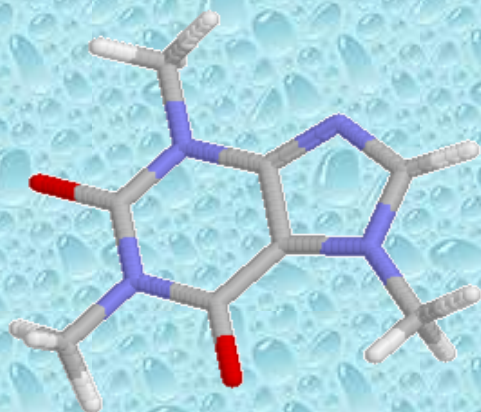


Ethylene is the gas that ripens fruit



Chapter (3)

Alkenes (Olefins) &

Alkynes (Acetylenes)



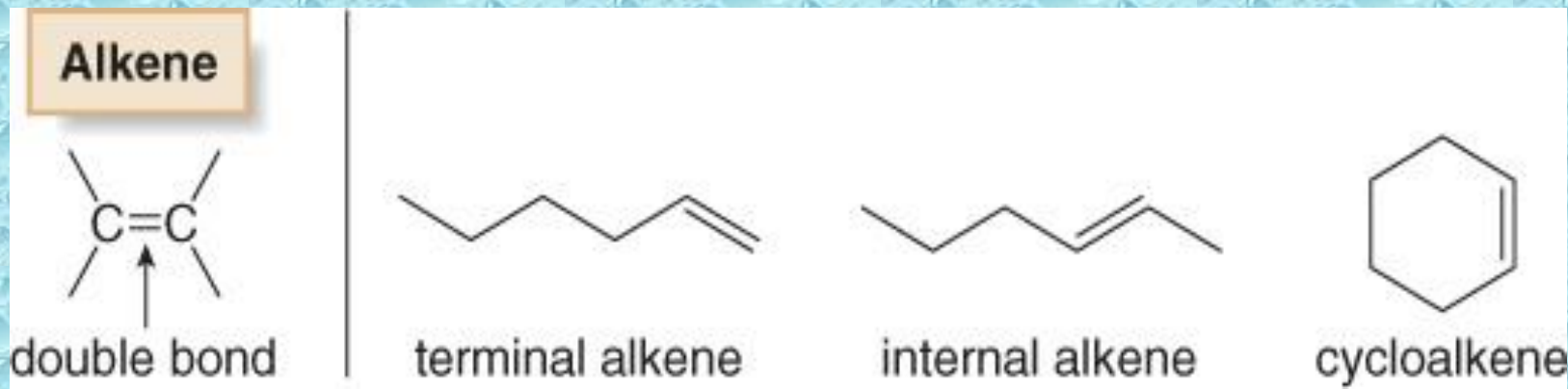
Capillin

an antifungal agent

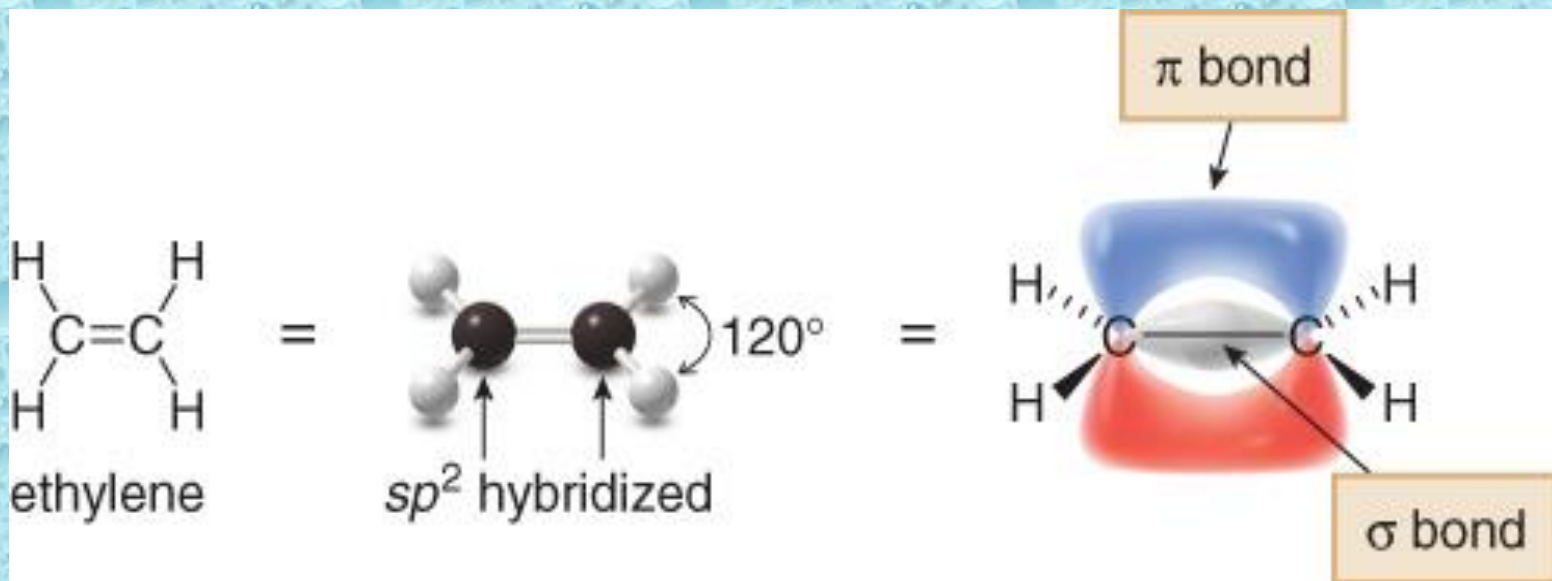


Alkenes (Olefins)

- ❑ Alkenes C_nH_{2n} are Unsaturated aliphatic hydrocarbons and contain at least one **C=C double bond** ($\sigma + \pi$ 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.



- ❑ 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°** .

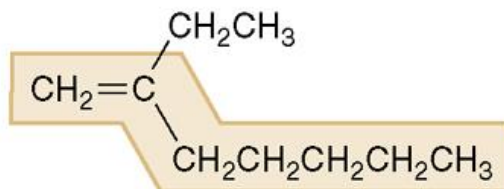


- Restricted rotation**
- **The rotation around the C–C double bond is restricted.** Rotation can only occur if the π bond breaks and then re-forms, a process that is unfavorable (Section 8.2B).
-
- Stereoisomerism**
- Whenever the two groups on each end of a C=C are different from each other, two diastereomers 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).



Nomenclature of Alkenes:

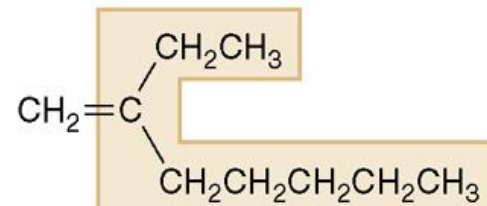
- Naming an alkene in which the longest carbon chain does not contain both atoms of the double bond



7 C's ----> heptene

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

Correct: 2-ethyl-1-heptene

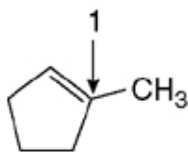


8 C's

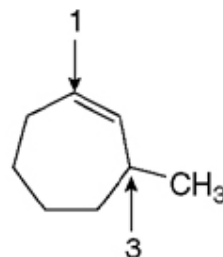
Both C's of the C=C are NOT contained in this long chain.

Incorrect

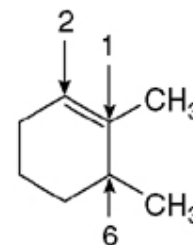
- Examples of cycloalkene nomenclature



1-methylcyclopentene



3-methylcycloheptene



1,6-dimethylcyclohexene

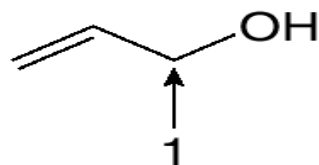
Number clockwise beginning at the C=C and place the CH₃ at C3.

Number counterclockwise beginning at the C=C and place the first CH₃ at C1.

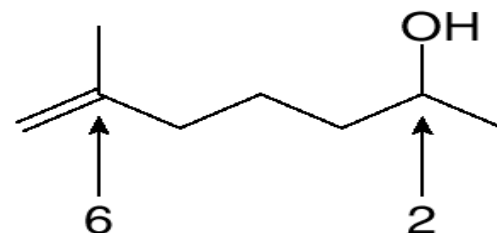
Nomenclature of Alkenes:

- Always choose the **longest chain** that **contains carbon atoms of the double bond**.

Ex: **alkenols**



2-propen-1-ol

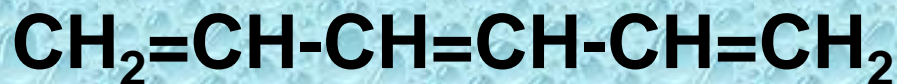


6-methyl-6-hepten-2-ol

- Compounds with **two double bonds** are named as **dienes** by changing the “-ane” ending of the parent alkane to the suffix “-diene”.
- Compounds with **three double bonds** are named as **triene**, and so forth.



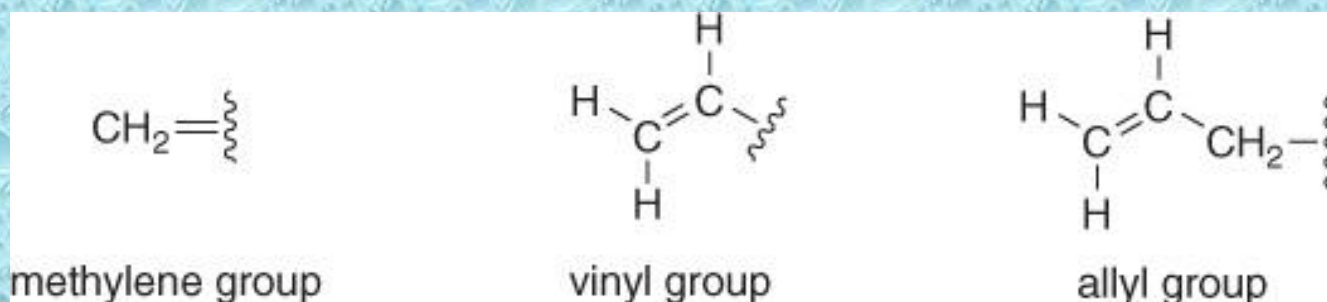
1,3-butadiene



1,3,5-hexatriene

Nomenclature of Alkenes:

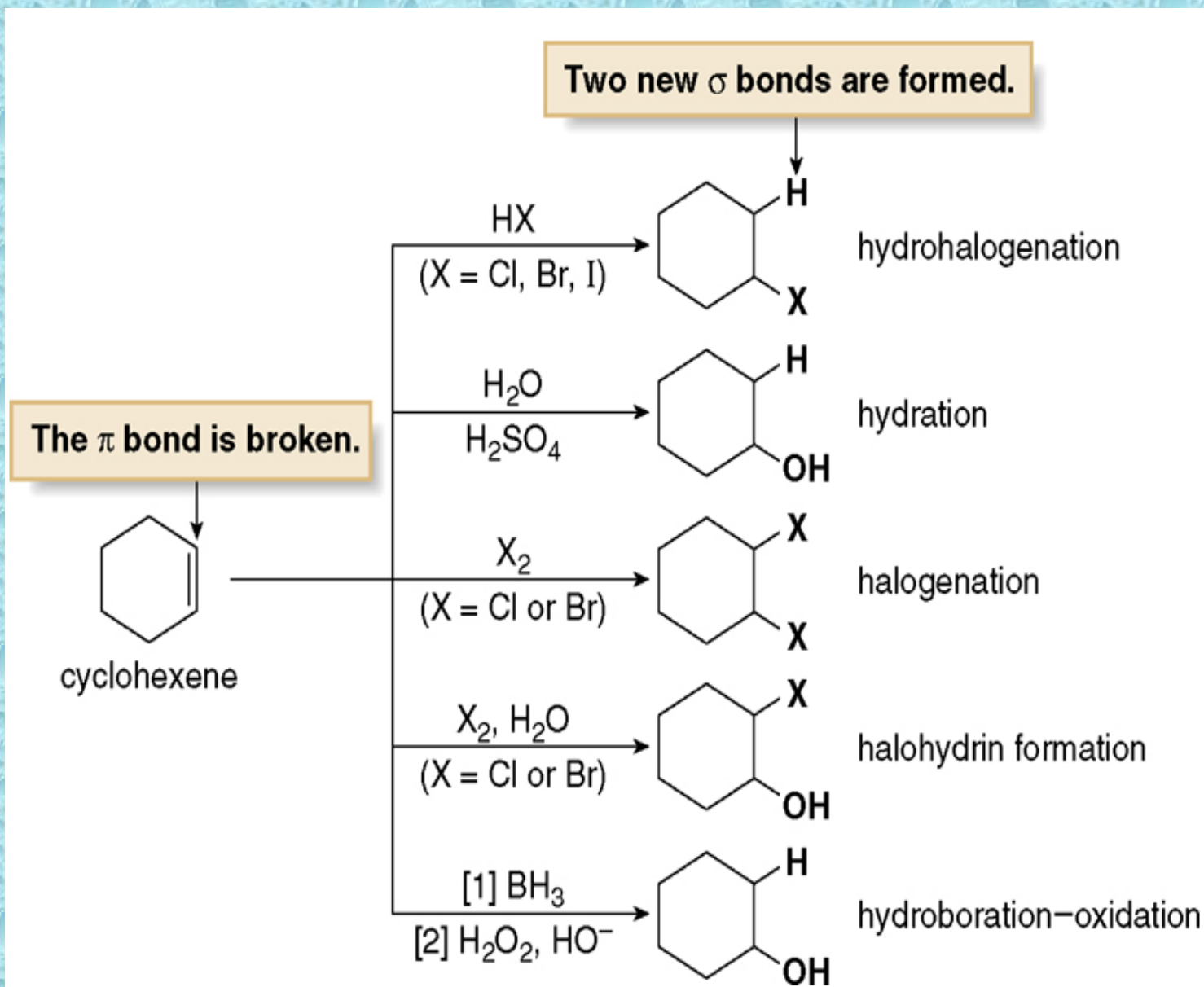
- Some alkene or alkenyl substituents have common names.
- The simplest alkene, $\text{CH}_2=\text{CH}_2$, named in the IUPAC system as ethene, is often called **ethylene**.



Naming alkenes with common substituent names



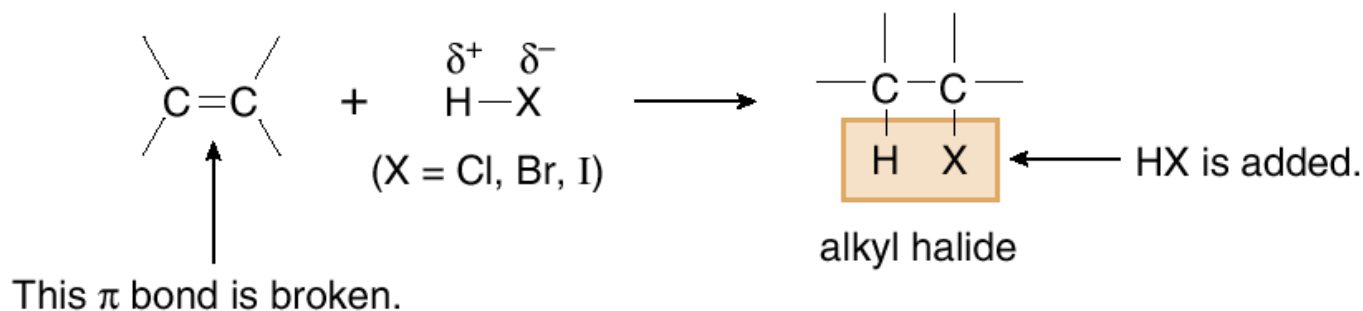
Five Addition Reactions of Cyclohexene



No π bond in products

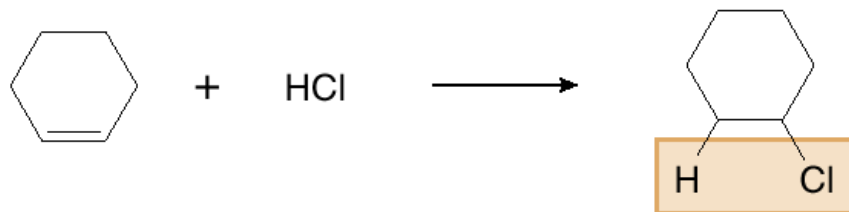
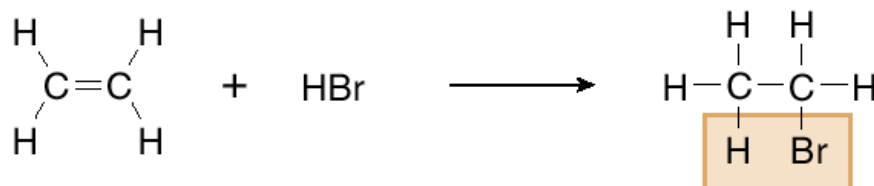
1- Hydrohalogenation: Electrophilic Addition of HX

Hydrohalogenation

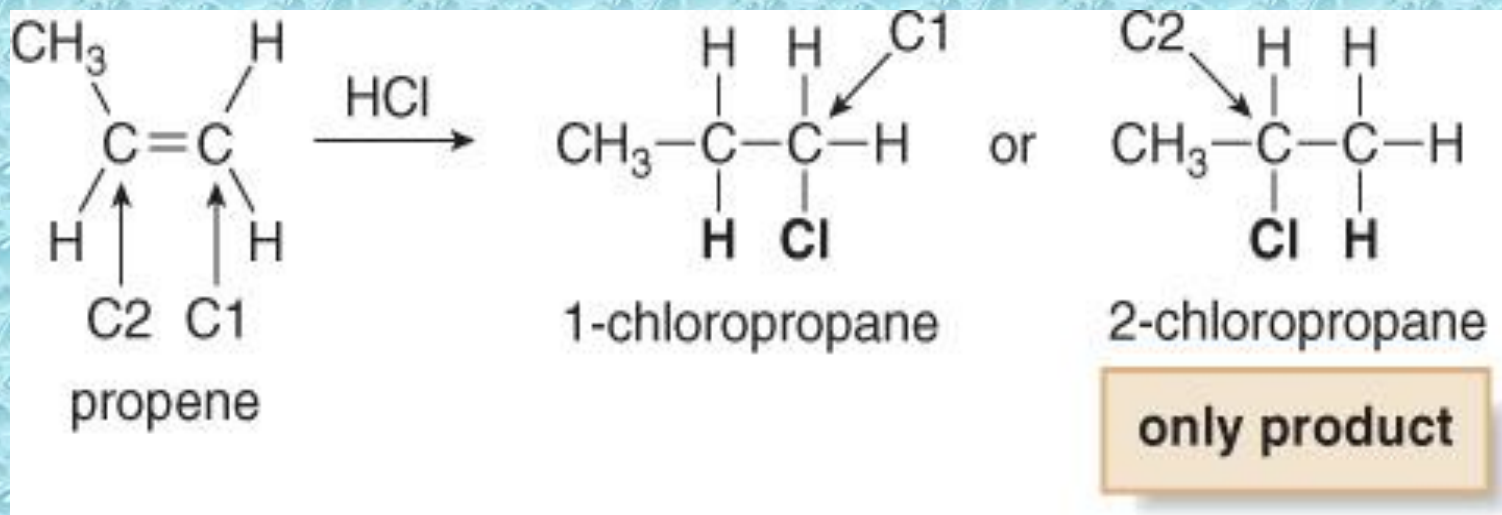


- The H—X bond is polarized, with a partial positive charge on H. Because the electrophilic H end of HX is attracted to the electron-rich double bond, these reactions are called **electrophilic additions**.

Examples



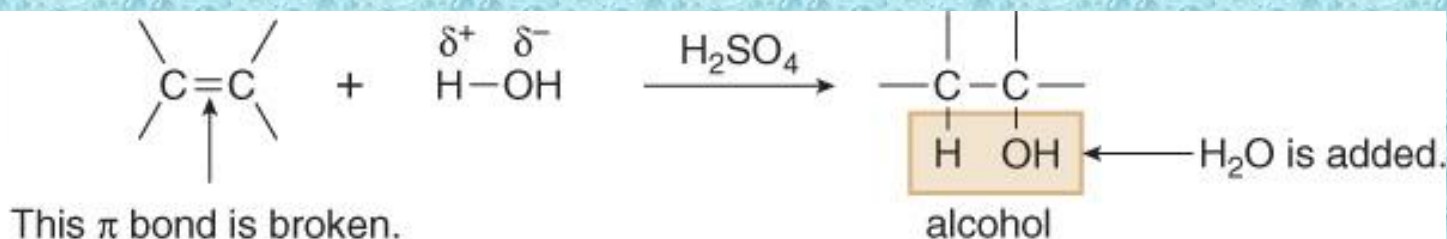
- *Markovnikov's rule* states that in the addition of **HX** to an unsymmetrical alkene, the H atom adds to the less substituted carbon atom, that is, ***the carbon that has the greater number of H atoms to begin with.***
- With an unsymmetrical alkene, **HX** can add to the double bond to give two constitutional isomers, but only one is actually formed:



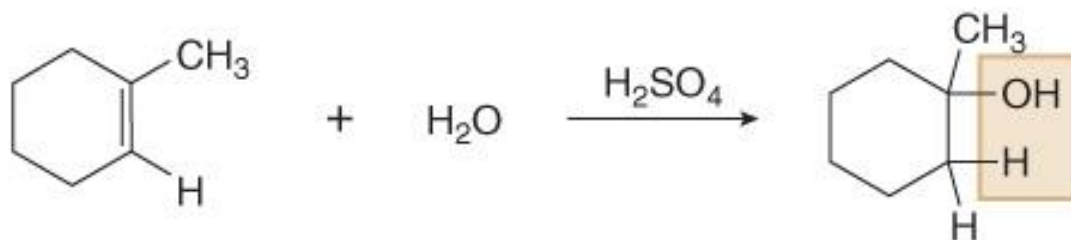
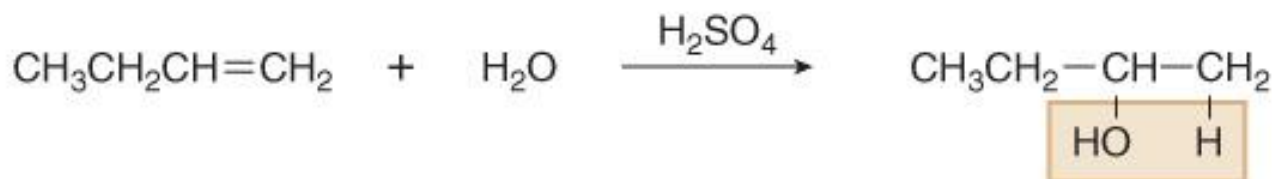
2- Hydration: Electrophilic Addition of Water

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

Hydration—
General reaction

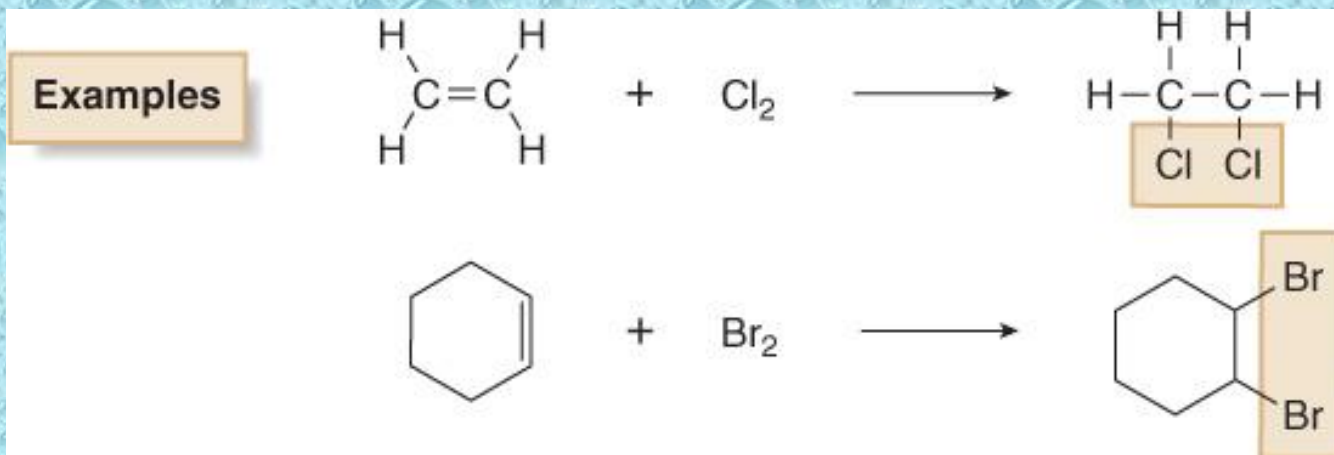
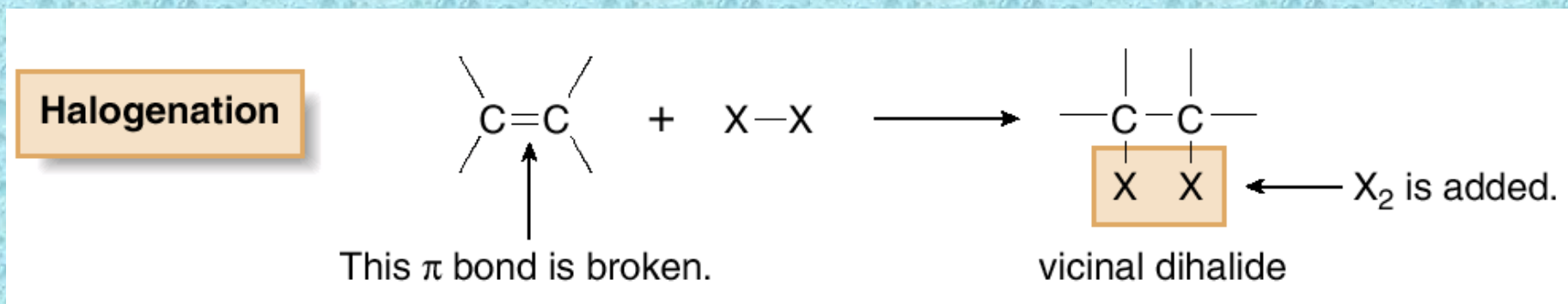


Examples



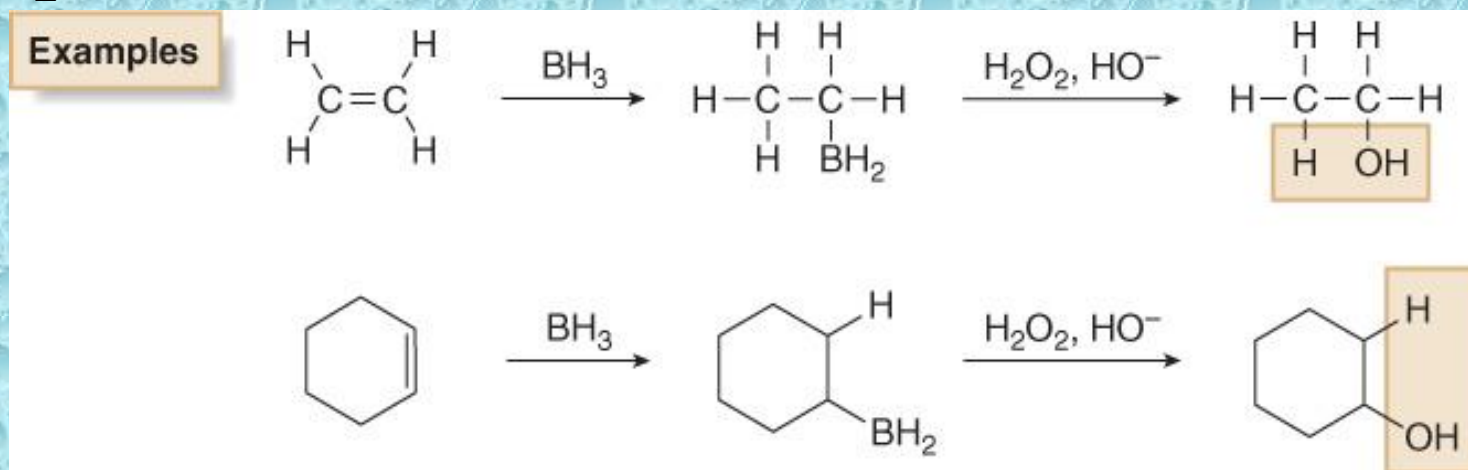
3- Halogenation: Addition of Halogen

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

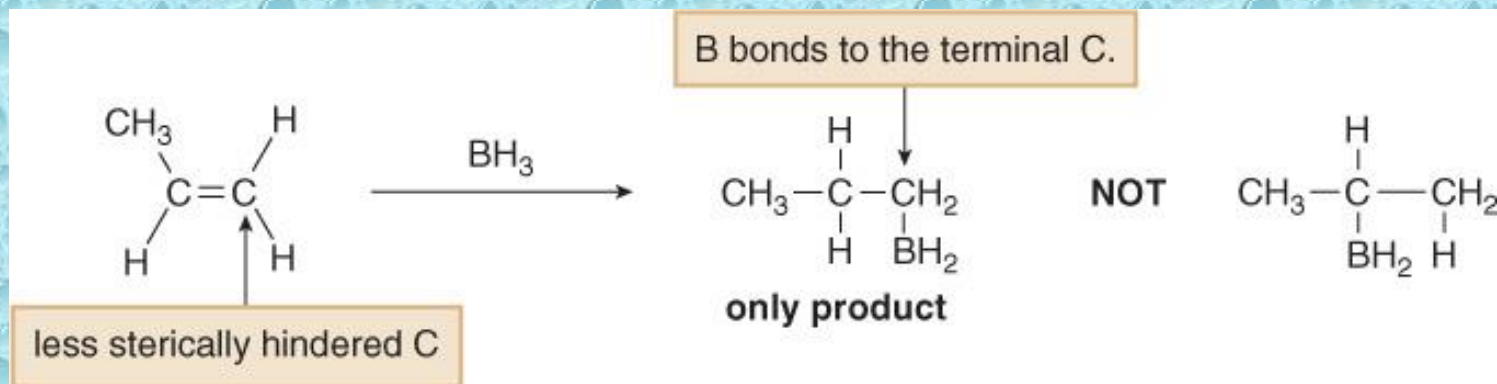


4- Hydroboration - Oxidation:

- Hydroboration—oxidation results in the indirect addition of H_2O to an alkene. **Anti Markovnikov Addition**

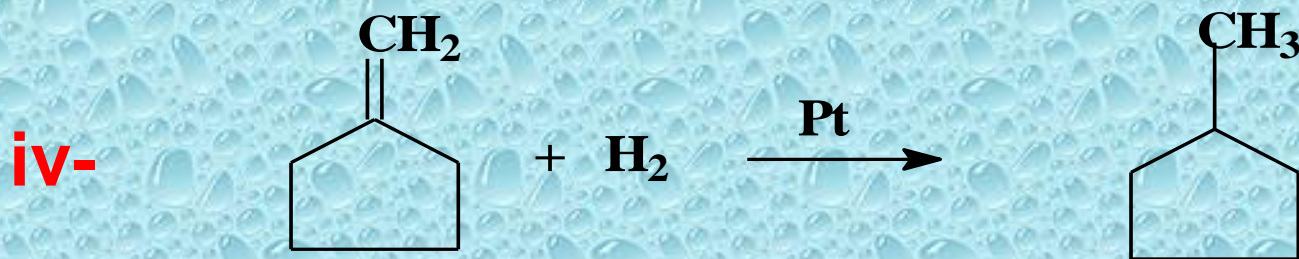
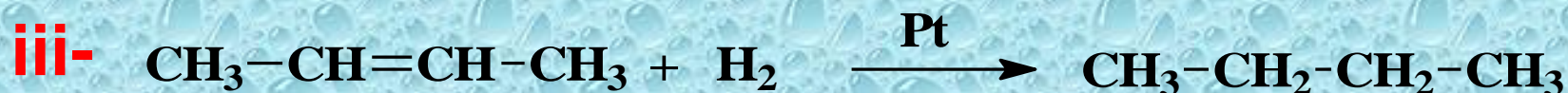
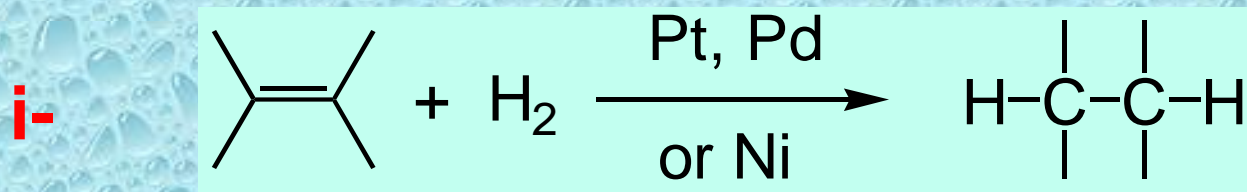


- With **unsymmetrical alkenes**, the boron atom bonds to the less substituted carbon atom.



5- Reduction (Hydrogenation): addition of hydrogens

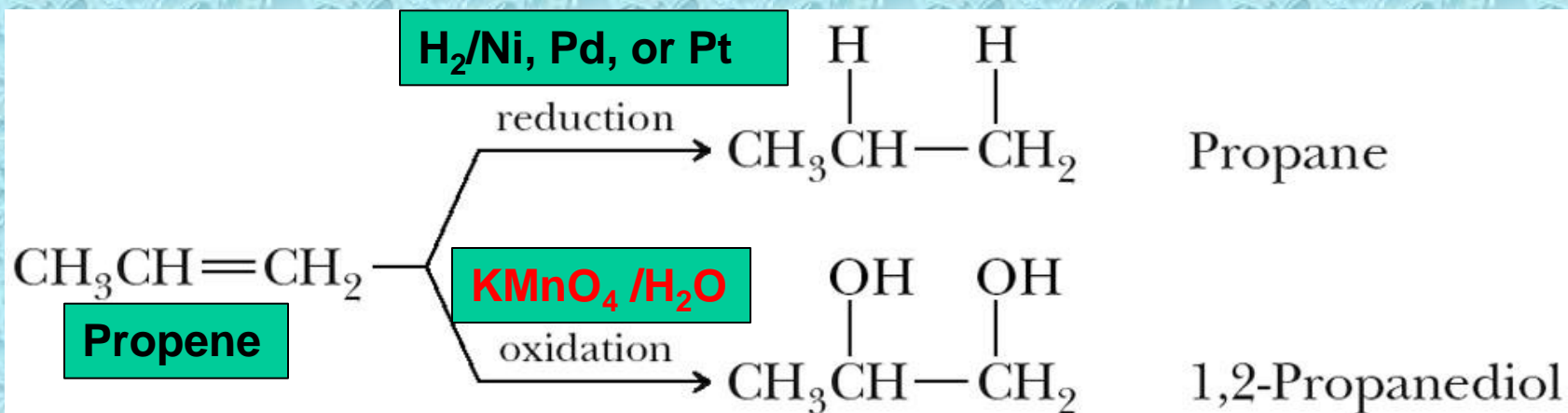
Addition of H_2 using **Ni**, **Pd**, or **Pt** as a catalyst produces alkane.



6- Oxidation of Alkenes:

i- Hydroxylation of Alkenes:

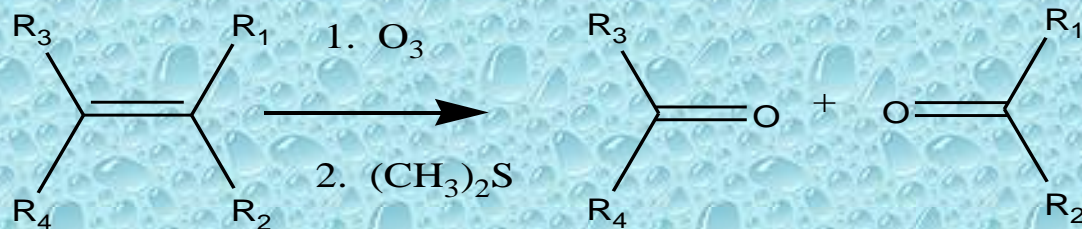
Addition of two Hydroxy groups by using dilute KMnO_4



© 2006 Brooks/Cole - Thomson

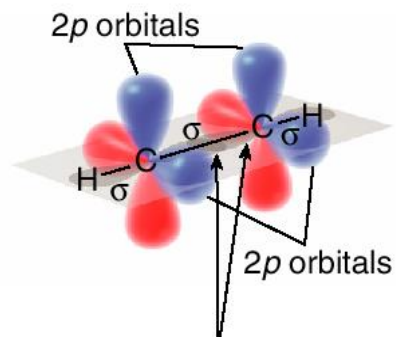
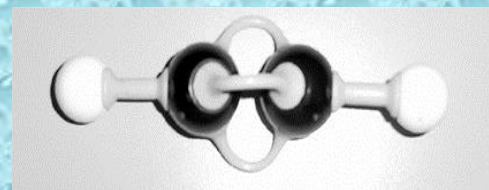
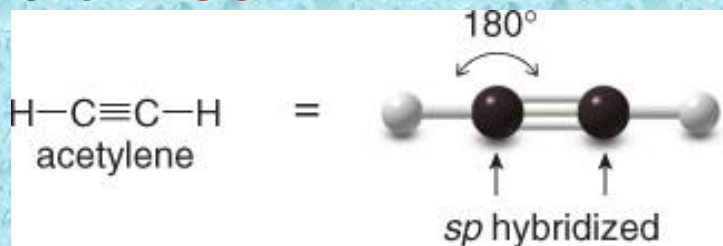
ii- Ozonolysis:

Reaction can be used to break larger molecule down into smaller parts for easy identification.



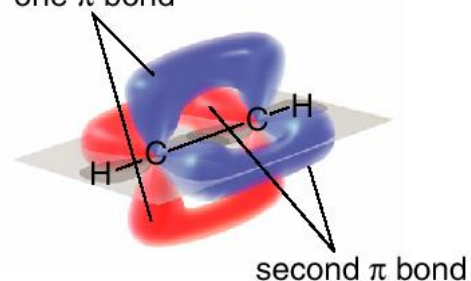
Alkynes (Acetylenes)

- The triple bond consists of 2 π bonds and 1 σ bond.
- Each carbon is *sp* hybridized with a **linear geometry** and bond angles of **180°**.



Overlap of the two *sp* hybrid orbitals forms the C—C σ bond.

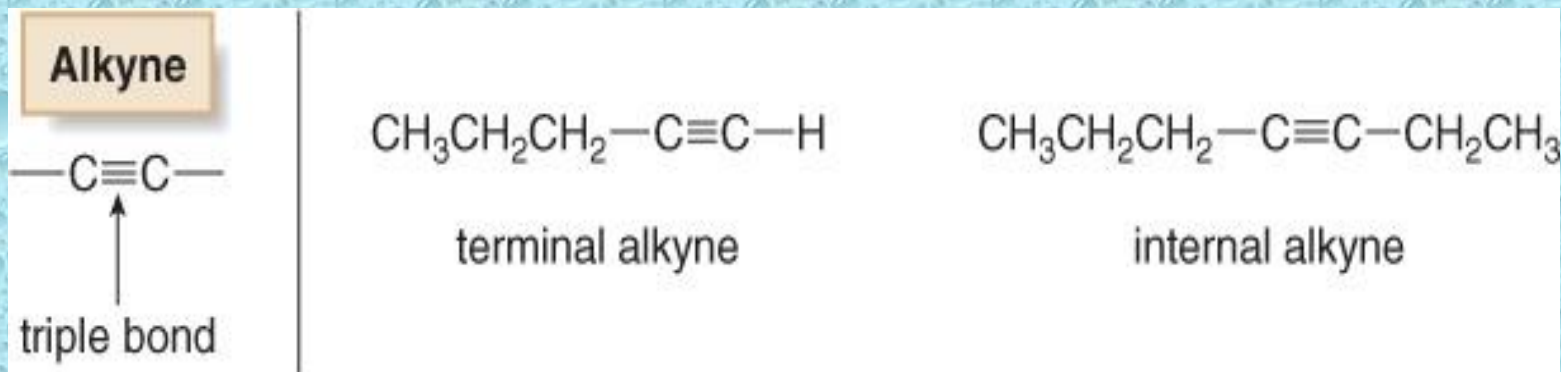
Two π bonds extend out from the axis of the linear molecule.
one π bond



Overlap of two sets of two 2*p* orbitals forms two C—C π bonds.

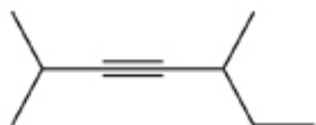
- The σ bond is formed by end-on overlap of the two *sp* hybrid orbitals.
- Each π bond is formed by side-by-side overlap of two 2*p* orbitals.

- ❑ Alkynes are Unsaturated aliphatic hydrocarbons and contain a **C≡C** triple bond.
- ❑ An alkyne has the **general molecular formula** **C_nH_{2n-2}**.
- ❑ Terminal alkynes have the triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond.
- ❑ Internal alkynes have a carbon atom bonded to each carbon atom of the triple bond.

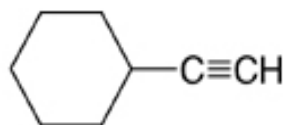


Nomenclature of Alkynes:

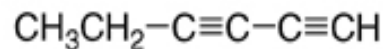
- Choose **the longest continuous chain** that **contains** carbons of the **triple bond**.
- Change the ***-ane*** ending of the parent alkane name to the suffix ***-yne***.
- Number the chain to give the triple bond the lower number.



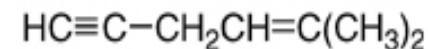
2,5-dimethyl-3-heptyne



ethynylcyclohexane



1,3-hexadiyne



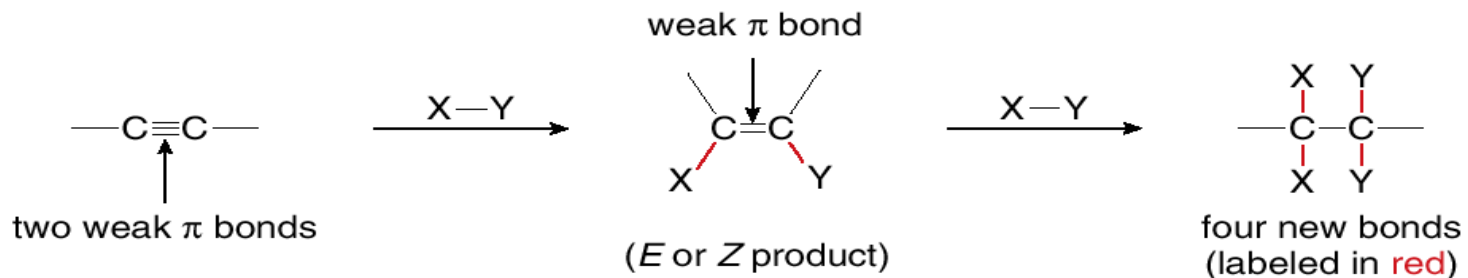
5-methyl-4-hexen-1-yne

- Compounds with two triple bonds are named as **diynes**, those with three are named as **triyne**s and so forth.

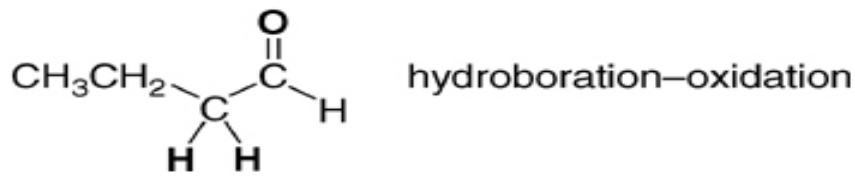
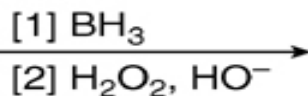
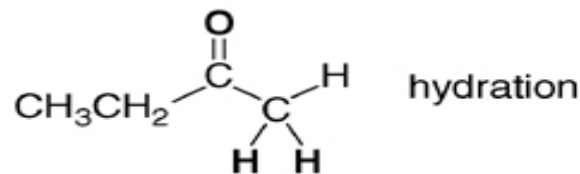
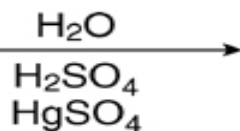
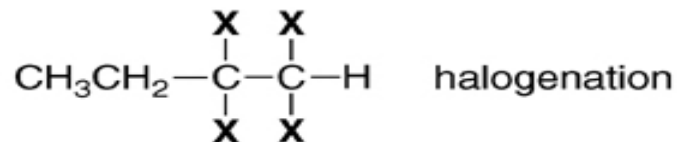
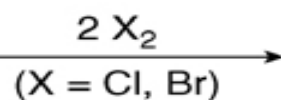
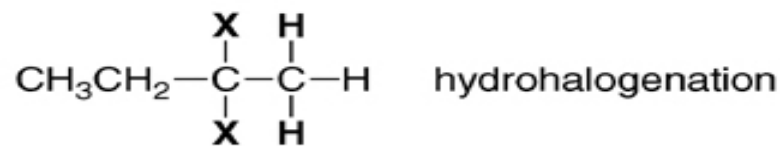
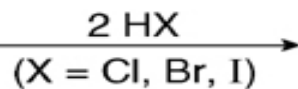
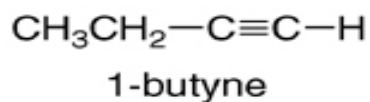
- ❑ Compounds **both a double and triple bond** are named as *enynes*.
- ❑ The chain is numbered to give the first site of unsaturation (either C=C or C≡C) the lower number.
- ❑ If numbering is equal the *ene* gets the lower number.
- ❑ However, *yne* is still the parent ending

Example

$\text{CH}_3\text{-C}\equiv\text{C-CH=CH-CH}_3$ is 2-hexen-4-yne

Addition reaction

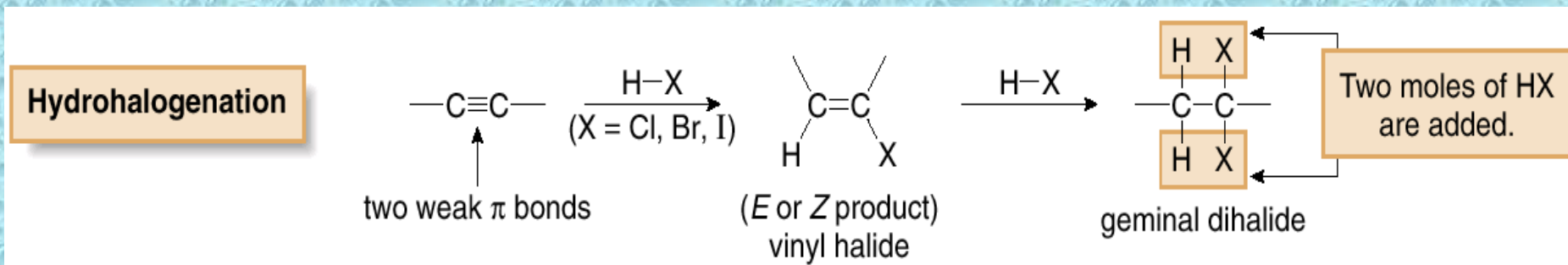
I. Addition Reactions of 1-butyne

Four new bonds are formed.**Both π bonds are broken.**

1. Hydrohalogenation:

Electrophilic Addition of Hydrogen halides(HX)

- Alkynes undergo hydrohalogenation,
- i.e the, addition of hydrogen halides, **HX (X = Cl, Br, I)**.

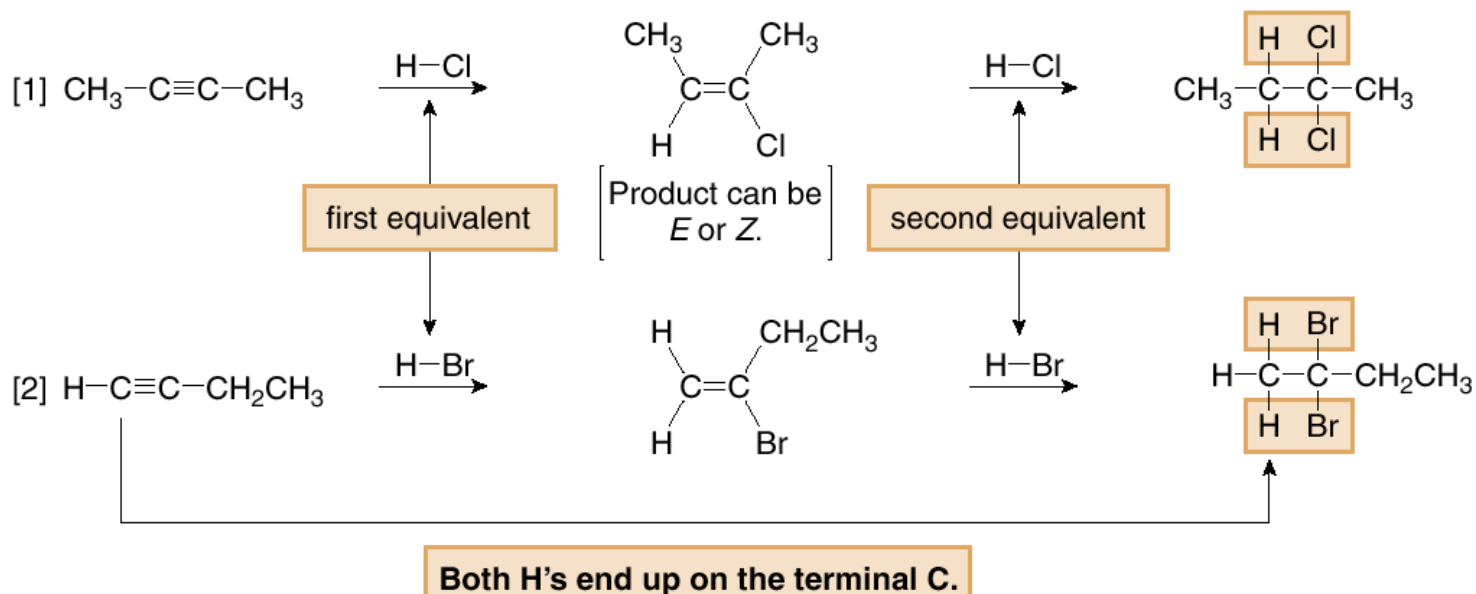


- Two equivalents of HX are usually used:
- addition of one mole forms a **vinyl halide**, which then reacts with a second mole of HX to form a **geminal dihalide**.

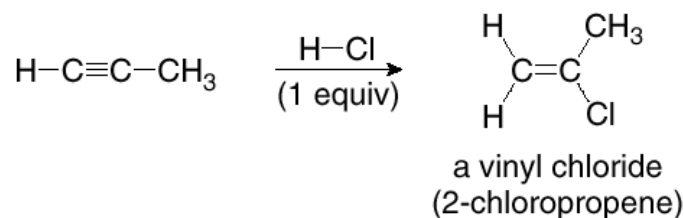
Hydrohalogenation: Electrophilic Addition of HX

- With two equivalents of HX, both H atoms bond to the *same* carbon.
- With a terminal alkyne, both H atoms bond to the *terminal* carbon; that is, the hydrohalogenation of alkynes follows Markovnikov's rule.

Examples



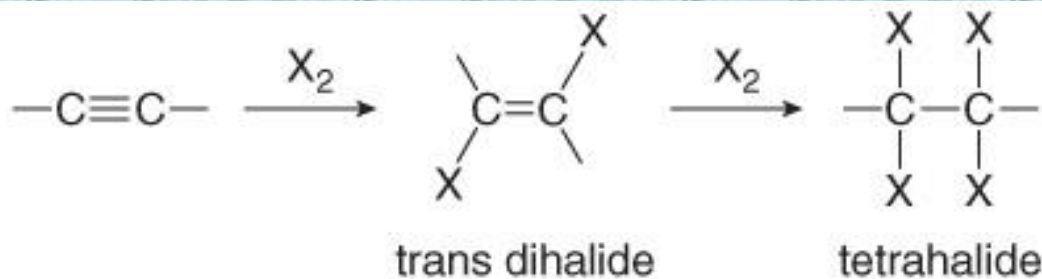
- With only one equivalent of HX, the reaction stops with formation of the vinyl halide.



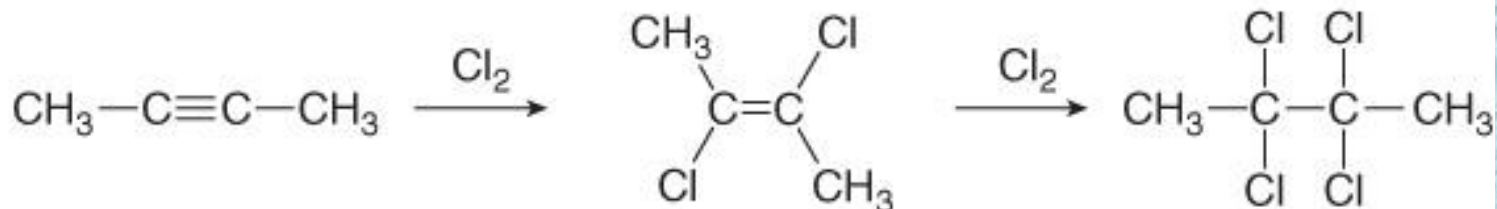
2- Halogenation: Addition of Halogen (X_2)

- Halogens X_2 ($X = \text{Cl}$ or Br) add to alkynes just as they do to alkenes.
- Addition of one mole of X_2 forms a trans dihalide, which can then react with a
- second mole of X_2 to yield a **tetrahalide**.

Halogenation—
General reaction



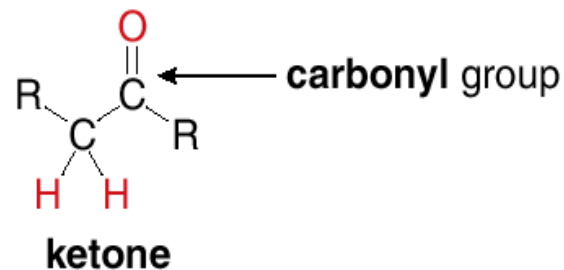
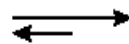
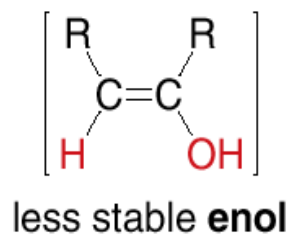
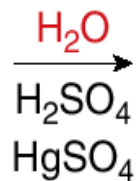
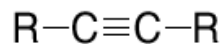
Example



3- Hydration: Electrophilic Addition of Water (H₂O)

- In the presence of strong acid (or Hg²⁺ catalyst), the elements of H₂O add to the triple bond. The initial addition product, an **enol**, is unstable and **rearranges** to a product containing a carbonyl group—that is, a C=O, before the second addition can occur. A carbonyl compound having two alkyl groups bonded to the **C=O** carbon is called a **ketone**.

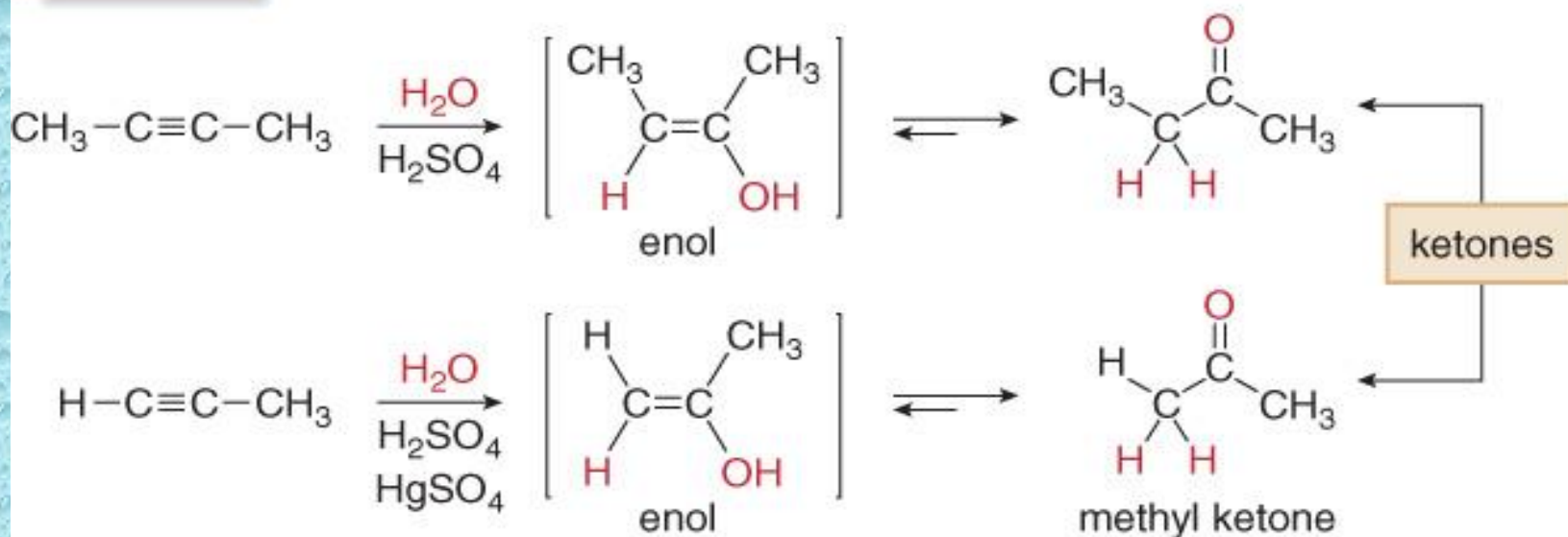
Hydration



H₂O has been added.

- Internal alkynes** undergo **hydration** with concentrated acid, whereas terminal alkynes require the presence of an additional Hg^{2+} catalyst—usually HgSO_4 —to yield methyl ketones by **Markovnikov addition** of water.

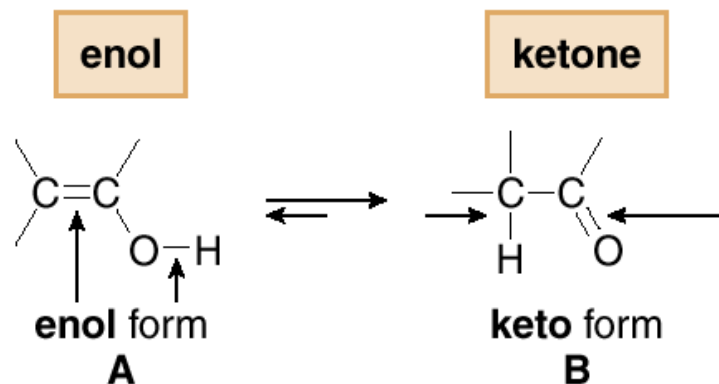
Examples



Markovnikov addition of H_2O

H adds to the terminal C.

- *Tautomers* are constitutional isomers that differ in the location of a double bond and a hydrogen atom. Two tautomers are in equilibrium with each other.

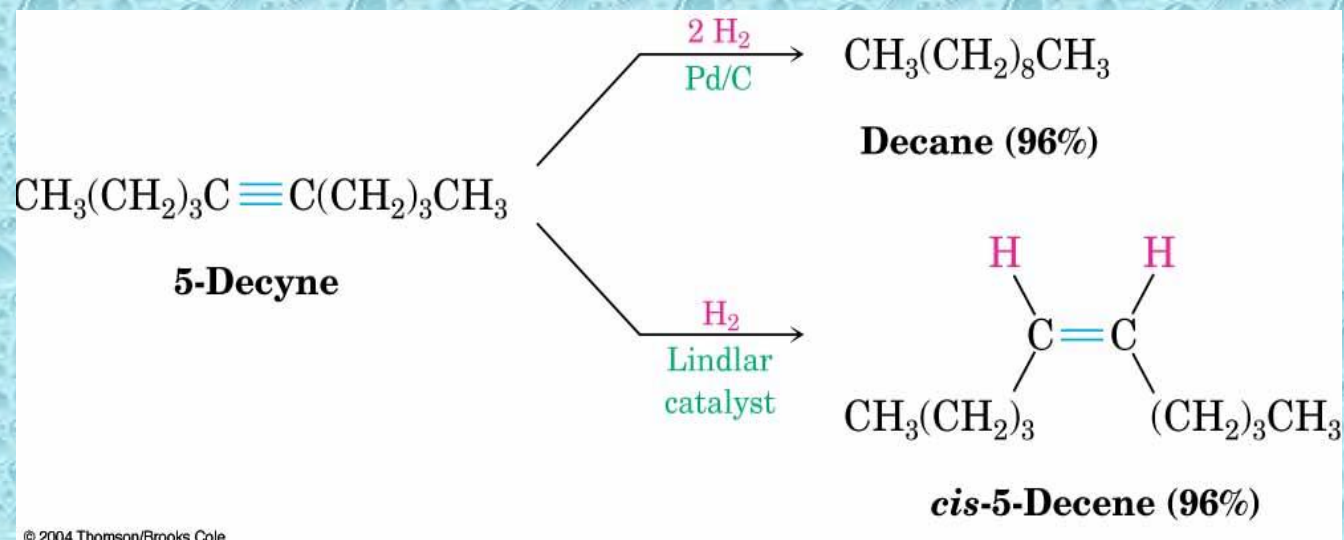


- An enol tautomer has an O–H group bonded to a C=C.
- A keto tautomer has a C=O and an additional C–H bond.

□ Equilibrium favors the **enol** \rightleftharpoons **keto** form largely because the C=O is much stronger than a C=C. Tautomerization, the process of converting one tautomer into another, is catalyzed by both acid and base.

4- Reduction of Alkynes: Conversion of *Alkynes* to *cis-Alkenes*

- **Addition of H₂** using chemically deactivated palladium on calcium carbonate as a **catalyst** (the *Lindlar catalyst*) produces a ***cis alkene***
- ***The two hydrogens add from the same side of the triple bond***



II- Substitution Reactions:

Acetylide anions

- Because *sp* hybridized C—H bonds are more acidic than *sp*² and *sp*³ hybridized C—H bonds, terminal alkynes are readily deprotonated with strong base in a Brønsted-Lowry acid-base reaction. The resulting ion is called the acetylide ion.



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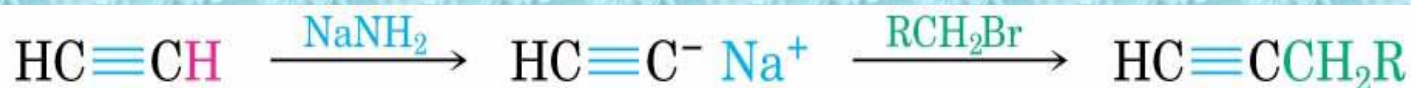
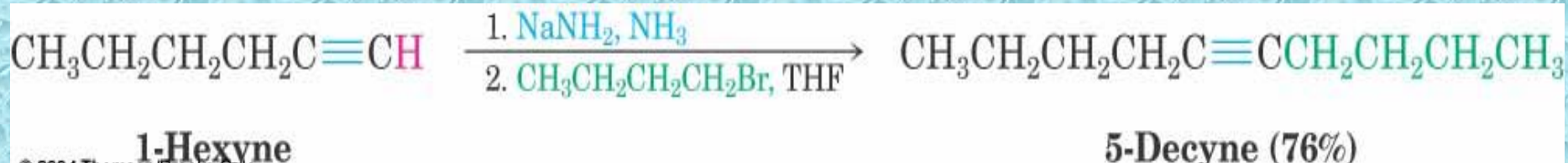
Table 11.1

A Comparison of Bases for Alkyne Deprotonation

	Base	pK_a of the conjugate acid
These bases are strong enough to deprotonate an alkyne.	{ $\text{ }^-\text{NH}_2$ H^-	38 35
These bases are not strong enough to deprotonate an alkyne.	{ $\text{ }^-\text{OH}$ $\text{ }^-\text{OR}$	15.7 15.5–18

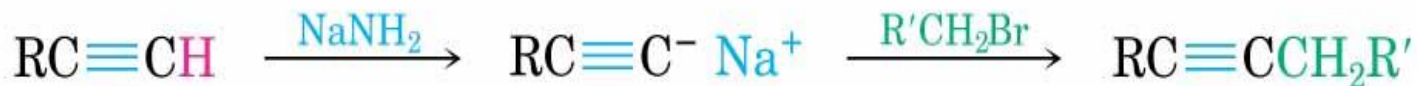
Reactions of Acetylide anions:

- **Acetylide** anions react with unhindered alkyl halides to yield products of **nucleophilic substitution**.



Acetylene

A terminal alkyne



A terminal alkyne

An internal alkyne