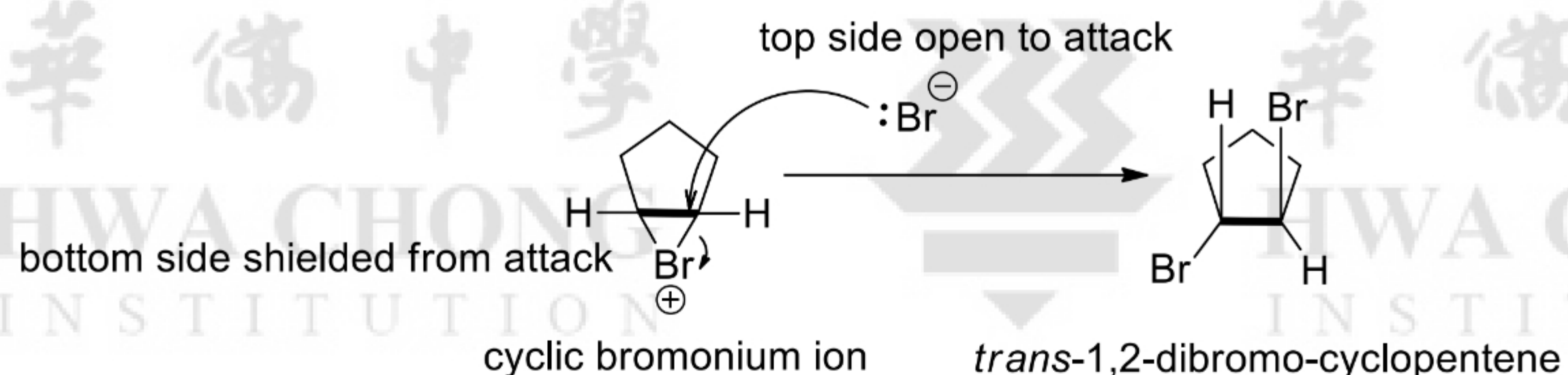
For instance, it was observed in the reaction of bromine with cyclopentene, that only the *trans* product is formed rather than an expected mixture of *cis* and *trans* products if a planar carbocation intermediate was involved.



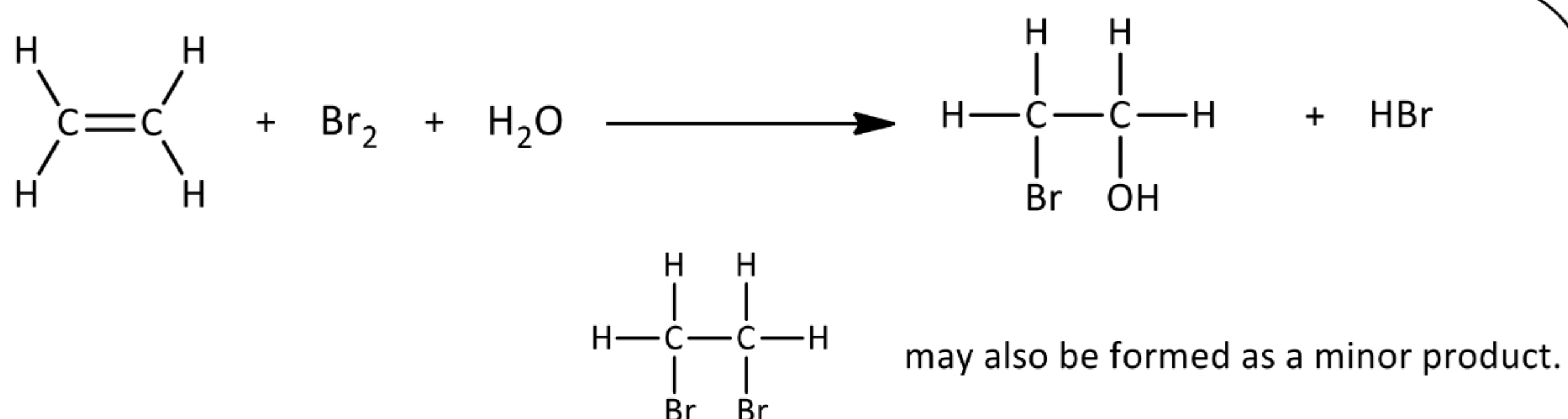
Hence, it was proposed that the intermediate in the mechanism was a cyclic three-membered bromonium ion during electrophilic addition of bromine on alkene.



This cyclic bromonium ion as an intermediate could explain the above observation because the second step of the mechanism (shown below) will then involve an S_N2 attack by bromide anion from the opposite side of the C–Br bond to be broken. The consequence of this S_N2 attack is the formation of a *trans* product in which the two Br atoms are on the opposite faces of the double bond. We shall look at S_N2 mechanism in greater detail in Topic 13 Halogen Derivatives.



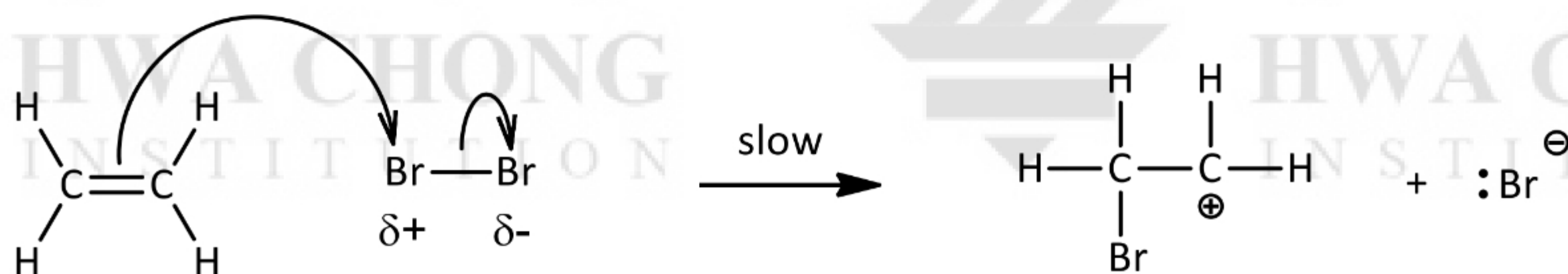
4.1.5 Electrophilic addition of bromine water



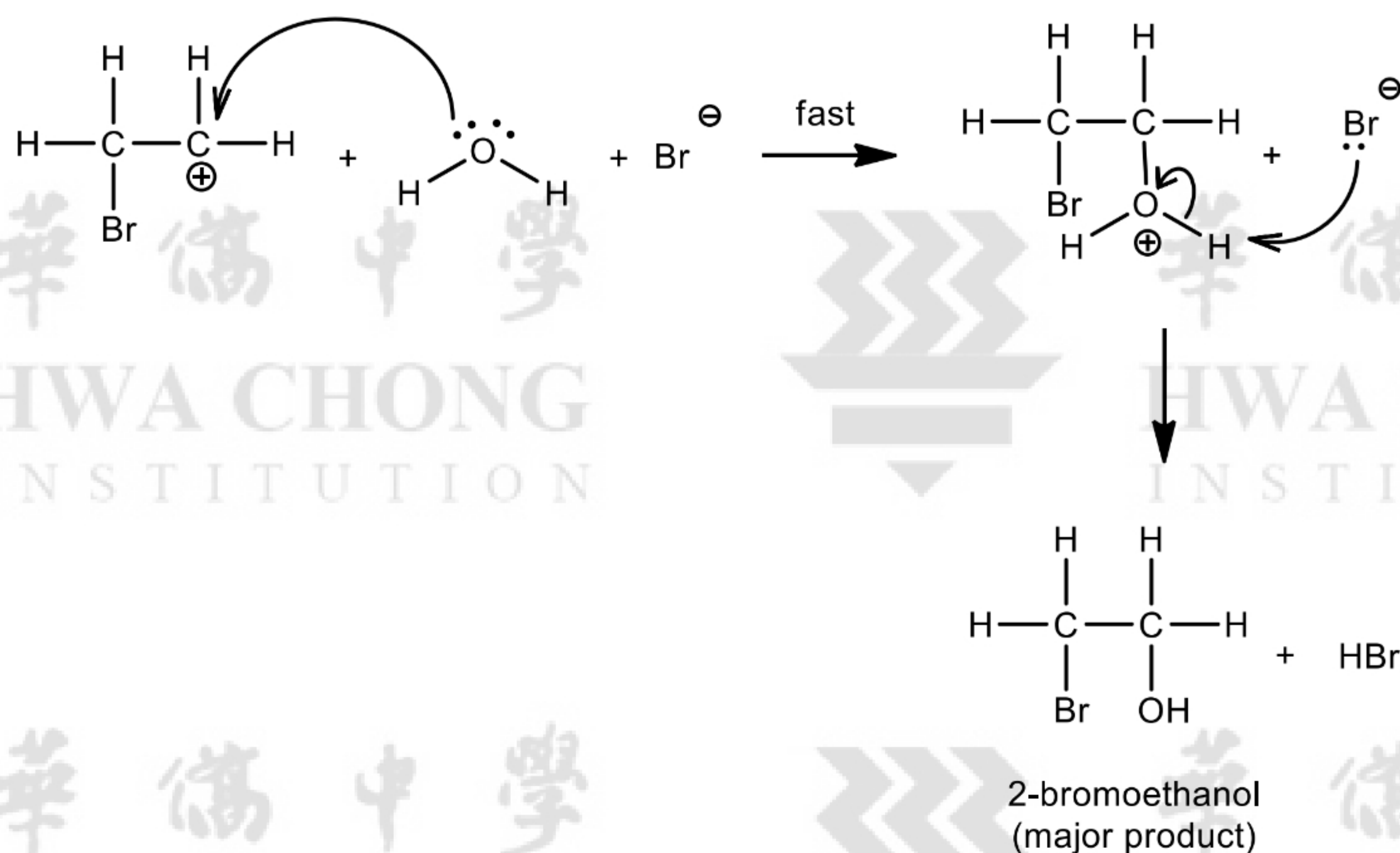
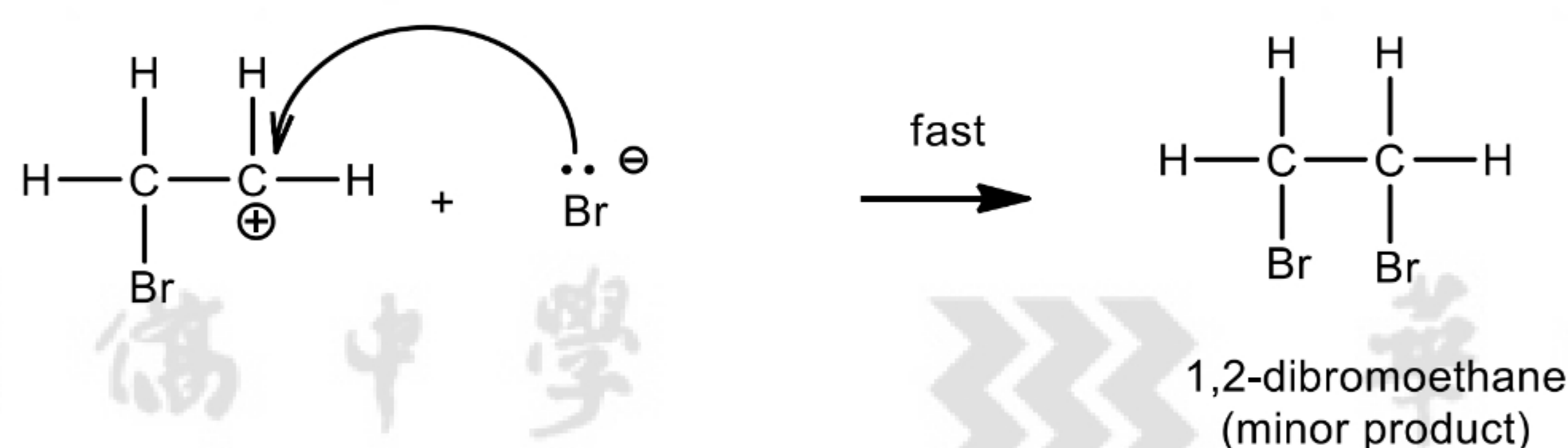
Reagents and conditions: $\text{Br}_2(\text{aq})$, room temperature
Observations: Yellow-orange $\text{Br}_2(\text{aq})$ decolourised (*distinguishing test)

Alkenes react with bromine water to form bromoalcohol (or bromohydrin) as the major product instead of the dibromo compound.

This is because the carbocation intermediate is susceptible to attack by any nucleophile present in the reaction mixture.



In the case of bromine water, after forming the carbocation intermediate in the rate-determining step, the carbocation intermediate can be attacked by any nucleophile in the reaction mixture. So, both water and bromide ion can act as nucleophiles to attack the carbocation. The major product generally depends on which nucleophile is present in excess.

Scenario 1: Nucleophilic attack by water

Scenario 2: Nucleophilic attack by bromide ion


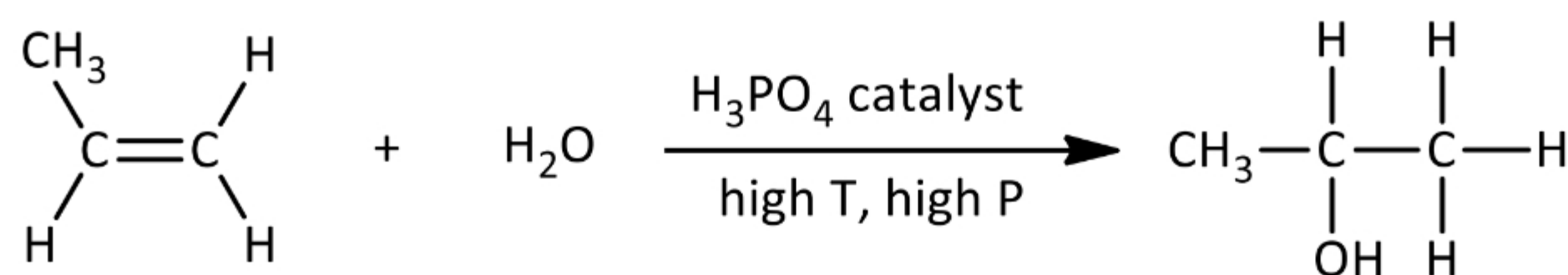
Water is present in a much higher concentration compared to the bromide ion and therefore attacks the intermediate preferentially in the second step of the reaction.

Lecture Exercise 4.1

Predict the products formed when propene reacts with bromine water that is contaminated by aqueous sodium chloride. Explain why it is not possible to obtain 1,2-dichloropropane.

4.1.6 Electrophilic addition of water/steam

Alkenes react with steam (H_2O) to form alcohols. The addition of steam to alkenes is similar to that of hydrogen halides. Phosphoric acid is added as a catalyst.



Industrial method

Reagents and conditions: steam; H_3PO_4 catalyst
High temperatures and high pressures

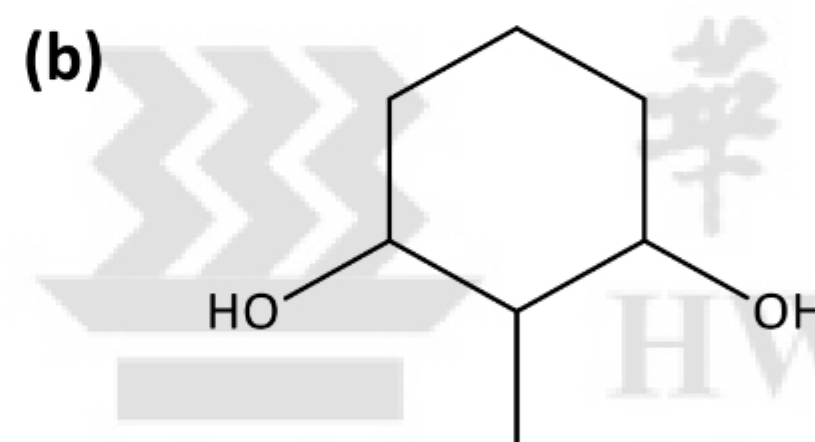
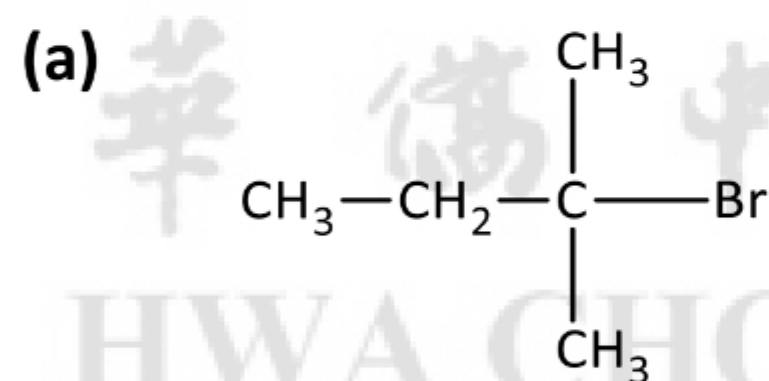
Lab method

Reagents and conditions: 1. concentrated H_2SO_4 , cold
2. H_2O

(Refer to Appendix for the mechanism)

Lecture Exercise 4.2

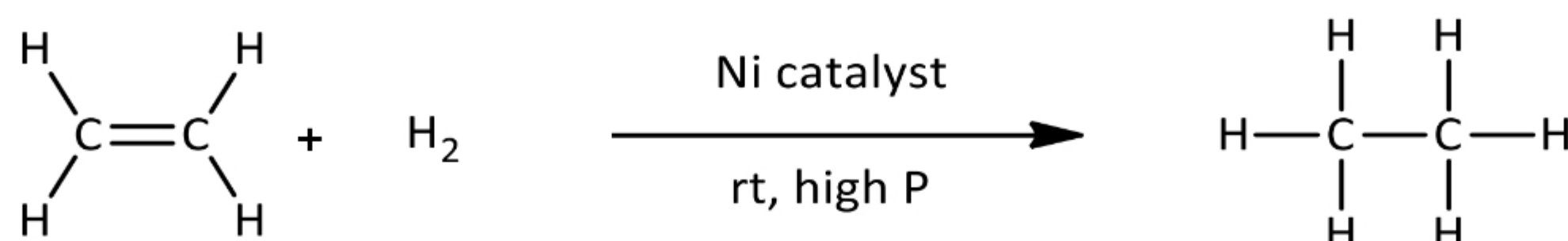
What alkenes would you start with to prepare the following compounds?



4.2 Reduction

Reduction via catalytic hydrogenation is often used to convert unsaturated alkenes to saturated alkanes. This process is commonly used in the food industry to produce margarine by converting unsaturated plant oil into the saturated soft margarine.

This is a form of heterogeneous catalysis. See Topic 6 Reaction Kinetics for the mechanism.



Reagents and conditions: H₂ gas; Ni catalyst
Room temperature and high pressure

Note: Platinum/Palladium catalyst at room temperature and pressure can also be used for this reduction.

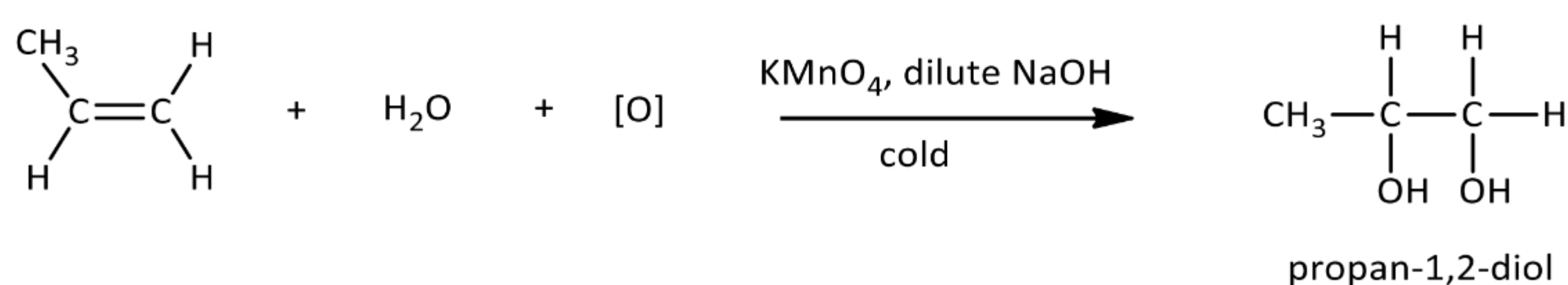
H₂ gas with nickel catalyst is also able to reduce other functional groups and these reactions will be discussed in the later organic chemistry topics.

4.3 Oxidation

Depending on the conditions, alkenes can undergo oxidation to form various products.

4.3.1 Mild oxidation

Cold alkaline potassium manganate(VII) can oxidise alkenes into the corresponding diols. The formation of diols from alkenes is considered as a type of mild oxidation.

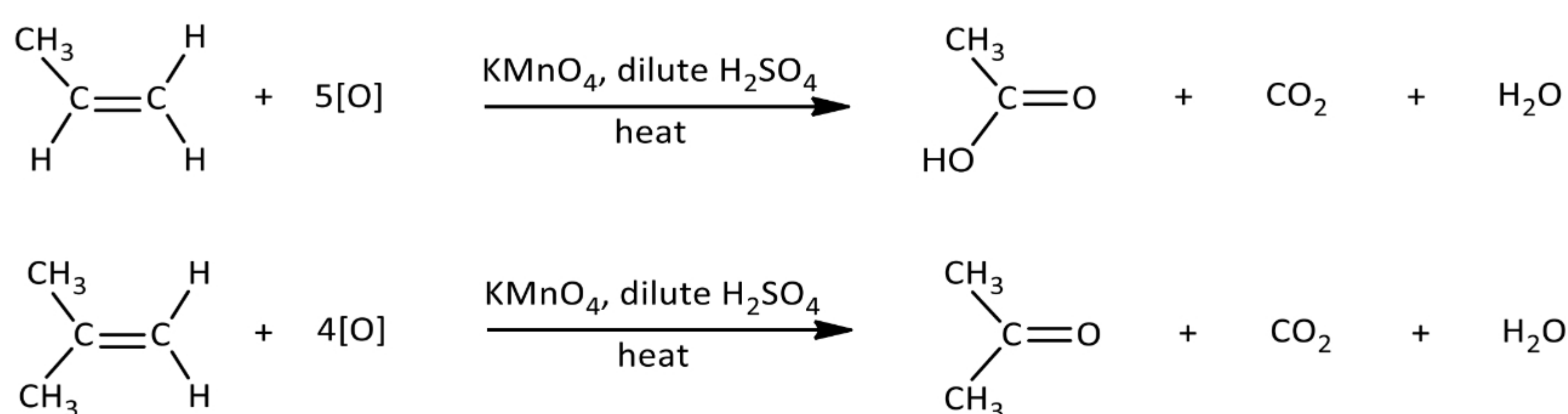


Reagents and conditions: KMnO₄, dilute NaOH, cold

Observations: Purple KMnO₄ is decolourised and a brown precipitate of MnO₂ is formed. (*distinguishing test)

4.3.2 Oxidative cleavage

Hot acidic potassium manganate(VII) can cleave the carbon-carbon double bond in alkenes to give carbonyl compounds and/or carboxylic acids as products. This oxidative cleavage of alkenes is considered as a type of strong oxidation.



Reagents and conditions: KMnO_4 , dilute H_2SO_4 , heat

Observations: Purple KMnO_4 is decolourised. Note that effervescence of carbon dioxide is possible for selected alkenes as mentioned below.

(*distinguishing test)

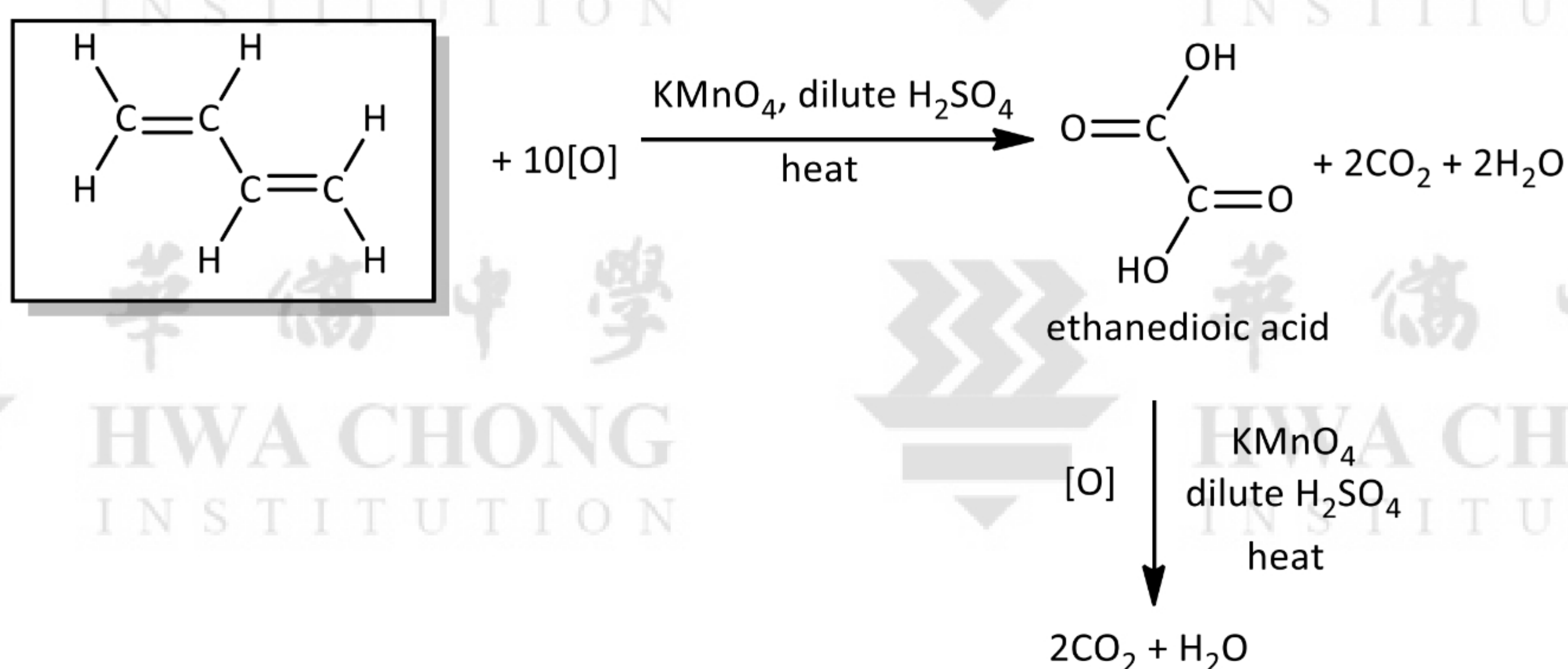
NOTE:

- Oxidation of alkenes CANNOT be carried out with potassium dichromate(VI).

Different substituents on the $\text{C}=\text{C}$ carbon atoms give rise to different products upon oxidative cleavage. The table below summarises the possible products arising from a different number of hydrogen atoms attached directly to the $\text{C}=\text{C}$ carbon atoms.

No. of hydrogen atoms on carbon	Structure	Products after oxidative cleavage
2	$ \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} $	$\text{CO}_2 + \text{H}_2\text{O}$
1	$ \begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{H} \end{array} $	$ \begin{array}{c} \text{R} \\ \diagdown \\ \text{O}=\text{C} \\ \diagup \\ \text{OH} \end{array} $ carboxylic acid
0	$ \begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}' \end{array} $	$ \begin{array}{c} \text{R} \\ \diagdown \\ \text{O}=\text{C} \\ \diagup \\ \text{R}' \end{array} $ ketone

Special case of oxidative cleavage:



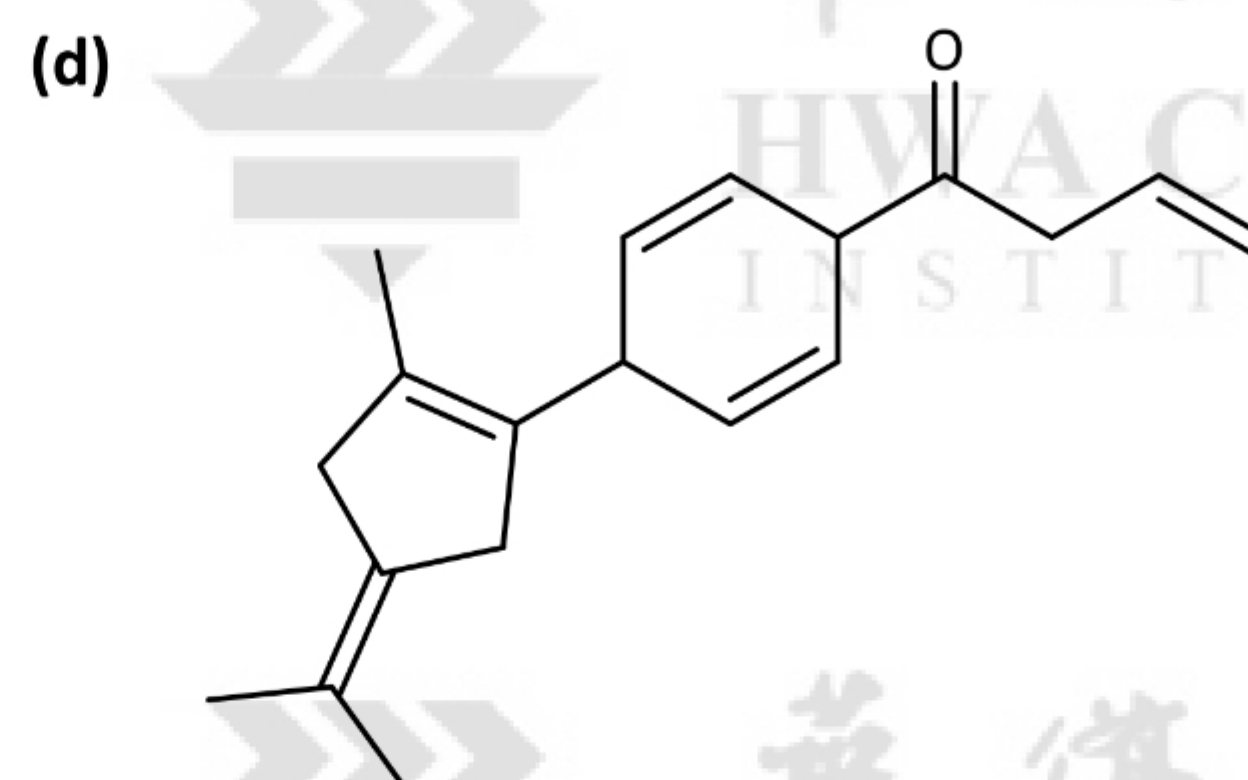
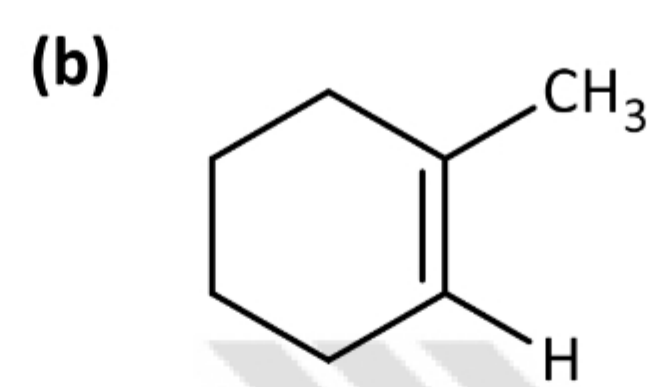
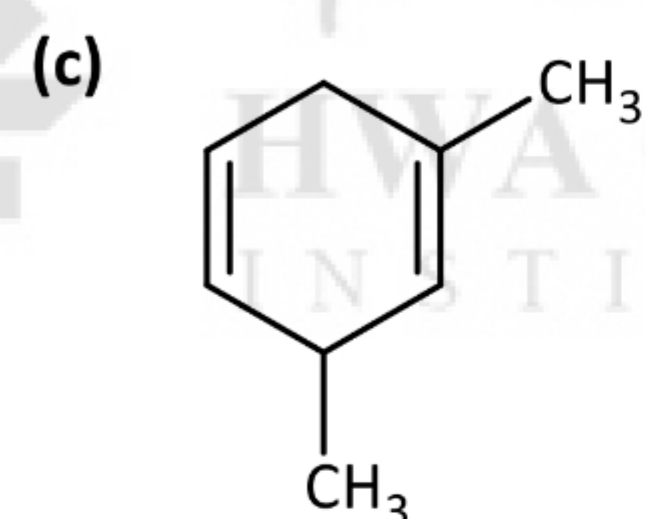
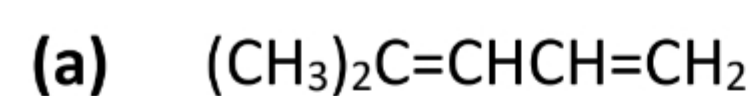
The special case of oxidative cleavage illustrated above should not be surprising as you have learnt about the redox titration of ethanedioic acid and potassium manganate(VII) under Topic 4 Reactions and Stoichiometry (try balancing the redox equation).

Usefulness of oxidative cleavage:

- Oxidative cleavage is a useful tool to establish the location of the alkene double bond in a hydrocarbon chain or ring.
- Oxidative cleavage using hot acidified KMnO_4 can be used as a test to **distinguish between alkenes with terminal $\text{C}=\text{C}$ double bonds ($=\text{CH}_2$) and those without**. Alkenes with terminal $\text{C}=\text{C}$ double bonds would, upon oxidation, evolve carbon dioxide gas. This distinguishes between the alkenes.

Lecture Exercise 4.3

Write down the products of the following compounds undergoing oxidative cleavage.



**Generic procedure for distinguishing test for alkenes****(a) Using acidified potassium manganate(VII), KMnO_4**

1. To prepare acidified KMnO_4 solution, add 5 drops of $\text{KMnO}_4(\text{aq})$ to 1 cm^3 of dilute H_2SO_4 in a test tube.
2. To 1 cm^3 of the unknown, add 2 – 3 drops of the acidified KMnO_4 dropwise.
3. Shake well.
4. Warm in a water bath.

(b) Using aqueous bromine (bromine water)

1. To 1 cm^3 of the unknown in a test tube, add aqueous bromine dropwise.
2. Shake well.

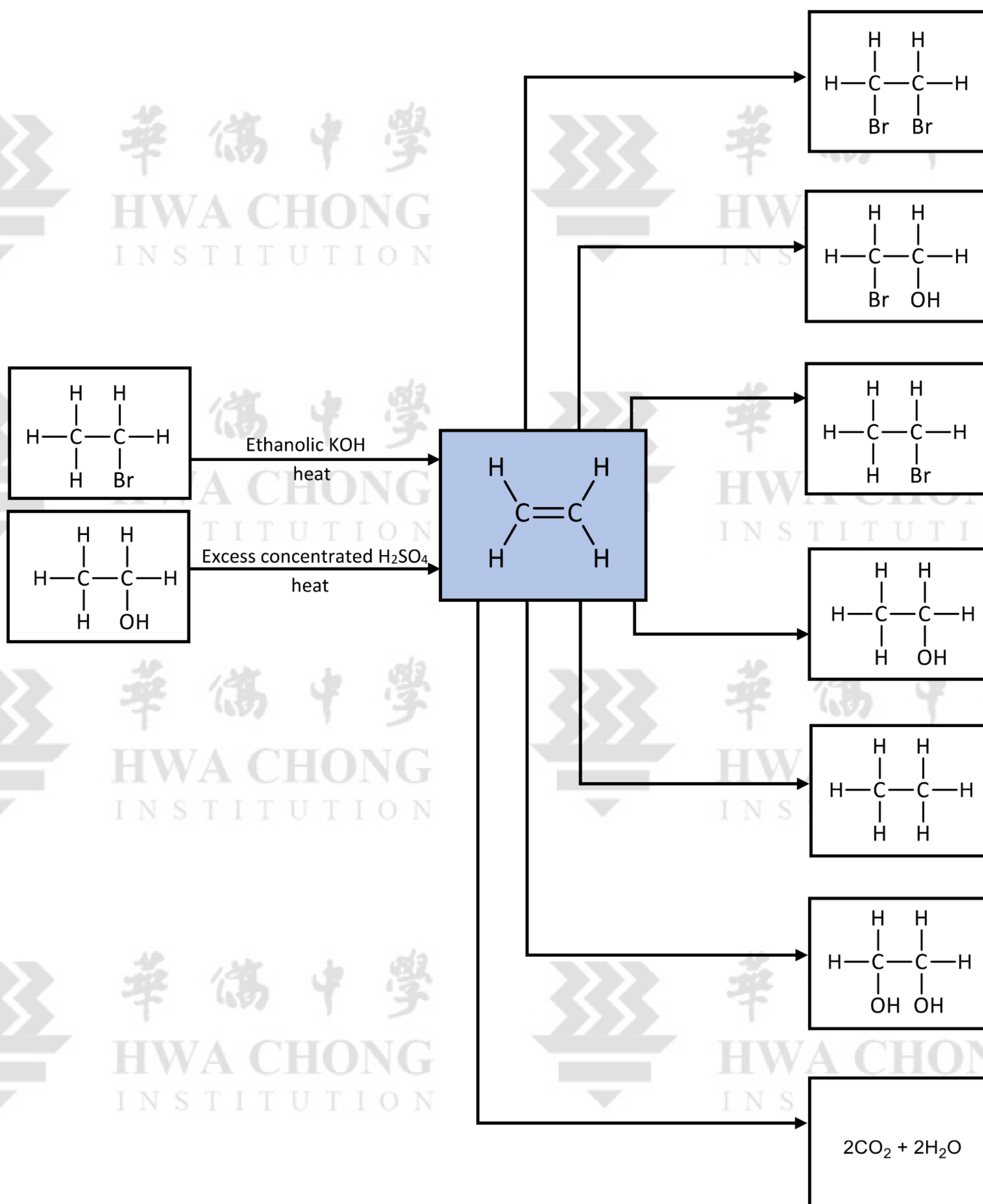
Self-Practice 4.3

Refer to the above distinguishing test and answer the following questions.

- i. Why should the KMnO_4 be added dropwise?
- ii. Why should the aqueous Br_2 be added dropwise?

Summary of reactions

Write the reagents and conditions needed for the conversions on the arrows below.

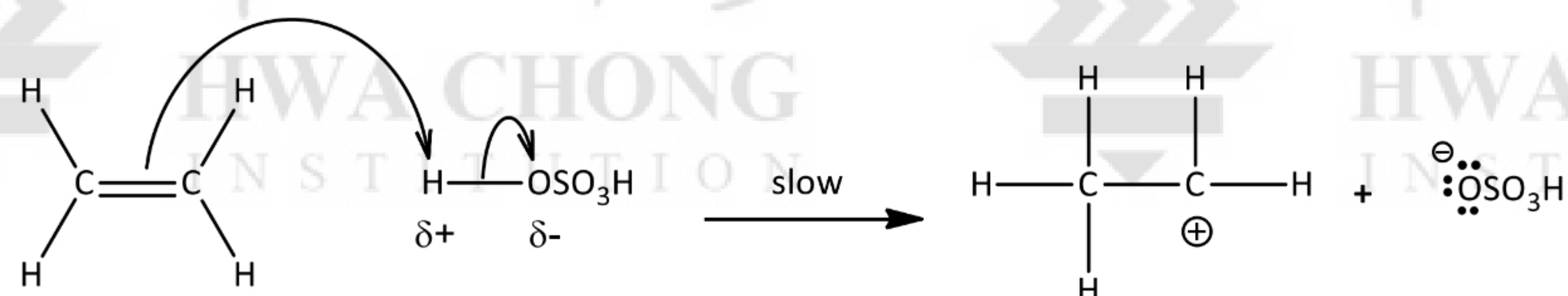


APPENDIX

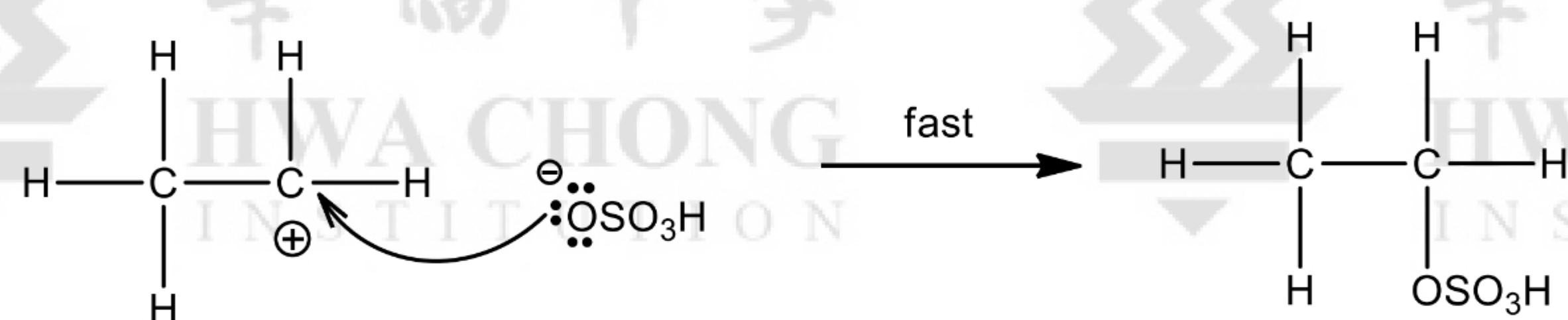
Electrophilic addition of water/steam mechanism:

Using ethene as an example, the mechanism for the acid-catalysed hydration of ethene is as follows:

Step 1: Protonation of the double bond to form a carbocation.



Step 2: Nucleophilic attack by HSO_4^- on carbocation to produce a hydrogensulfate.



The hydrogensulfate is then added to cold water. Water acts as a nucleophile to attack the hydrogensulfate. The $-\text{OSO}_3\text{H}$ group is substituted with $-\text{OH}$ group, producing the alcohol and regenerating the sulfuric acid catalyst.



