B.Sc.(H) Chemistry
Semester - II
Core Course - III (CC-III)
Organic Chemistry - I

III. Chemistry of Aliphatic Hydrocarbons
B. Carbon-Carbon pi bonds

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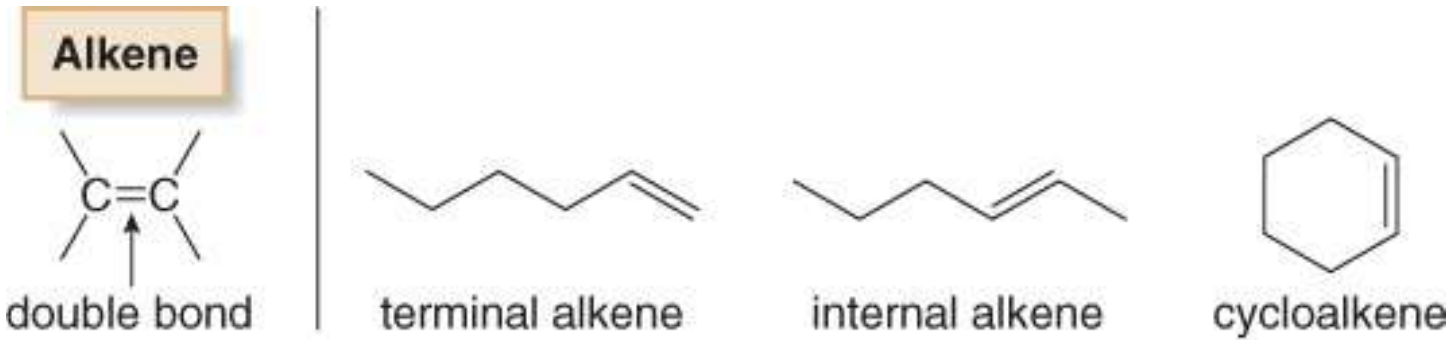
Carbon-Carbon pi bonds

Chapter Topics:

- **Chemical and physical properties**
- **Degrees of unsaturation**
- **Naming**
- **E,Z isomers**
- **Preparation: 1. Dehydrohalogenation**
  2. Dehydration
  3. Catalytic cracking
- **Reactions (addition):**
  1. HX ; 2. H_2O ; 3. Br_2 or Cl_2 ;
  4. Br_2/HOH or Cl_2/HOH
  5. Hydroboration/Oxidation
  6. Oxymercuration/demercuration

Alkenes : Introduction, Structure and Bonding

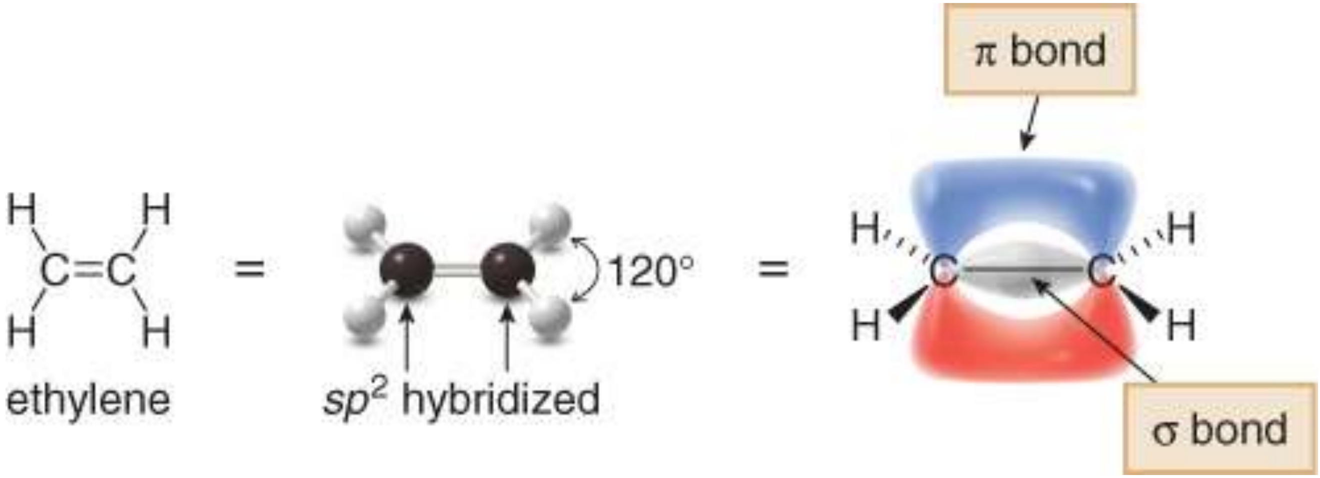
- **Alkenes are also called olefins.**
- **Alkenes contain a carbon—carbon double bond.**
- **Terminal alkenes have the double bond at the end of the carbon chain.**
- **Internal alkenes have at least one carbon atom bonded to each end of the double bond.**
- **Cycloalkenes contain a double bond in a ring.**



Introduction: Structure and Bonding

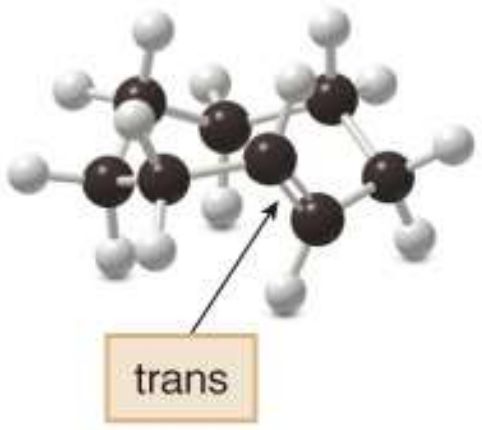
- Recall that the double bond consists of a π bond and a σ bond. The σ bond is stronger than the π bond.

- Each carbon is *sp*^{2} hybridized and trigonal planar, with bond angles of approximately 120°.

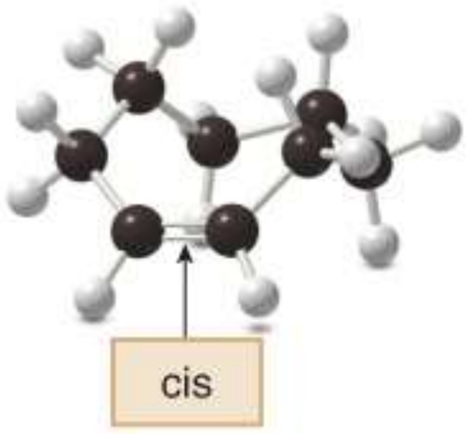


Introduction: Structure and Bonding

- **Cycloalkenes having fewer than eight carbon atoms have a cis geometry. A trans cycloalkene must have a carbon chain long enough to connect the ends of the double bond without introducing too much strain.**
- ***trans*-Cyclooctene is the smallest isolable trans cycloalkene. It is considerably less stable than *cis*-cyclooctene, making it one of the few alkenes having a higher energy trans isomer.**



trans-cyclooctene

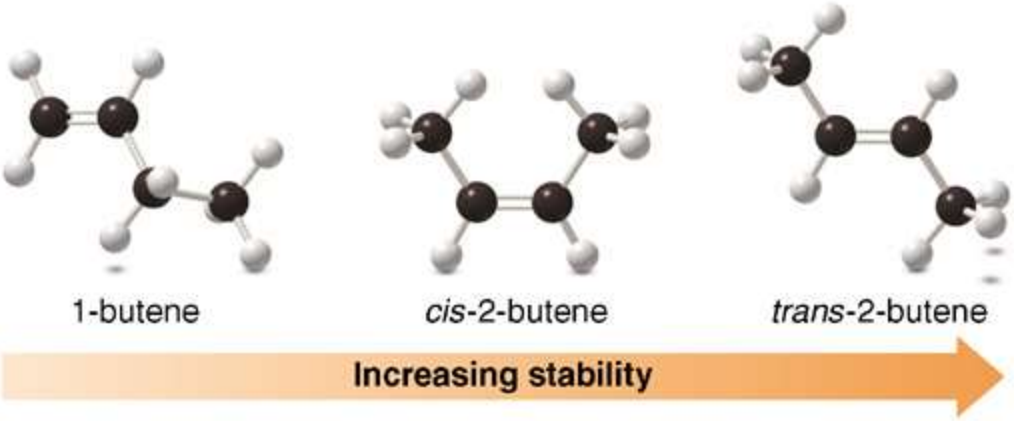


cis-cyclooctene

Carbon-Carbon pi bonds

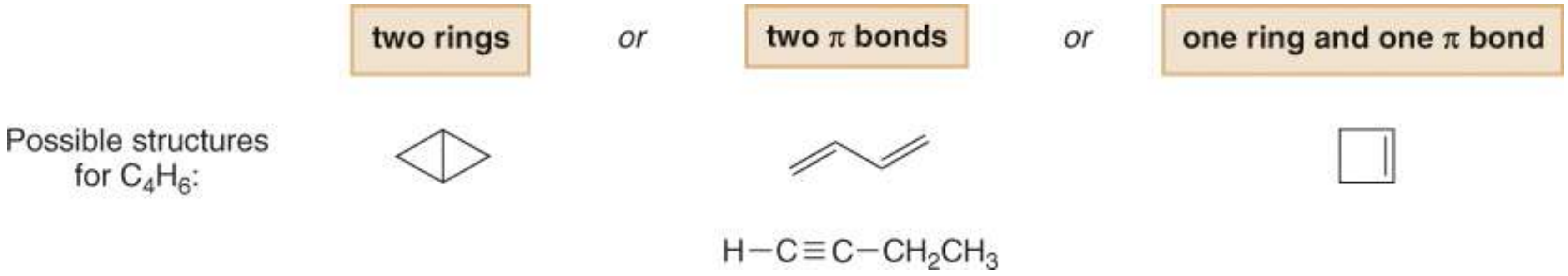
Introduction: Structure and Bonding

Table 10.1	Properties of the Carbon–Carbon Double Bond
Restricted rotation	• **The rotation around the C–C double bond is restricted.** Rotation can only occur if the π bond breaks and then re-forms, a process that is unfavorable (Section 8.2B).
Stereoisomerism	• Whenever the two groups on each end of a C=C are different from each other, two diastereomers are possible. *Cis*- and *trans*-2-butene (drawn at the bottom of Table 10.1) are diastereomers (Section 8.2B).
Stability	• **Trans** alkenes are generally more stable than **cis** alkenes. • **The stability of an alkene increases as the number of R groups on the C=C increases** (Section 8.2C).



Calculating Degrees of Unsaturation:

- An acyclic alkene and a cycloalkane both have the general formula C_nH_{2n}.
- Alkenes are unsaturated hydrocarbons because they have fewer than the maximum number of hydrogen atoms per carbon.
- 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 C_nH_{2n+2}. This procedure gives the total number of rings and/or π bonds in a molecule.



Degrees of Unsaturation, examples:000

1. Calculate # unsaturations for the molecular formula $C_6H_6O_2$.

   Maximum #Hs for 6 carbons = C_nH_{2n+2} = 14

   # unsaturations in the given compound:

   14 – 6 = 8 and 8/2 = 4 unsaturations

2. Calculate # unsaturations for the molecular formula $C_7H_{13}N$.

   Maximum #Hs for 6 carbons = $C_nH_{2n+2+1 \text{ for each N}}$ = 17

   # unsaturations in the given compound:

   17 – 13 = 4 and 4/2 = 2 unsaturations

3. Calculate # unsaturations for the molecular formula C_3H_5Cl.

   Maximum #Hs for 6 carbons = $C_nH_{2n+2-1 \text{ for each X}}$ = 7

   # unsaturations in the given compound:

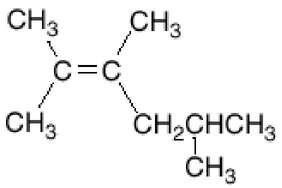
   7 – 5 = 2 and 2/2 = 1 unsaturation

Carbon-Carbon pi bonds

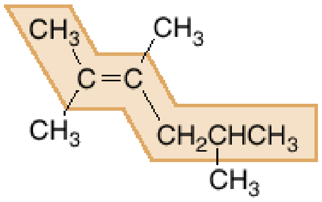
Nomenclature of Alkenes:

How To Name an Alkene

Example Give the IUPAC name of the following alkene:



Step [1] Find the longest chain that contains *both* carbon atoms of the double bond.



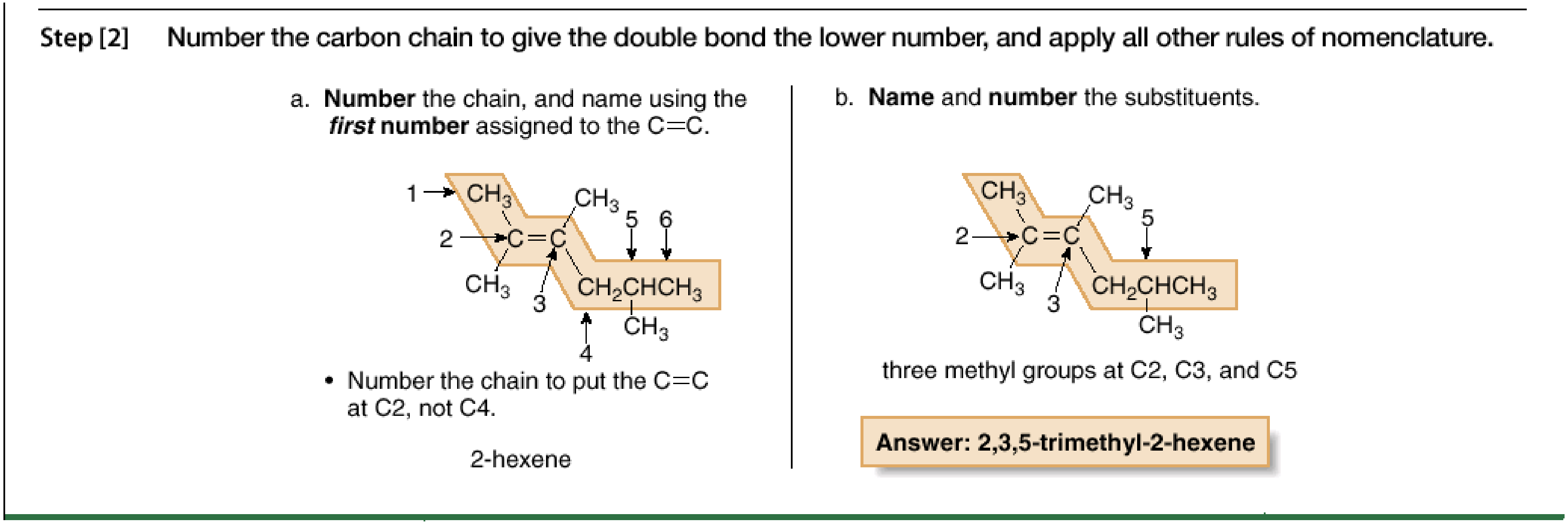
6 C's in the longest chain

hex*ane* ----→ **hex*ene***

- Change the ***-ane*** ending of the parent alkane to ***-ene.***

Carbon-Carbon pi bonds

Nomenclature of Alkenes:



Step [2] Number the carbon chain to give the double bond the lower number, and apply all other rules of nomenclature.

a. **Number** the chain, and name using the ***first* number** assigned to the C=C.

- Number the chain to put the C=C at C2, not C4.

2-hexene

b. **Name** and **number** the substituents.

three methyl groups at C2, C3, and C5

Answer: 2,3,5-trimethyl-2-hexene

Nomenclature of Alkenes:

- **Always choose the longest chain that contains both atoms of the double bond.**
- **Compounds with two double bonds are named as dienes by changing the "-ane" ending of the parent alkane to the suffix "–adiene". Compounds with three double bonds are named as trienes, and so forth.**

$CH_2{=}CH{-}CH{=}CH_2$

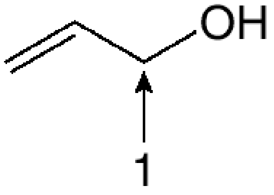
1,3-butadiene

$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$

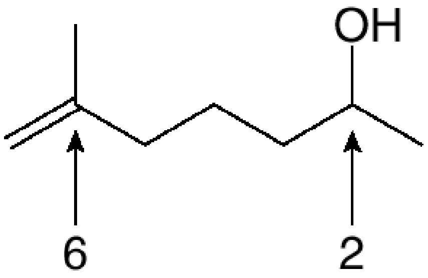
1,3,5-hexatriene

Nomenclature of Alkenes:

- **In naming cycloalkenes, the double bond is located between C1 and C2, and the “1” is usually omitted in the name. The ring is numbered clockwise or counterclockwise to give the first substituent the lower number.**
- **Compounds that contain both a double bond and a hydroxy group are named as alkenols and the chain (or ring) is numbered to give the OH group the lower number.**



2-propen-1-ol

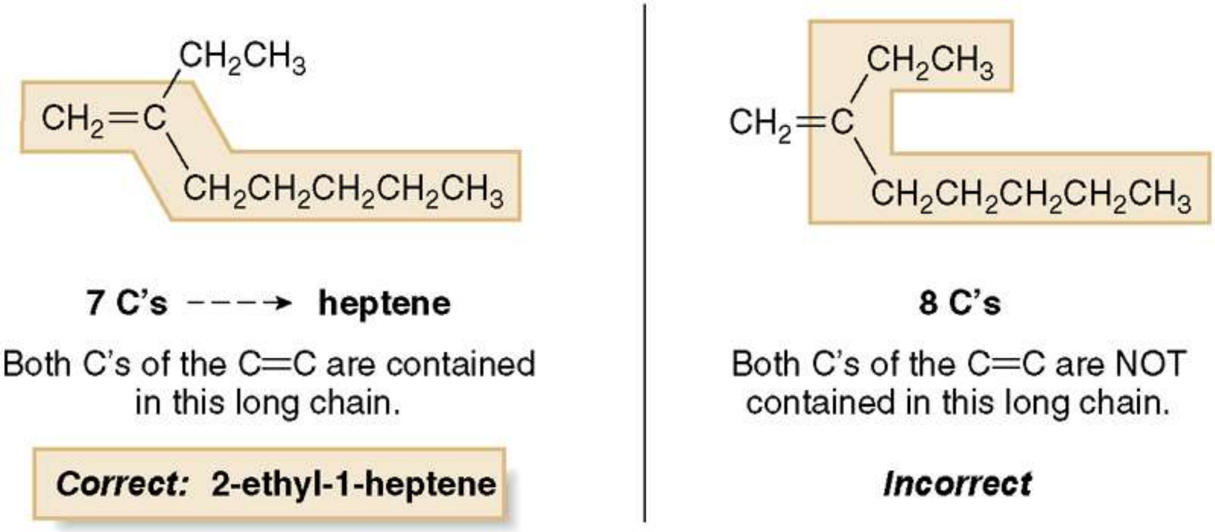


6-methyl-6-hepten-2-ol

Carbon-Carbon pi bonds

Nomenclature of Alkenes:

Figure 10.1 **Naming an alkene in which the longest carbon chain does not contain both atoms of the double bond**



7 C's ---→ heptene

Both C's of the C=C are contained in this long chain.

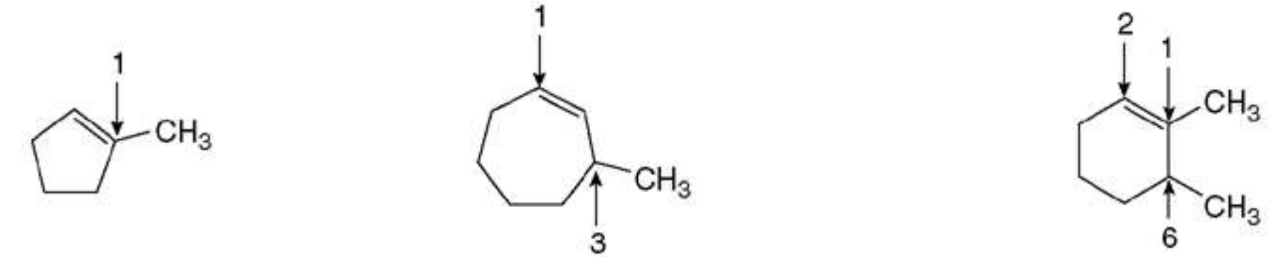
Correct: **2-ethyl-1-heptene**

8 C's

Both C's of the C=C are NOT contained in this long chain.

Incorrect

Figure 10.2 **Examples of cycloalkene nomenclature**



1-methylcyclopentene

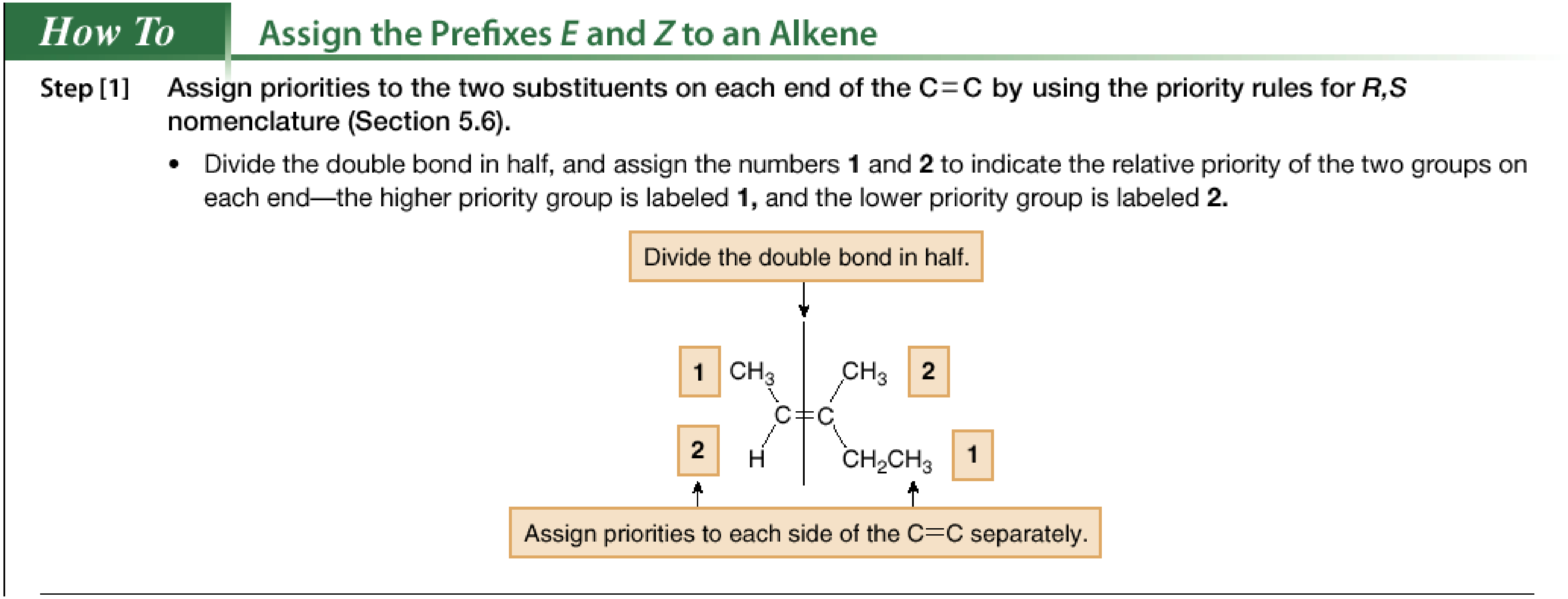
3-methylcycloheptene

Number clockwise beginning at the C=C and place the CH_3 at C3.

1,6-dimethylcyclohexene

Number counterclockwise beginning at the C=C and place the first CH_3 at C1.

Nomenclature of Alkenes:



How To **Assign the Prefixes *E* and *Z* to an Alkene**

Step [1] Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R*,*S* nomenclature (Section 5.6).

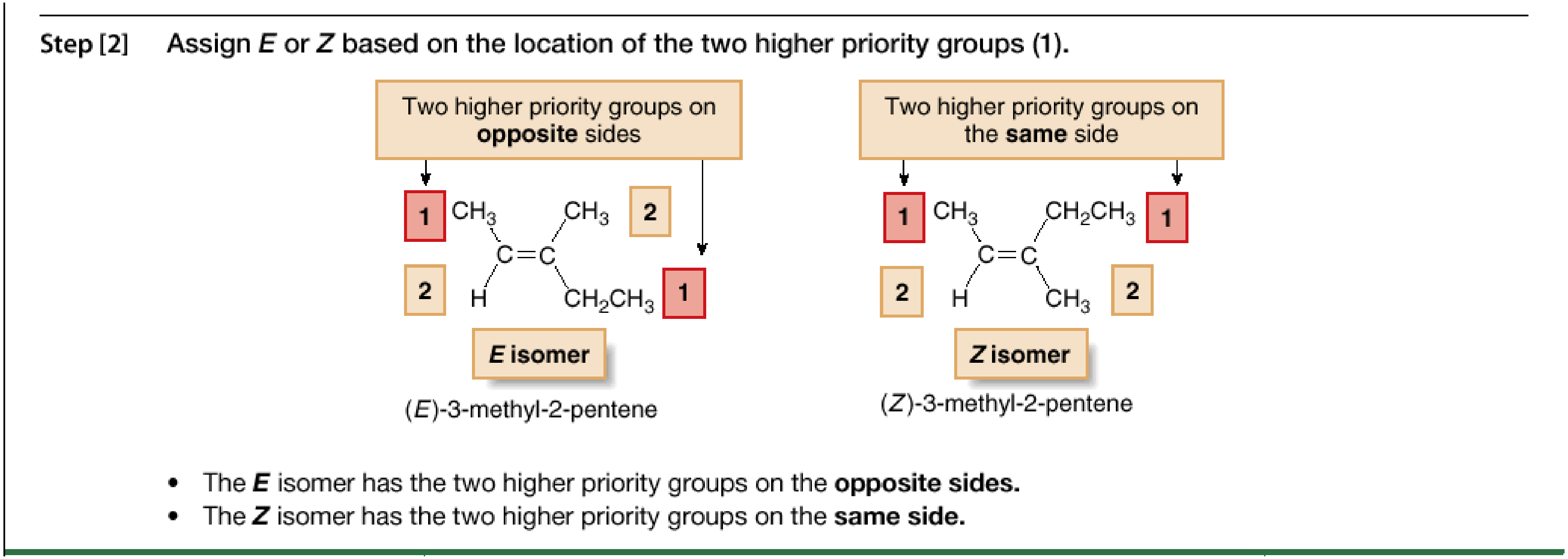
- Divide the double bond in half, and assign the numbers **1** and **2** to indicate the relative priority of the two groups on each end—the higher priority group is labeled **1,** and the lower priority group is labeled **2.**

Divide the double bond in half.

Assign priorities to each side of the C=C separately.

Carbon-Carbon pi bonds

Nomenclature of Alkenes:



Step [2] Assign *E* or *Z* based on the location of the two higher priority groups (1).

***E* isomer**

(*E*)-3-methyl-2-pentene

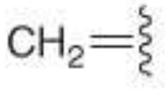
***Z* isomer**

(*Z*)-3-methyl-2-pentene

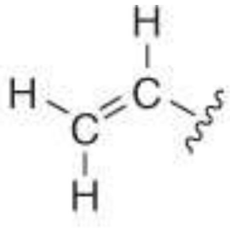
- The ***E*** isomer has the two higher priority groups on the **opposite sides.**
- The ***Z*** isomer has the two higher priority groups on the **same side.**

Nomenclature of Alkenes:

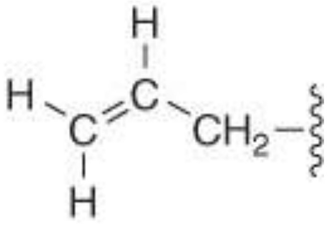
- **Some alkene or alkenyl substituents have common names.**
- **The simplest alkene, CH_2=CH_2, named in the IUPAC system as ethene, is often called ethylene.**



methylene group



vinyl group



allyl group

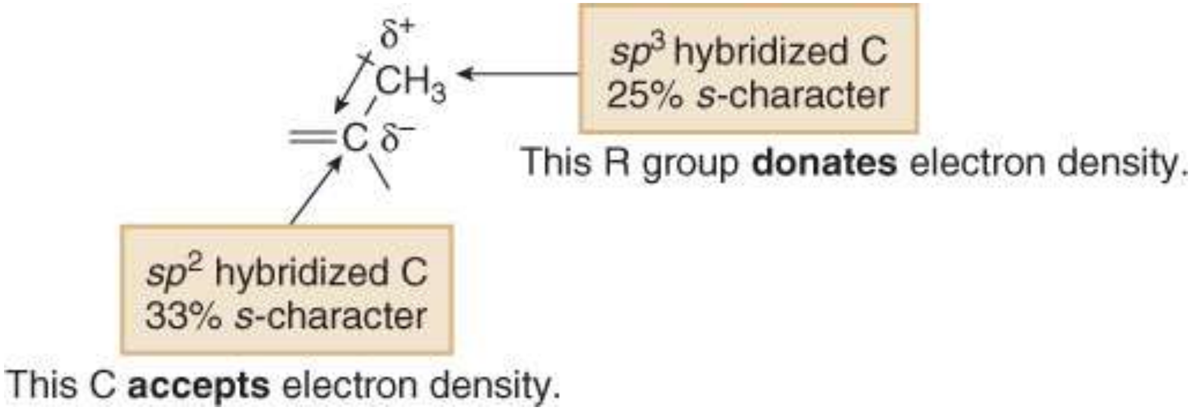
Figure 10.3 **Naming alkenes with common substituent names**

methylenecyclohexane

1-vinylcyclohexene

Physical Properties:

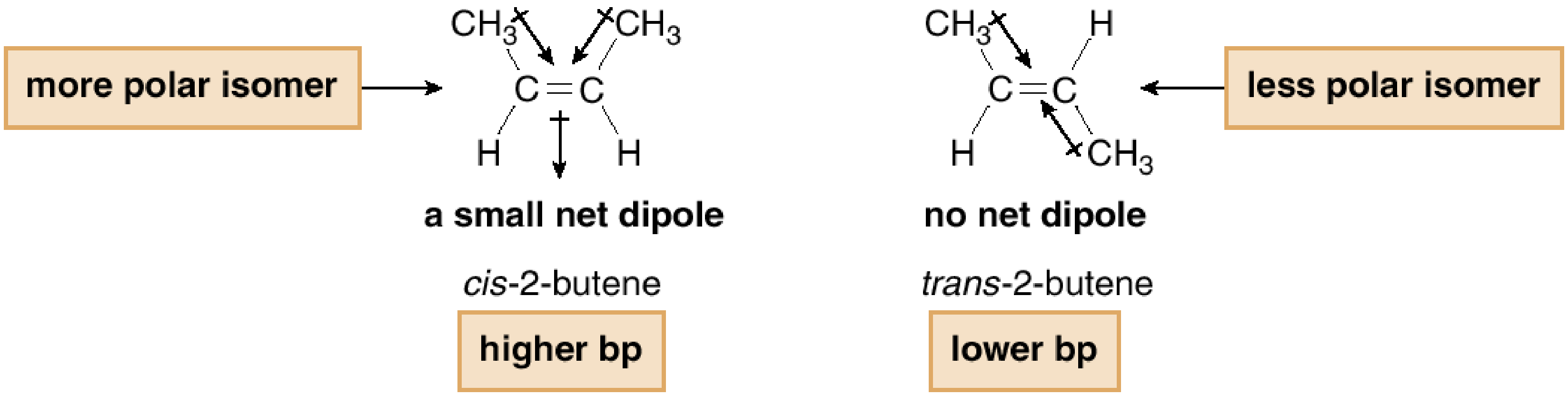
- **Most alkenes exhibit only weak van der Waals interactions, so their physical properties are similar to alkanes of comparable molecular weight.**
- **Alkenes have low melting points and boiling points.**
- **Melting and boiling points increase as the number of carbons increases because of increased surface area.**
- **Alkenes are soluble in organic solvents and insoluble in water.**
- **The C—C single bond between an alkyl group and one of the double bond carbons of an alkene is slightly polar because the *sp*^{3} hybridized alkyl carbon donates electron density to the *sp*^{2} hybridized alkenyl carbon.**



Carbon-Carbon pi bonds

Physical Properties:

- A consequence of this dipole is that cis and trans isomeric alkenes often have somewhat different physical properties.
- *cis*-2-Butene has a higher boiling point (4°C) than *trans*-2-butene (1°C).
- In the cis isomer, the two C_{sp^3}—C_{sp^2} bond dipoles reinforce each other, yielding a small net molecular dipole. In the trans isomer, the two bond dipoles cancel.



more polar isomer →

a small net dipole

cis-2-butene

higher bp

← **less polar isomer**

no net dipole

trans-2-butene

lower bp

- A cis alkene is more polar than a trans alkene, giving it a slightly higher boiling point and making it more soluble in polar solvents.

Carbon-Carbon pi bonds

Interesting Alkenes:

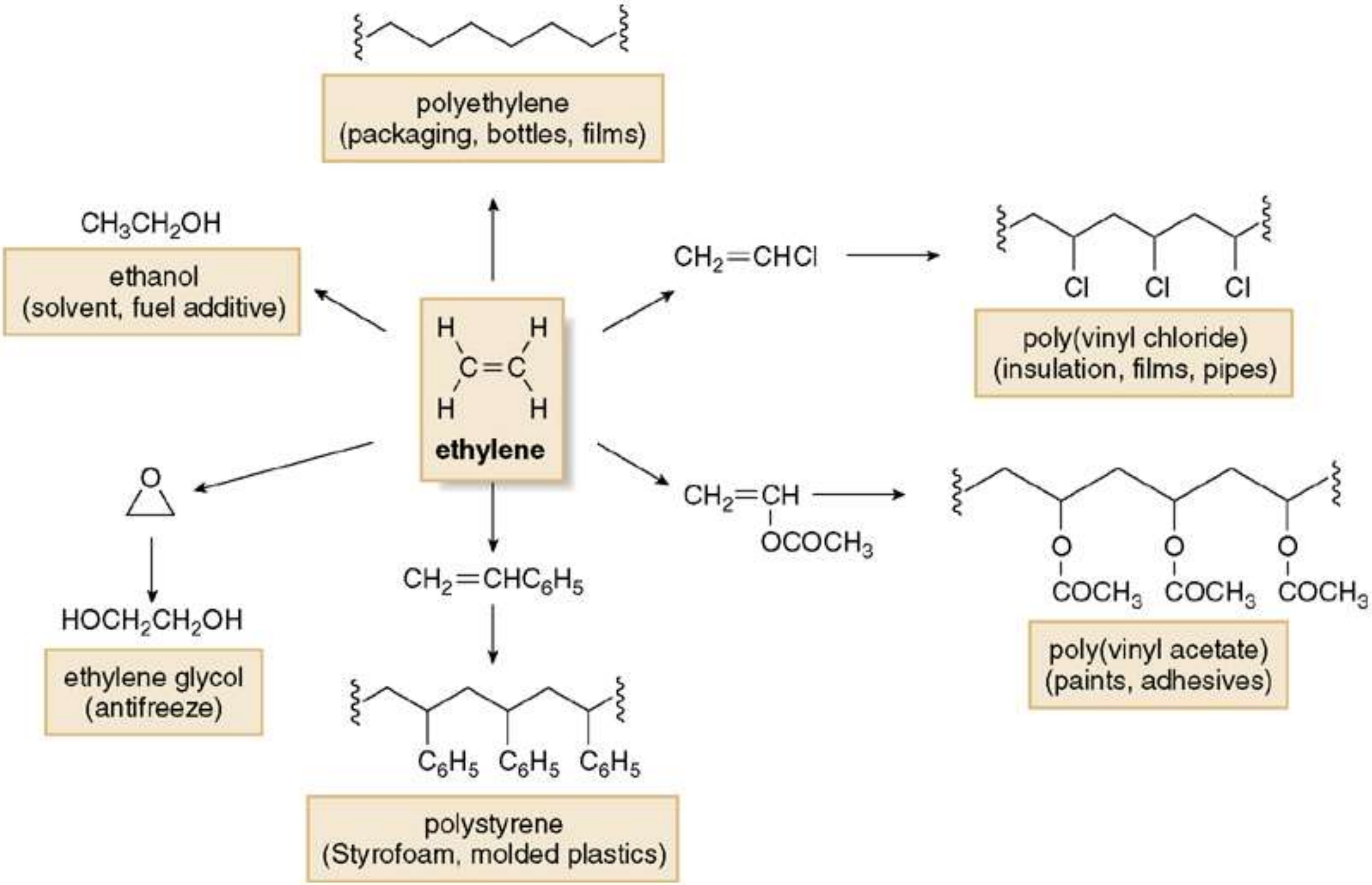


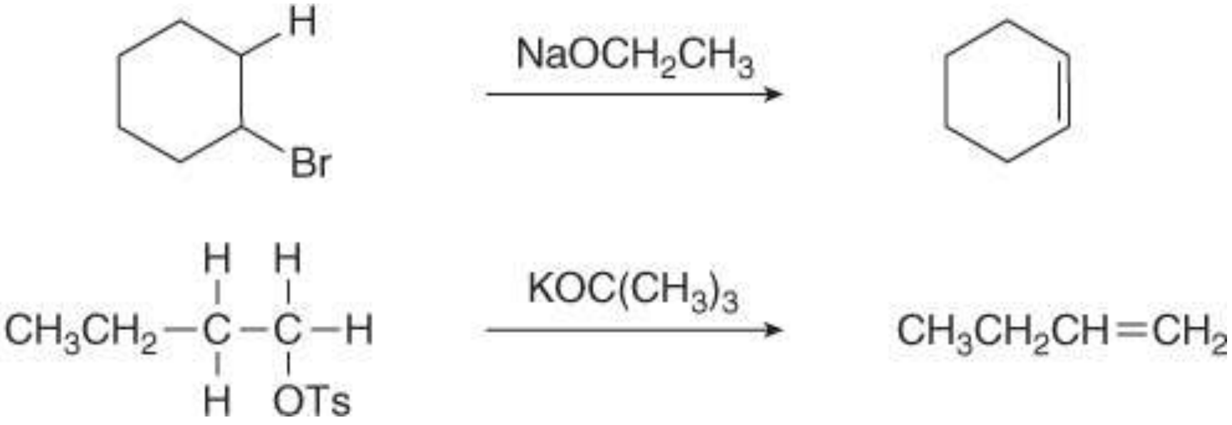
Figure 10.4 **Ethylene, an industrial starting material for many useful products**

Preparation of Alkenes:

- **Alkenes can be prepared using elimination reactions:**

1. Dehydrohalogenation of alkyl halides.

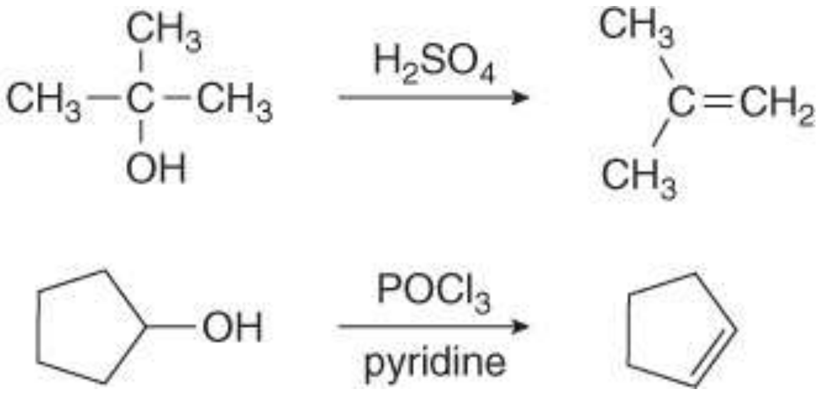
Examples



$$CH_3CH_2CH_2CH_2OTs \xrightarrow{KOC(CH_3)_3} CH_3CH_2CH{=}CH_2$$

2. Dehydration of alcohols.

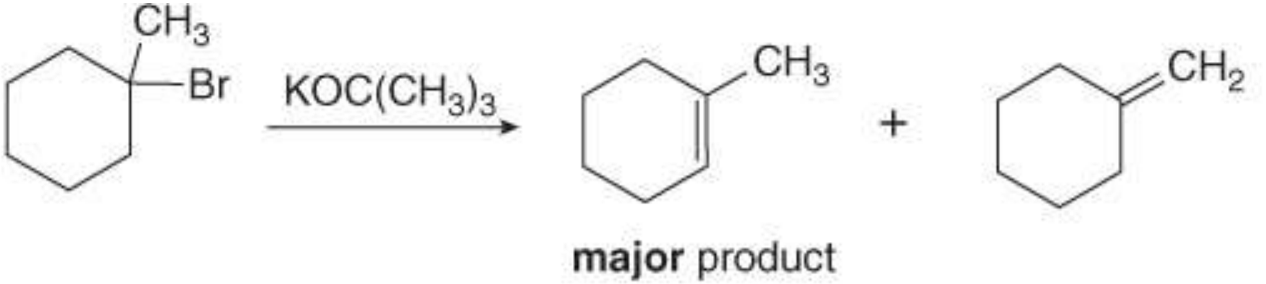
Examples

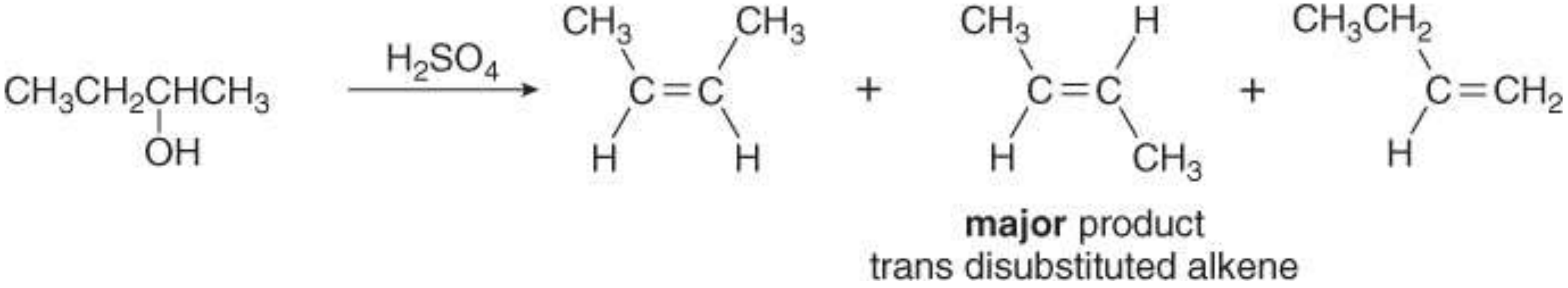


$$(CH_3)_3COH \xrightarrow{H_2SO_4} (CH_3)_2C{=}CH_2$$

Preparation of Alkenes:

- **Remember, these elimination reactions are regioselective and stereoselective, so the most stable alkene is usually formed as the major product.**

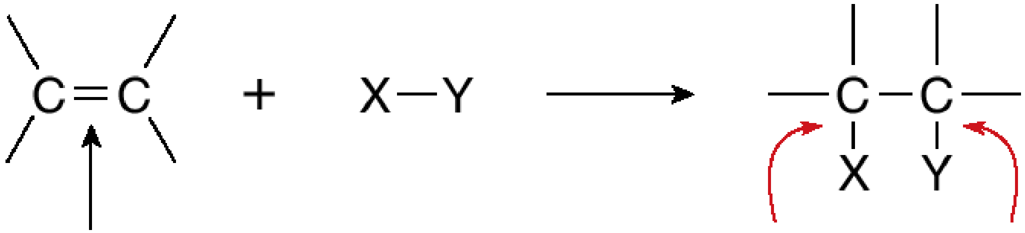




Introduction to Addition Reactions (see also Chapt. 6):

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

Addition reaction



No pi bond

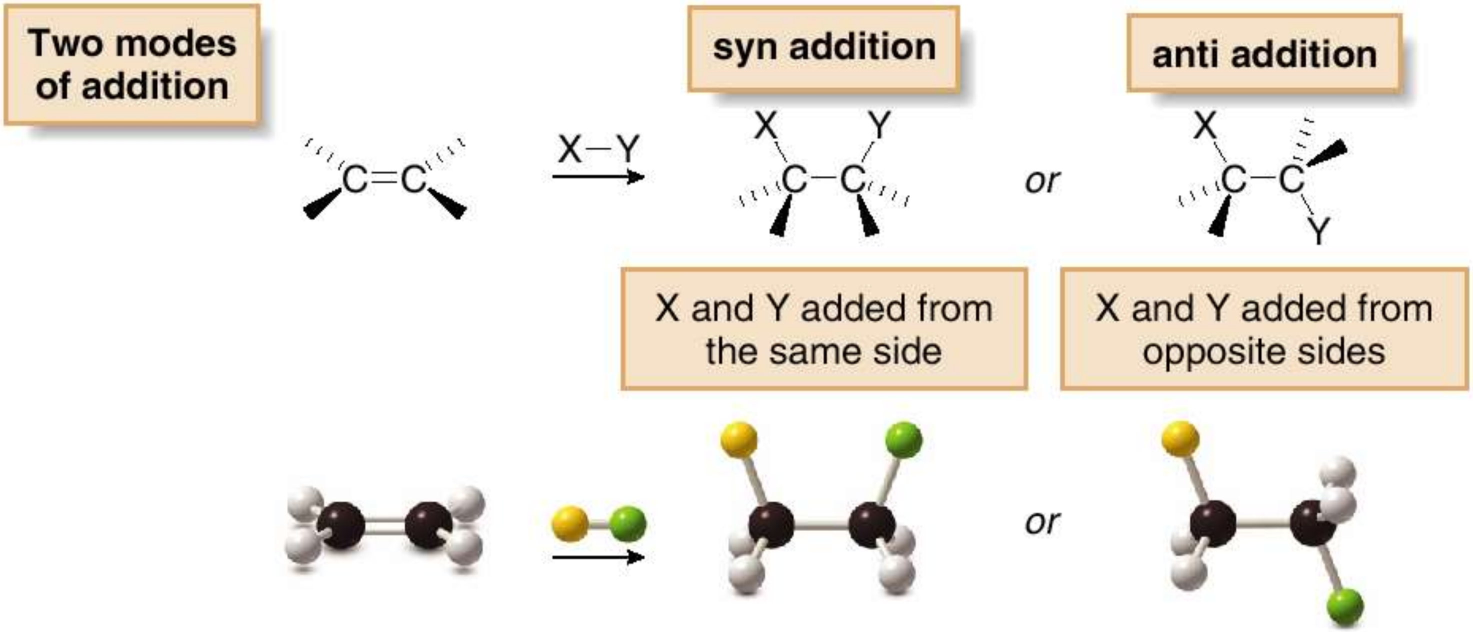
This π bond is broken.

Two σ bonds are formed.

- Alkenes have exposed electrons, with the electron density of the π bond 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.

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.**

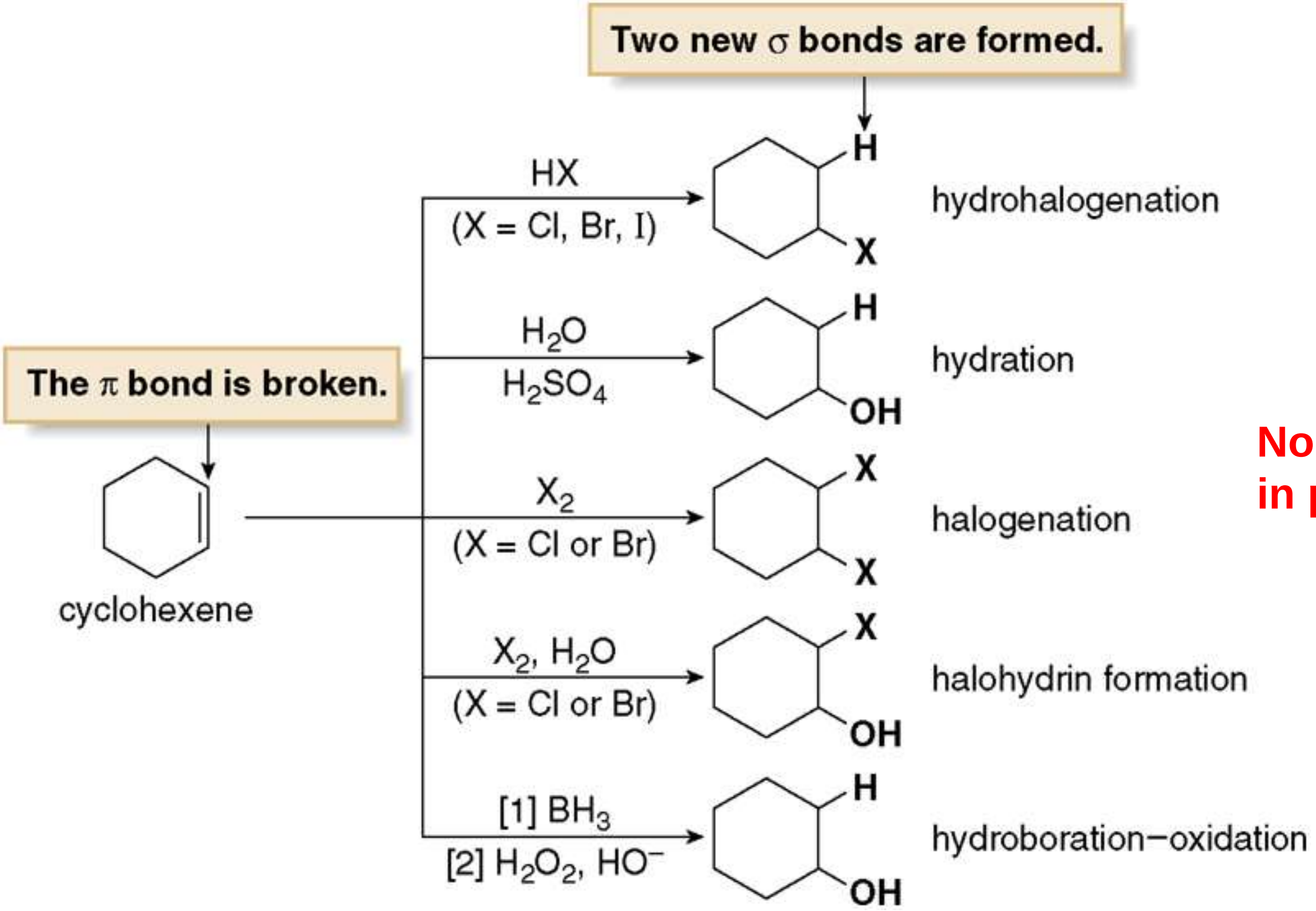


- *Syn addition* takes place when both X and Y are added from the *same* side.
- *Anti addition* takes place when X and Y are added from *opposite* sides.

Carbon-Carbon pi bonds

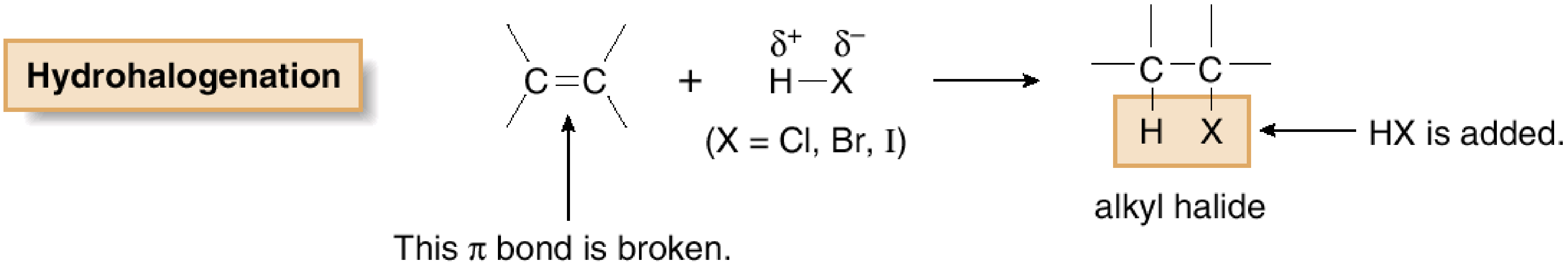
Introduction to Addition Reactions:

Figure 10.8 **Five addition reactions of cyclohexene**



No pi bond
in products

Hydrohalogenation: Electrophilic Addition of HX



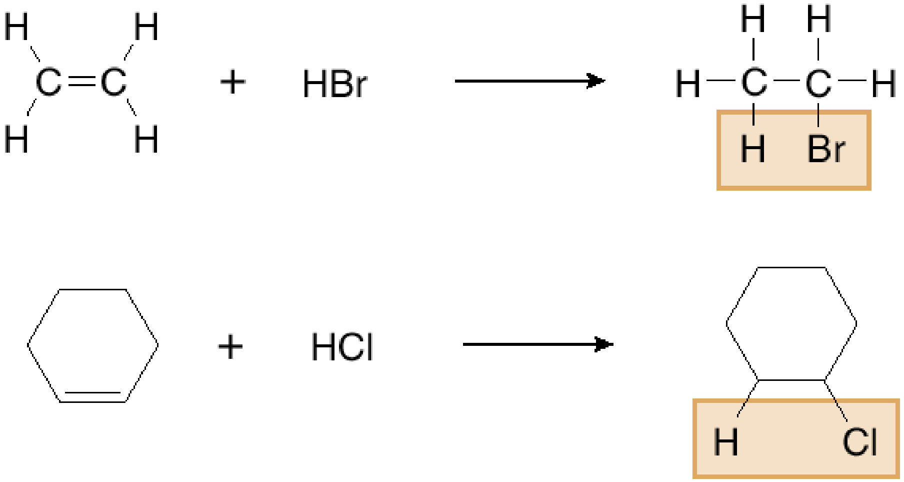
- **Two bonds are broken in this reaction: the weak π bond of the alkene and the HX bond, and two new σ bonds are formed: one to H and one to X.**
- **Recall that the H—X bond is polarized, with a partial positive charge on H. Because the electrophilic H end of HX is attracted to the electron-rich double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

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.

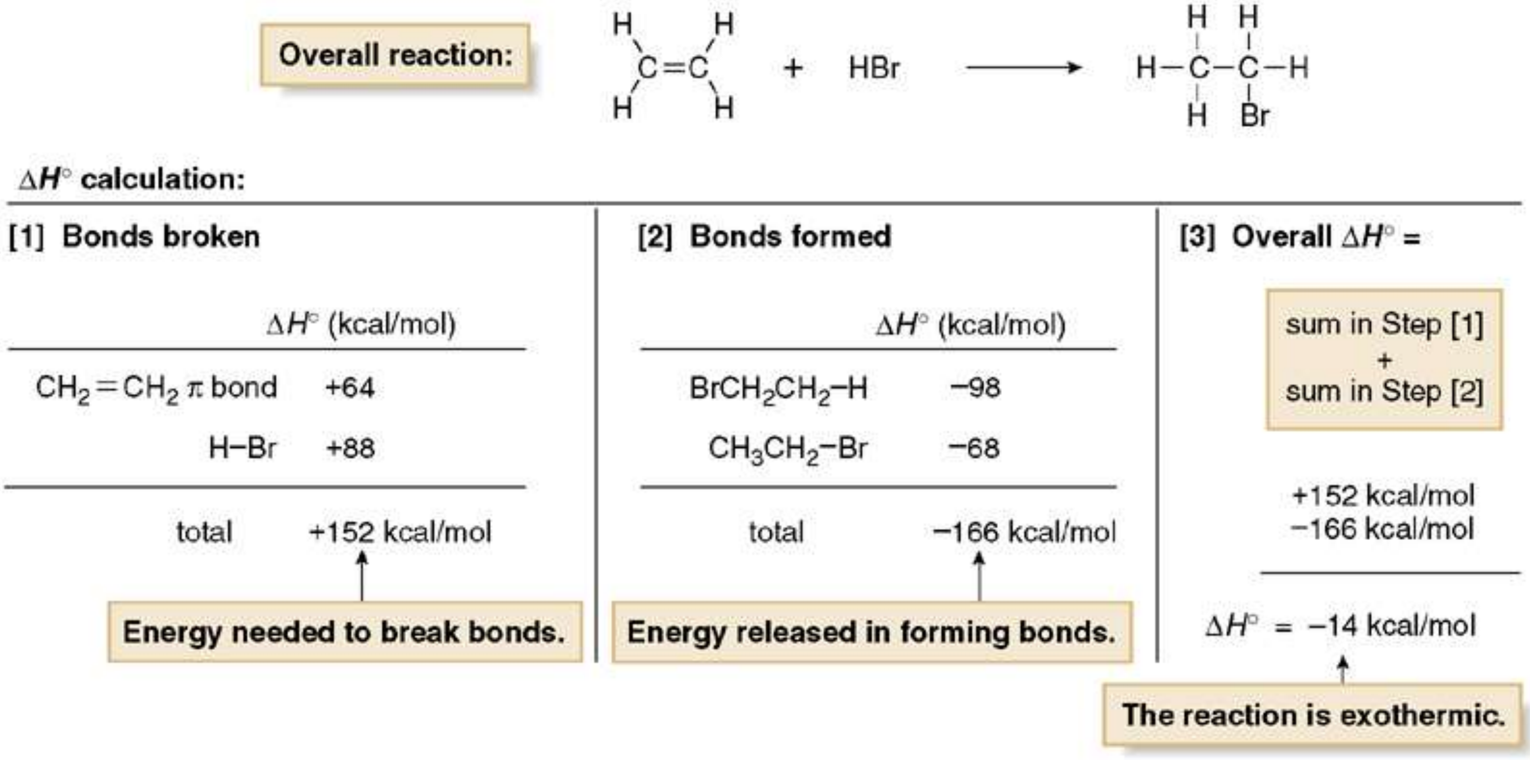
Examples



Hydrohalogenation: Electrophilic Addition of HX

- Addition reactions are exothermic because the two σ bonds formed in the product are stronger than the σ and π bonds broken in the reactants. For example, ΔH° for the addition of HBr to ethylene is –14 kcal/mol, as illustrated below.

Figure 10.9 The addition of HBr to $CH_2=CH_2$, An exothermic reaction.



ΔH° calculation:

[1] Bonds broken

	ΔH° (kcal/mol)
$CH_2=CH_2$ π bond	+64
H–Br	+88
total	+152 kcal/mol

Energy needed to break bonds.

[2] Bonds formed

	ΔH° (kcal/mol)
$BrCH_2CH_2$–H	−98
CH_3CH_2–Br	−68
total	−166 kcal/mol

Energy released in forming bonds.

[3] Overall ΔH° =

sum in Step [1]
+
sum in Step [2]

+152 kcal/mol
−166 kcal/mol

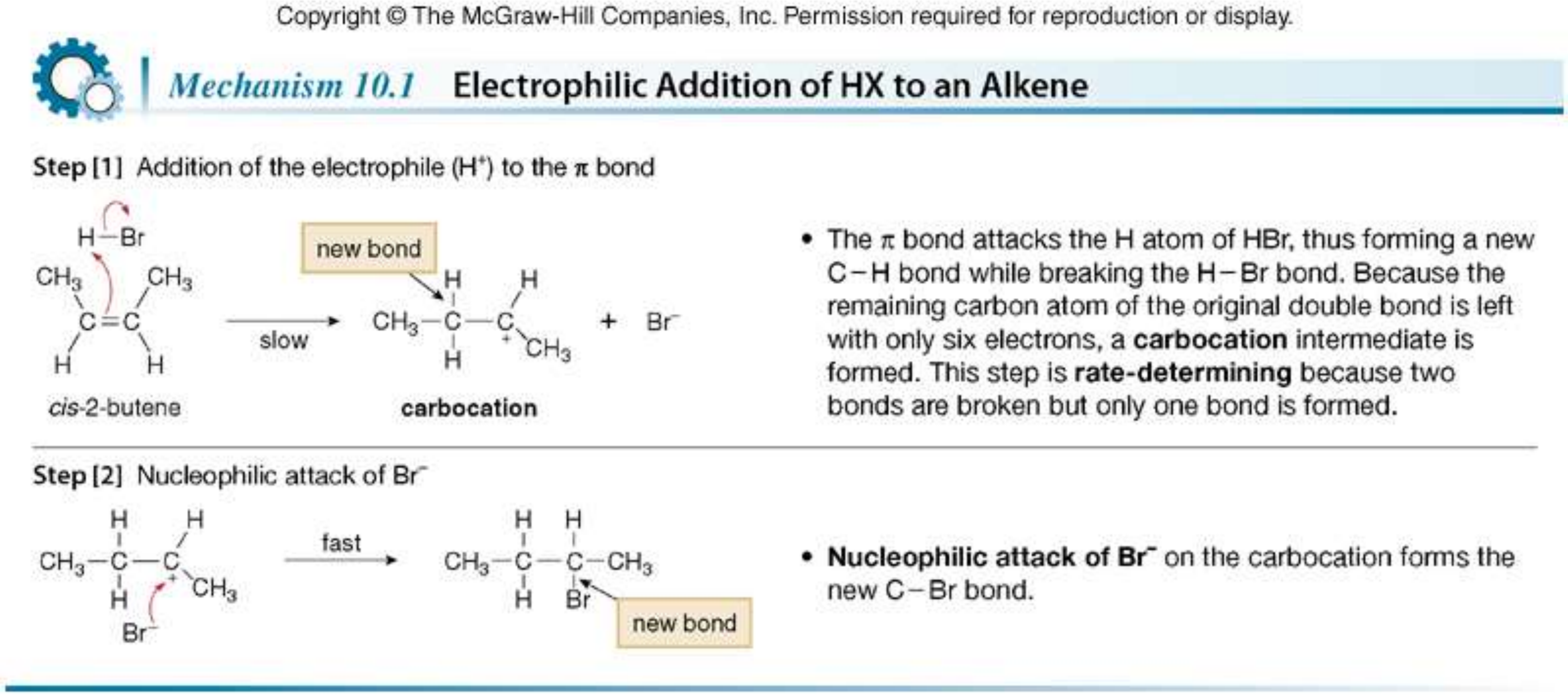
ΔH° = −14 kcal/mol

The reaction is exothermic.

Carbon-Carbon pi bonds

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.



Mechanism 10.1 **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.

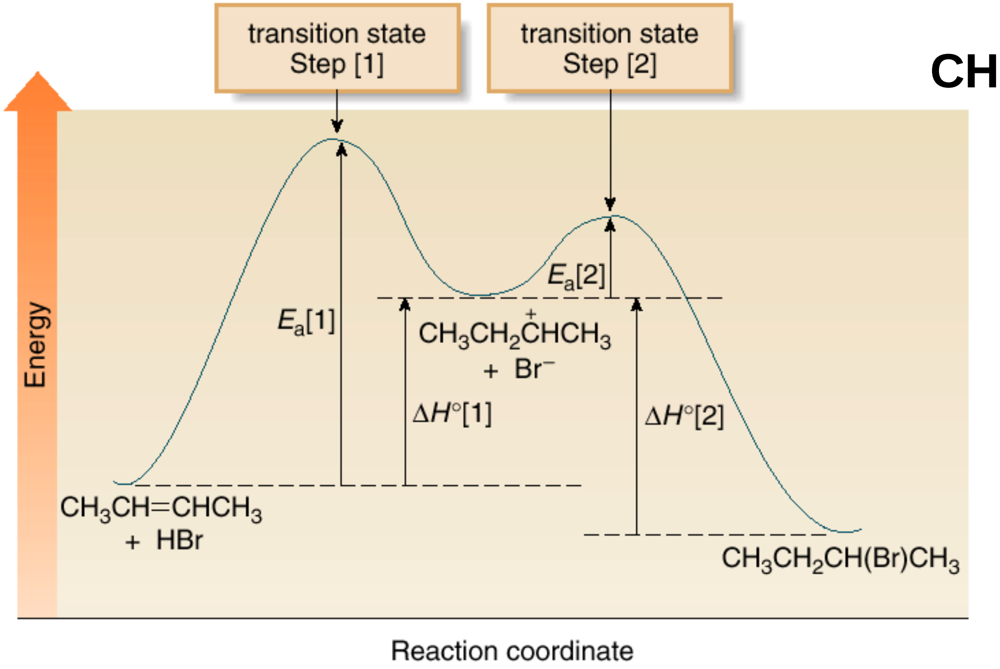
Step [2] Nucleophilic attack of Br^-

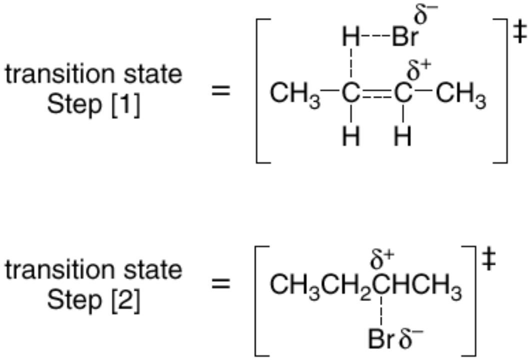
- **Nucleophilic attack of Br^-** on the carbocation forms the new C–Br bond.

Hydrohalogenation: Electrophilic Addition of HX

- **In the representative energy diagram below, each step has its own energy barrier with a transition state energy maximum. Since step 1 has a higher energy transition state, it is rate-determining. ΔH° for step 1 is positive because more bonds are broken than formed, whereas ΔH° for step 2 is negative because only bond making occurs.**

Figure 10.10 **Energy diagram for electrophilic addition: $CH_3CH_2{=}CH_2$ + HBr → $CH_3CH_2CH(Br)CH_3$**

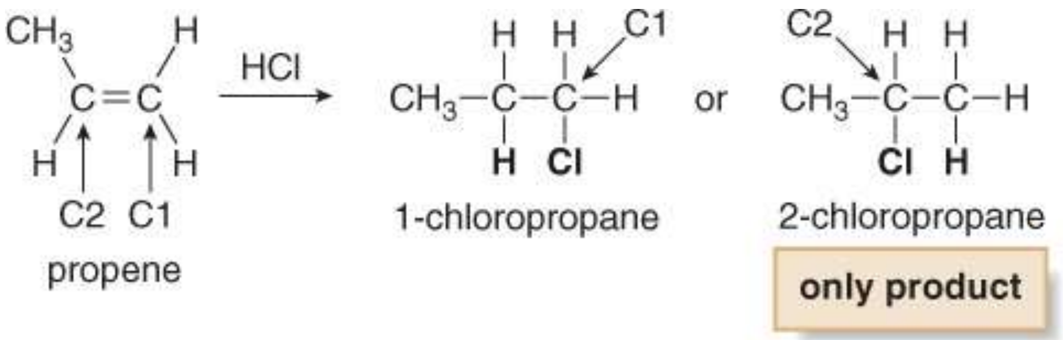




- The mechanism has two steps, so there are two energy barriers.
- Step [1] is rate-determining.

Hydrohalogenation: Markovnikov’s Rule

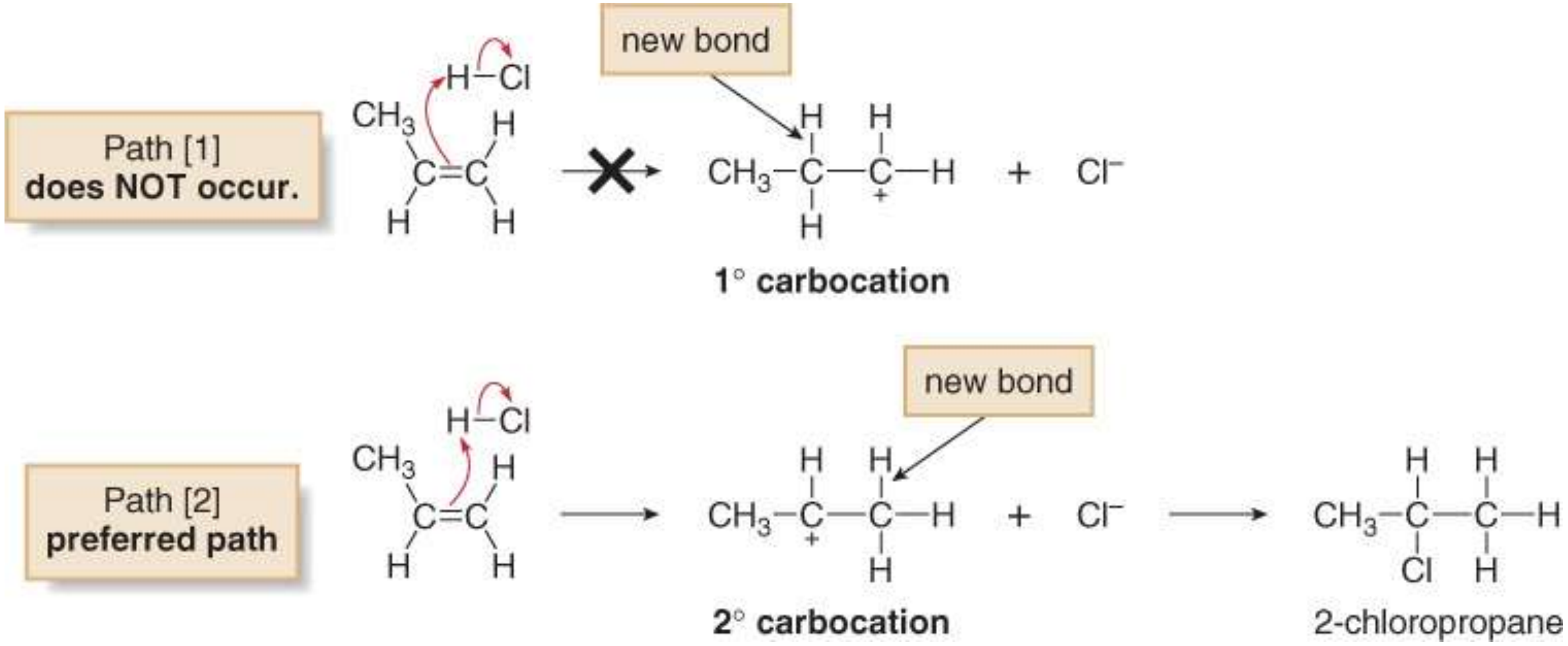
- With an unsymmetrical alkene, HX can add to the double bond to give two constitutional isomers, but only one is actually formed:



- 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.

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.

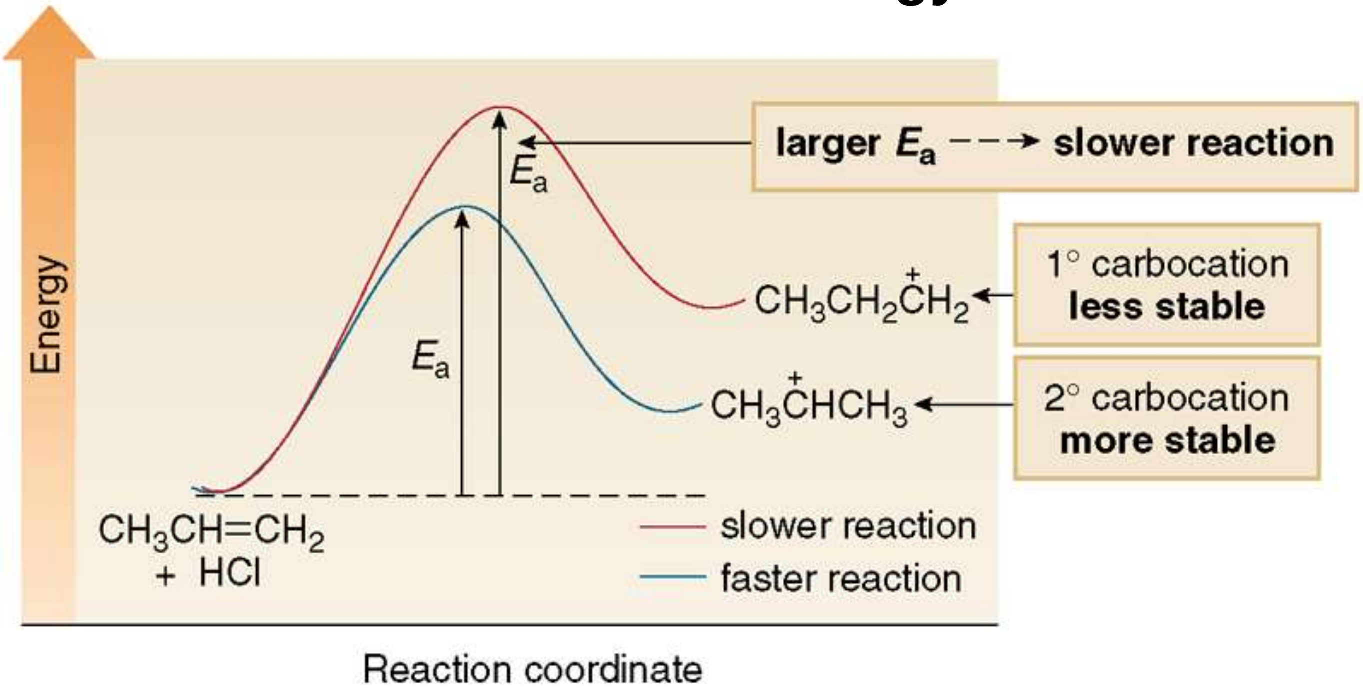


Hydrohalogenation: Markovnikov’s Rule

Figure 10.11 **Electrophilic addition and the Hammond postulate**

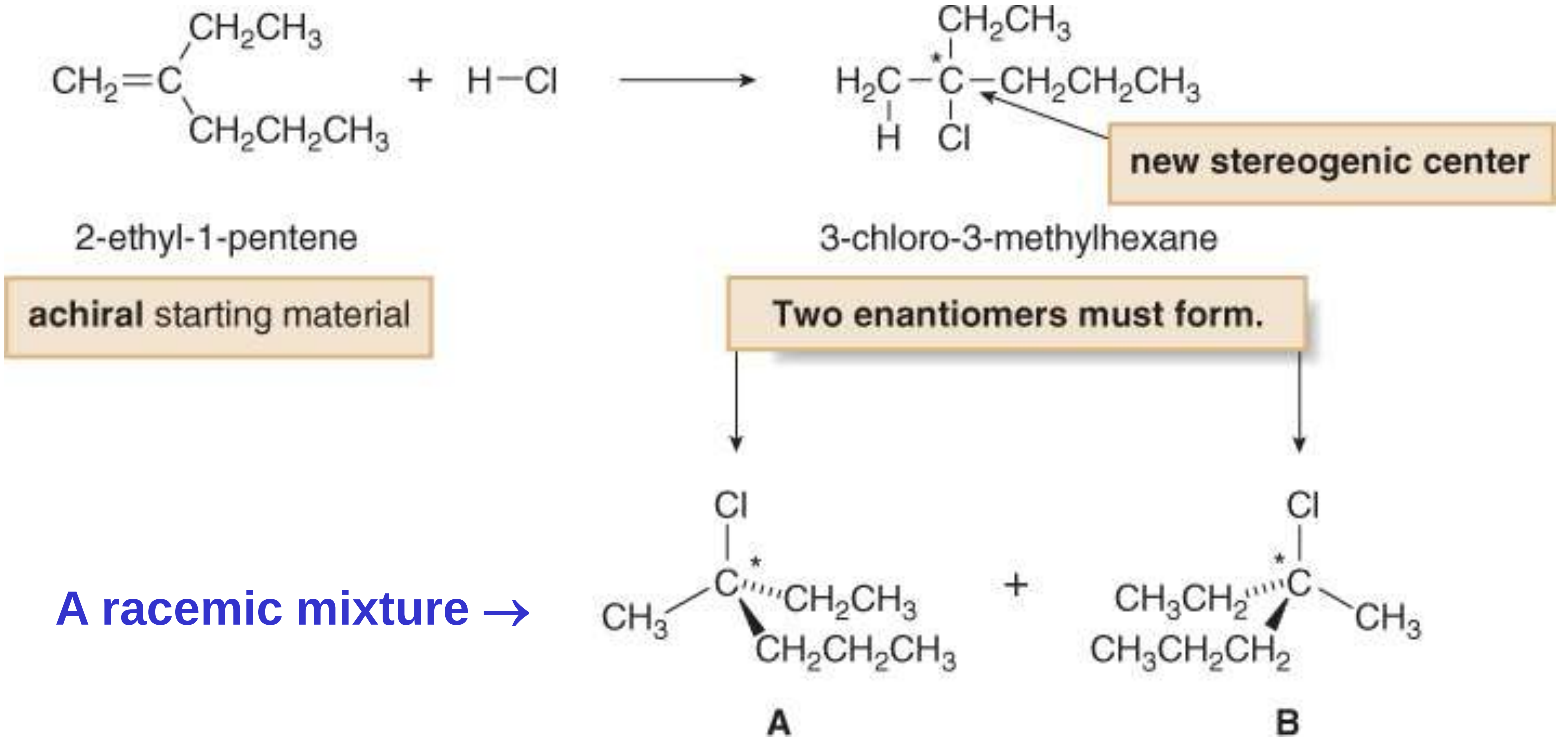
- The E_a for formation of the more stable 2° carbocation is lower than the E_a for formation of the 1° carbocation. The 2° carbocation is formed faster.

According to the Hammond postulate, Path [2] is faster because formation of the carbocation is an endothermic process. Thus, the transition state to form the more stable 2° carbocation is lower in energy.



Hydrohalogenation: Reaction Stereochemistry

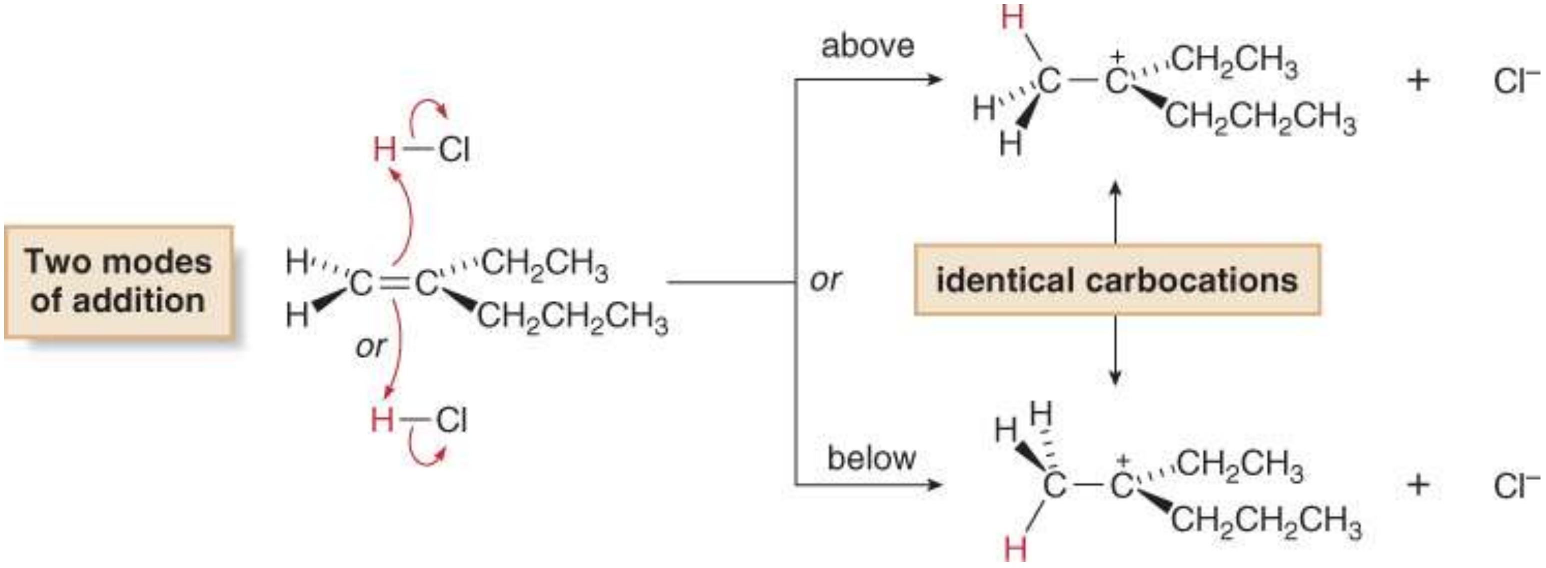
- Recall that trigonal planar atoms react with reagents from two directions with equal probability.
- Achiral starting materials yield achiral products.
- Sometimes new stereogenic centers are formed from hydrohalogenation:



A racemic mixture →

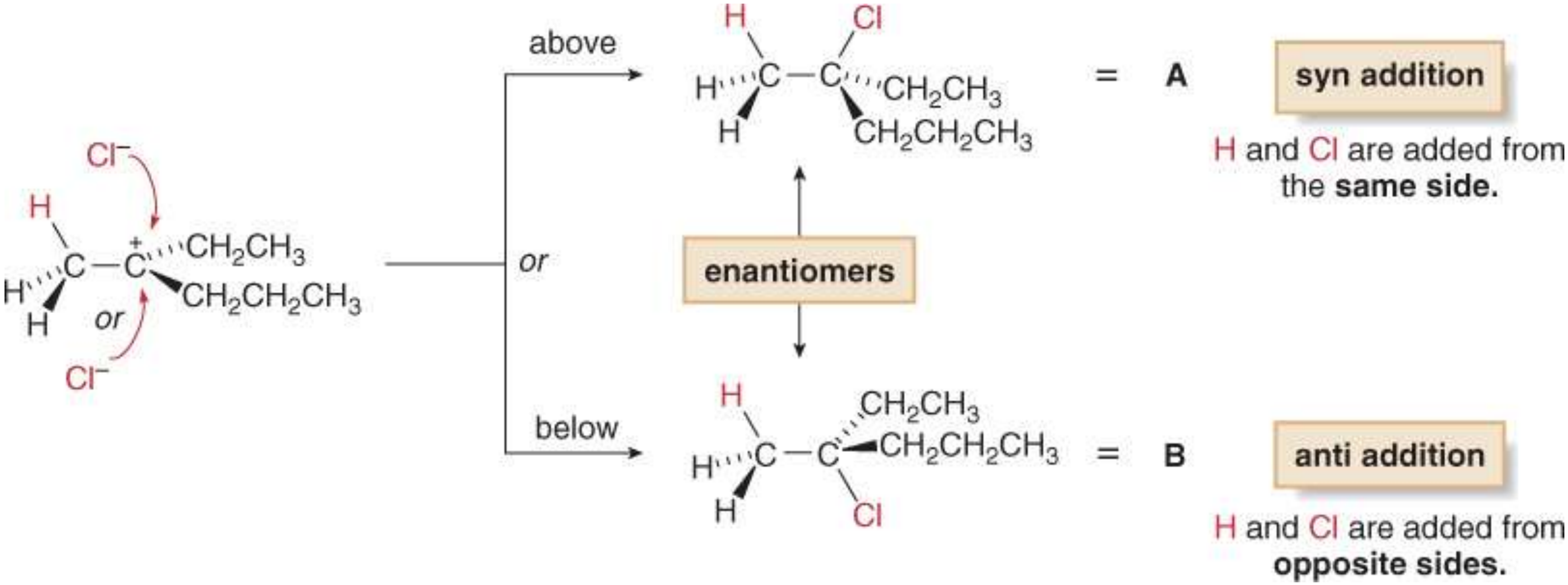
Hydrohalogenation: Reaction Stereochemistry

- 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.



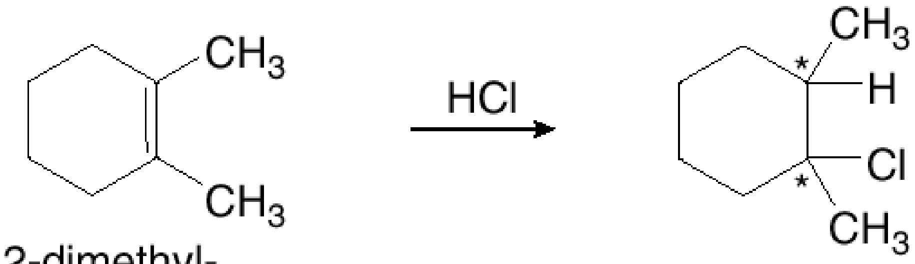
Hydrohalogenation: Reaction Stereochemistry

- 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.



Hydrohalogenation: Reaction Stereochemistry

- Hydrohalogenation occurs with syn and anti addition of HX.
- The terms cis and trans refer to the arrangement of groups in a particular compound, usually an alkene or disubstituted cycloalkene.
- The terms syn and anti describe stereochemistry of a process, for example, how two groups are added to a double bond.
- Addition of HX to 1,2-dimethylcyclohexene forms two new stereogenic centers, resulting in the formation of four stereoisomers (2 pairs of enantiomers).



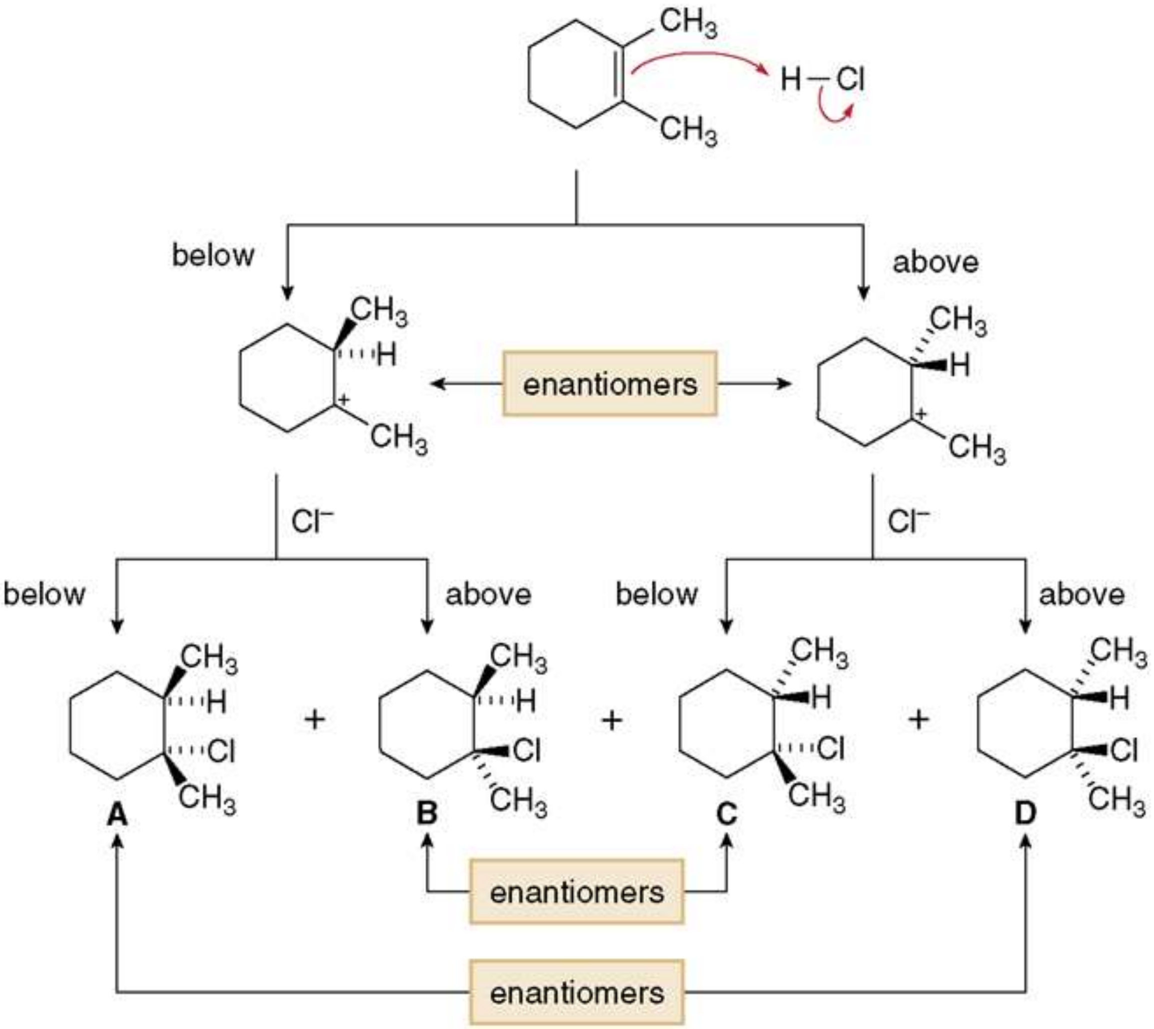
1,2-dimethyl-cyclohexene

Two new stereogenic centers are formed.

* denotes a stereogenic center

Hydrohalogenation: Reaction Stereochemistry

Figure 10.12 **Reaction of 1,2-dimethylcyclohexene with HCl**



Four stereoisomers are formed:

- Compounds **A** and **D** are enantiomers formed in equal amounts.
- Compounds **B** and **C** are enantiomers formed in equal amounts.

Hydrohalogenation: Summary

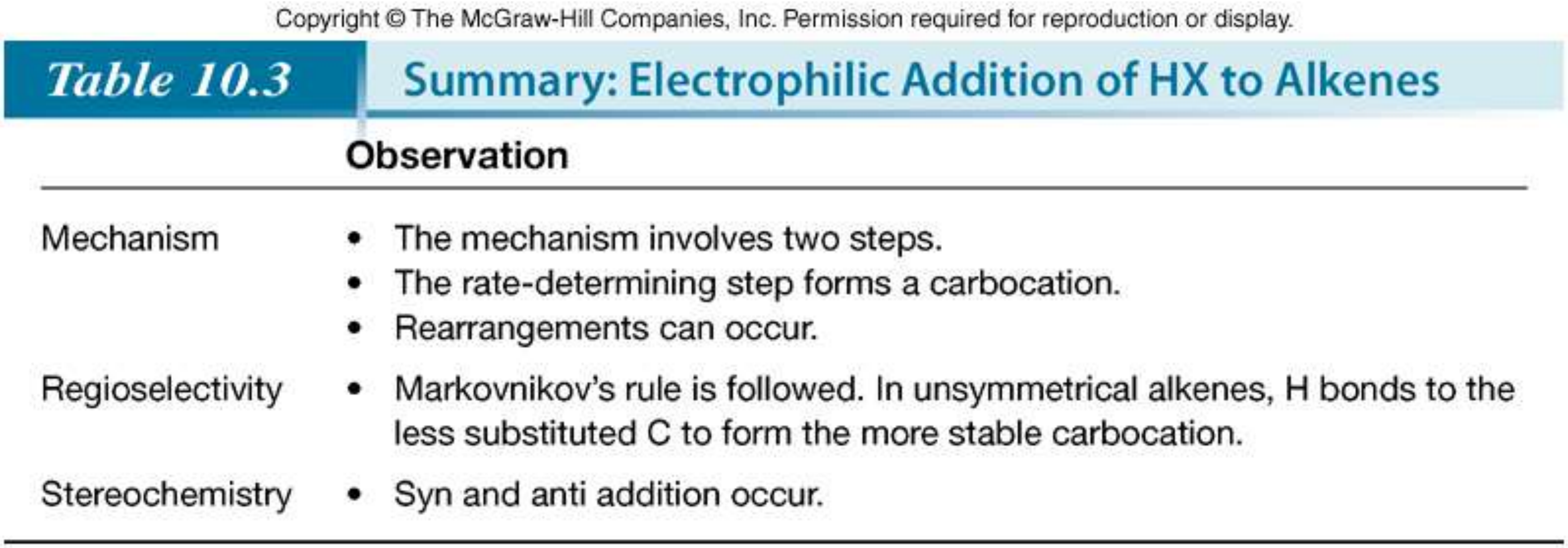
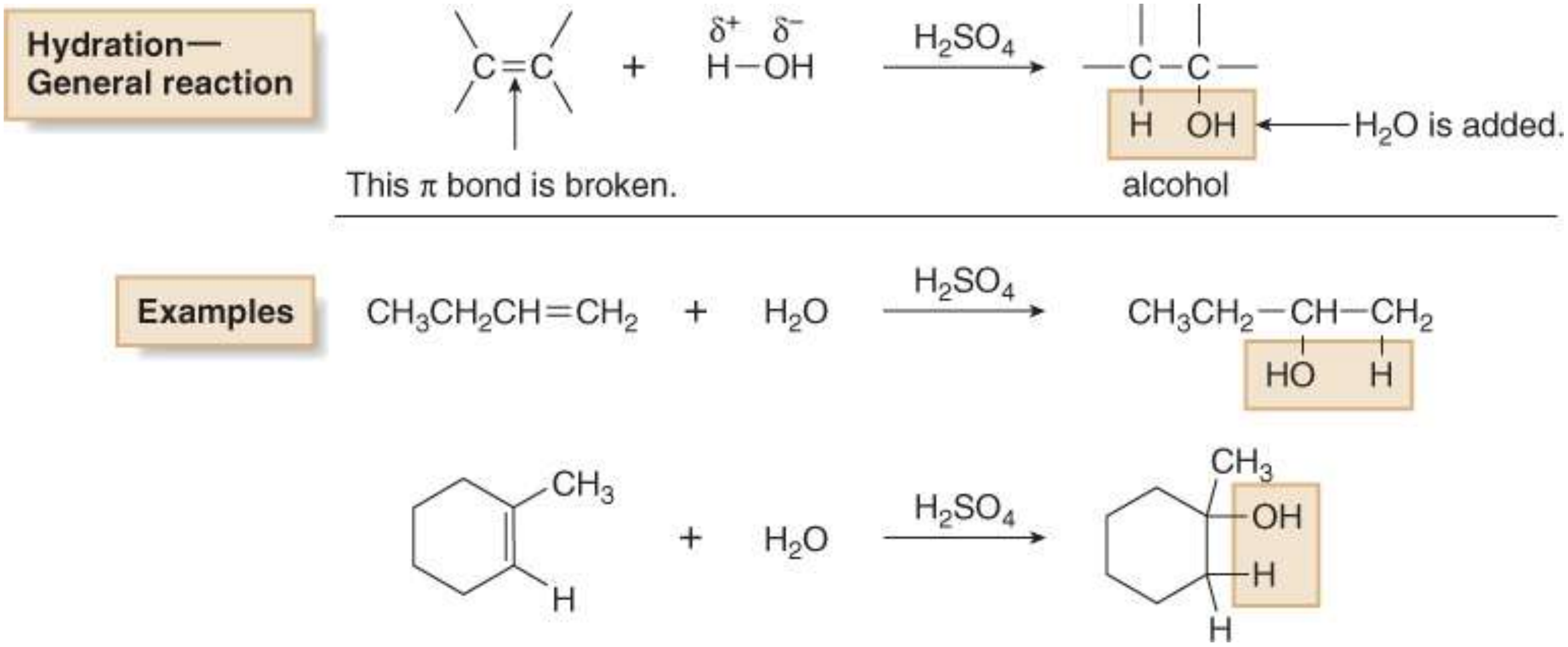


Table 10.3 Summary: Electrophilic Addition of HX to Alkenes

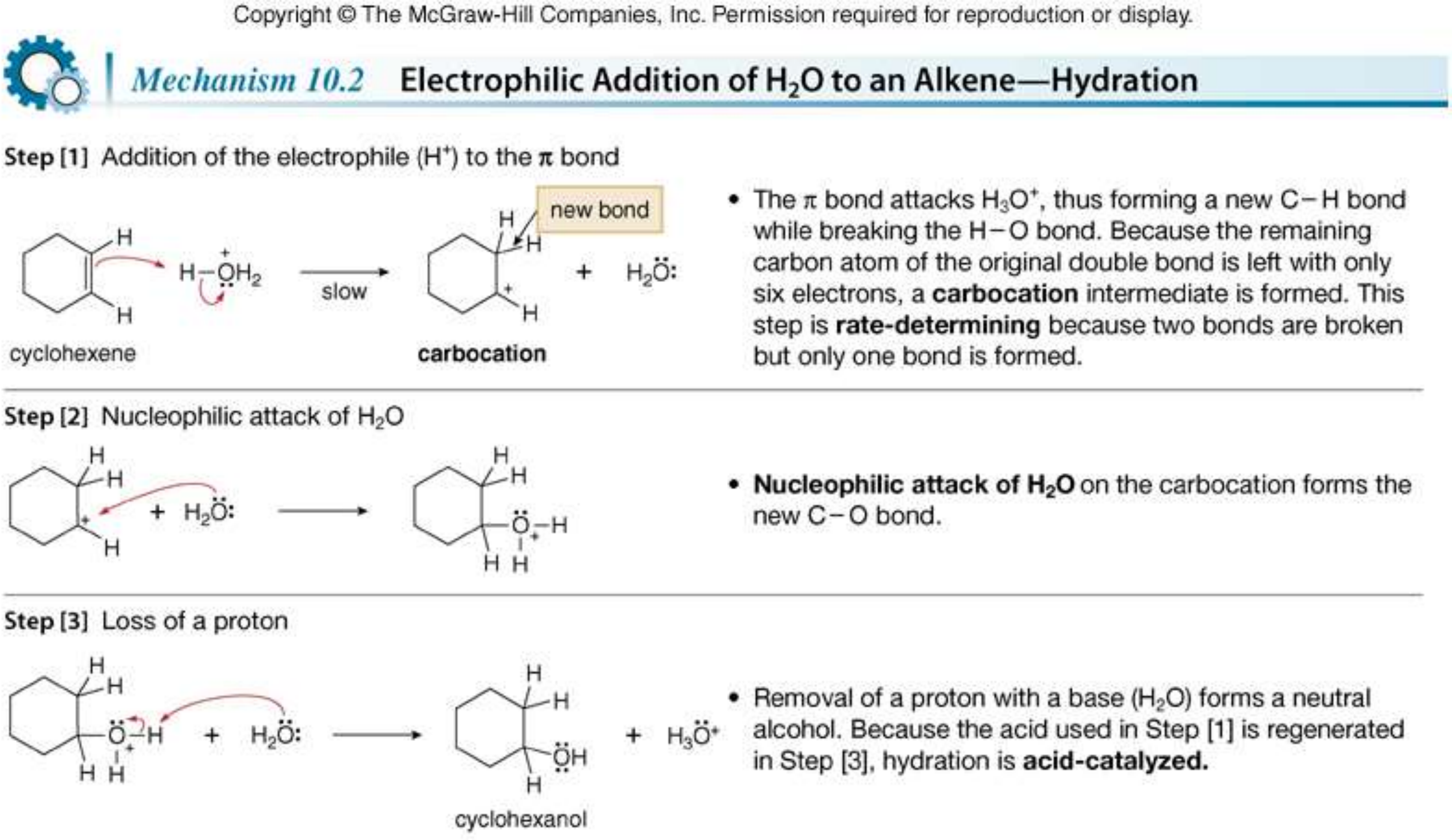
	Observation
Mechanism	• The mechanism involves two steps. • The rate-determining step forms a carbocation. • Rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	•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

Hydration: Electrophilic Addition of Water

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



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.

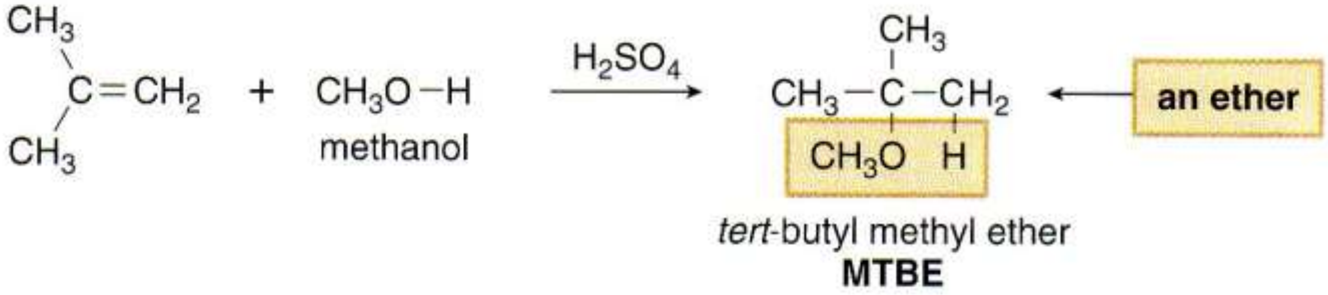
Step [3] Loss of a proton

- 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.**

Carbon-Carbon pi bonds

Hydration: Electrophilic Addition of Alcohols

- **Alcohols add to alkenes, forming ethers by the same mechanism. For example, addition of CH_3OH to 2-methylpropene, forms *tert*-butyl methyl ether (MTBE), a high octane fuel additive.**

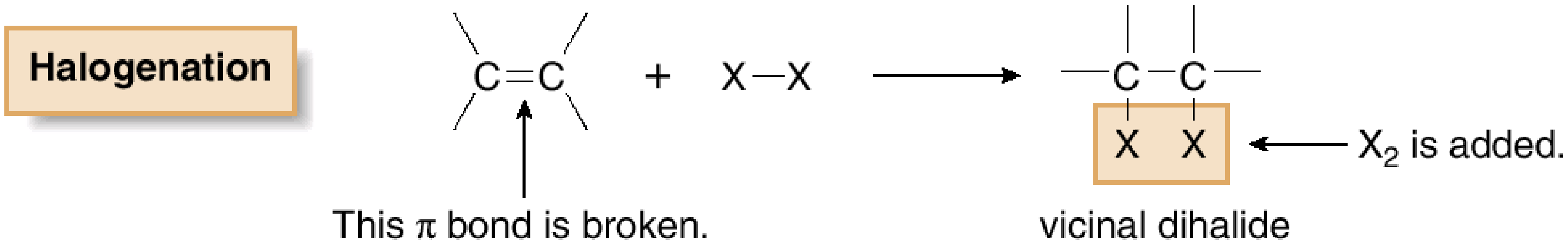


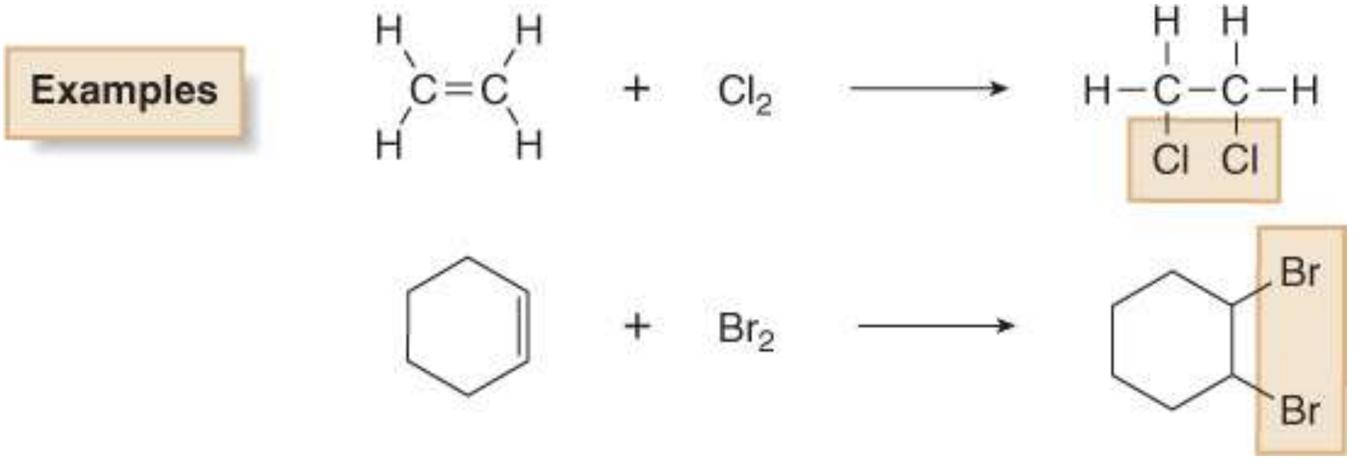
tert-butyl methyl ether
MTBE

- **Note that there are three consequences to the formation of carbocation intermediates:**
  1. **Markovnikov’s rule holds.**
  2. **Addition of H and OH occurs in both syn and anti fashion.**
  3. **Carbocation rearrangements can occur.**

Halogenation: Addition of Halogen

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

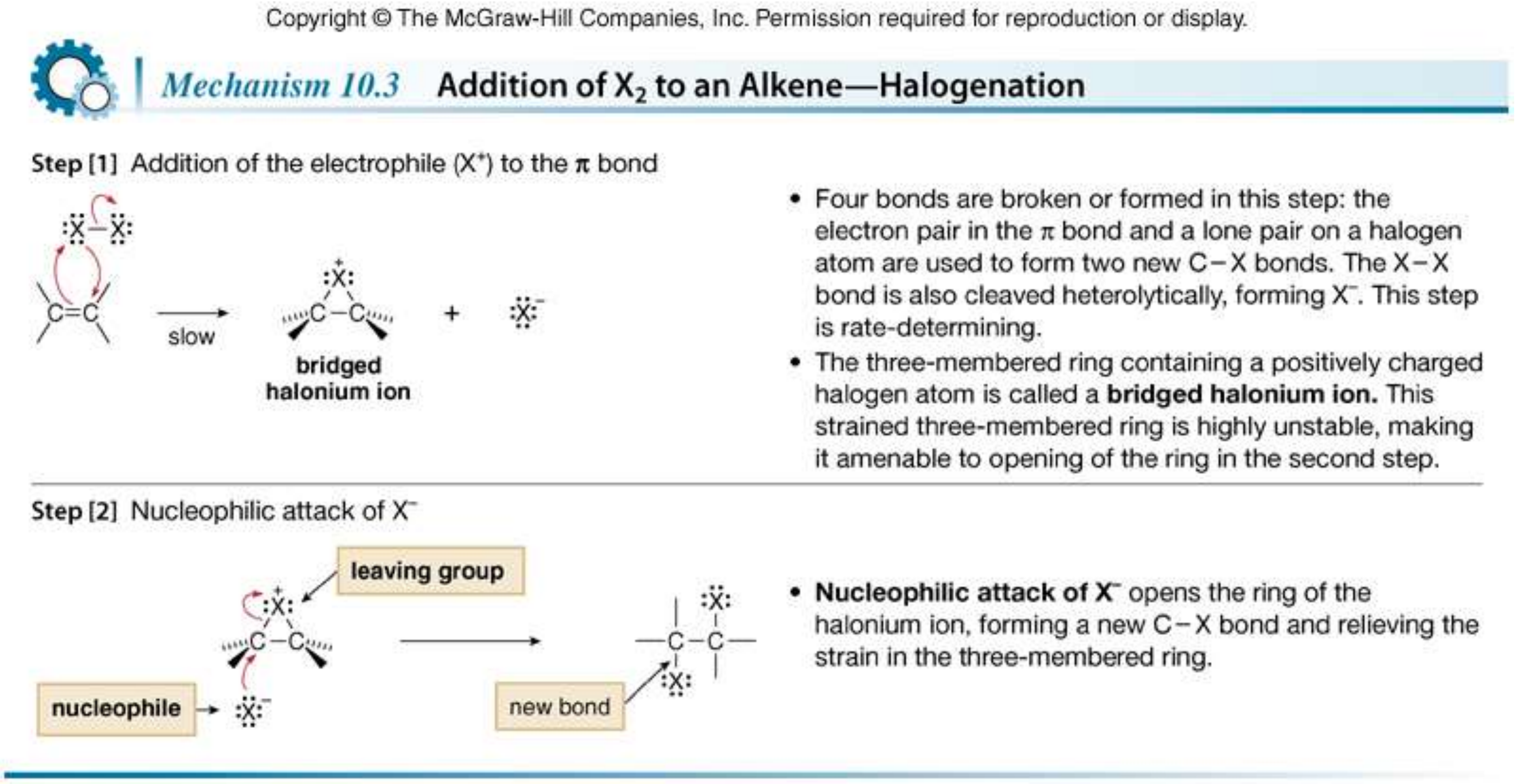




Halogenation: Addition of Halogen

- 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.

Halogenation: Addition of Halogen



Mechanism 10.3 **Addition of X_2 to an Alkene—Halogenation**

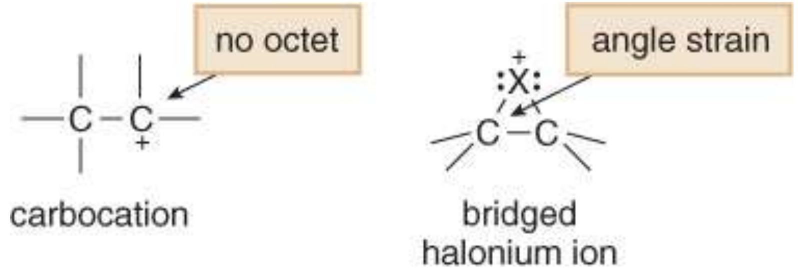
Step [1] Addition of the electrophile (X^+) to the π bond

- 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^-

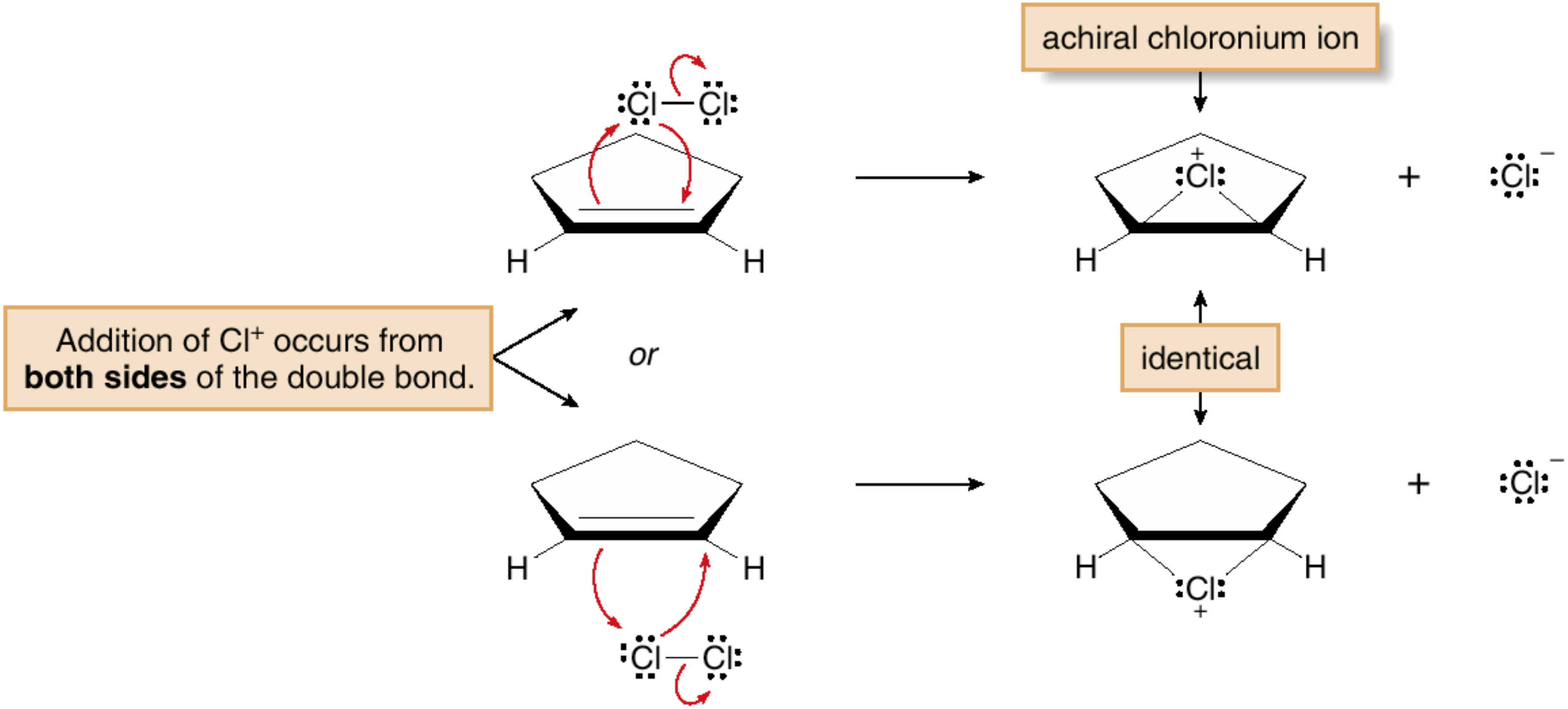
- **Nucleophilic attack of X^-** opens the ring of the halonium ion, forming a new C−X bond and relieving the strain in the three-membered ring.

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



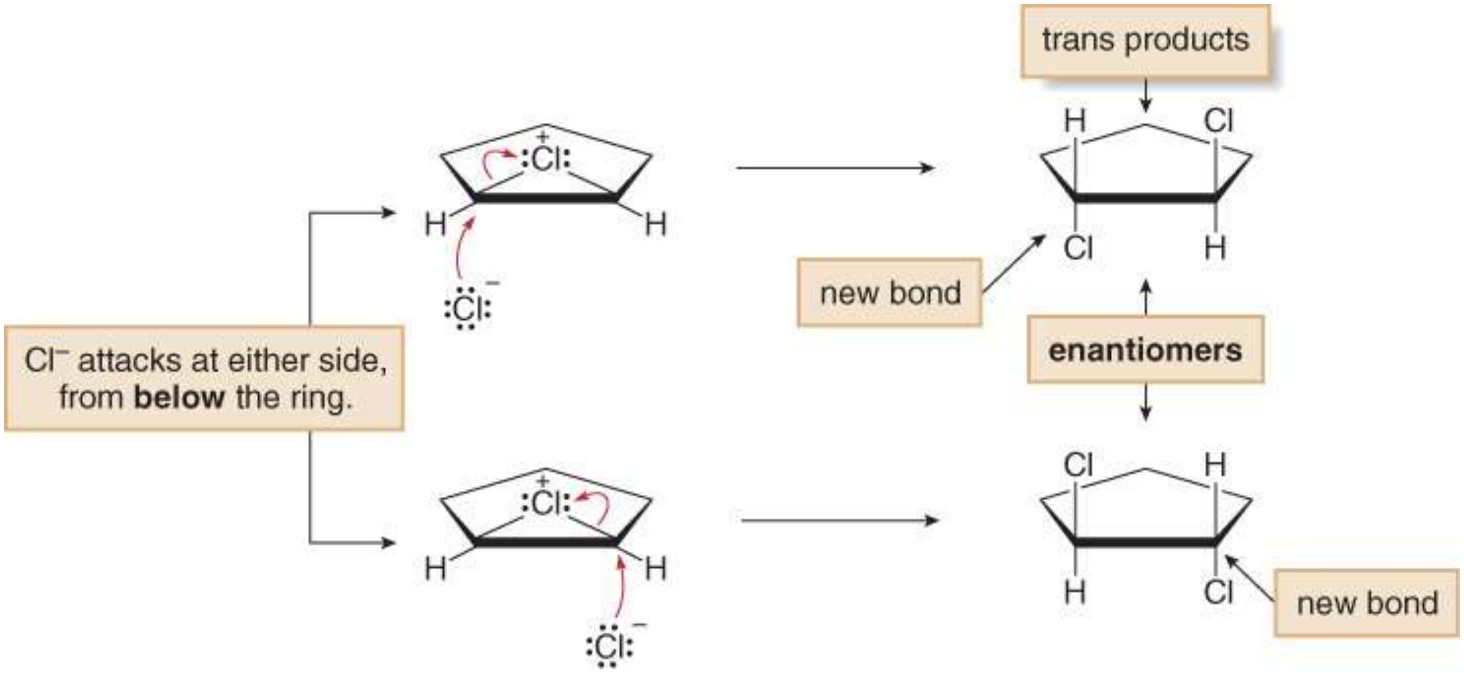
Halogenation: Reaction Stereochemistry

- **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.**



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

new bond

enantiomers

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

new bond

Halogenation: Reaction Stereochemistry

***cis*-2-Butene yields two enantiomers, whereas *trans*-2-butene yields a single achiral meso compound.**

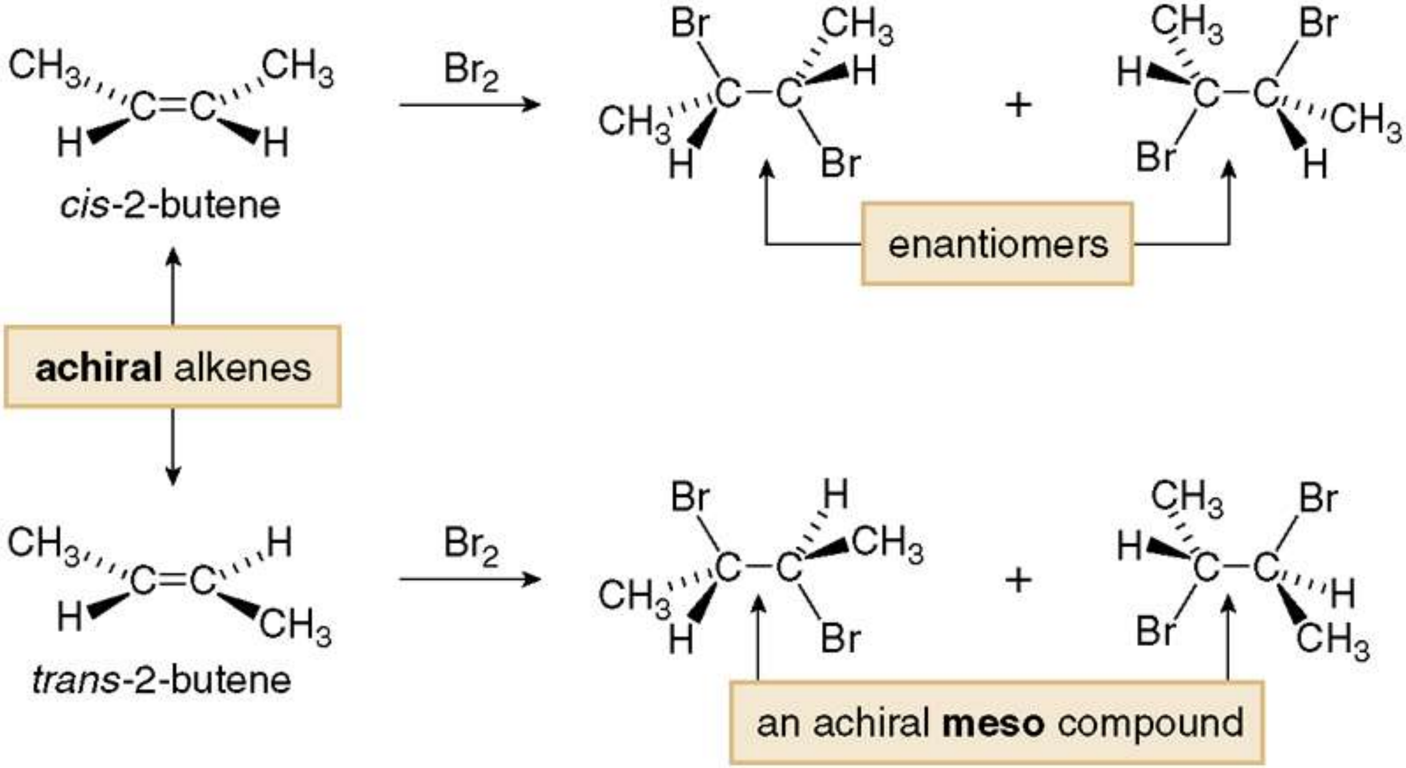


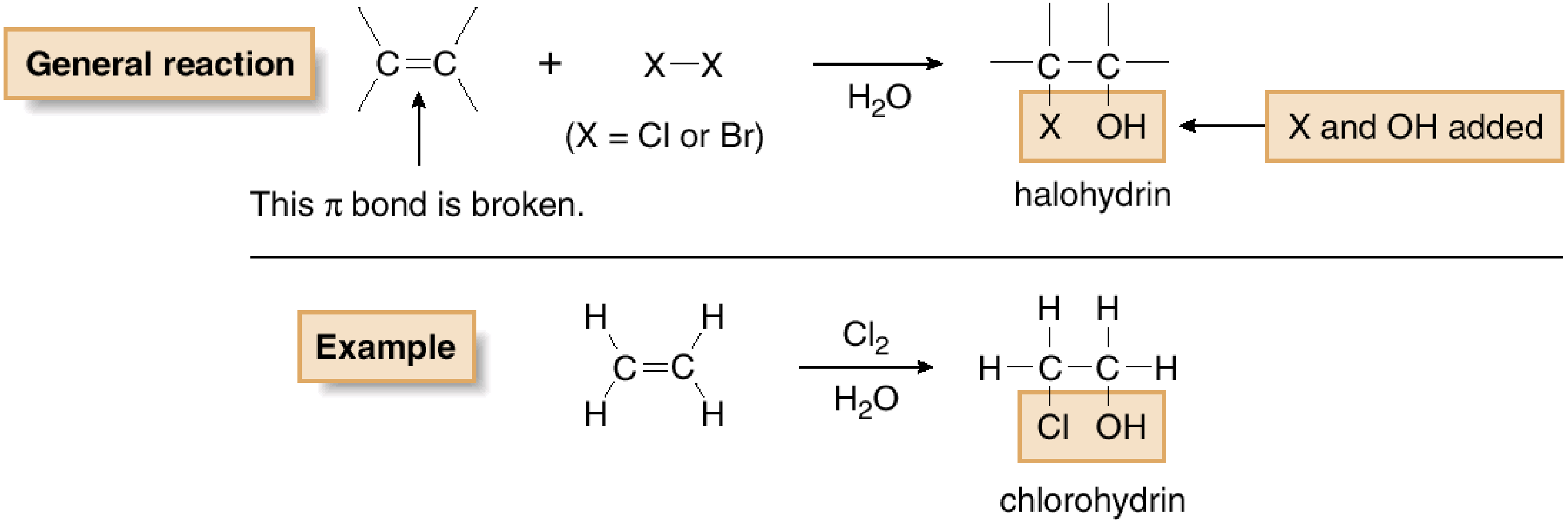
Figure 10.13
Halogenation of *cis*- and *trans*-2-butene

To draw the products of halogenation:

- Add Br_2 in an **anti** fashion across the double bond, leaving all other groups in their original orientations. Draw the products such that a given Br atom is above the plane in one product and below the plane in the other product.
- Sometimes this reaction produces two stereoisomers, as in the case of *cis*-2-butene, which forms an equal amount of two enantiomers. Sometimes it produces a single compound, as in the case of *trans*-2-butene, where a meso compound is formed.

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.

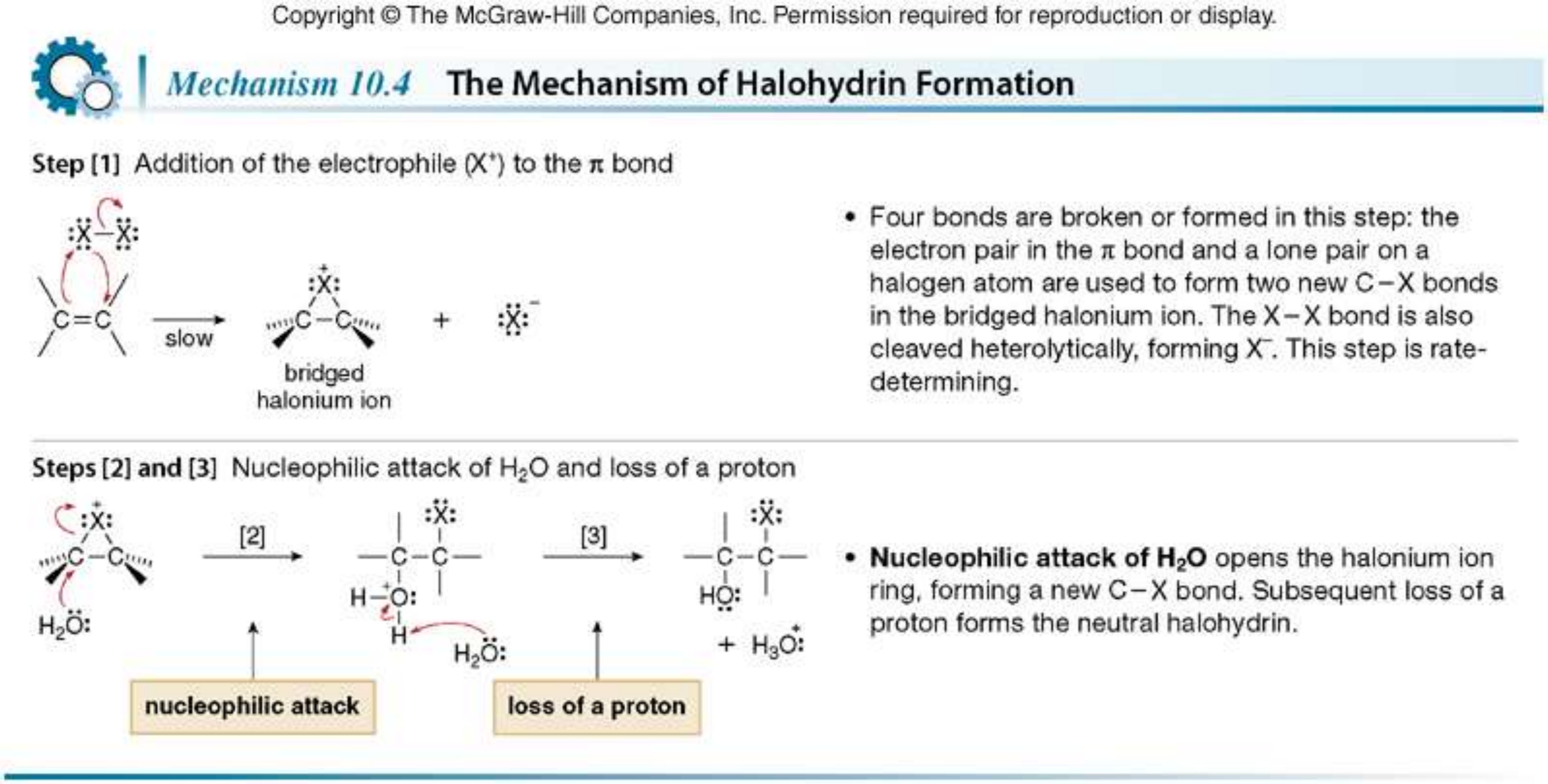


This π bond is broken.

halohydrin

chlorohydrin

Halohydrin Formation:



Mechanism 10.4 **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.

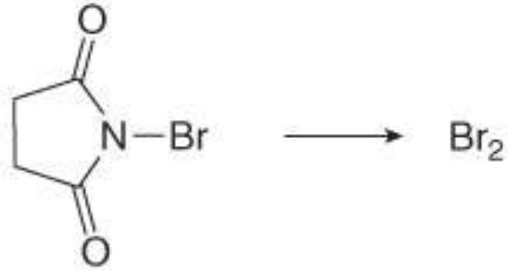
Steps [2] and [3] Nucleophilic attack of H_2O and loss of a proton

- **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.

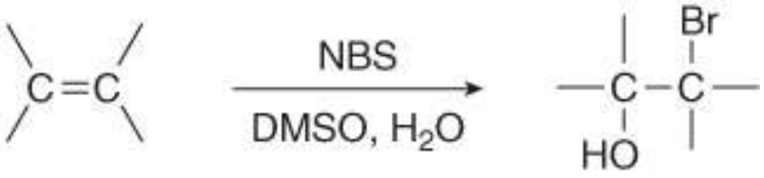
Even though $X^–$ is formed in step [1] of the mechanism, its concentration is small compared to H_2O (often the solvent), so H_2O and not $X^–$ is the nucleophile.

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.



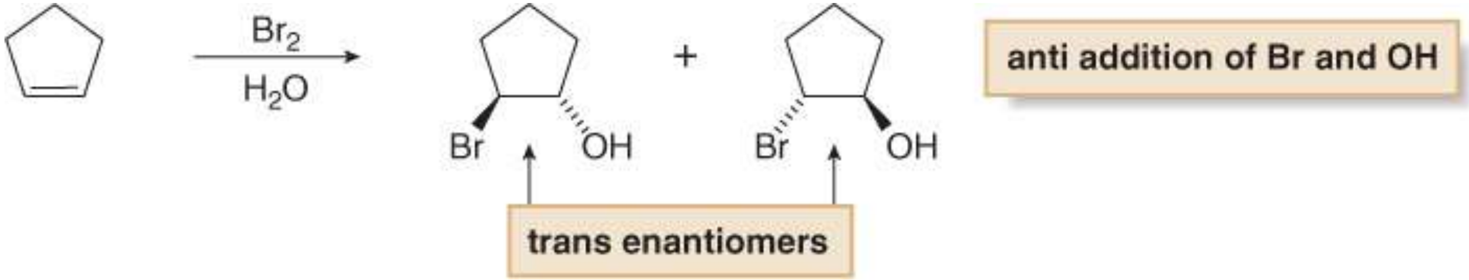
N-bromosuccinimide
NBS



bromohydrin

Halohydrin Formation:

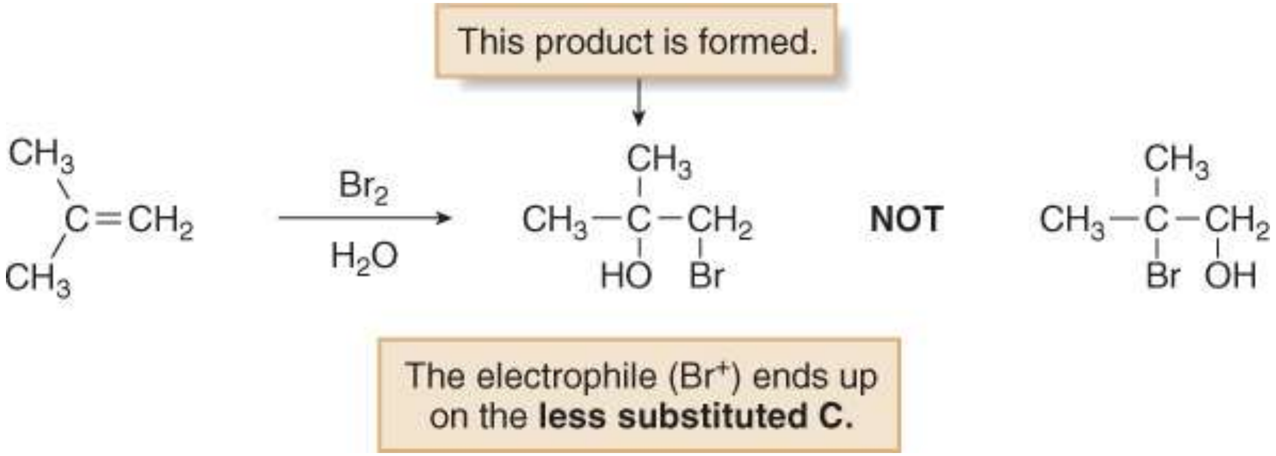
Because the bridged halonium ion is opened by backside attack of H_2O, addition of X and OH occurs in an anti fashion and trans products are formed.



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.



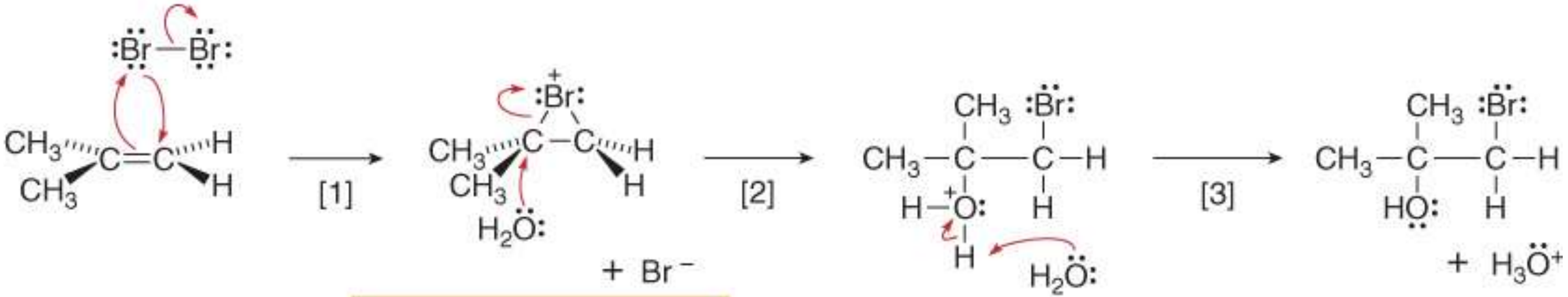
This product is formed.

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

Halohydrin Formation:

As in the acid catalyzed ring opening of epoxides, nucleophilic attack occurs at the more substituted carbon end of the bridged halonium ion because that carbon is better able to accommodate the partial positive charge in the transition state.

Halohydrin formation in an unsymmetrical alkene



nucleophilic attack at the
more substituted C

Halohydrin Formation:

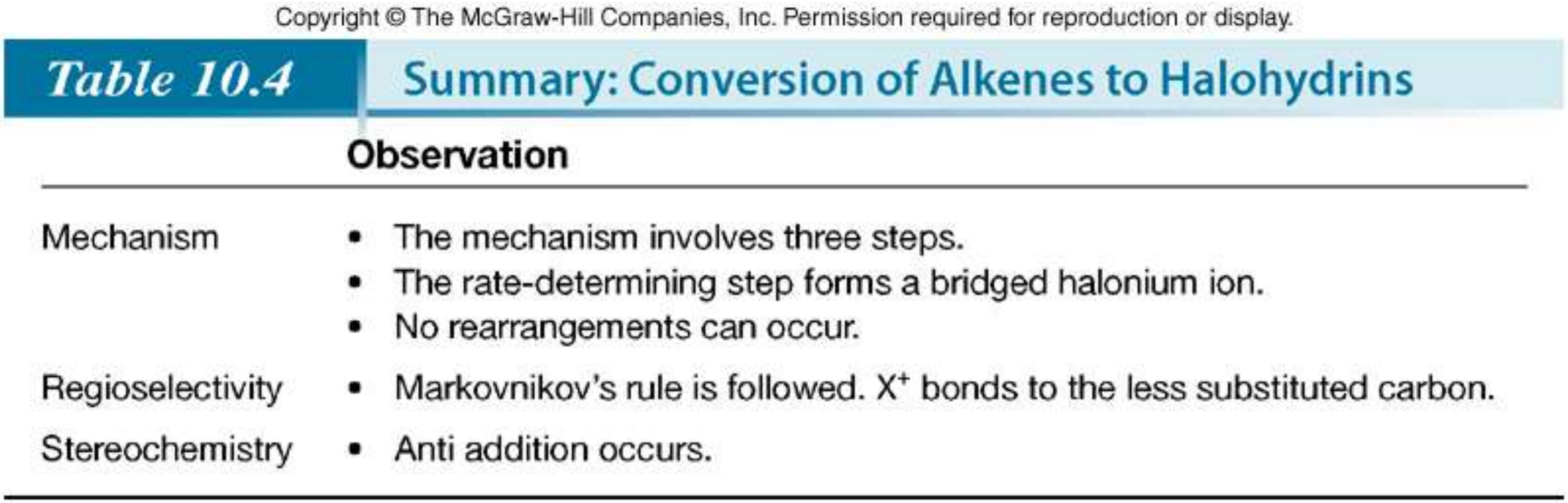
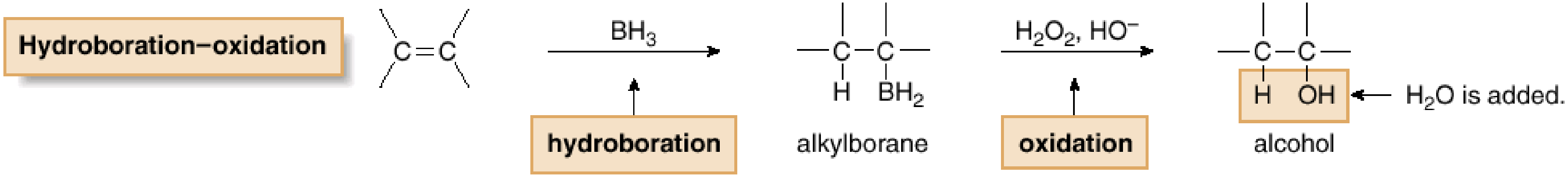


Table 10.4 Summary: Conversion of Alkenes to Halohydrins

	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.

Hydroboration - Oxidation:

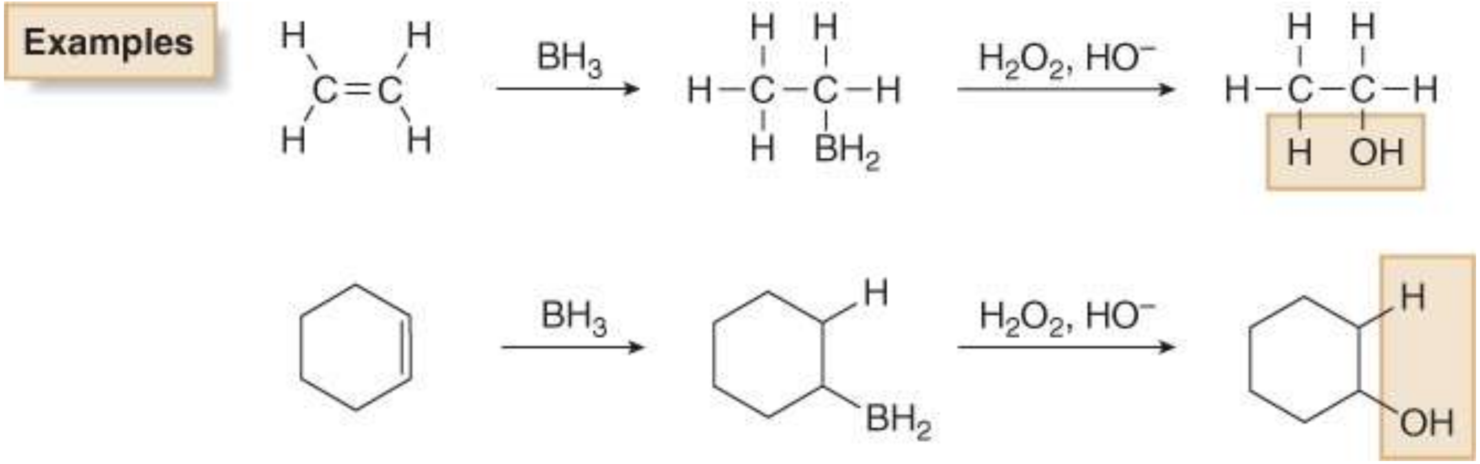
Hydroboration—oxidation is a two-step reaction sequence that converts an alkene into an alcohol.



- *Hydroboration* is the addition of borane (BH_3) to an alkene, forming an alkylborane.
- *Oxidation* converts the C−B bond of the alkylborane to a C−O bond.

Hydroboration - Oxidation:

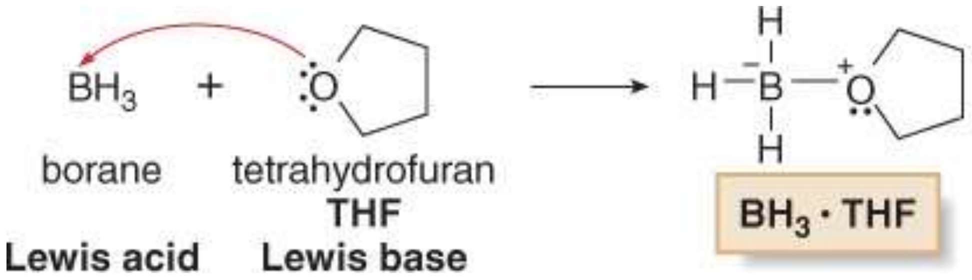
Hydroboration—oxidation results in the addition of H_2O to an alkene.



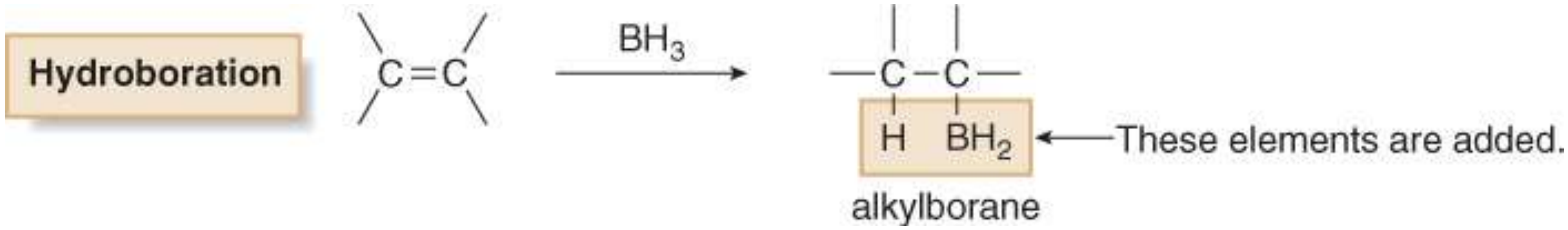
Carbon-Carbon pi bonds

Hydroboration - Oxidation:

BH_3 is a reactive gas that exists mostly as a dimer, diborane (B_2H_6). Borane is a strong Lewis acid that reacts readily with Lewis bases. For ease of handling in the laboratory, it is commonly used as a complex with tetrahydrofuran (THF).

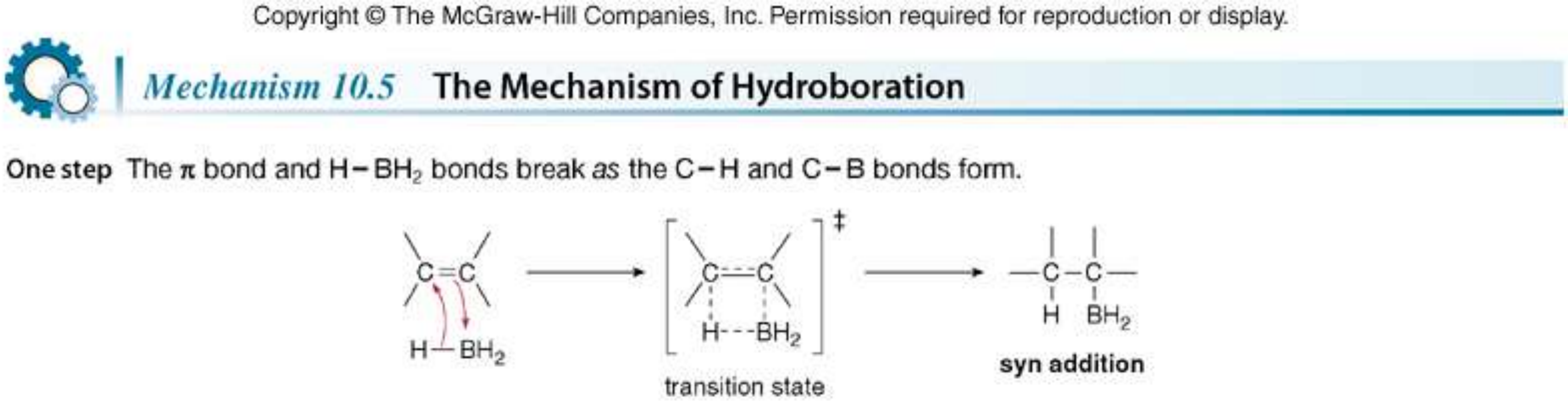


The first step in hydroboration—oxidation is the addition of the elements of H and BH_2 to the π bond of the alkene, forming an intermediate alkylborane.



Hydroboration - Oxidation:

- **The proposed mechanism involves concerted addition of H and BH_2 from the same side of the planar double bond: the π bond and H—BH_2 bond are broken as two new σ bonds are formed.**
- **Because four atoms are involved, the transition state is said to be four-centered.**



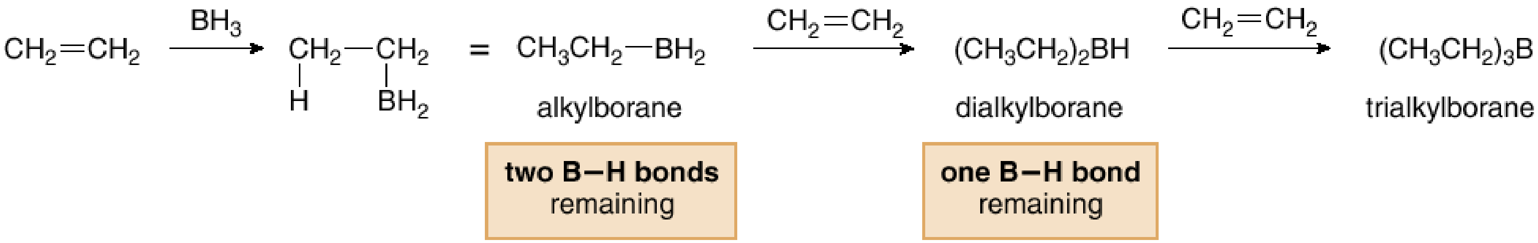
Mechanism 10.5 **The Mechanism of Hydroboration**

One step The π bond and H–BH_2 bonds break *as* the C–H and C–B bonds form.

Hydroboration - Oxidation:

Because the alkylborane formed by the reaction with one equivalent of alkene still has two B—H bonds, it can react with two more equivalents of alkene to form a trialkylborane.

Figure 10.15 Conversion of BH_3 to a trialkylborane with three equivalents of $CH_2{=}CH_2$



$$CH_2{=}CH_2 \xrightarrow{BH_3} \underset{H\quad\; BH_2}{CH_2{-}CH_2} = CH_3CH_2{-}BH_2 \xrightarrow{CH_2{=}CH_2} (CH_3CH_2)_2BH \xrightarrow{CH_2{=}CH_2} (CH_3CH_2)_3B$$

- We often draw hydroboration as if addition stopped after one equivalent of alkene reacts with BH_3. Instead, all three B–H bonds actually react with three equivalents of an alkene to form a trialkylborane. The term **organoborane** is used for any compound with a carbon–boron bond.

Carbon-Carbon pi bonds

Hydroboration - Oxidation:

Since only one B-H bond is needed for hydroboration, commercially available dialkylboranes having the general structure R_2BH are sometimes used instead of BH_3. A common example is 9-borabicyclo[3.3.1]nonane (9-BBN).

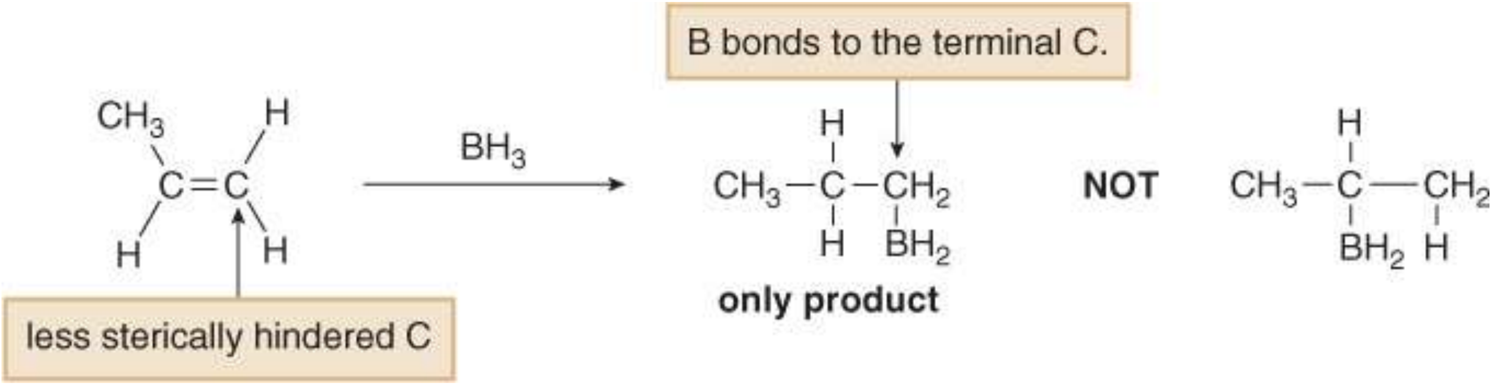
9-borabicyclo[3.3.1]nonane
9-BBN

Hydroboration with 9-BBN

Carbon-Carbon pi bonds

Hydroboration - Oxidation:

With unsymmetrical alkenes, the boron atom bonds to the less substituted carbon atom.



B bonds to the terminal C.

less sterically hindered C

only product

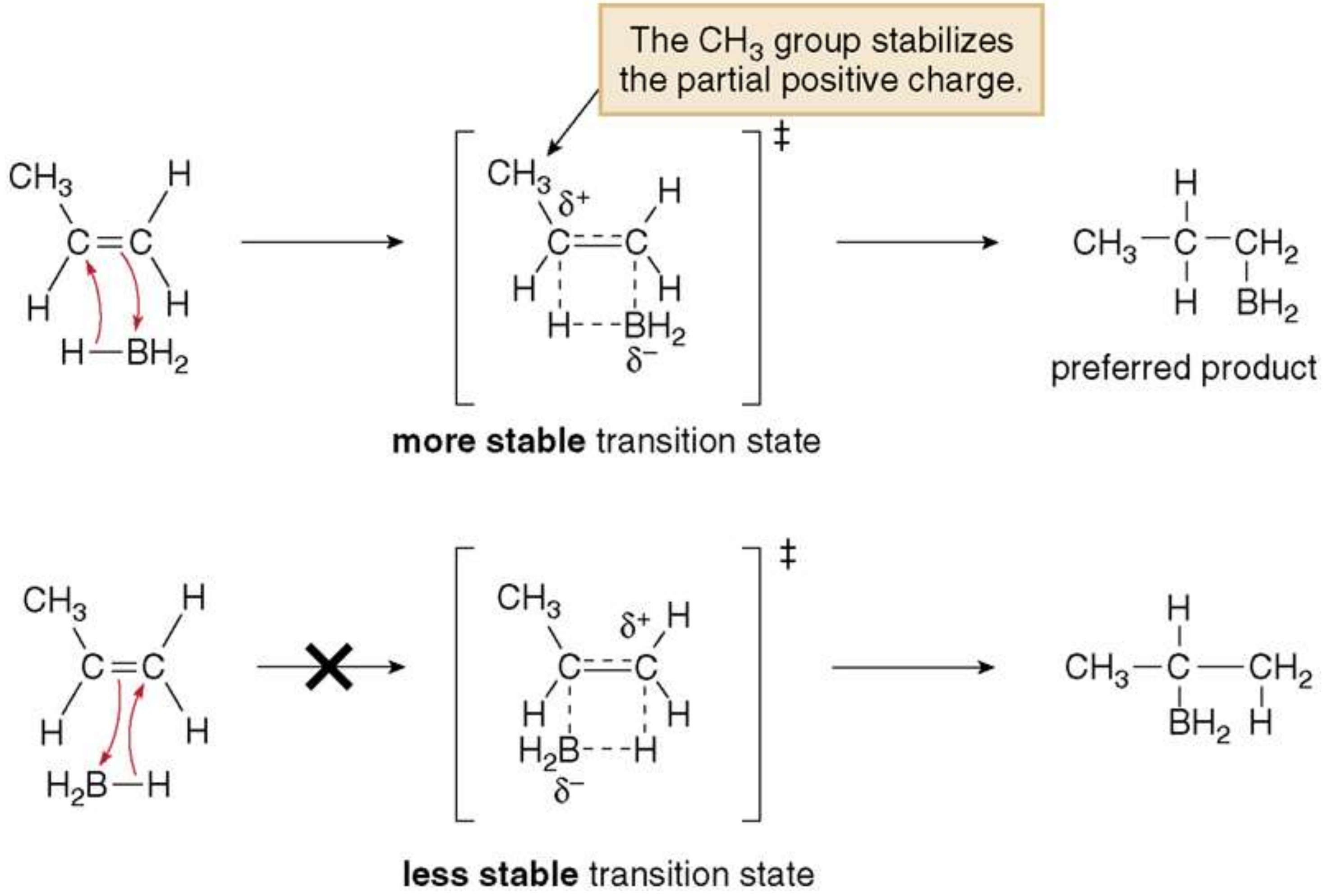
NOT

Hydroboration - Oxidation:

- This regioselectivity can be explained by considering steric factors. The larger boron atom bonds to the less sterically hindered, more accessible carbon atom.
- Electronic factors are also used to explain this regioselectivity. If bond making and bond breaking are not completely symmetrical, boron bears a δ- charge in the transition state and carbon bears a δ+ charge. Since alkyl groups stabilize a positive charge, the more stable transition state has the partial positive charge on the more substituted carbon.

Hydroboration - Oxidation:

Figure 10.16 **Hydroboration of an unsymmetrical alkene**



The CH_3 group stabilizes the partial positive charge.

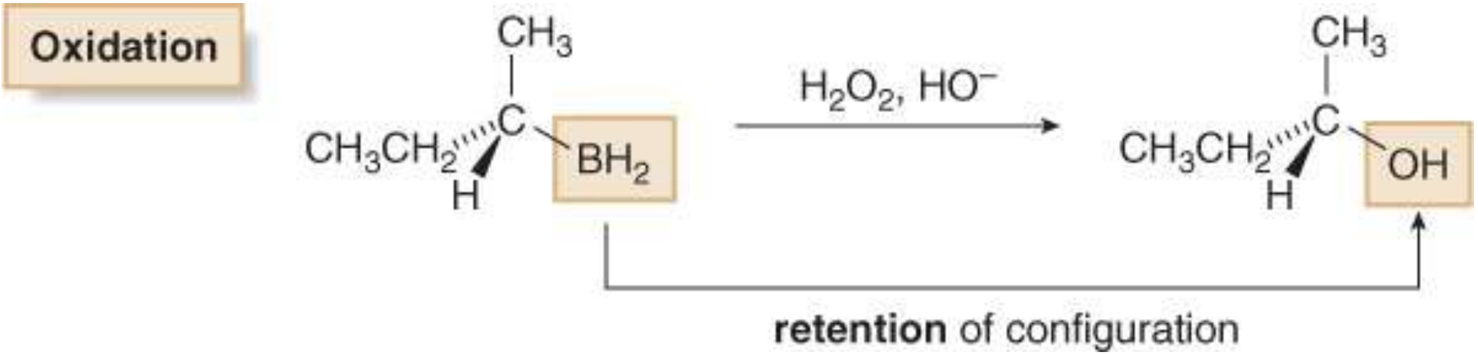
more stable transition state

preferred product

less stable transition state

Hydroboration - Oxidation:

- Since alkylboranes react rapidly with water and spontaneously burn when exposed to air, they are oxidized, without isolation, with basic hydrogen peroxide (H_2O_2, ^{-}OH).
- Oxidation replaces the C—B bond with a C—O bond, forming a new OH group with retention of configuration.
- The overall result of this two-step sequence is syn addition of the elements of H and OH to a double bond in an "anti-Markovnikov" fashion.



Hydroboration - Oxidation:

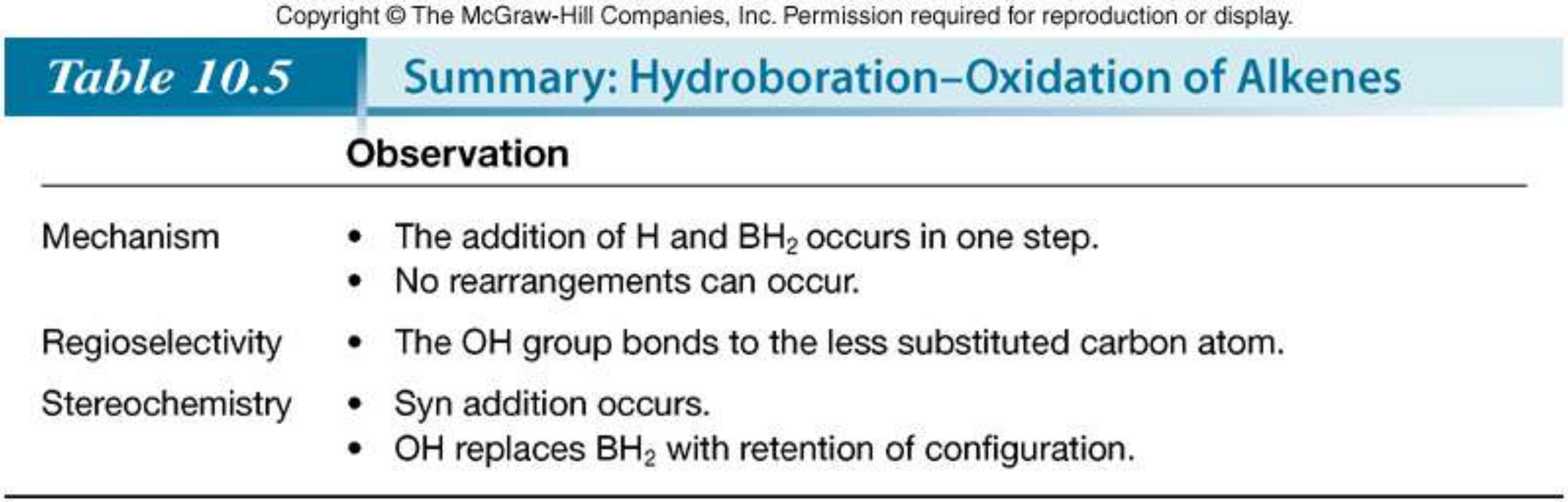


Table 10.5 **Summary: Hydroboration–Oxidation of Alkenes**

	Observation
Mechanism	• The addition of H and BH_2 occurs in one step. • No rearrangements can occur.
Regioselectivity	• The OH group bonds to the less substituted carbon atom.
Stereochemistry	• Syn addition occurs. • OH replaces BH_2 with retention of configuration.

Oxymercuration – Demercuration:

This is a two step reaction.

1. Oxymercuration using $Hg(OAc)_2$ and HOH
2. Reduction using $NaBH_4$ and OH^-

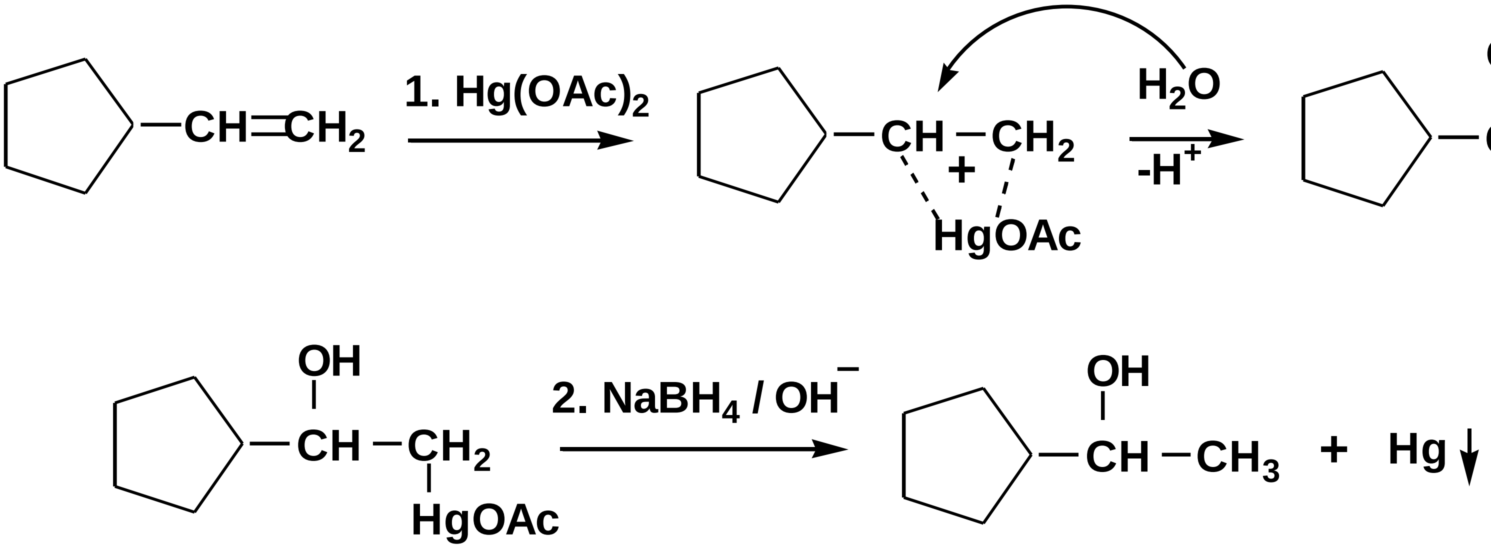
Step 1 of the mechanism forms a cyclic mercurinium ion requiring anti attack of the nucleophile (HOH).

Step 2 is a sodium borohydride reduction of the C-HgOAc bond.

Water yields a Markovnikov alcohol, however, no C+ is formed so, no rearrangement is possible.

The benefit of this reaction is a Markovnikov product with no rearrangement.

Oxymercuration – Demercuration:



Alkoxymercuration – Demercuration:

Mechanism is the same as before.

1. Alkoxymercuration using $Hg(OAc)_2$ and ROH
2. Reduction using $NaBH_4$ and OH^-

Step 1 of the mechanism forms a cyclic mercurinium ion requiring anti attack of the nucleophile (ROH).

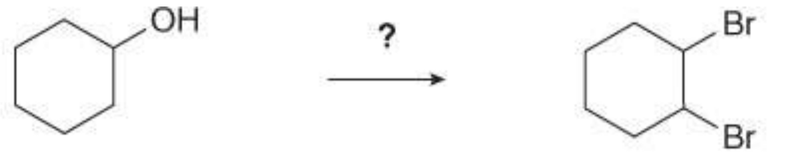
Step 2 is a sodium borohydride reduction of the C-HgOAc bond.

An alcohol yields a Markovnikov ether, again, no C+ is formed so, no rearrangement is possible.

The benefit of this reaction is a Markovnikov product with no rearrangement.

Alkenes in Organic Synthesis:

Suppose we wish to synthesize 1,2-dibromocyclohexane from cyclohexanol.



cyclohexanol

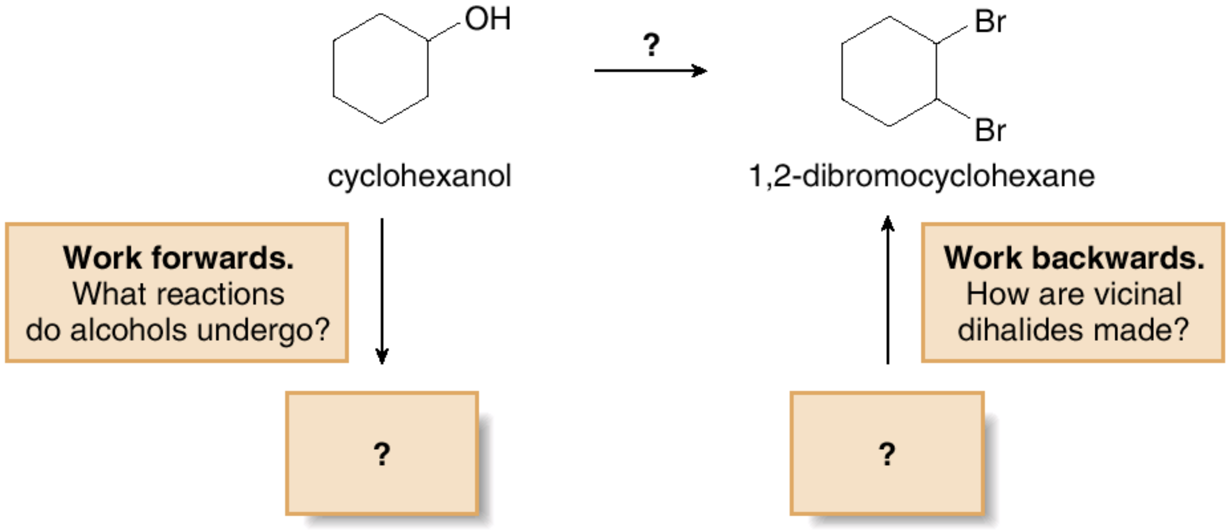
starting material

1,2-dibromocyclohexane

product

To solve this problem we must:

- Work backwards from the product by asking: What type of reactions introduce the functional groups in the product?
- Work forwards from the starting material by asking: What type of reactions does the starting material undergo?



cyclohexanol

1,2-dibromocyclohexane

Work forwards.
What reactions
do alcohols undergo?

Work backwards.
How are vicinal
dihalides made?

?

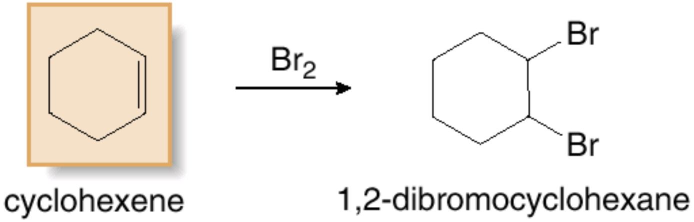
?

Alkenes in Organic Synthesis:

Working backwards from the product to determine the starting material from which it is made is called retrosynthetic analysis.

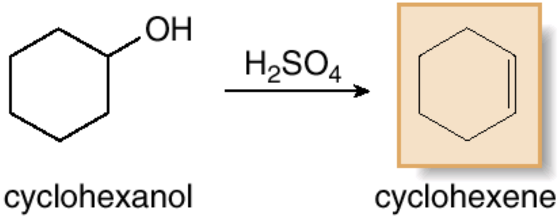
Working backwards:

[1] 1,2-Dibromocyclohexane, a vicinal dibromide, can be prepared by the addition of Br_2 to **cyclohexene.**



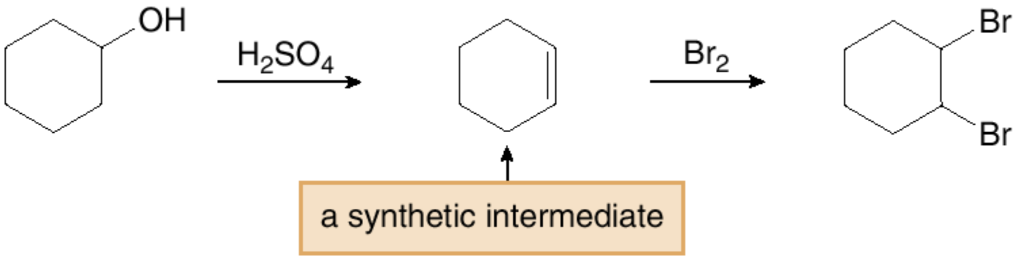
Working forwards:

[2] Cyclohexanol can undergo acid-catalyzed dehydration to form **cyclohexene.**

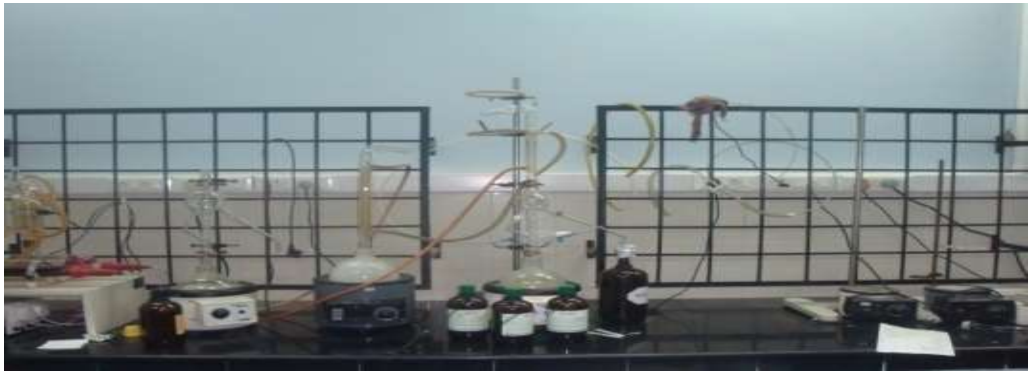


Cyclohexene is called a **synthetic intermediate,** or simply an **intermediate,** because it is the **product of one step and the starting material of another.** We now have a two-step sequence to convert cyclohexanol to 1,2-dibromocyclohexane, and the synthesis is complete. Take note of the central role of the alkene in this synthesis.

A two-step synthesis



Thank You



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