Organic Chemistry

Alkenes (2)

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Alkenes
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http://ocw.ump.edu.my/course/view.php?id=152

Expected Outcomes

In the completion of this chapter, student will have the ability to:

- Describe characteristics and physical properties of alkene
- Draw and name alkene using IUPAC nomenclature
- Write alkene reaction mechanism

Contents

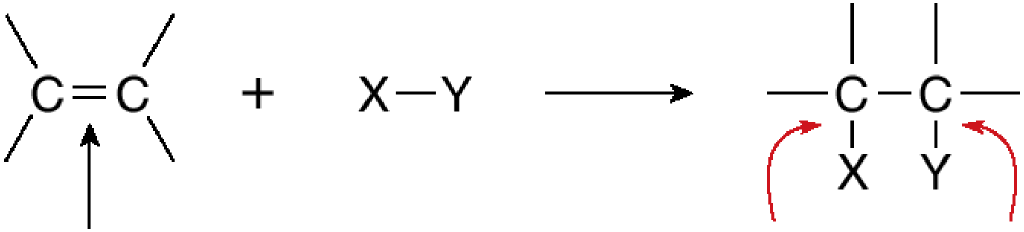
- Alkenes
- Physical properties
- Nomenclature
- Alkene reaction mechanisms

Alkenes

Introduction to Addition Reactions

- **The characteristic reaction of alkenes is addition—the π bond is broken and two new σ bonds are formed.**

Addition reaction



This π bond is broken.

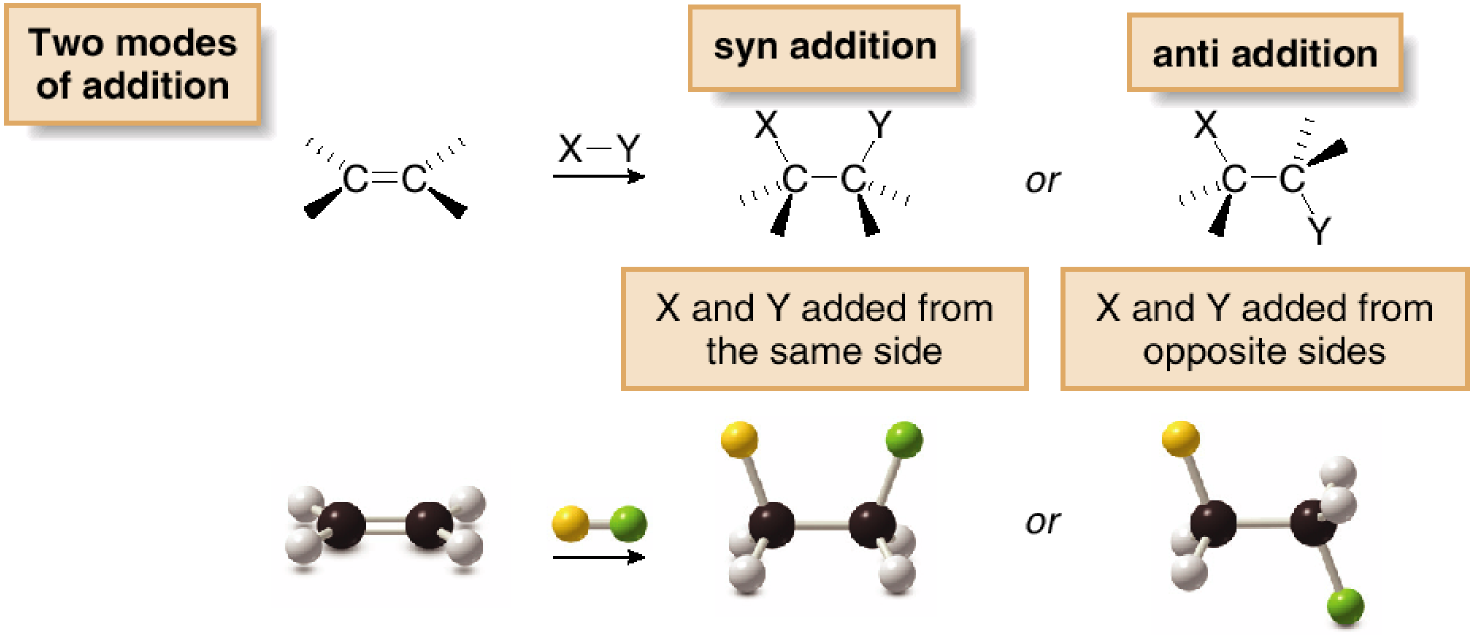
Two σ bonds are formed.

- **Alkenes are electron rich, with the electron density of the π bond concentrated above and below the plane of the molecule.**
- **Because alkenes are electron rich, simple alkenes do not react with nucleophiles or bases, reagents that are themselves electron rich. Alkenes react with electrophiles.**

Alkenes

Introduction to Addition Reactions

- **Because the carbon atoms of a double bond are both trigonal planar, the elements of X and Y can be added to them from the same side or from opposite sides.**



Two modes of addition

syn addition

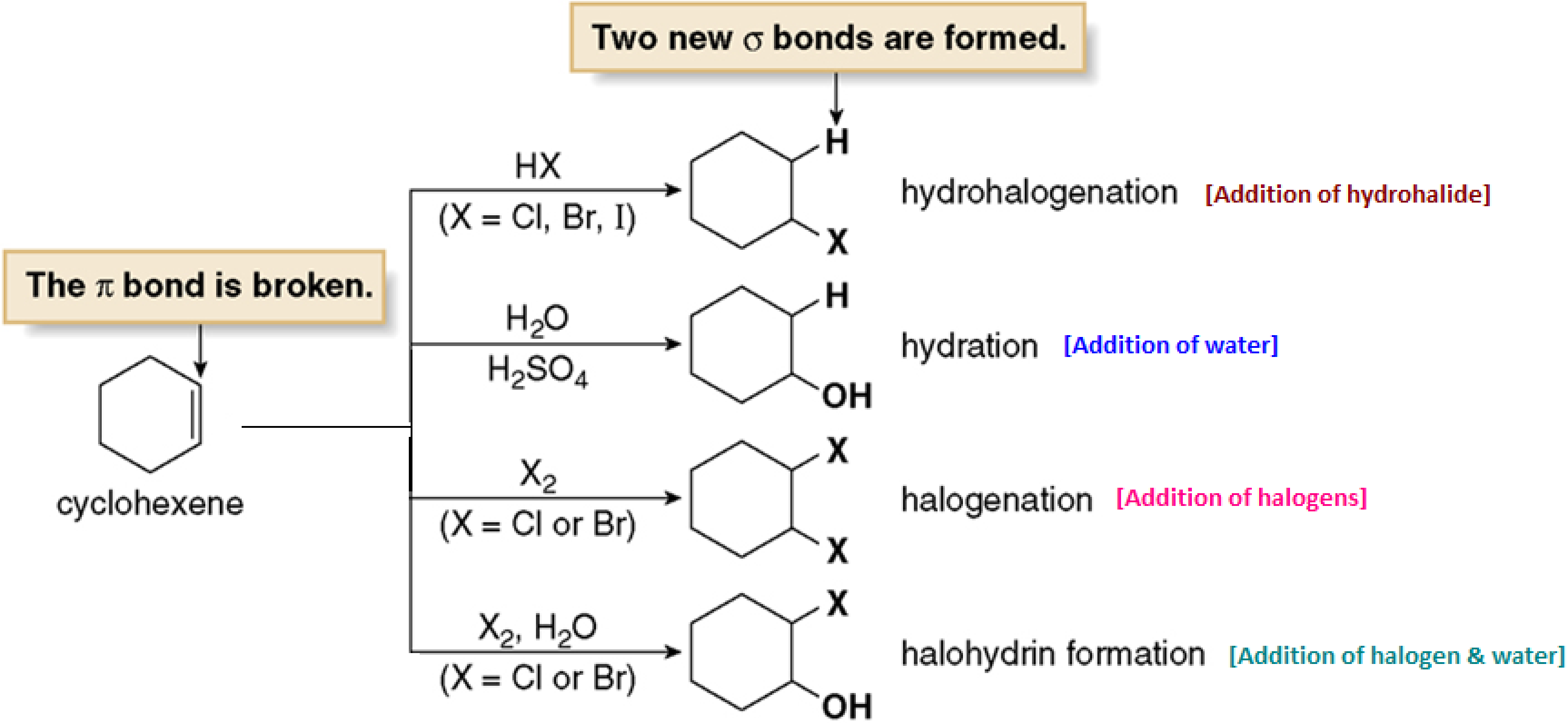
anti addition

X and Y added from the same side

X and Y added from opposite sides

- *Syn addition* takes place when both X and Y are added from the *same* side.
- *Anti addition* takes place when X and Y are added from *opposite* sides.

Introduction to Addition Reactions



Two new σ bonds are formed.

The π bond is broken.

cyclohexene

HX (X = Cl, Br, I) → hydrohalogenation [Addition of hydrohalide]

H_2O, H_2SO_4 → hydration [Addition of water]

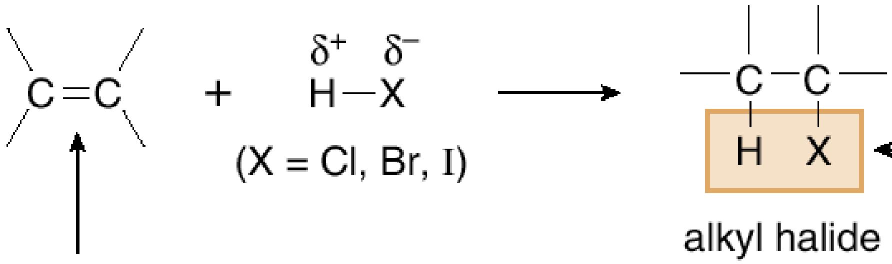
X_2 (X = Cl or Br) → halogenation [Addition of halogens]

X_2, H_2O (X = Cl or Br) → halohydrin formation [Addition of halogen & water]

Alkenes

Hydrohalogenation—Electrophilic Addition of HX

Hydrohalogenation



HX is added.

alkyl halide

This π bond is broken.

- **Two bonds are broken in this reaction—the weak π bond of the alkene and the HX bond—and two new σ bonds are formed—one to H and one to X.**
- **Recall that the H—X bond is polarized, with a partial positive charge on H. Because the electrophilic H end of HX is attracted to the electron-rich double bond, these reactions are called electrophilic additions.**

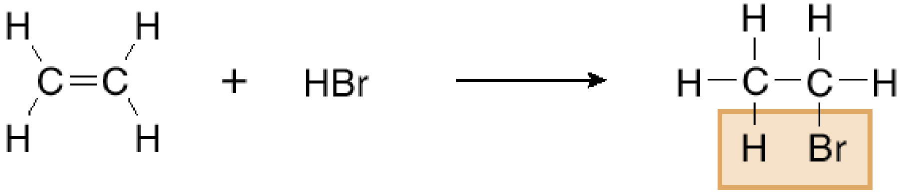
Alkenes

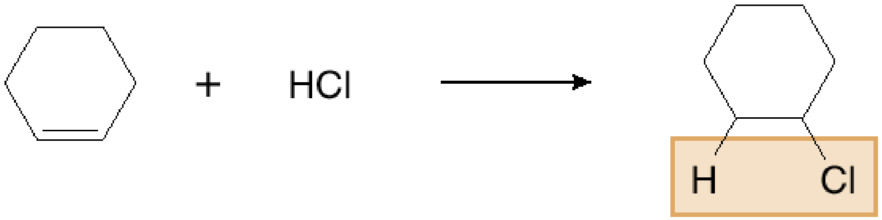
Hydrohalogenation—Electrophilic Addition of HX

To draw the products of an addition reaction:

- Locate the C – C double bond.
- Identify the σ bond of the reagent that breaks—namely, the H – X bond in hydrohalogenation.
- Break the π bond of the alkene and the σ bond of the reagent, and form two new σ bonds to the C atoms of the double bond.

Examples

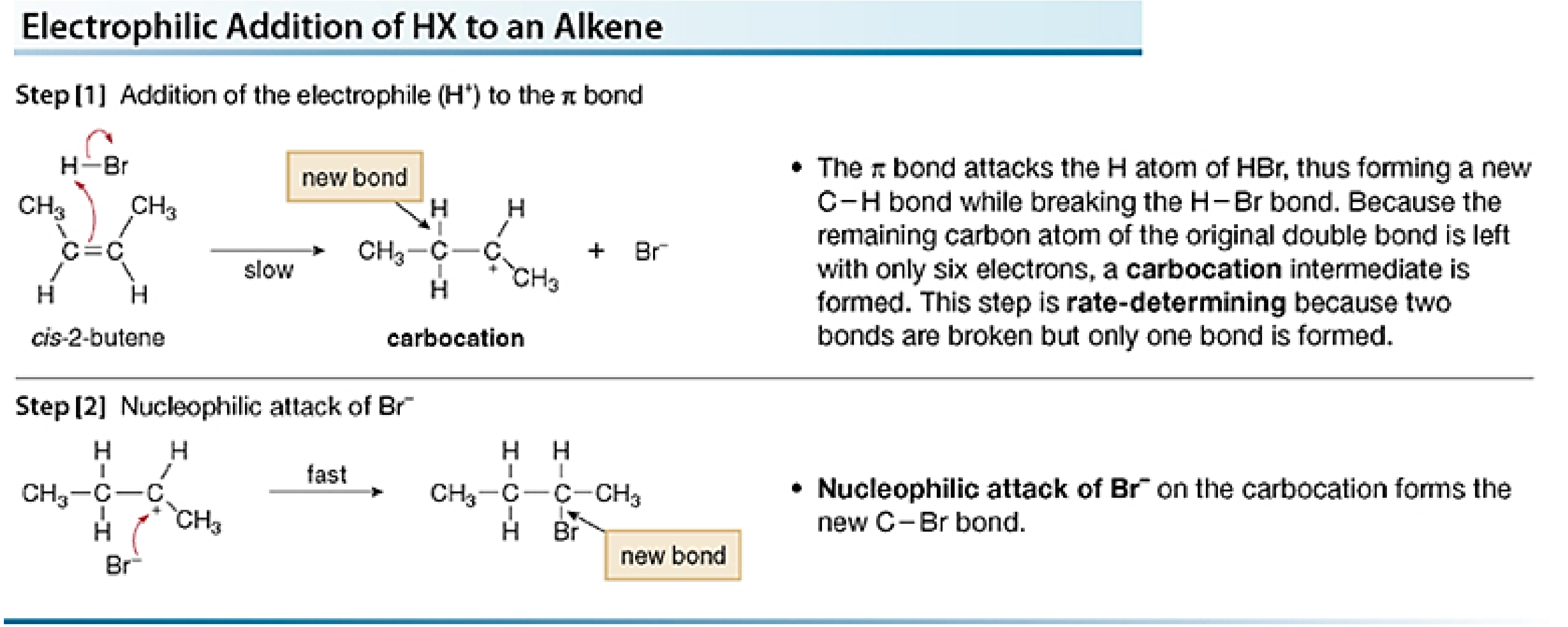




Alkenes

Hydrohalogenation—Electrophilic Addition of HX

- The mechanism of electrophilic addition consists of two successive Lewis acid-base reactions. In step 1, the alkene is the Lewis base that donates an electron pair to H—Br, the Lewis acid, while in step 2, Br^- is the Lewis base that donates an electron pair to the carbocation, the Lewis acid.



Electrophilic Addition of HX to an Alkene

Step [1] Addition of the electrophile (H^+) to the π bond

- The π bond attacks the H atom of HBr, thus forming a new C–H bond while breaking the H–Br bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond is formed.

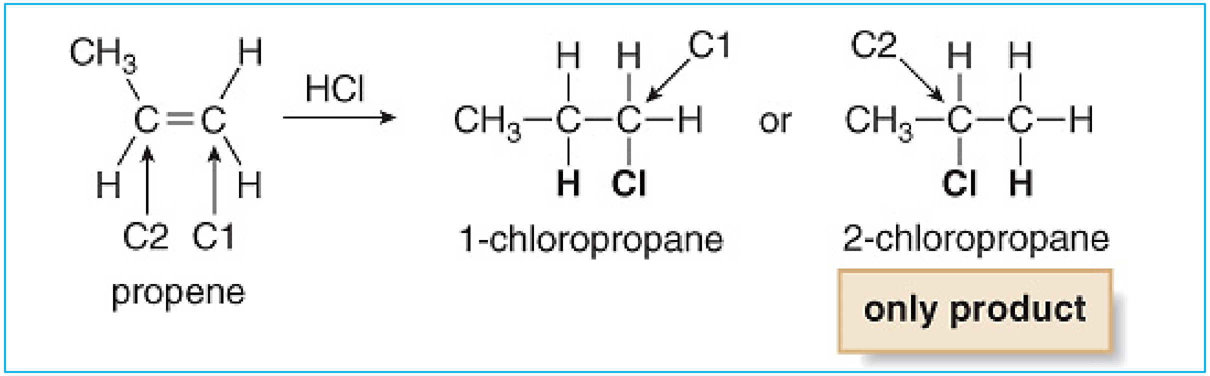
Step [2] Nucleophilic attack of Br^-

- **Nucleophilic attack of Br^-** on the carbocation forms the new C–Br bond.

Alkenes

Hydrohalogenation—Markovnikov’s Rule

- **With an unsymmetrical alkene, HX can add to the double bond to give two constitutional isomers, but only one is actually formed:**



- **This is a specific example of a general trend called Markovnikov’s rule.**
- **Markovnikov’s rule states that in the addition of HX to an unsymmetrical alkene, the H atom adds to the less substituted carbon atom—that is, the carbon that has the greater number of H atoms to begin with.**

Markovnikov’s Rule

In the ionic addition of an acid to the carbon-carbon double bond of an alkene, the hydrogen of the acid attaches itself to the carbon atom which already holds the *greater* number of hydrogens.

–“Them that has, gets!”

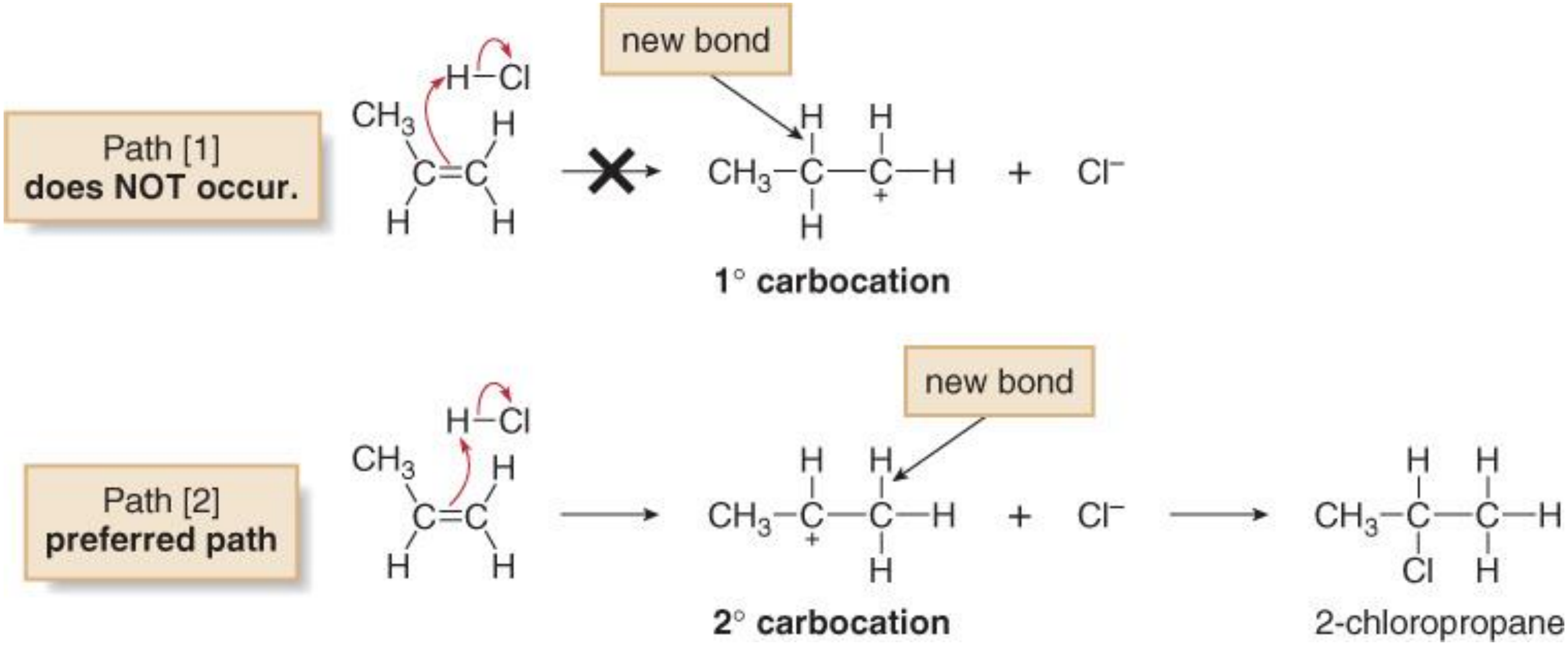
–“The richer get richer!”

(V. W. Markovnikov -- 1838 - 1904)

Alkenes

Hydrohalogenation—Markovnikov's Rule

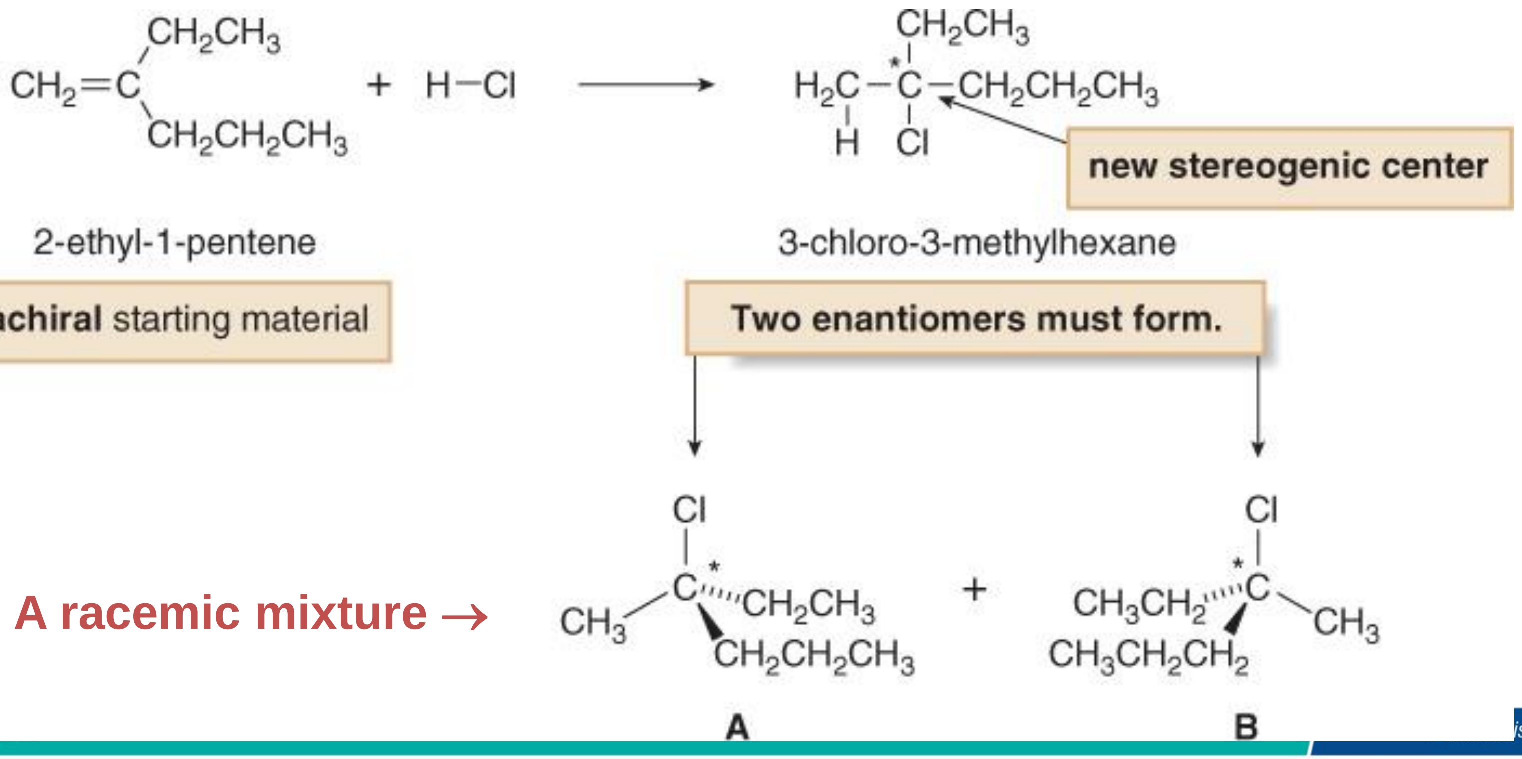
- **The basis of Markovnikov's rule is the formation of a carbocation in the rate-determining step of the mechanism.**
- **In the addition of HX to an unsymmetrical alkene, the H atom is added to the less substituted carbon to form the more stable, more substituted carbocation.**



Alkenes

Hydrohalogenation—Reaction Stereochemistry

- **Recall that trigonal planar atoms react with reagents from two directions with equal probability.**
- **Achiral starting materials yield achiral products.**
- **Sometimes new stereogenic centers are formed from hydrohalogenation:**

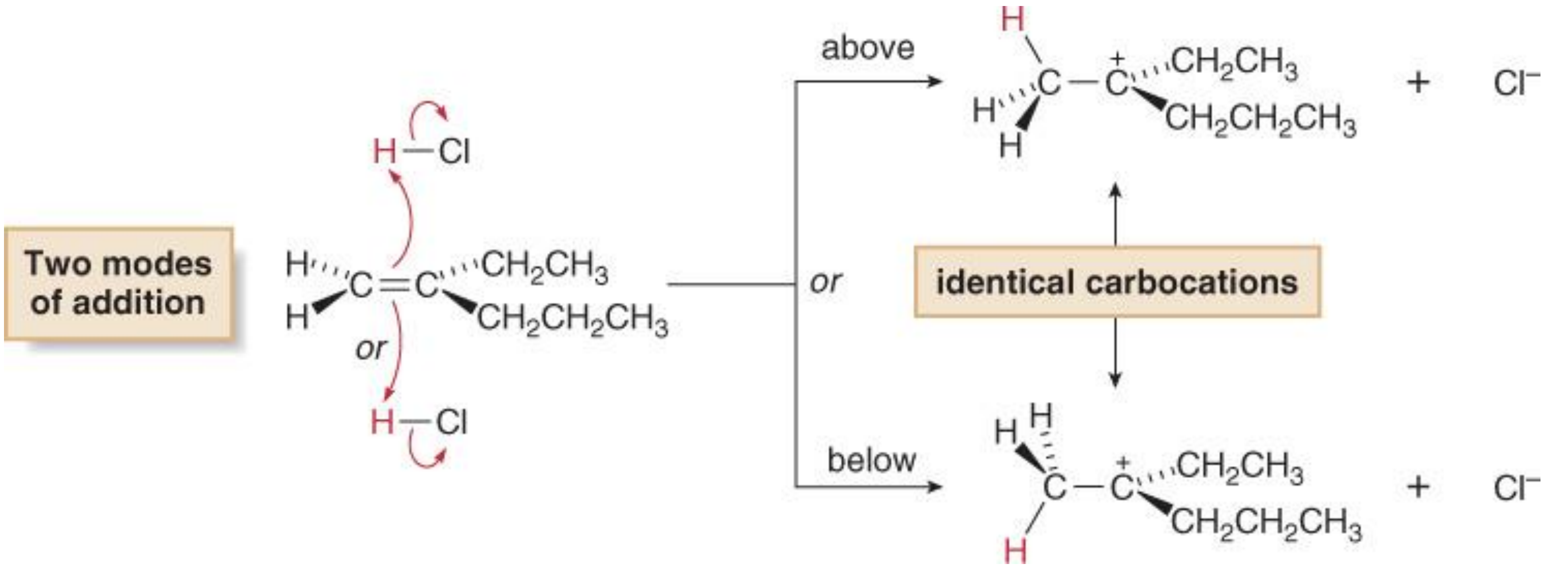


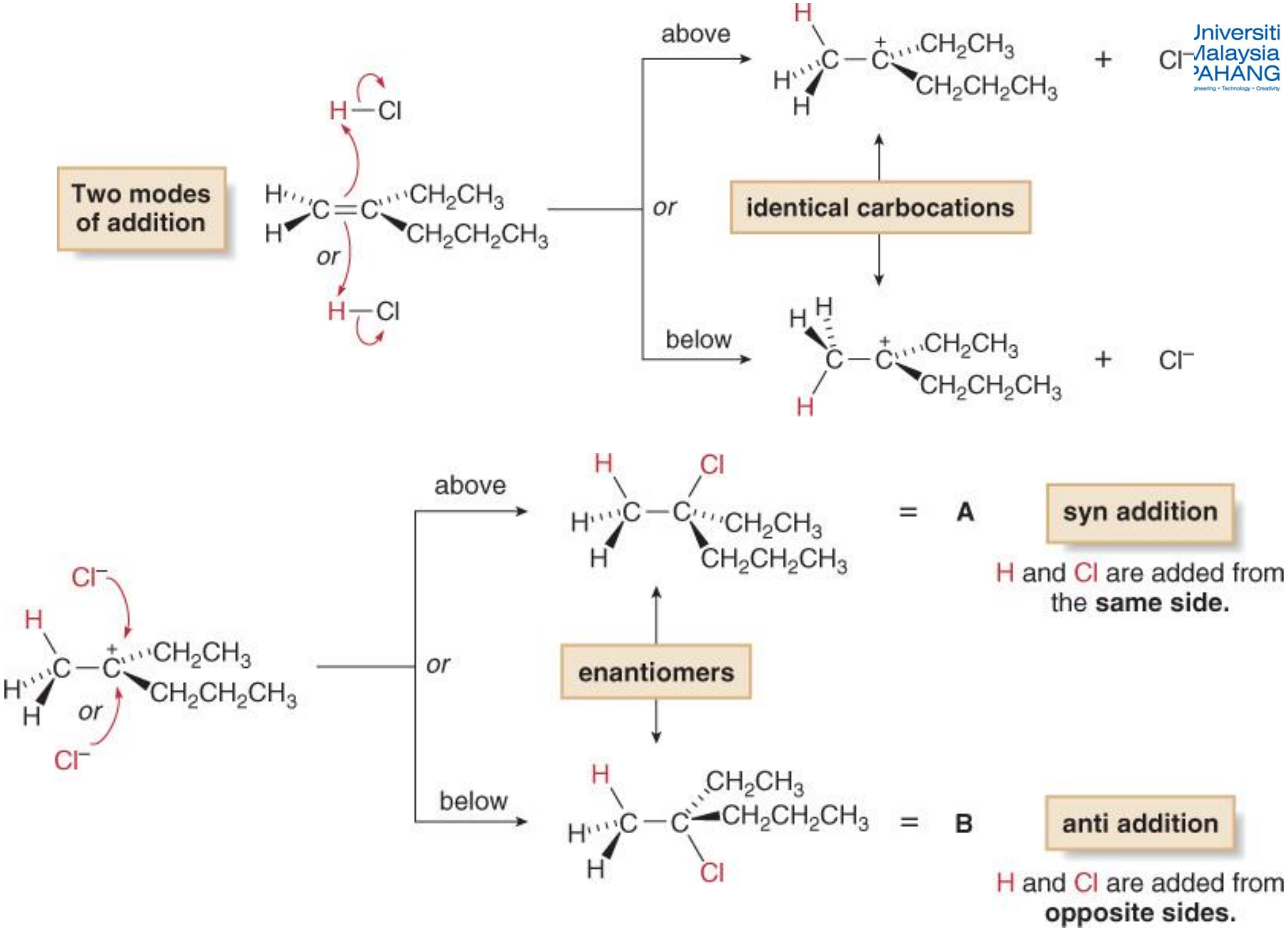
A racemic mixture →

Alkenes

Hydrohalogenation—Reaction Stereochemistry

- The mechanism of hydrohalogenation illustrates why two enantiomers are formed. Initial addition of H^+ occurs from either side of the planar double bond.
- Both modes of addition generate the same achiral carbocation. Either representation of this carbocation can be used to draw the second step of the mechanism.





Two modes of addition

identical carbocations

enantiomers

syn addition

H and Cl are added from the **same side.**

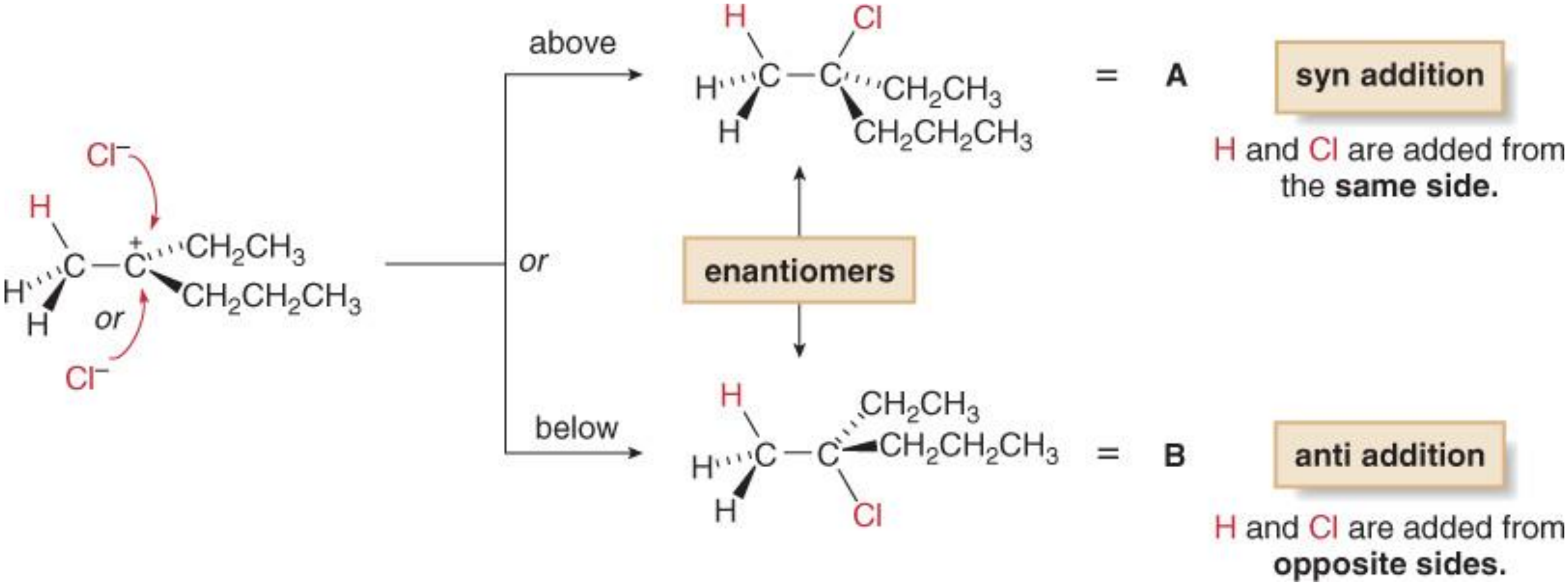
anti addition

H and Cl are added from **opposite sides.**

Alkenes

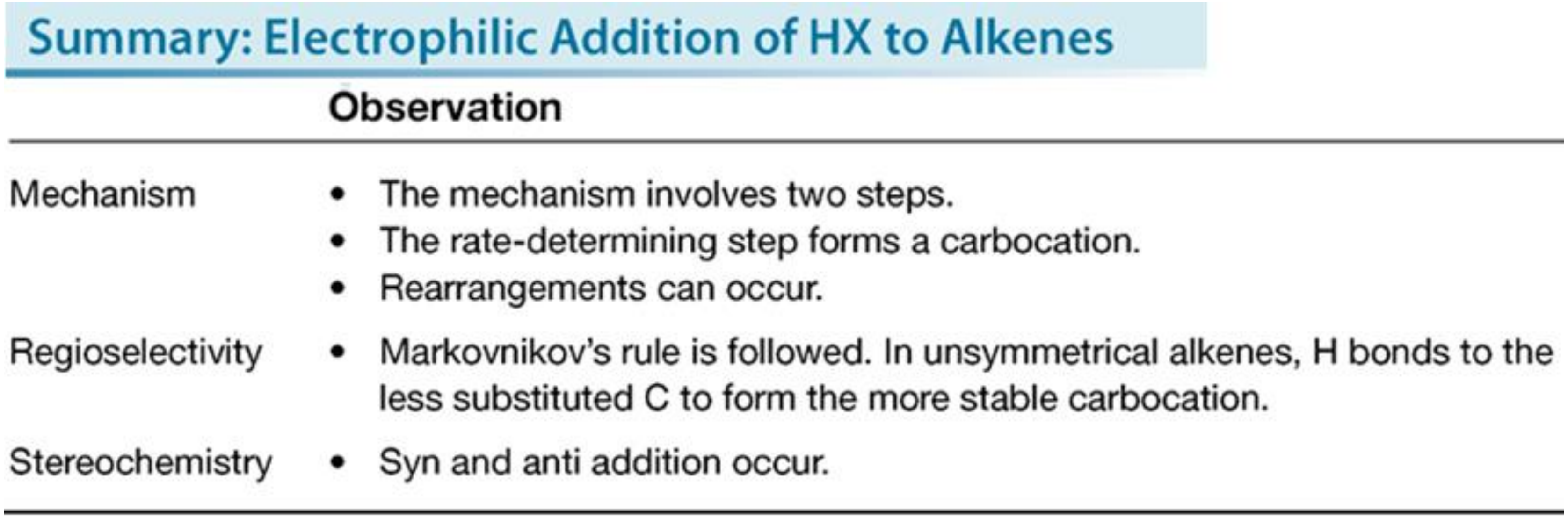
Hydrohalogenation—Reaction Stereochemistry

- Nucleophilic attack of Cl^{-} on the trigonal planar carbocation also occurs from two different directions, forming two products, A and B, having a new stereogenic center.
- A and B are enantiomers. Since attack from either direction occurs with equal probability, a racemic mixture of A and B is formed.



Alkenes

Hydrohalogenation—Summary



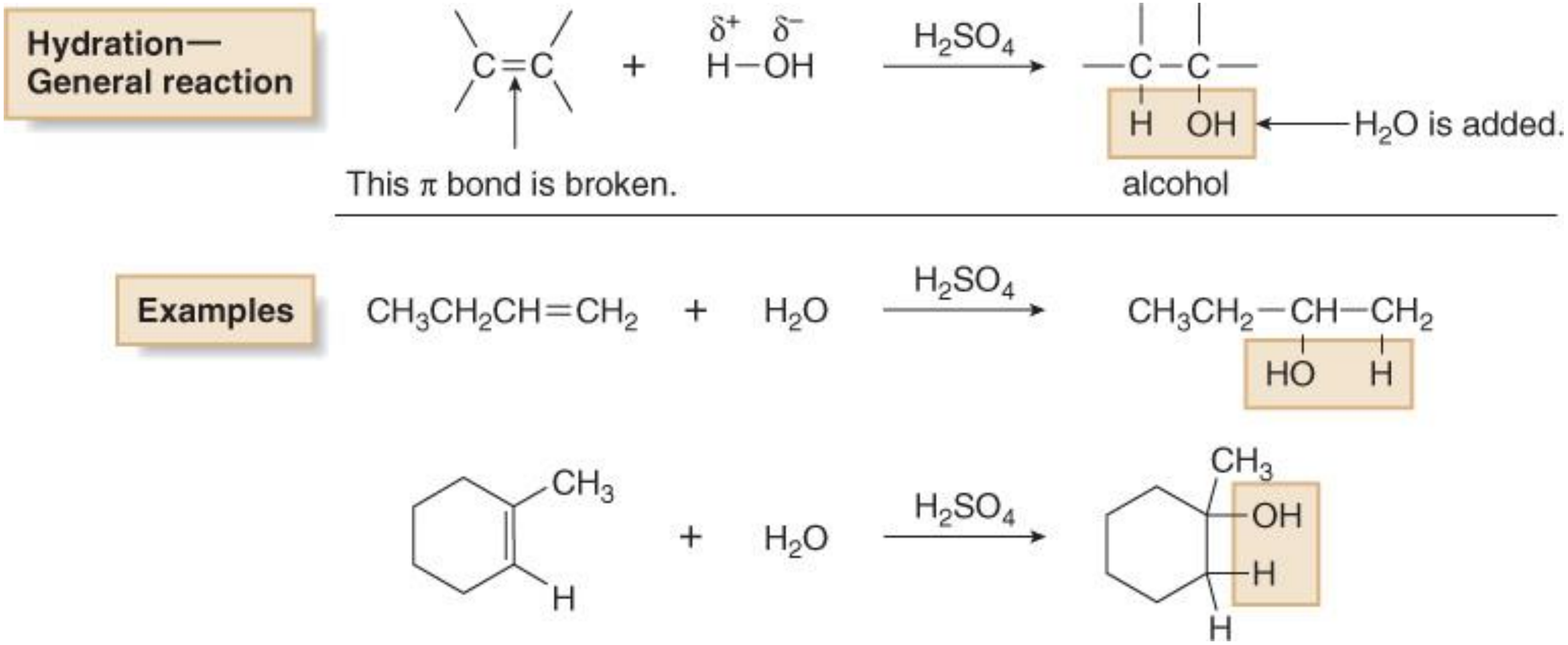
Summary: Electrophilic Addition of HX to Alkenes

	Observation
Mechanism	• The mechanism involves two steps. • The rate-determining step forms a carbocation. • Rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	• Syn and anti addition occur.

Alkenes

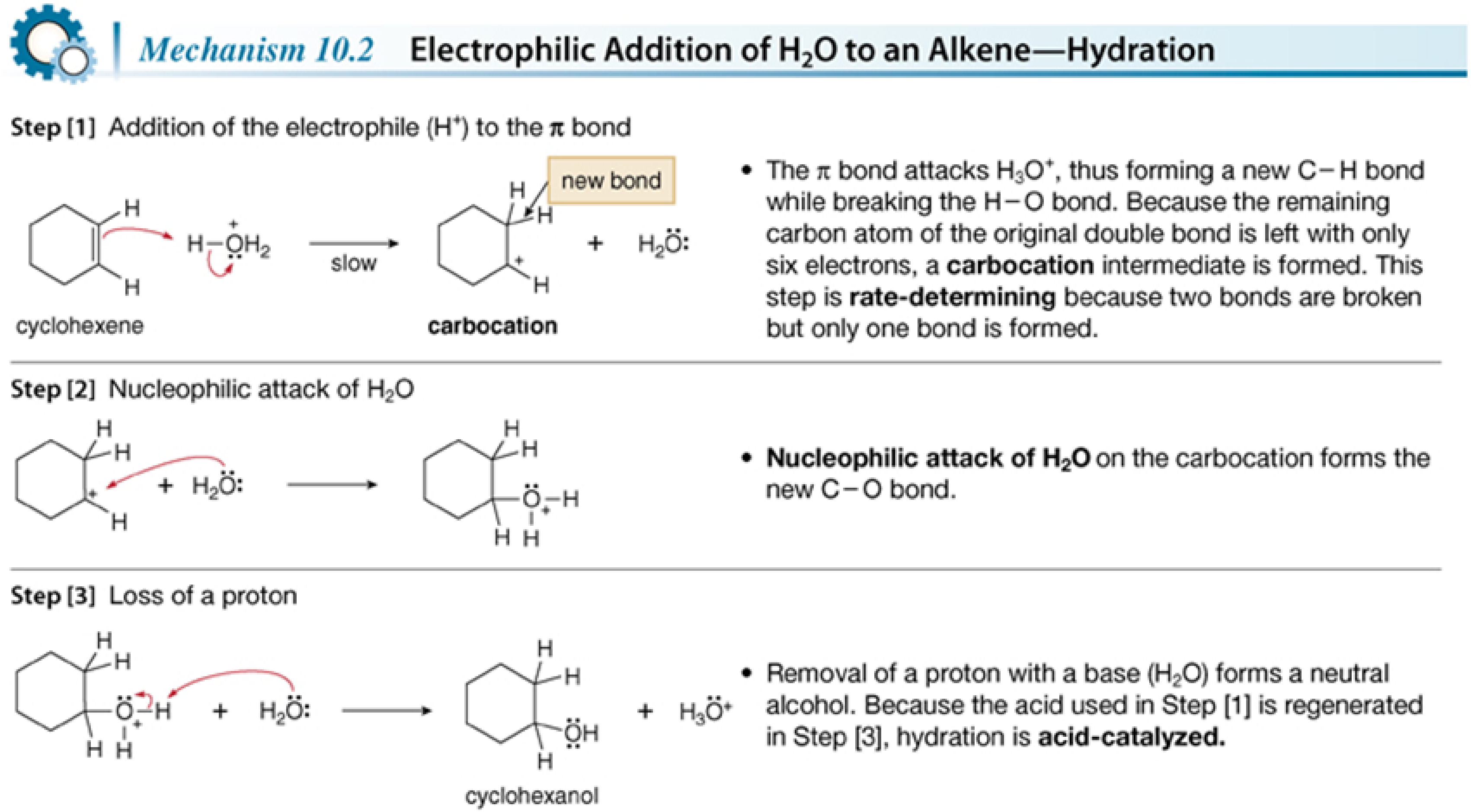
Hydration—Electrophilic Addition of Water

- Hydration is the addition of water to an alkene to form an alcohol.



Alkenes

Hydration—Electrophilic Addition of Water



Mechanism 10.2 Electrophilic Addition of H_2O to an Alkene—Hydration

Step [1] Addition of the electrophile (H^+) to the π bond

- The π bond attacks H_3O^+, thus forming a new C–H bond while breaking the H–O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond is formed.

Step [2] Nucleophilic attack of H_2O

- **Nucleophilic attack of H_2O** on the carbocation forms the new C–O bond.

Step [3] Loss of a proton

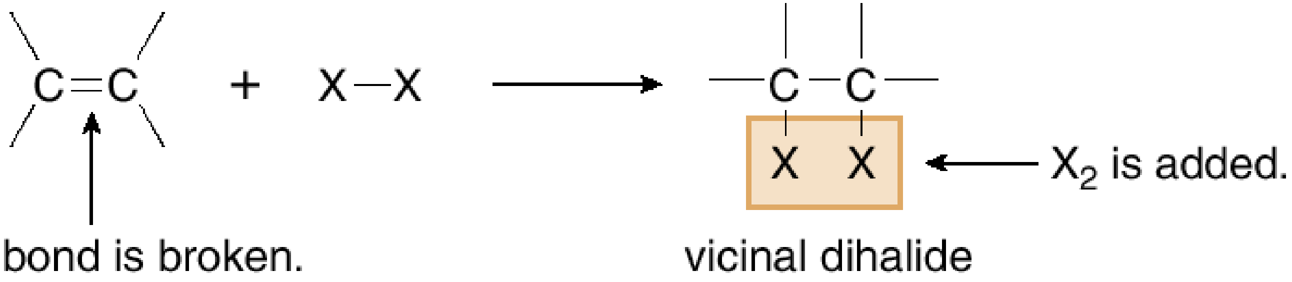
- Removal of a proton with a base (H_2O) forms a neutral alcohol. Because the acid used in Step [1] is regenerated in Step [3], hydration is **acid-catalyzed.**

Alkenes

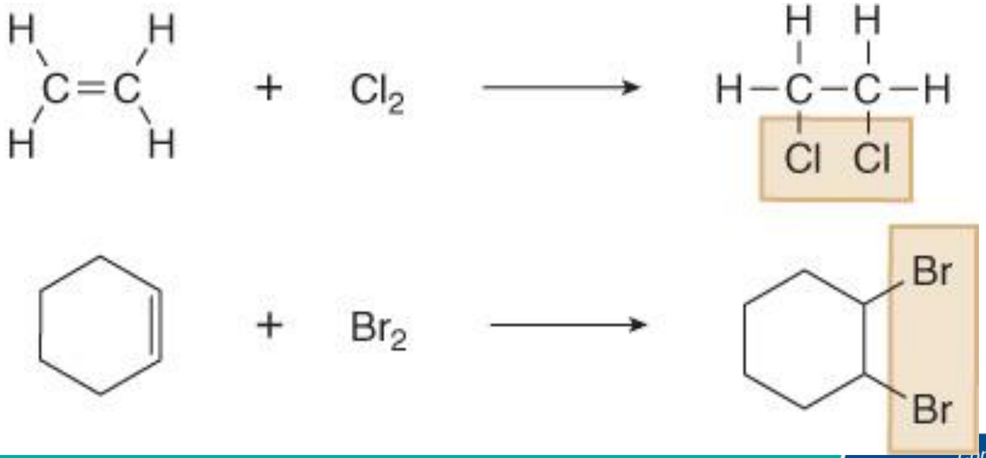
Halogenation—Addition of Halogen

- Halogenation is the addition of X_2 (X = Cl or Br) to an alkene to form a vicinal dihalide.

Halogenation



Examples



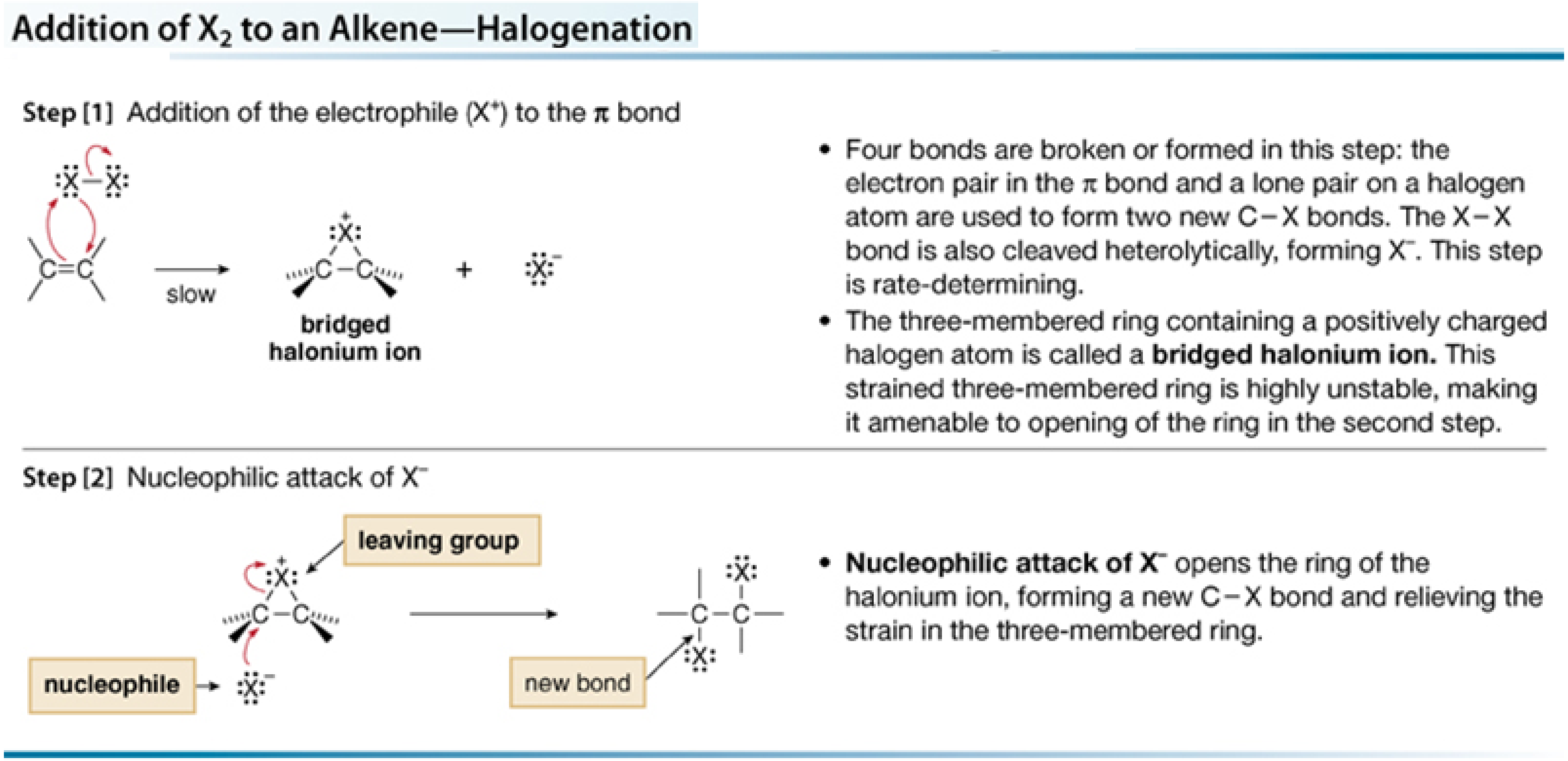
Alkenes

Halogenation—Addition of Halogen

- Halogens add to π bonds because halogens are polarizable.
- The electron rich double bond induces a dipole in an approaching halogen molecule, making one halogen atom electron deficient and the other electron rich ($X^{\delta+}—X^{\delta-}$).
- The electrophilic halogen atom is then attracted to the nucleophilic double bond, making addition possible.
- Two facts demonstrate that halogenation follows a different mechanism from that of hydrohalogenation or hydration.
  - No rearrangements occur
  - Only anti addition of X_2 is observed
  - These facts suggest that carbocations are not intermediates.

Alkenes

Halogenation—Addition of Halogen



Addition of X_2 to an Alkene—Halogenation

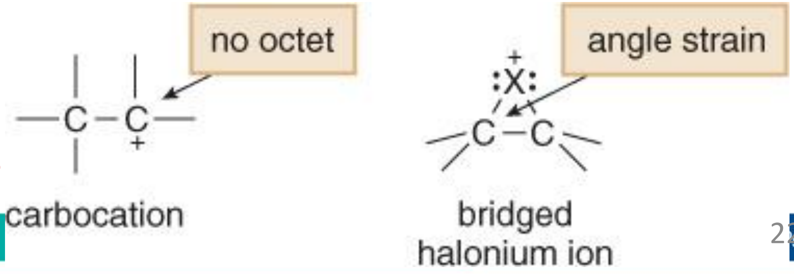
Step [1] Addition of the electrophile (X^+) to the π bond

- Four bonds are broken or formed in this step: the electron pair in the π bond and a lone pair on a halogen atom are used to form two new C–X bonds. The X–X bond is also cleaved heterolytically, forming X^-. This step is rate-determining.
- The three-membered ring containing a positively charged halogen atom is called a **bridged halonium ion.** This strained three-membered ring is highly unstable, making it amenable to opening of the ring in the second step.

Step [2] Nucleophilic attack of X^-

- **Nucleophilic attack of X^-** opens the ring of the halonium ion, forming a new C–X bond and relieving the strain in the three-membered ring.

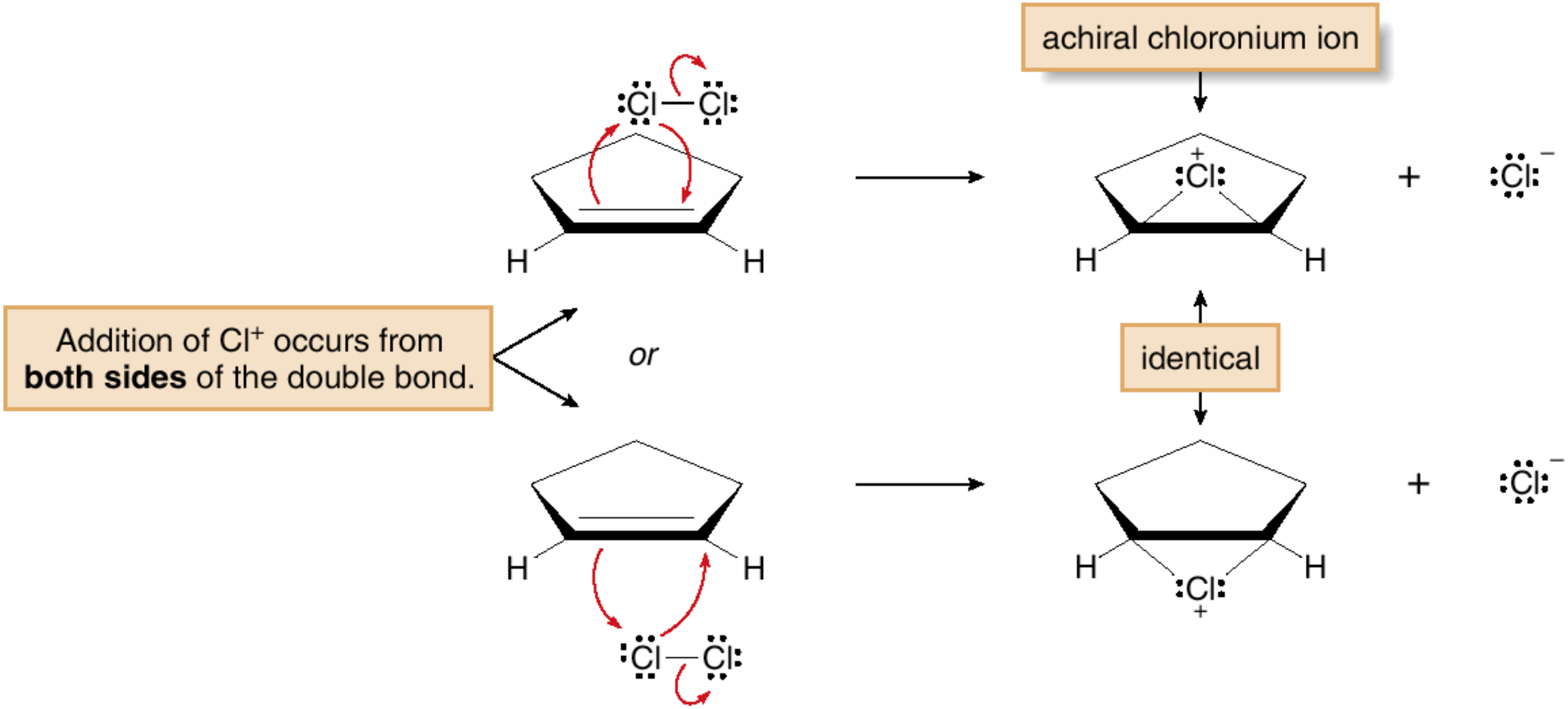
Carbocations are unstable because they have only six electrons around carbon. Halonium ions are unstable because of ring strain.



Alkenes

Halogenation—Reaction Stereochemistry

- Consider the chlorination of cyclopentene to afford both enantiomers of *trans*-1,2-dichlorocyclopentane, with no cis products.
- Initial addition of the electrophile Cl^+ from (Cl_2) occurs from either side of the planar double bond to form a bridged chloronium ion.



achiral chloronium ion

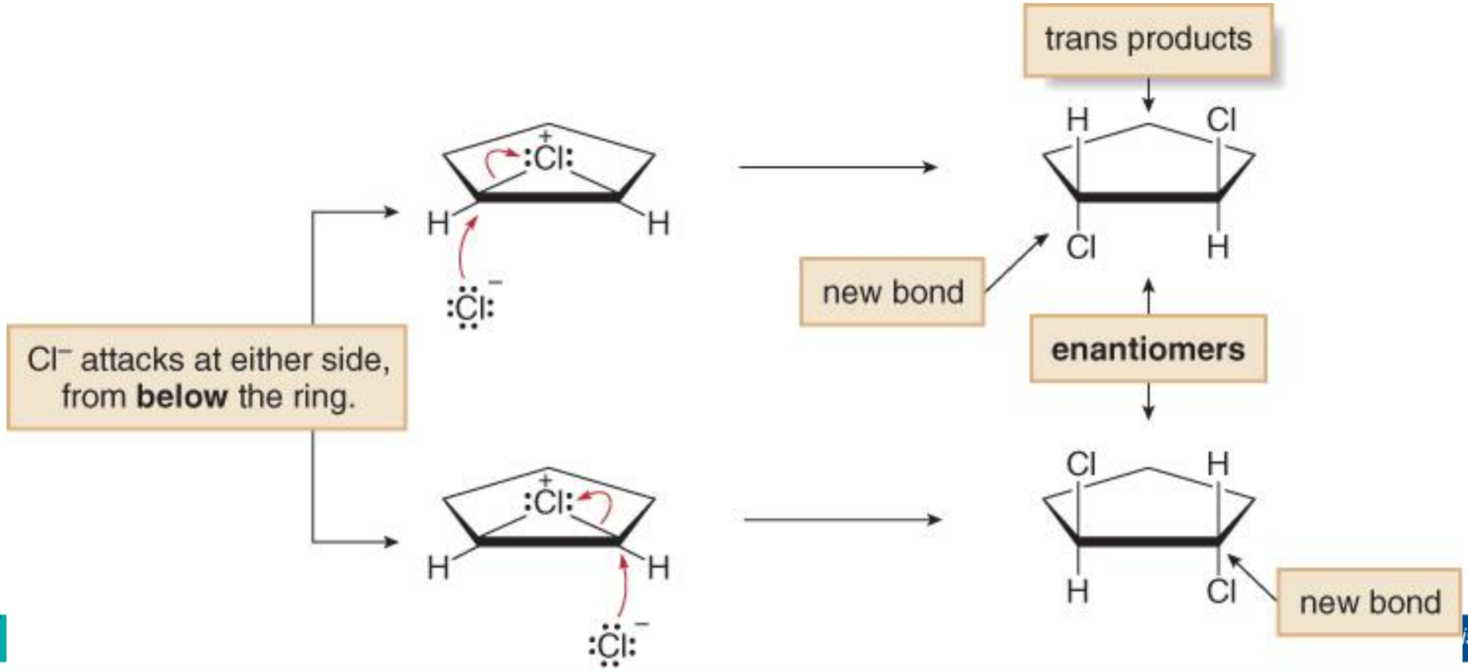
identical

Addition of Cl^+ occurs from **both sides** of the double bond.

Alkenes

Halogenation—Reaction Stereochemistry

- In the second step, nucleophilic attack of Cl^- must occur from the backside.
- Since the nucleophile attacks from below and the leaving group departs from above, the two Cl atoms in the product are oriented trans to each other.
- Backside attack occurs with equal probability at either carbon of the three-membered ring to yield a racemic mixture.



trans products

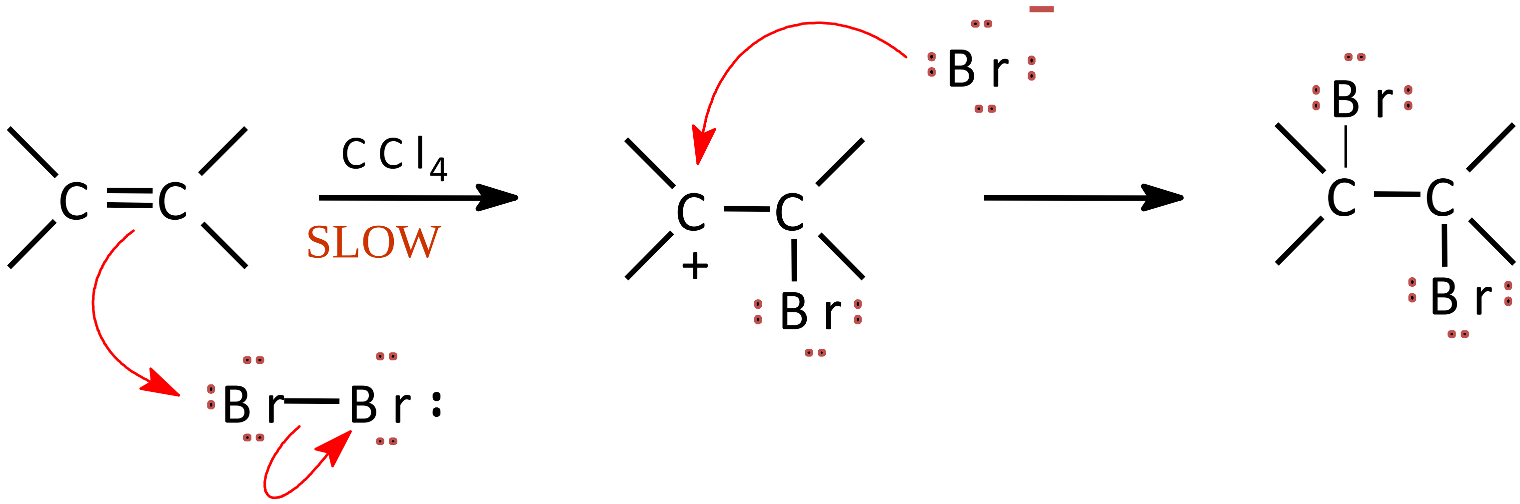
Cl⁻ attacks at either side, from **below** the ring.

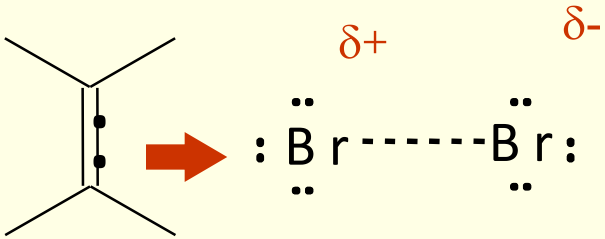
new bond

enantiomers

new bond

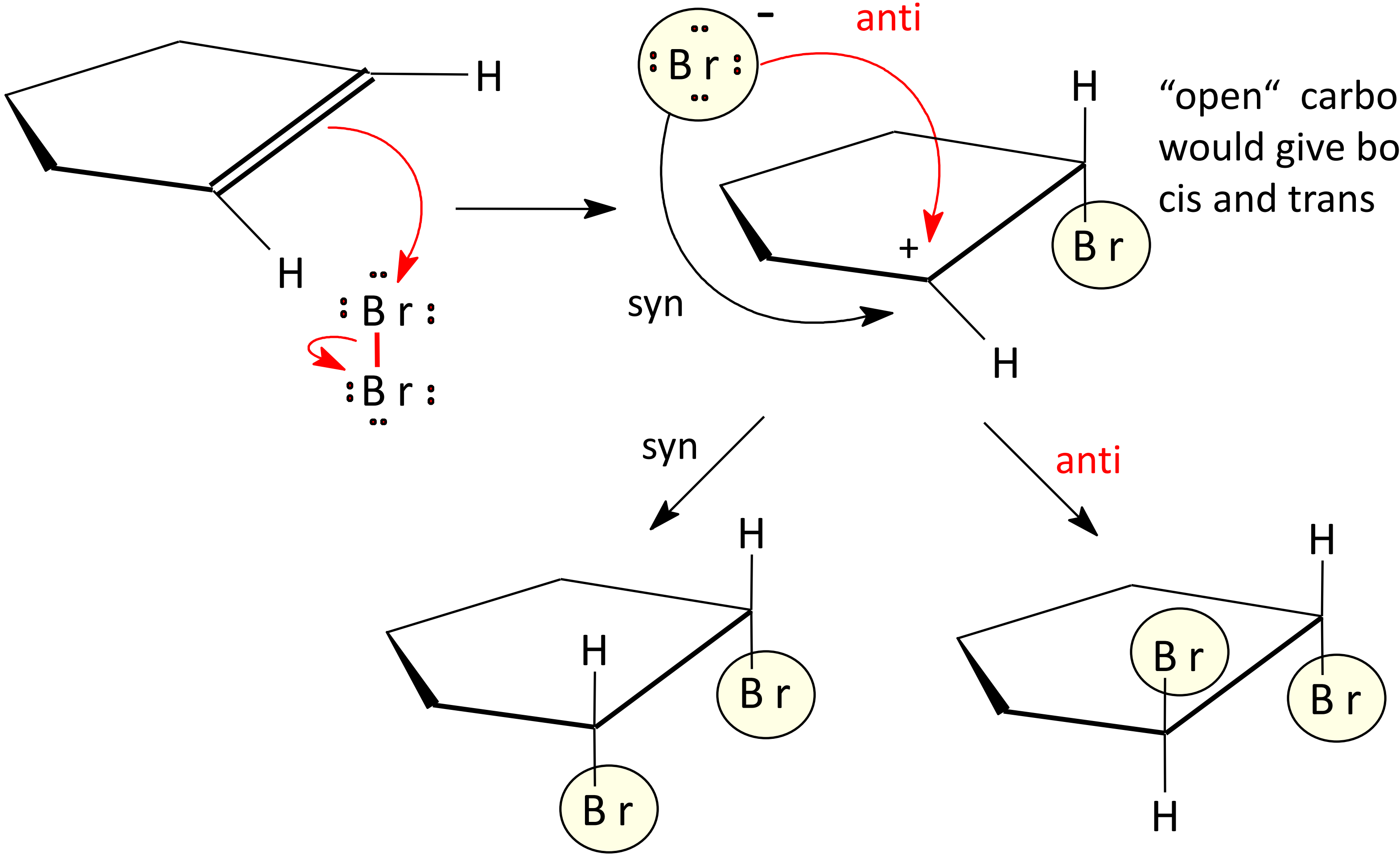
ADDITION OF BROMINE





alkene polarizes bromine

ANTI ADDITION



"open" carbocation would give both cis and trans

cis compound

NOT OBSERVED

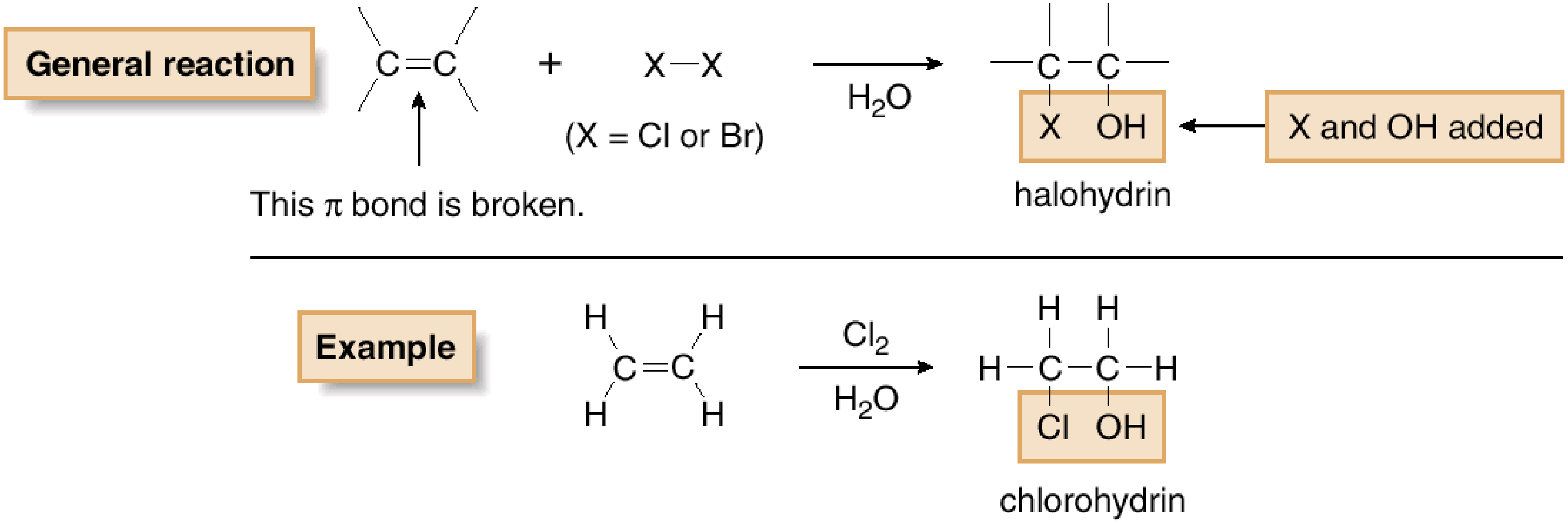
trans compound

ACTUAL PRODUCT

Alkenes

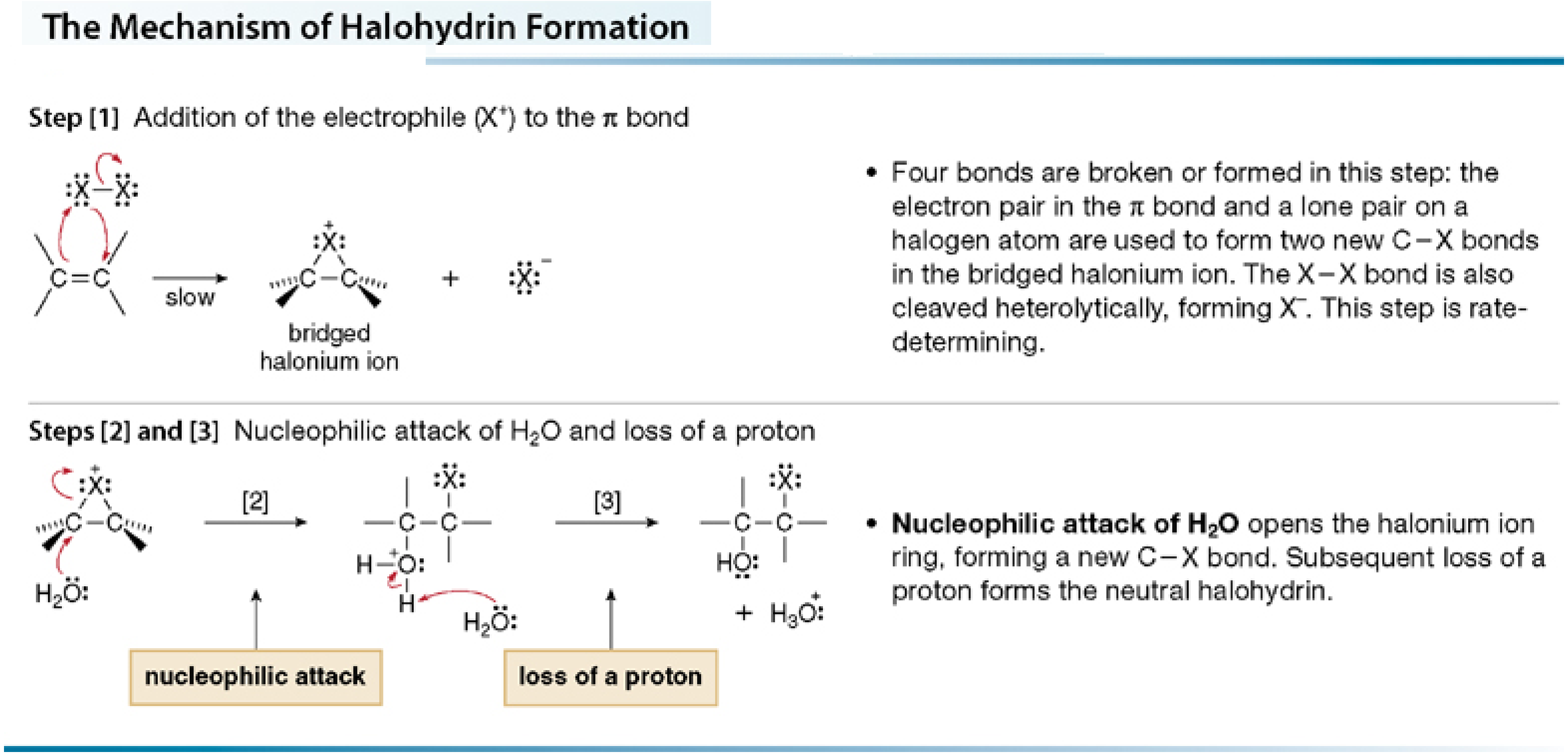
Halohydrin Formation

Treatment of an alkene with a halogen X_2 and H_2O forms a halohydrin by addition of the elements of X and OH to the double bond.



Alkenes

Halohydrin Formation



The Mechanism of Halohydrin Formation

Step [1] Addition of the electrophile (X^+) to the π bond

- Four bonds are broken or formed in this step: the electron pair in the π bond and a lone pair on a halogen atom are used to form two new C–X bonds in the bridged halonium ion. The X–X bond is also cleaved heterolytically, forming X^-. This step is rate-determining.

Steps [2] and [3] Nucleophilic attack of H_2O and loss of a proton

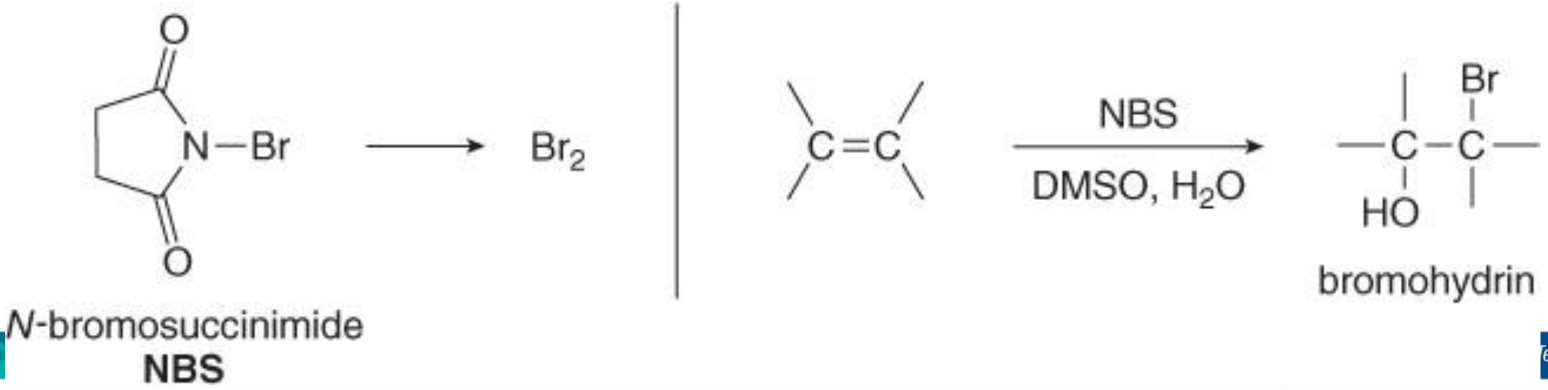
- **Nucleophilic attack of H_2O** opens the halonium ion ring, forming a new C–X bond. Subsequent loss of a proton forms the neutral halohydrin.

Even though $X^–$ is formed in step [1] of the mechanism, its concentration is small compared to H_2O (often the solvent), so H_2O and not $X^–$ is the nucleophile.

Alkenes

Halohydrin Formation

- **Although the combination of Br_2 and H_2O effectively forms bromohydrins from alkenes, other reagents can also be used.**
- **Bromohydrins are also formed with *N*-bromosuccinimide (NBS) in aqueous DMSO $[(CH_3)_2S{=}O]$.**
- **In H_2O, NBS decomposes to form Br_2, which then goes on to form a bromohydrin by the same reaction mechanism.**



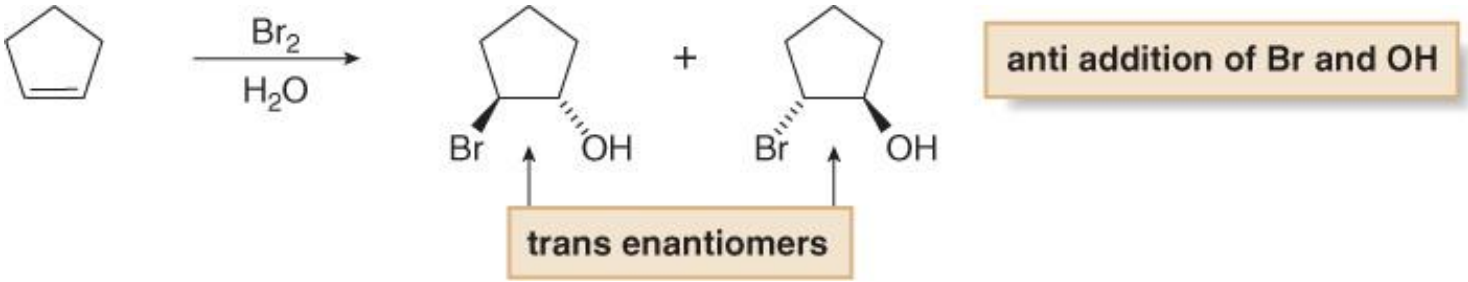
N-bromosuccinimide
NBS

bromohydrin

Alkenes

Halohydrin Formation

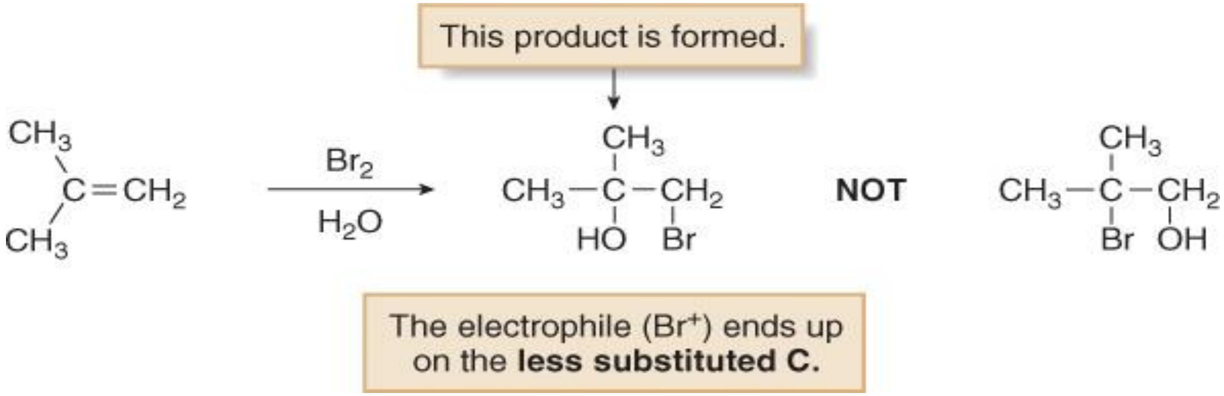
Because the bridged halonium ion is opened by backside attack of H_2O, addition of X and OH occurs in an anti fashion and trans products are formed.



anti addition of Br and OH

trans enantiomers

With unsymmetrical alkenes, the preferred product has the electrophile X^+ bonded to the less substituted carbon, and the nucleophile (H_2O) bonded to the more substituted carbon.



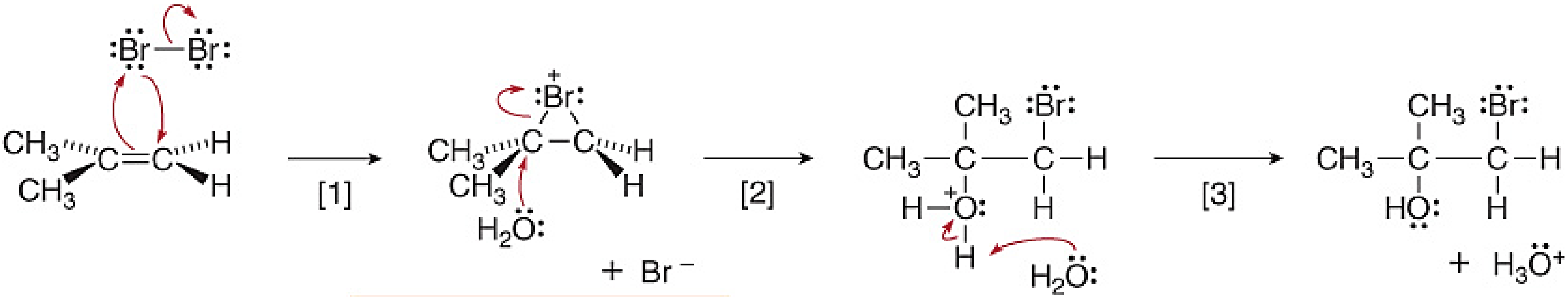
This product is formed.

The electrophile (Br^+) ends up on the **less substituted C.**

Alkenes

Halohydrin Formation

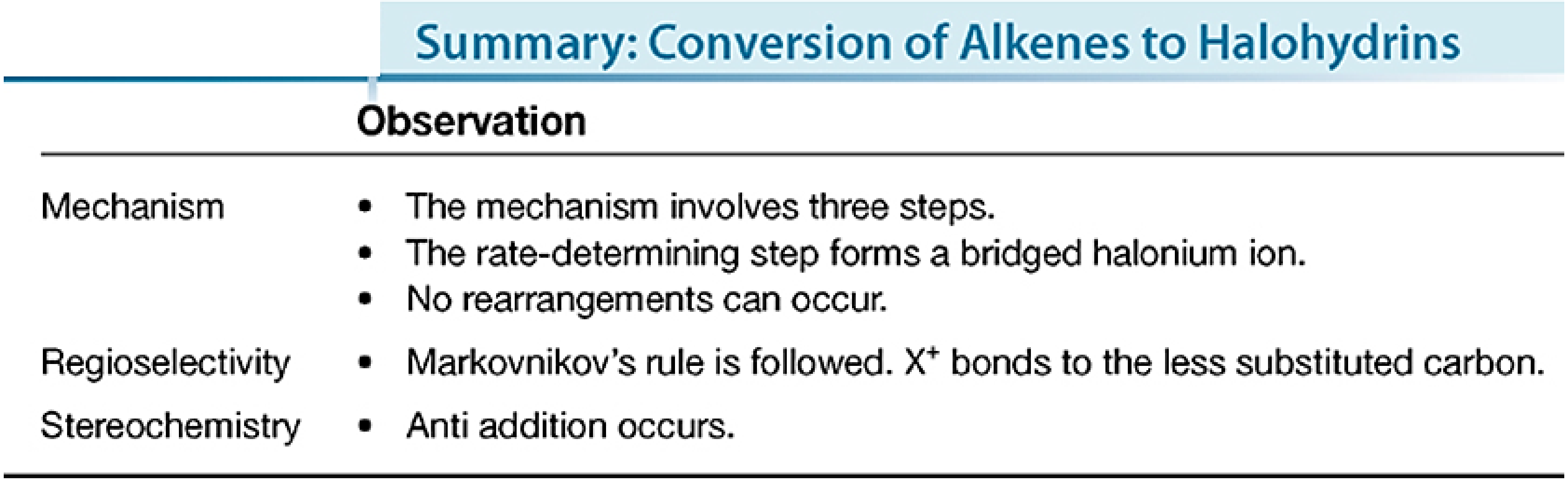
Halohydrin formation in an unsymmetrical alkene



nucleophilic attack at the **more substituted C**

Alkenes

Halohydrin Formation



Summary: Conversion of Alkenes to Halohydrins

	Observation
Mechanism	• The mechanism involves three steps. • The rate-determining step forms a bridged halonium ion. • No rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. X^+ bonds to the less substituted carbon.
Stereochemistry	• Anti addition occurs.

Alkenes

Calculating Degrees of Unsaturation

- An acyclic alkene has the general structural formula C_nH_{2n}.
- Alkenes are unsaturated hydrocarbons because they have fewer than the maximum number of hydrogen atoms per carbon.
- Cycloalkanes also have the general formula C_nH_{2n}.
- Each π bond or ring removes two hydrogen atoms from a molecule, and this introduces one degree of unsaturation.
- The number of degrees of unsaturation for a given molecular formula can be calculated by comparing the actual number of H atoms in a compound to the maximum number of H atoms possible for the number of carbons present if the molecule were a straight chain alkane.
- This procedure gives the total number of rings and/or π bonds in a molecule.

Possible structures for C_4H_6: