Organic Chemistry

Alkenes

by

Nurlin Abu Samah, Dr. Md. Shaheen & Dr. Nadeem Akhtar
Faculty of Industrial Sciences & Technology
nurlin@ump.edu.my

Chapter Description

- Aims
  - The students should **understand** the fundamental of organic chemistry in terms of alkenes
  - The students should be able to **explain** the fundamental of organic chemistry in terms of alkenes

- Expected Outcomes
  - Explain the basic knowledge in alkenes
  - Describe the chemical reactions and conditions for alkenes reactions
  - Describe the synthesis reactions involving alkenes in certain industrial application

- References
  - Janice Gorzynski Smith (2008), Organic chemistry,Mc Graw-Hill
  - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
  - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem

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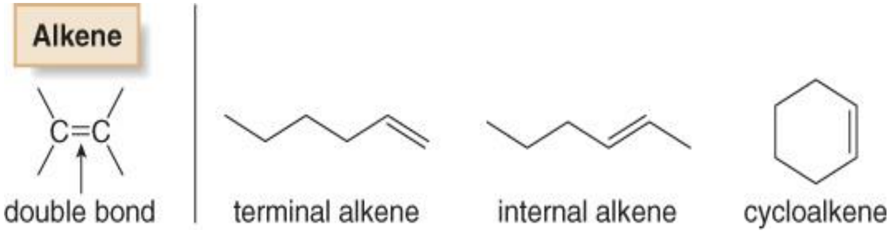
Alkenes

Alkenes

Introduction—Structure and Bonding

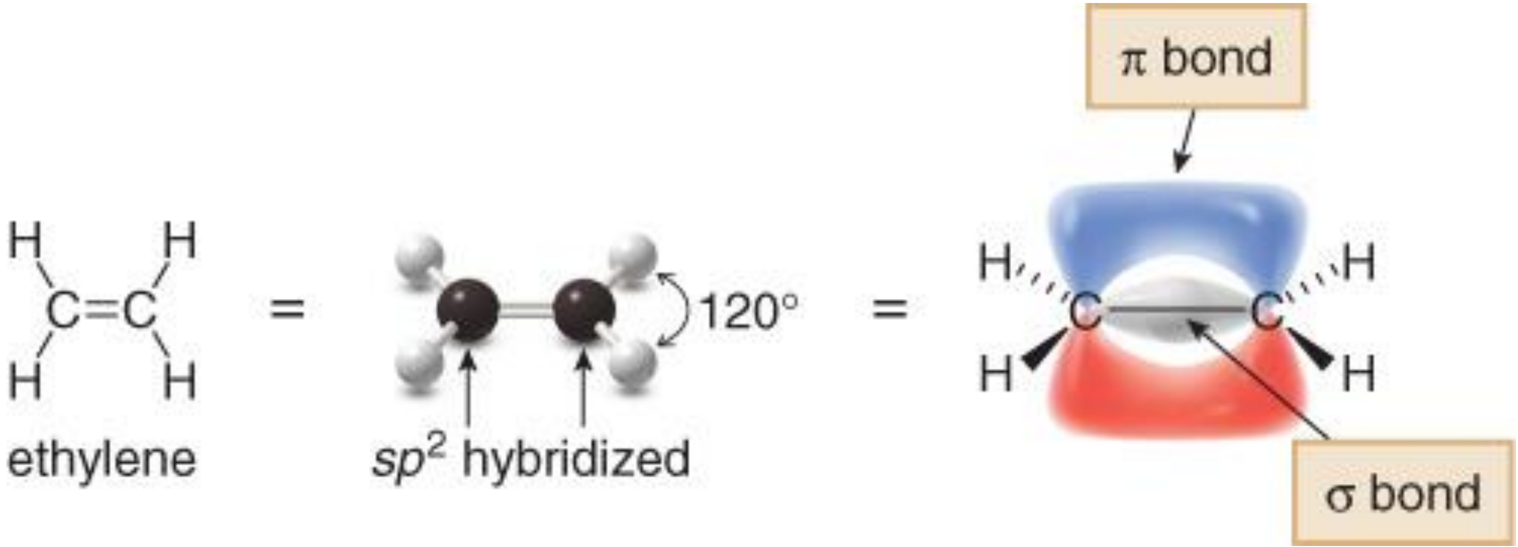
- Alkenes are also called olefins.
- Alkenes contain a C—C double bond.
- Terminal alkenes have the double bond at the end of the carbon chain.
- Internal alkenes have at least one carbon atom bonded to each end of the double bond.
- Cycloalkenes contain a double bond in a ring.



Alkenes

Introduction—Structure and Bonding

- Recall that the double bond consists of a π bond and a σ bond.
- Each carbon is *sp*² hybridized and trigonal planar, with bond angles of approximately 120°



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Introduction—Structure and Bonding

- Bond dissociation energies of the C—C bonds in ethane (a σ bond only) and ethylene (one σ and one π bond) can be used to estimate the strength of the π component of the double bond.

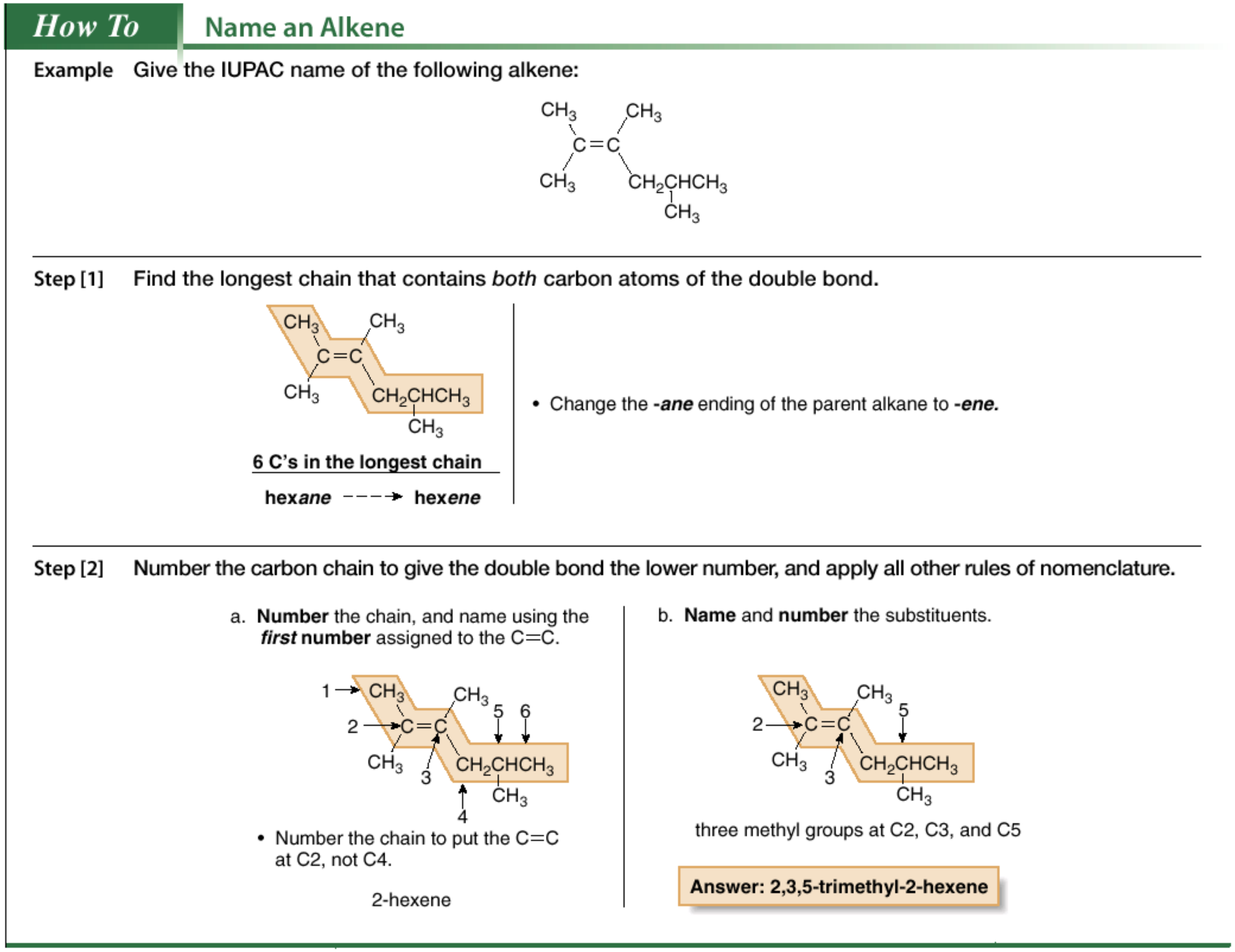
$$\underset{(\sigma + \pi\ \text{bond})}{\overset{CH_2{=}CH_2}{152\ \text{kcal/mol}}} \quad - \quad \underset{(\sigma\ \text{bond})}{\overset{CH_3{-}CH_3}{88\ \text{kcal/mol}}} \quad = \quad \underset{\uparrow}{64\ \text{kcal/mol}}$$

π bond only

- The π bond is much weaker than the σ bond of a C−C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not.

Alkenes

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.***

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

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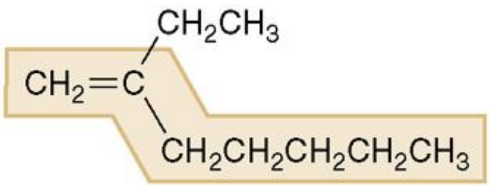
Nomenclature of Alkenes

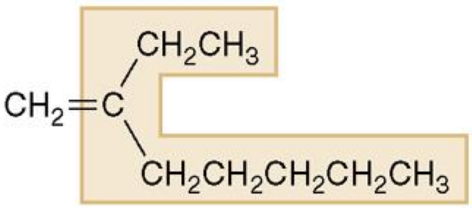
Naming an alkene in which the longest carbon chain does not contain both atoms of the double bond



7 C's ---→ heptene

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

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

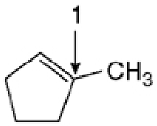


8 C's

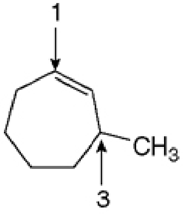
Both C's of the C=C are NOT contained in this long chain.

Incorrect

Examples of cycloalkene nomenclature

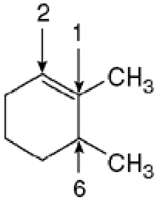


1-methylcyclopentene



3-methylcycloheptene

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

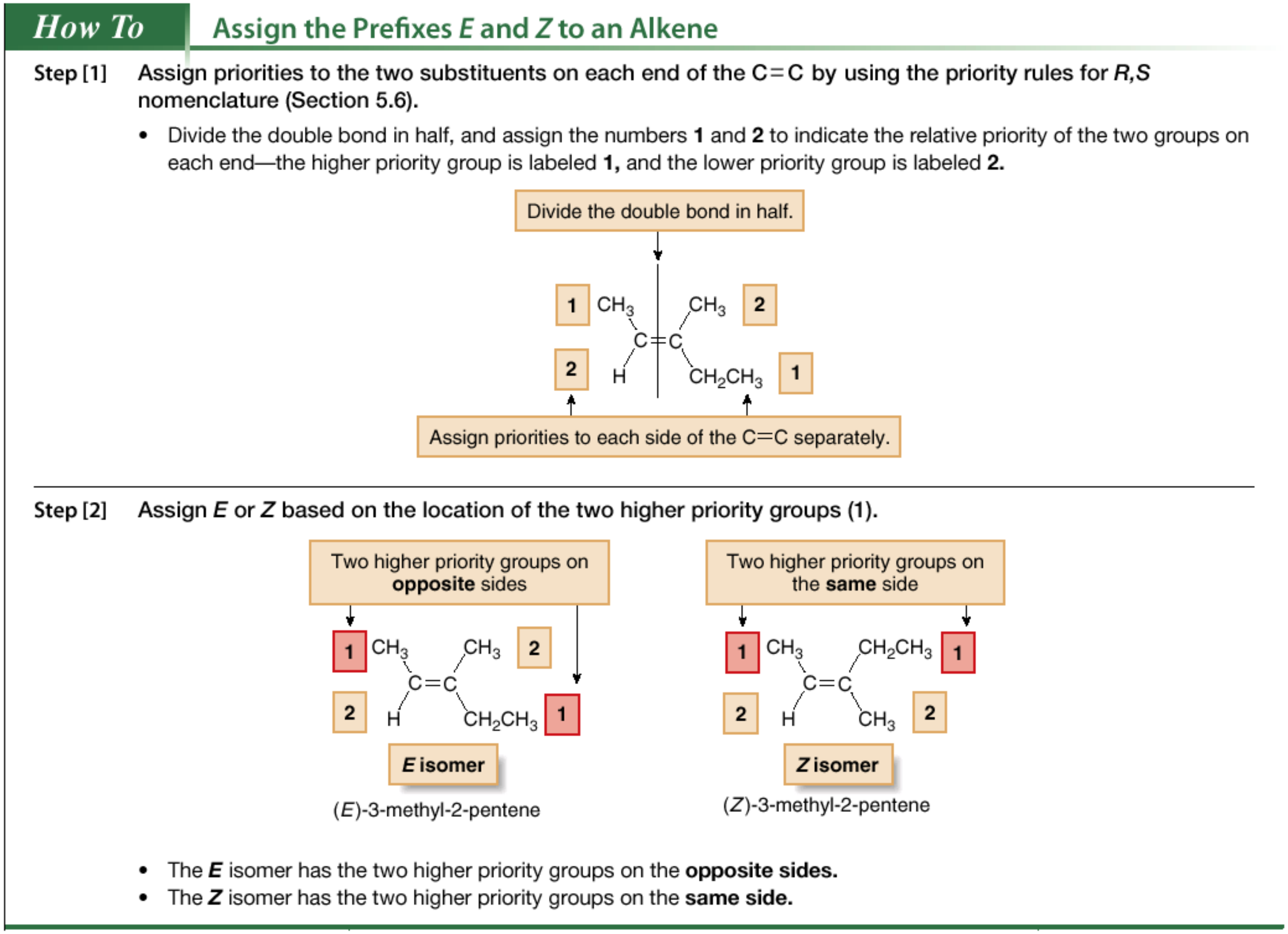


1,6-dimethylcyclohexene

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

Alkenes

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.

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

Two higher priority groups on **opposite** sides

***E* isomer**

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

Two higher priority groups on the **same** side

***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.**

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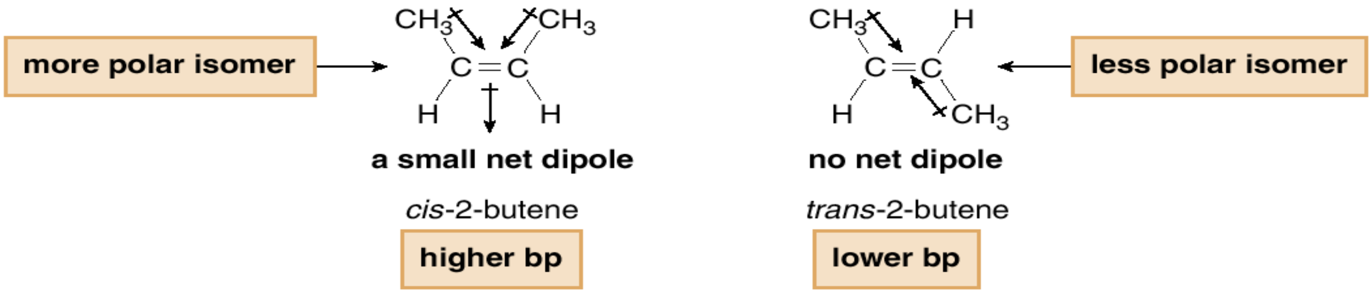
Alkenes

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 →

← **less polar isomer**

a small net dipole

cis-2-butene

higher bp

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.

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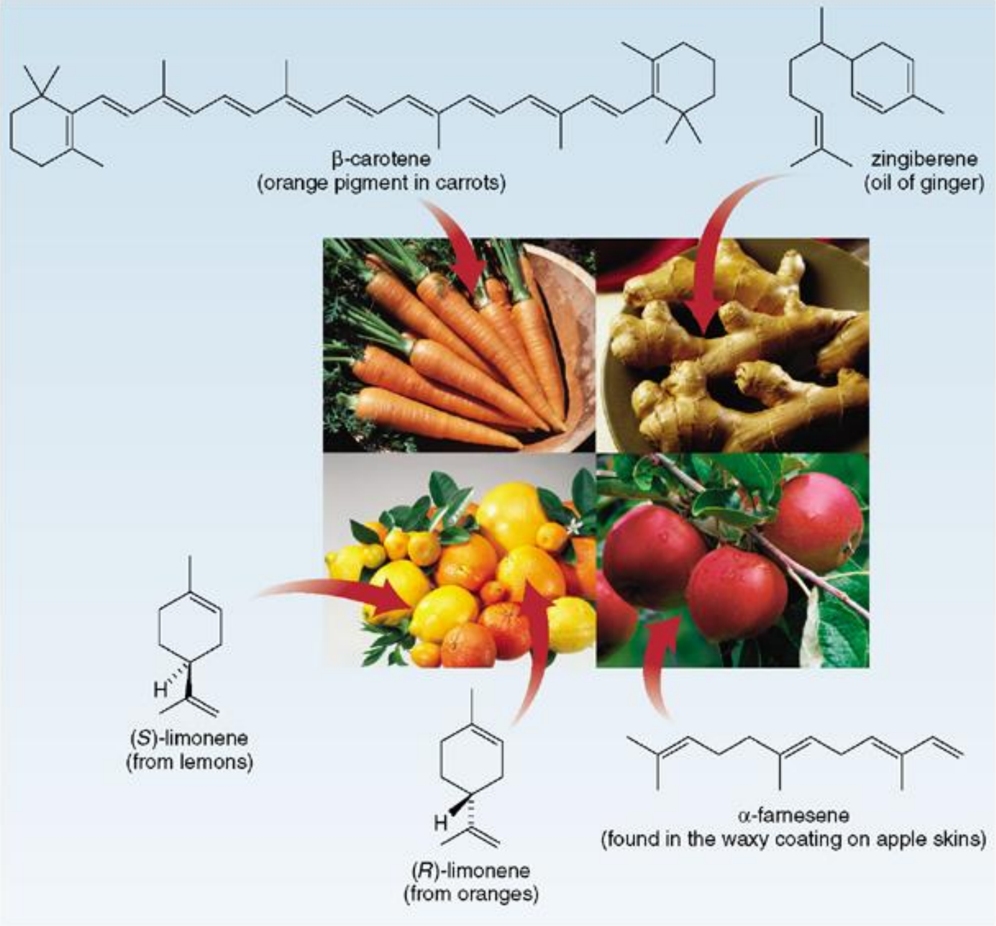
Interesting Alkenes

Five naturally occurring alkenes



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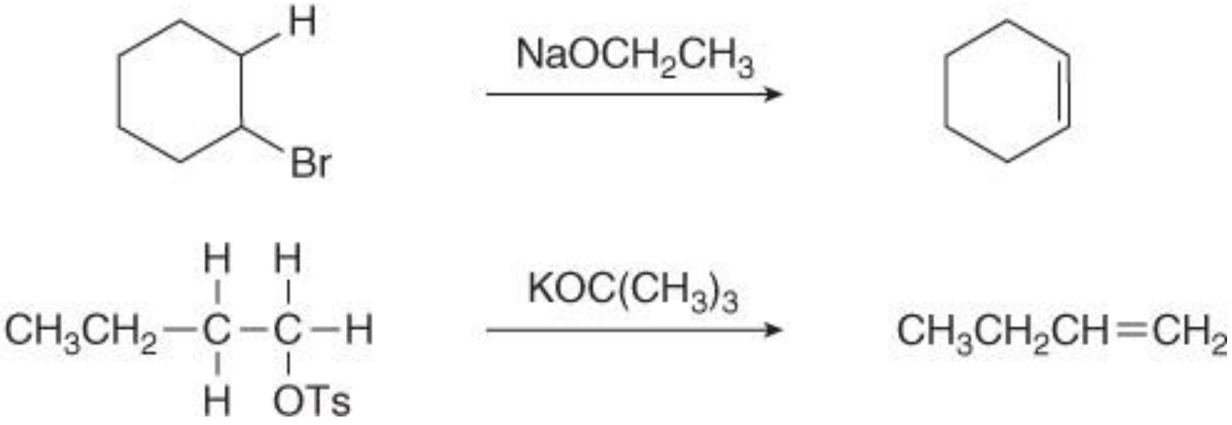
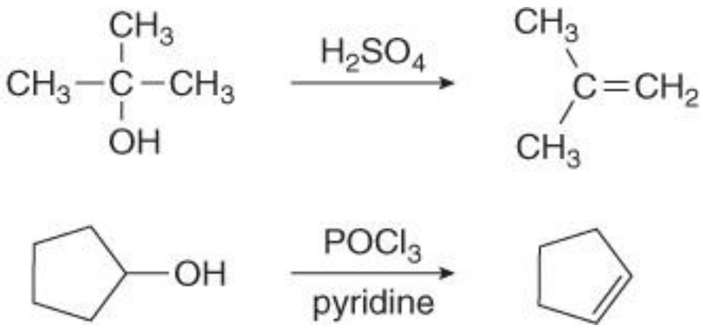
Preparation of Alkenes

- Recall that alkenes can be prepared from alkyl halides and alcohols via elimination reactions.

Examples



Examples

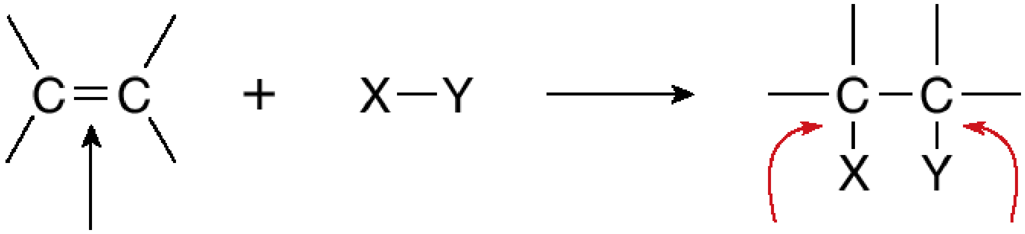


Alkenes

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.
- ☐ Alkenes are electron rich, simple alkenes do not react with nucleophiles or bases, reagents that are themselves electron rich. Alkenes react with electrophiles.

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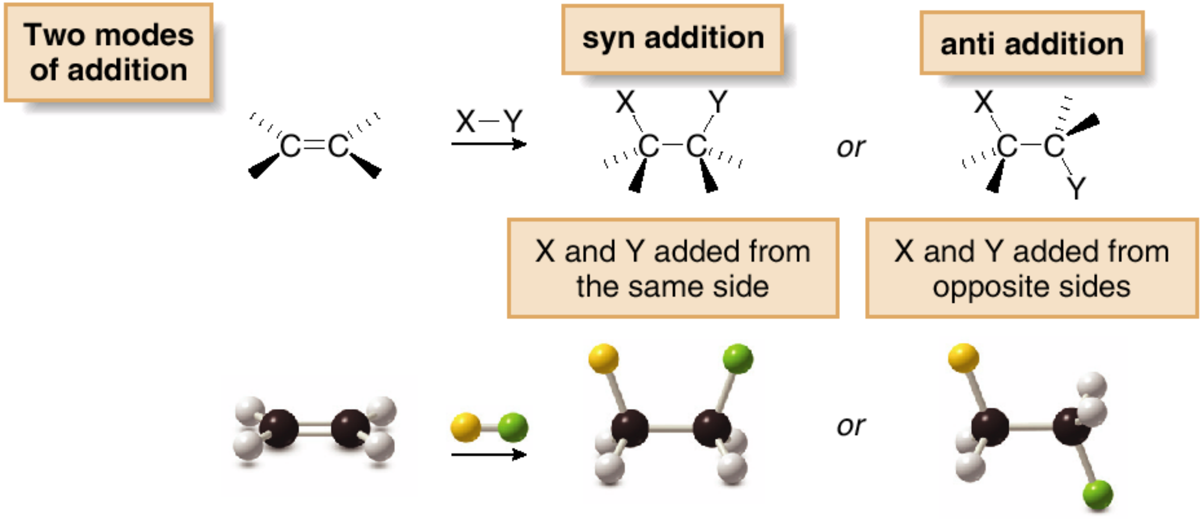
Introduction to Addition Reactions

- 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.

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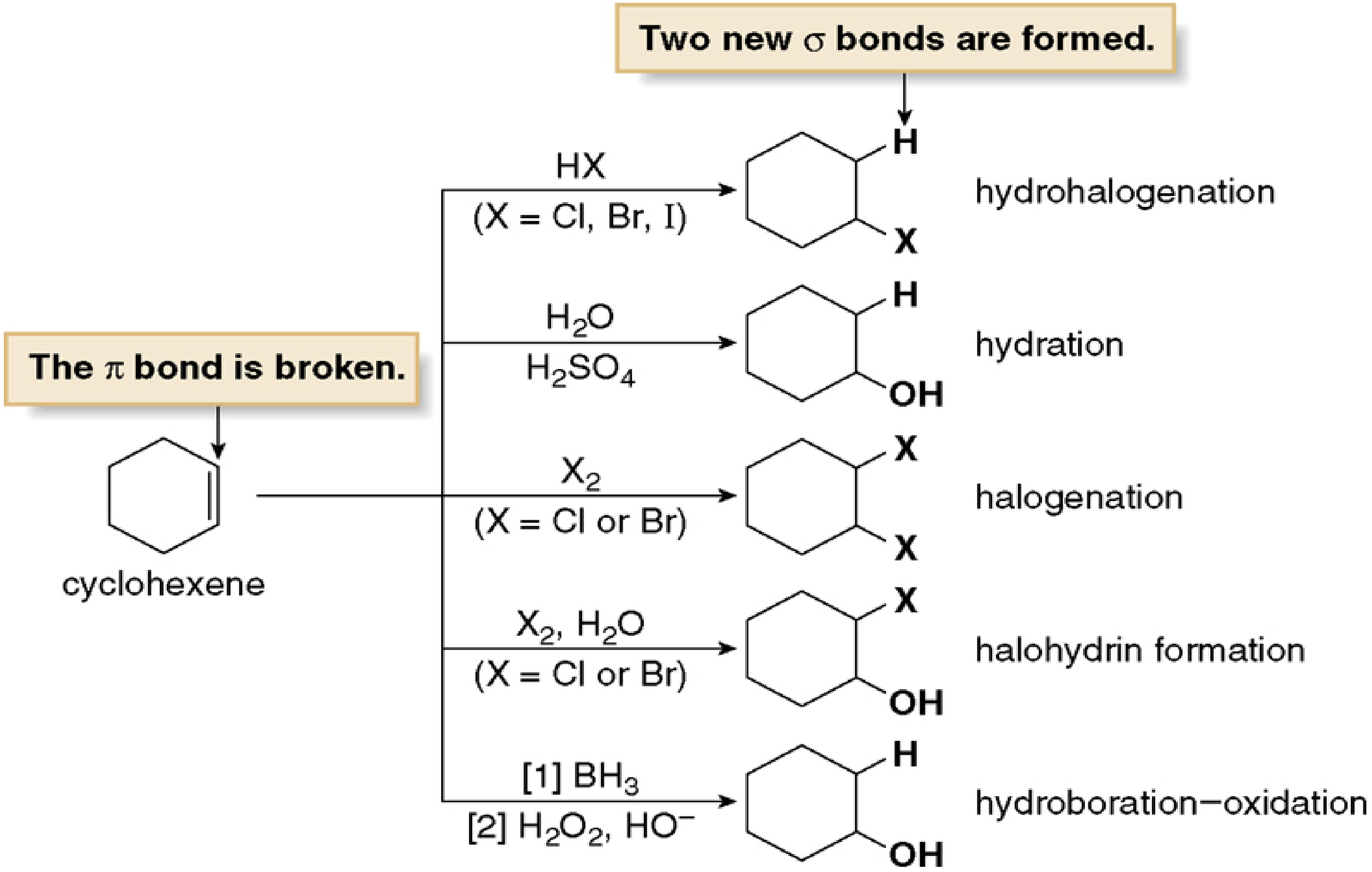
Introduction to Addition Reactions

Five addition reactions of cyclohexene



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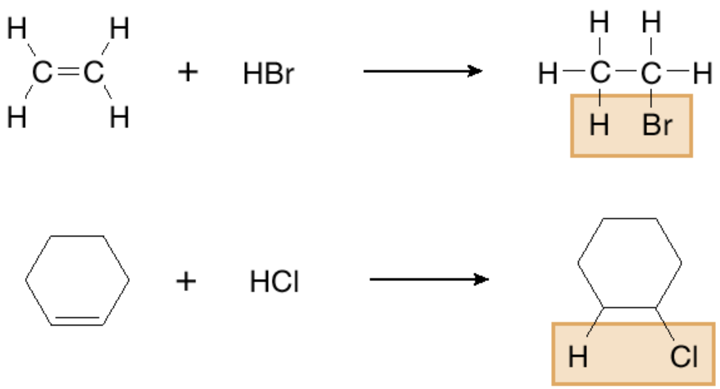
Hydrohalogenation—Electrophilic Addition of HX

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



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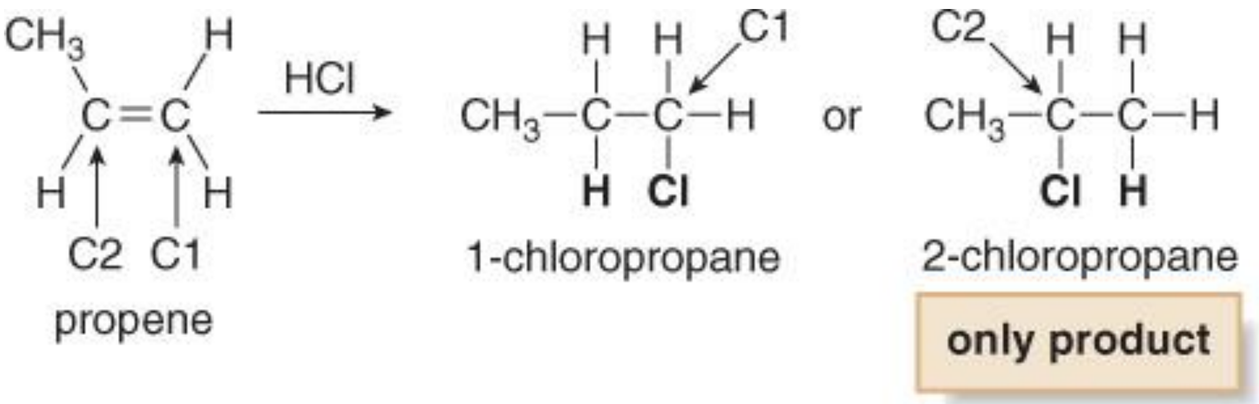
Hydrohalogenation—Markovnikov's Rule

- 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.

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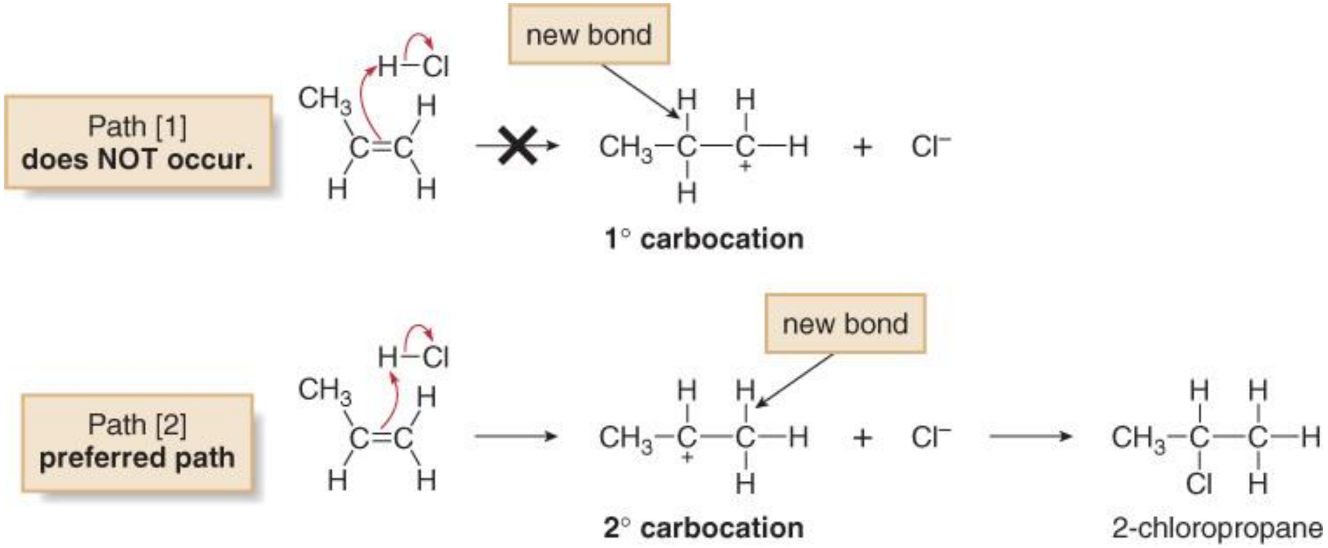
Hydrohalogenation—Markovnikov's Rule

- 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.



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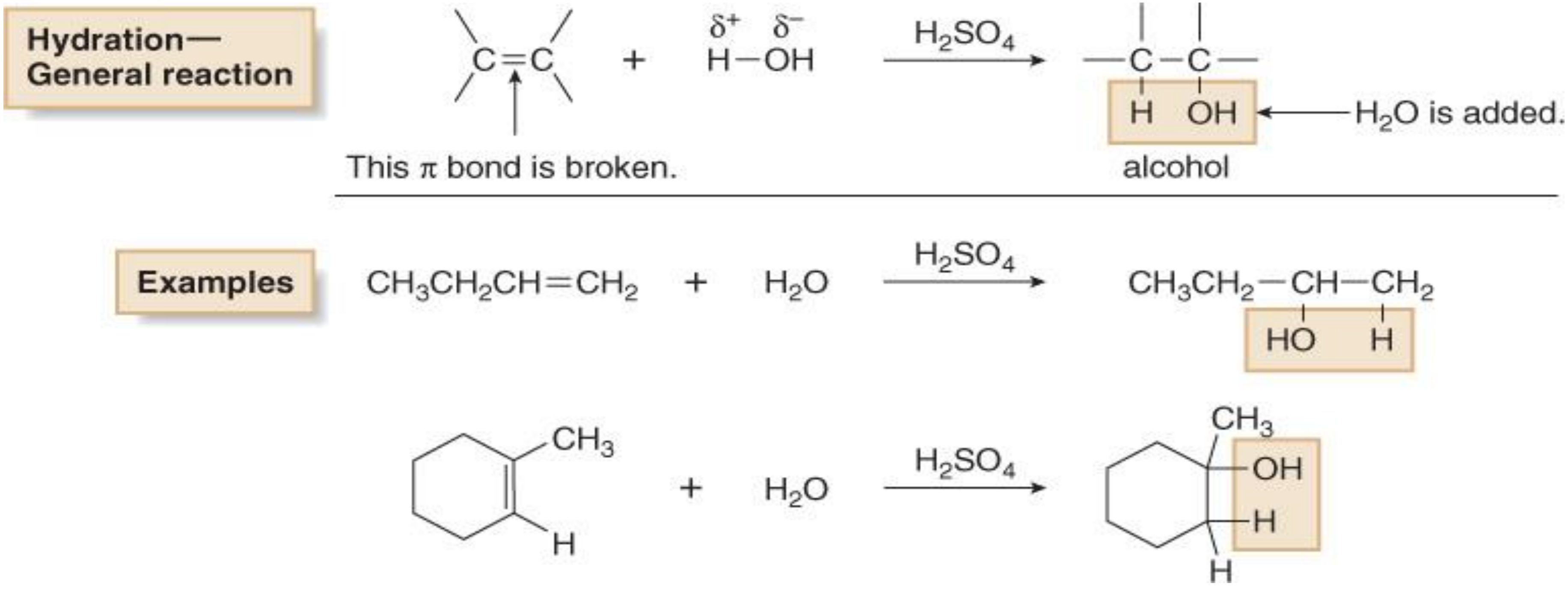
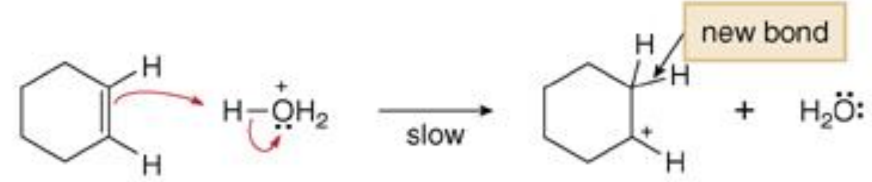
Hydration—Electrophilic Addition of Water

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



Hydration—Electrophilic Addition of Water

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

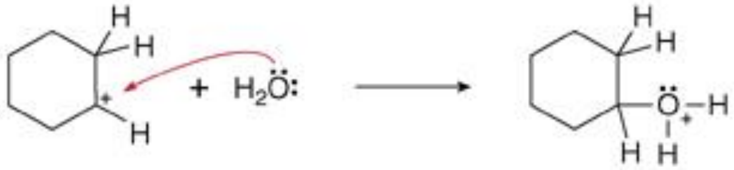


cyclohexene

carbocation

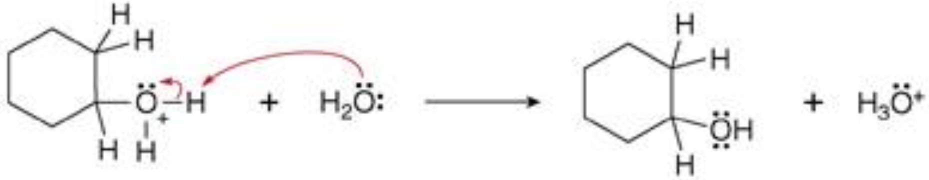
- The π bond attacks H_3O^+, thus forming a new C−H bond while breaking the H−O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond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



cyclohexanol

- 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.**

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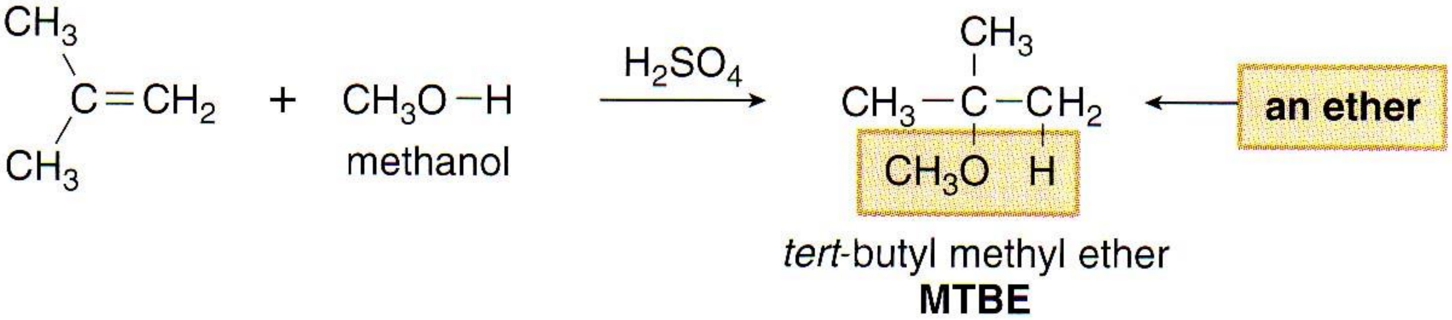
Hydration—Electrophilic Addition of Alcohols

- 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.



- 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.

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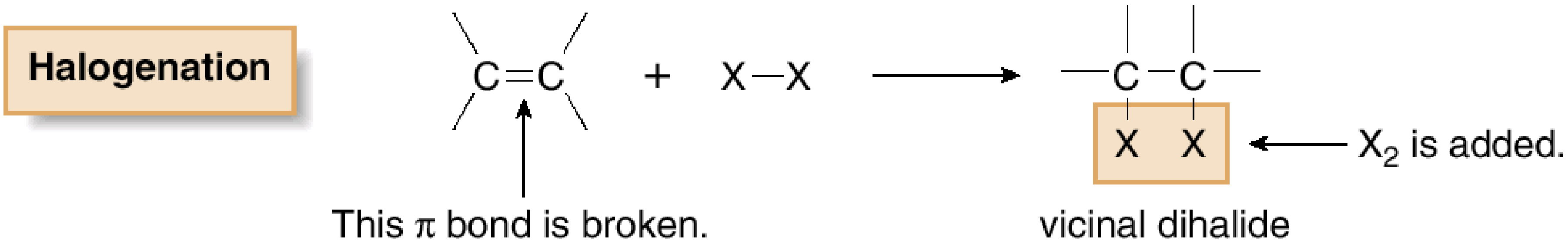
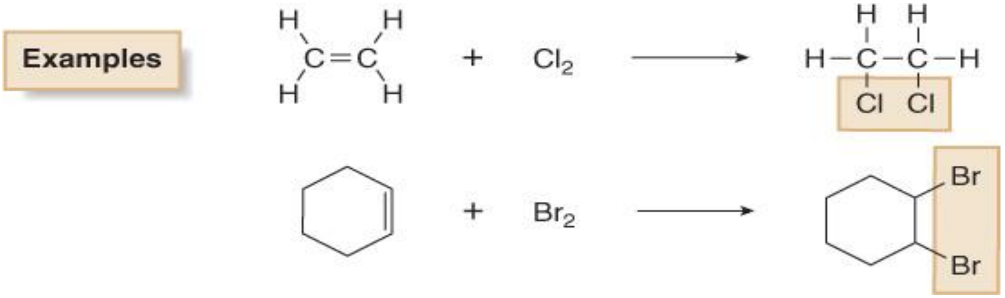
Halogenation—Addition of Halogen

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





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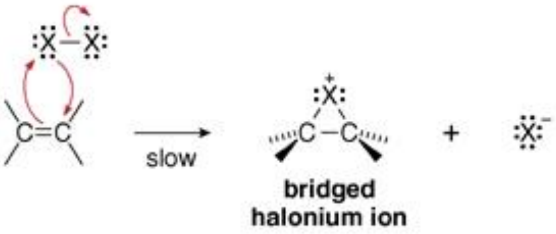
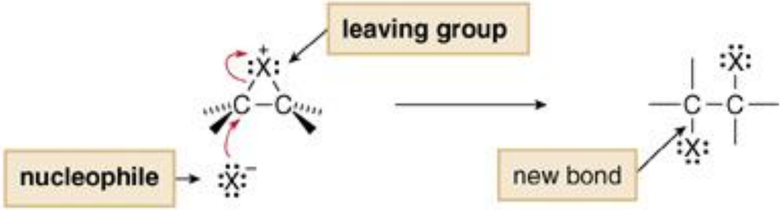
Halogenation—Addition of Halogen

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



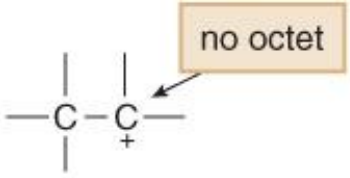
- Four bonds are broken or formed in this step: the electron pair in the π bond and a lone pair on a halogen atom are used to form two new C−X bonds. The X−X bond is also cleaved heterolytically, forming X^-. This step is rate-determining.
- The three-membered ring containing a positively charged halogen 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^-

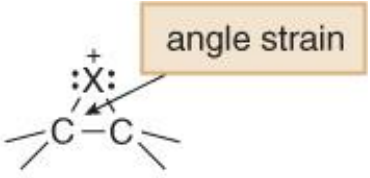


- **Nucleophilic attack of X^-** opens the ring of the halonium ion, forming a new C−X bond and relieving the strain in the three-membered ring.

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



carbocation



bridged halonium ion

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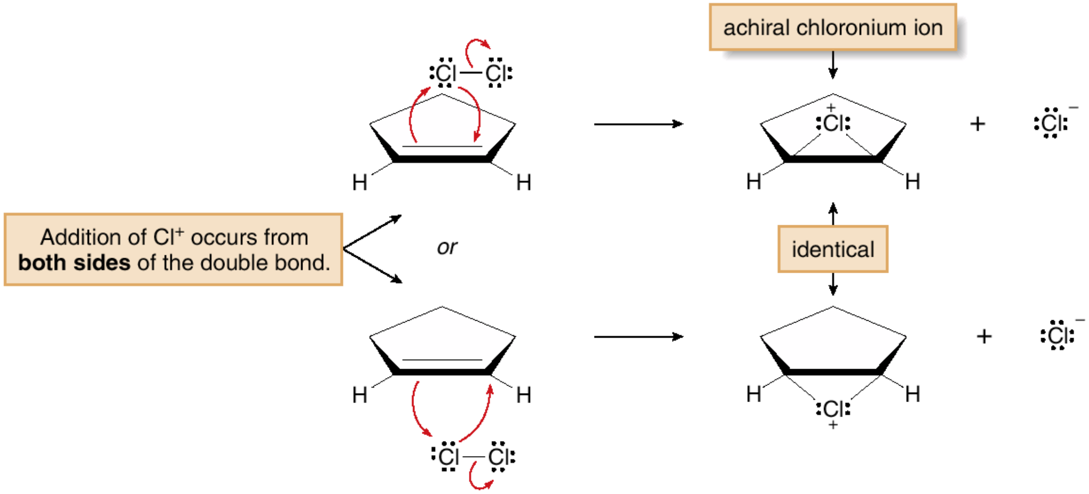
Halogenation—Reaction Stereochemistry

- 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

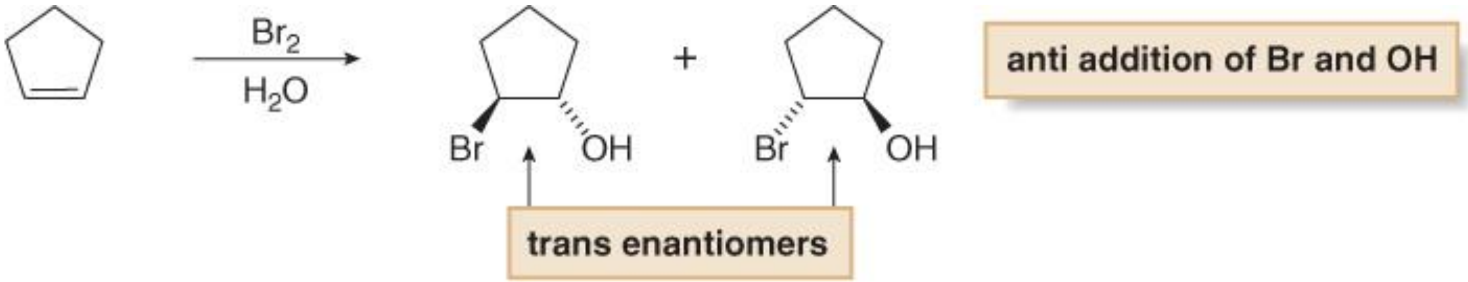
Addition of Cl^+ occurs from **both sides** of the double bond.

identical

Alkenes

Halohydrin Formation

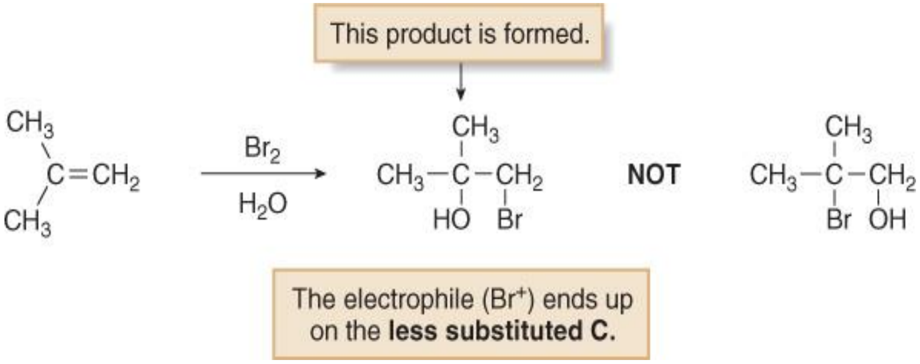
Because the bridged halonium ion is opened by backside attack of H_2O, addition of X and OH occurs in an anti fashion and trans products are formed.



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.

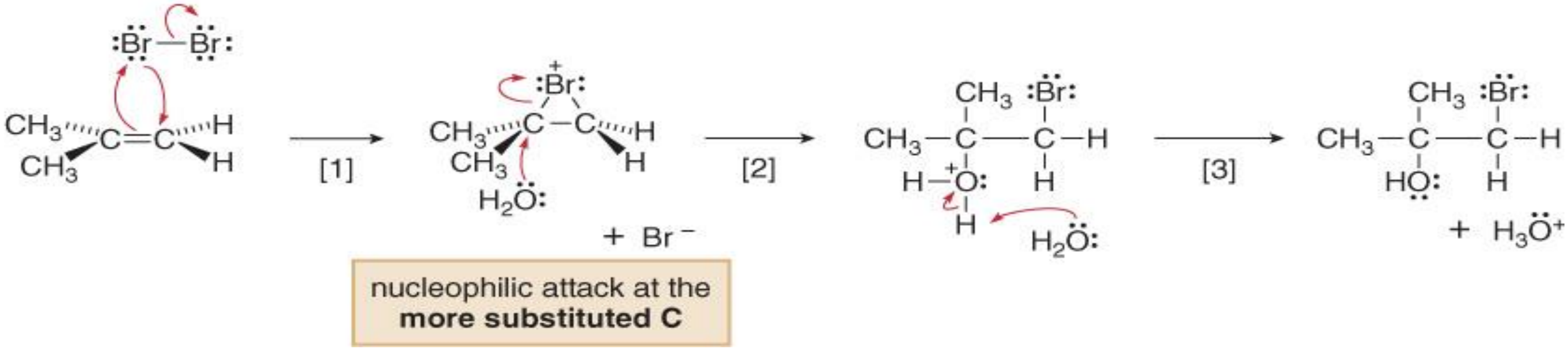
The electrophile (Br^+) ends up on the **less substituted C.**

Alkenes

Halohydrin Formation

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



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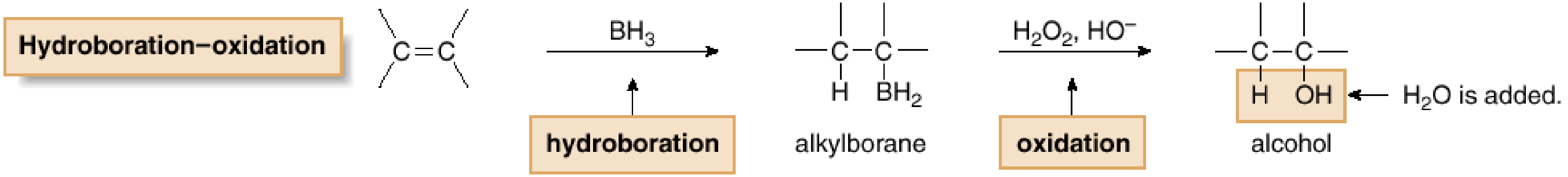
Hydroboration—Oxidation

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.

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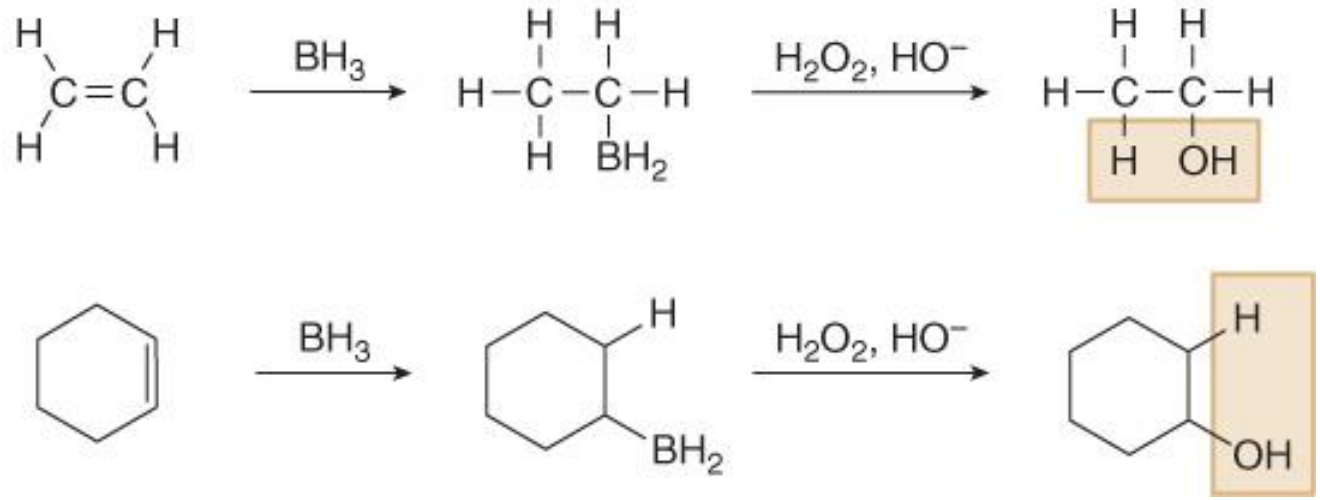
Hydroboration—Oxidation

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

Examples



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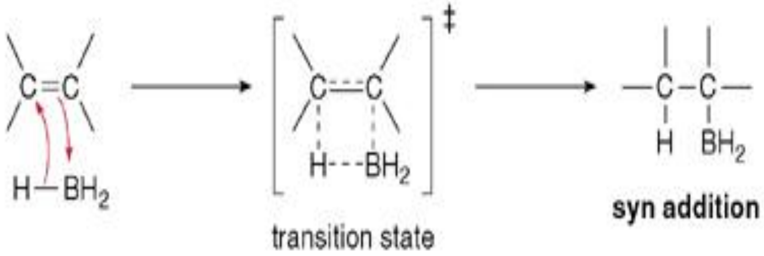
Hydroboration—Oxidation

- 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.

One step The π bond and $H-BH_2$ bonds break as the C−H and C−B bonds form.



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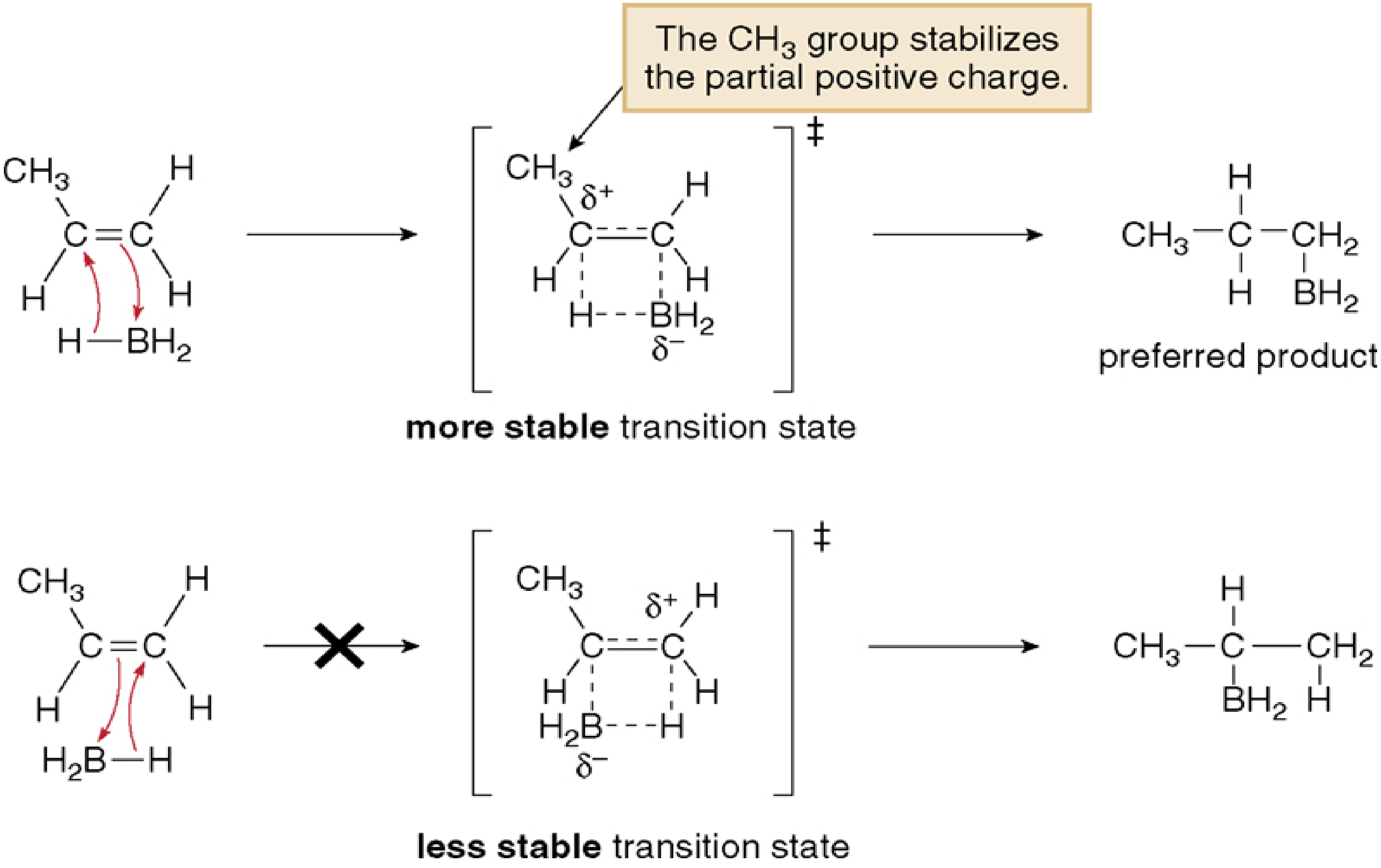
Hydroboration—Oxidation

Hydroboration of an unsymmetrical alkene



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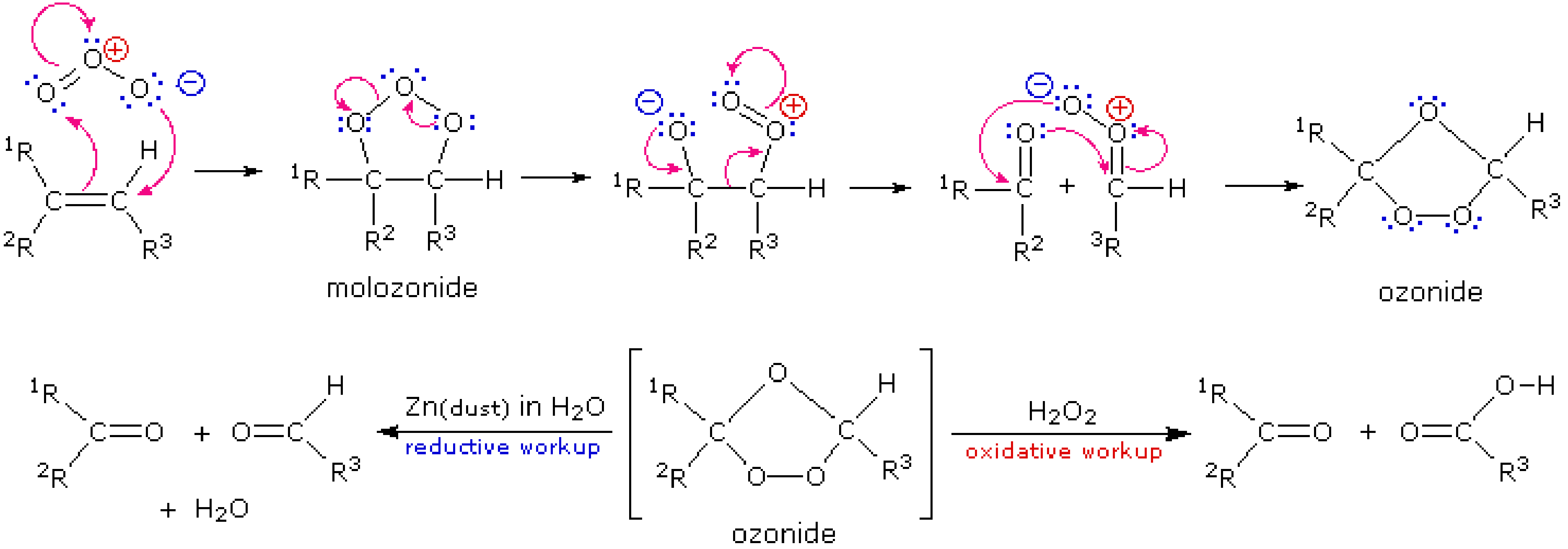
Ozonolysis

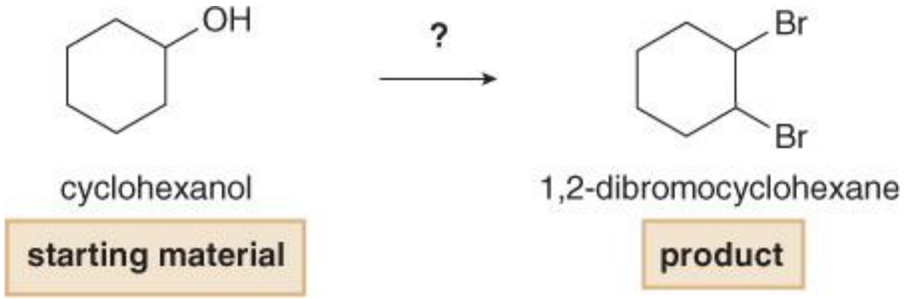
Alkenes can be oxidized with ozone to form alcohols, aldehydes or ketones, or carboxylic acid



Alkenes

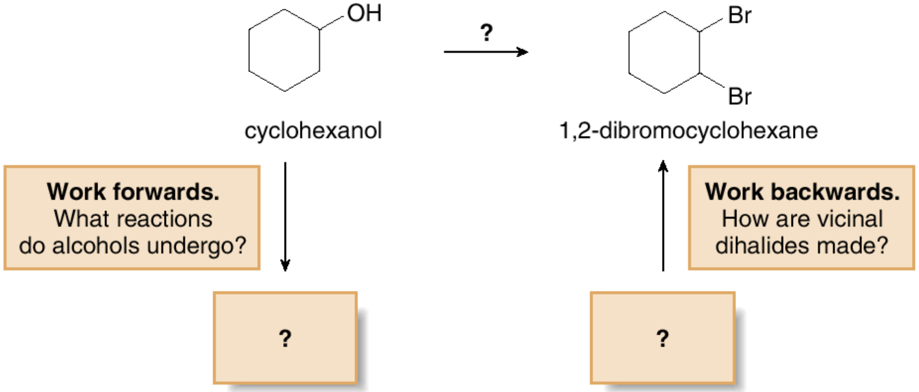
Alkenes in Organic Synthesis

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



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?



Conclusion of The Chapter

- Conclusion #1
  - The fundamental of alkenes with its nomenclature were understandable.
- Conclusion #2
  - The fundamental of alkenes included its reactions involves were practically explained.
- Conclusion #3
  - The synthesis of alkenes was understandable.

Co-author Information

Nurlin Abu Samah is an analytical chemistry lecturer since 2010 and currently she further her PhD study in Universitat Autonoma de Barcelona, Spain. She was graduated from Universiti Kebangsaan Malaysia for her Master of Science in Chemistry. During her undergraduate, she was studied in Universiti Sains Malaysia, Penang.

nurlin@ump.edu.my