



Chapter 4

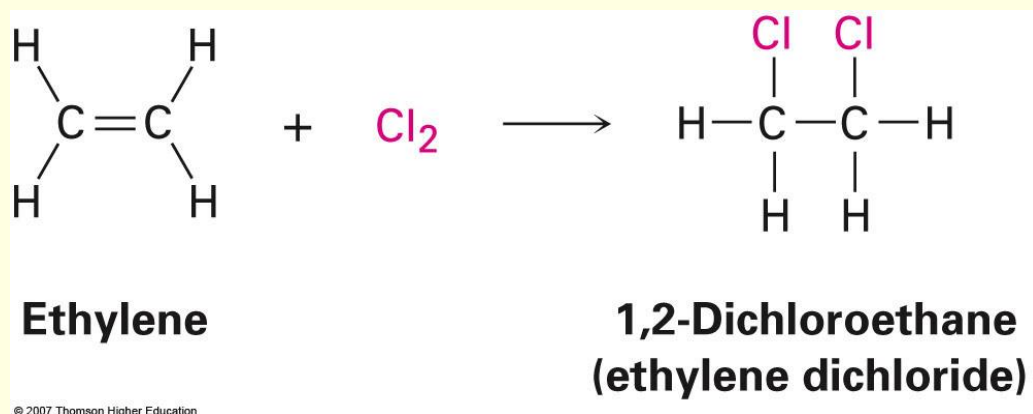
Reactions of Alkenes and Alkynes

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4.4 Addition of **Halogens** to Alkenes

Bromine and chlorine, for instance, add readily to yield 1,2-dihaloalkanes, a process called **halogenation**.



- Bromine and chlorine add to alkenes to give 1,2-dihalides, an industrially important process
 - F₂ is too reactive and I₂ does not add

Why halogenation is not done with fluorine and iodine?

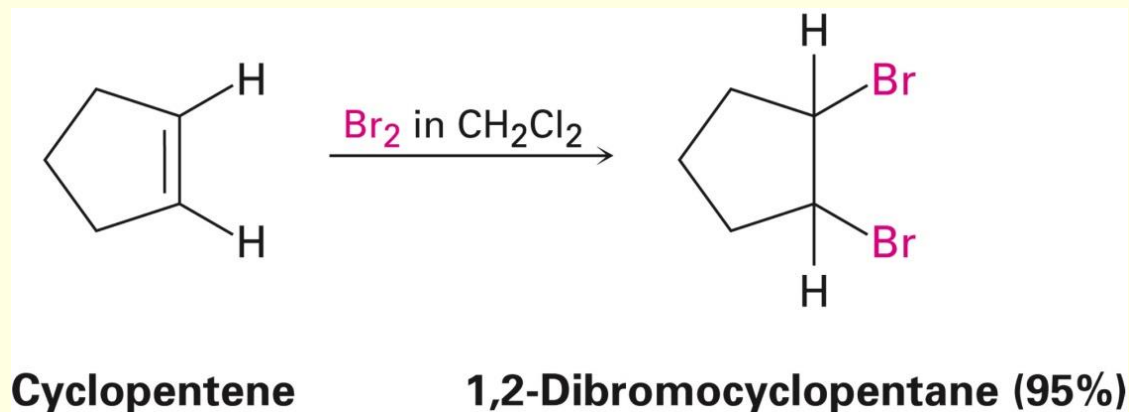
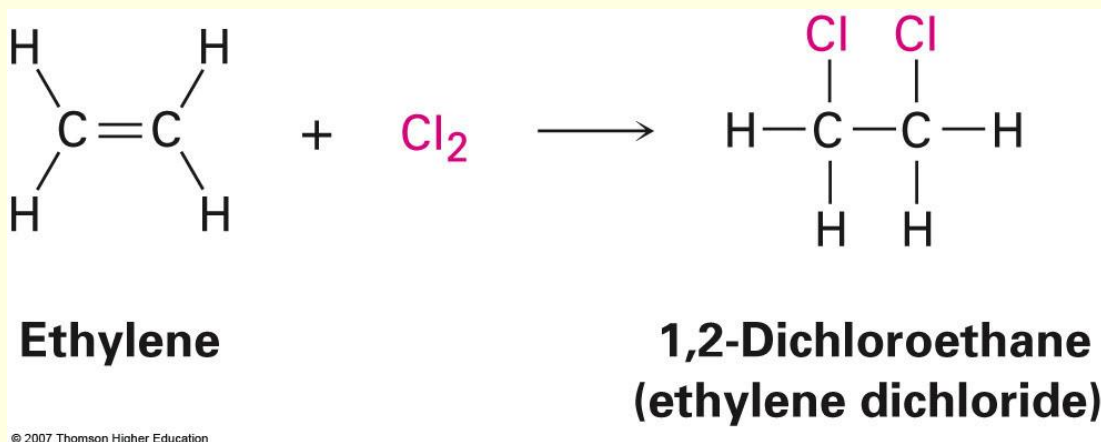
The facility of halogenation is influenced by the halogen.

Because **F₂ is so reactive** and the C–F bond is so stable, it's not considered useful in most synthetic pathways. The required bond breaking simply cannot be done under normal conditions.

The reaction with iodine often produces very low yields.

4.4 Addition of **Halogens** to Alkenes

- Cl_2 reacts as $\text{Cl}^+ \text{Cl}^-$
 - Br_2 is similar

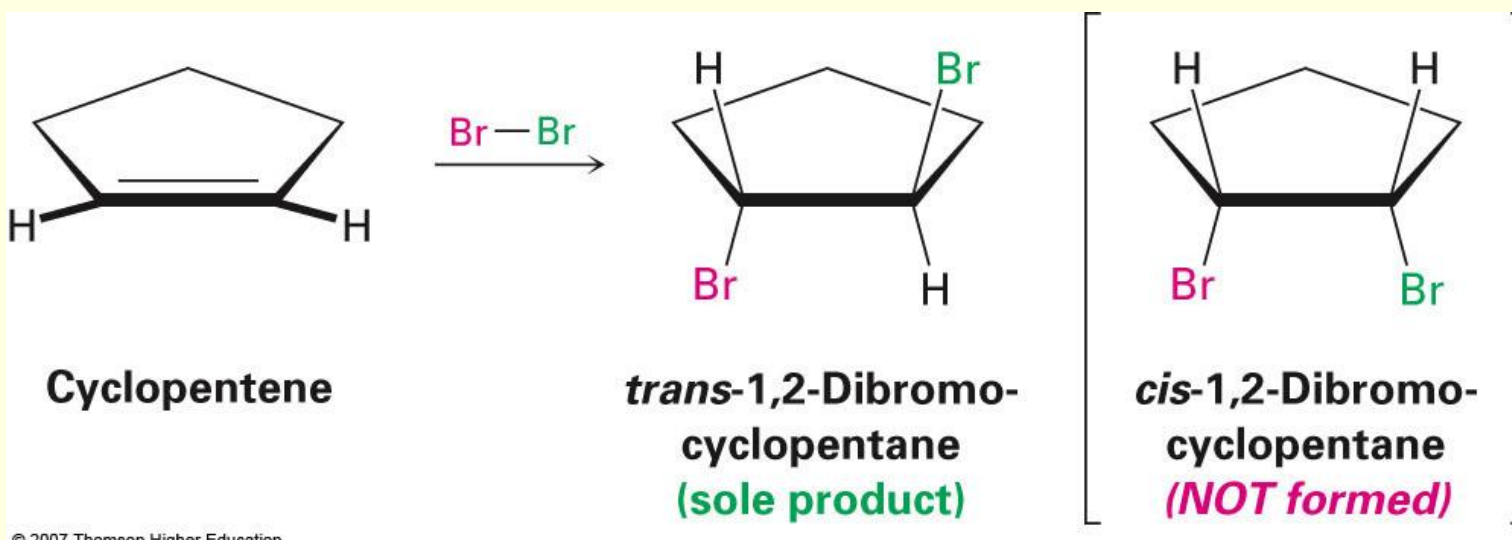


Addition of Br₂ to Cyclopentene

- Addition is exclusively trans : anti stereochemistry

When the halogenation reaction is carried out on a cycloalkene, such as **cyclopentene**, only ***trans*-1,2-dibromocyclopentane** is formed rather than the mixture of **cis and trans products** that might have been expected if a planar carbocation intermediate were involved.

We say that the reaction occurs with **anti stereochemistry**, meaning that the two bromine atoms come from opposite faces of the double bond **approximately 180° apart**.



Mechanism of Bromine Addition

- Br^+ adds to an alkene producing a **cyclic ion**
- Bromonium ion, bromine shares charge with carbon
 - Gives trans addition

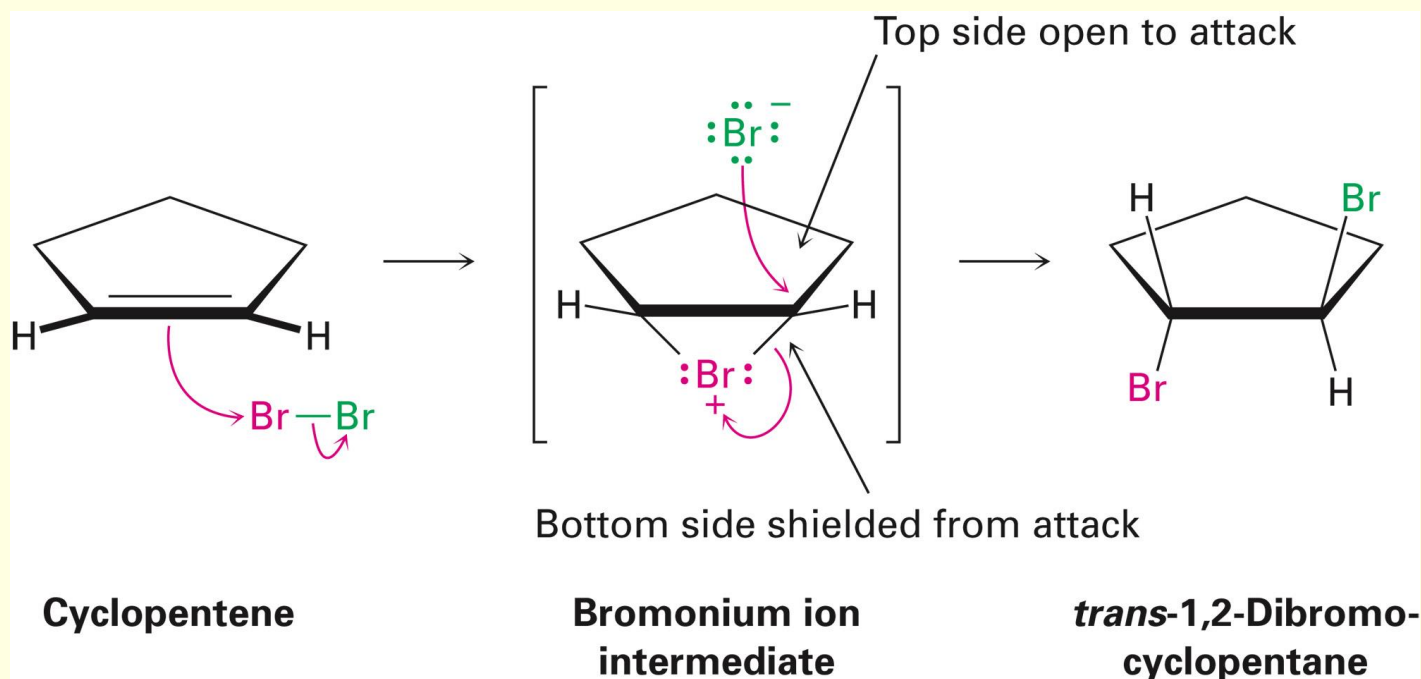
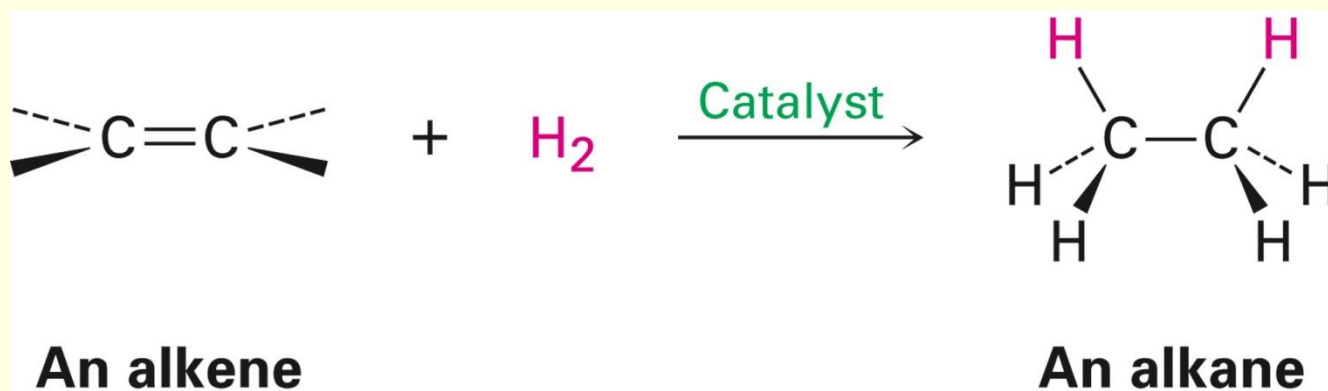


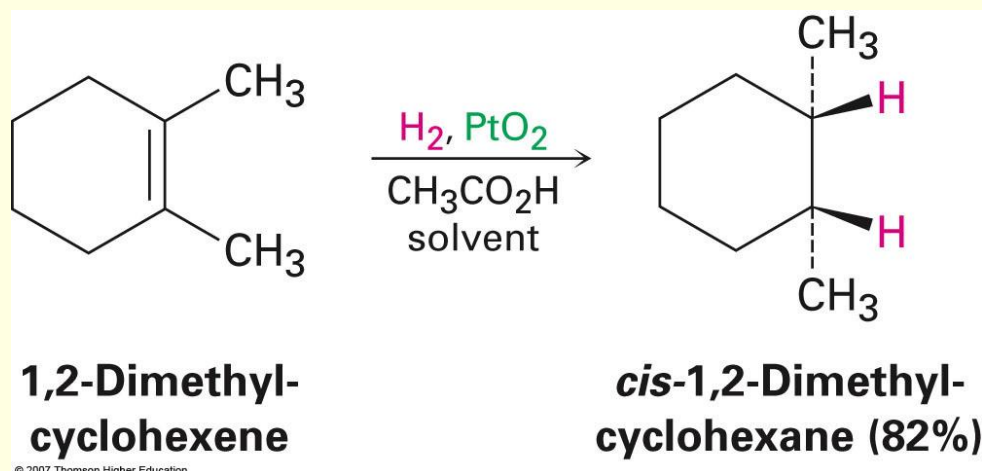
Figure 4.3

Mechanism of the addition of Br_2 to an alkene. A **bromonium ion intermediate** is formed, shielding one face of the double bond and resulting in trans stereochemistry for the addition product.

4.5 Reduction of Alkenes: Hydrogenation

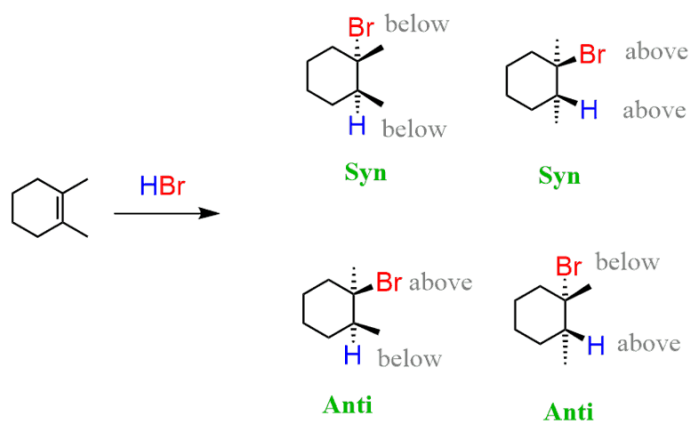


- Addition of H-H across $C=C$
- Reduction in general is addition of H_2
- Requires Pt or Pd as powders on carbon and H_2
- Hydrogen is first adsorbed on catalyst



Mechanism of Catalytic Hydrogenation

- Addition of H-H is **syn**

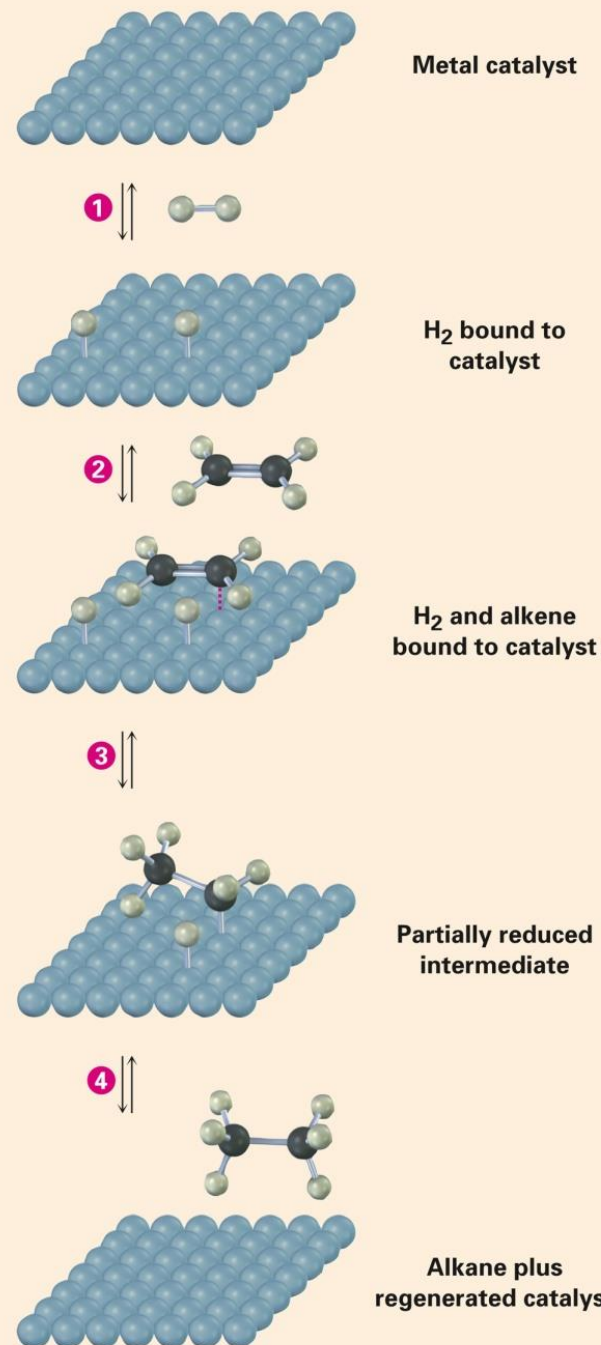


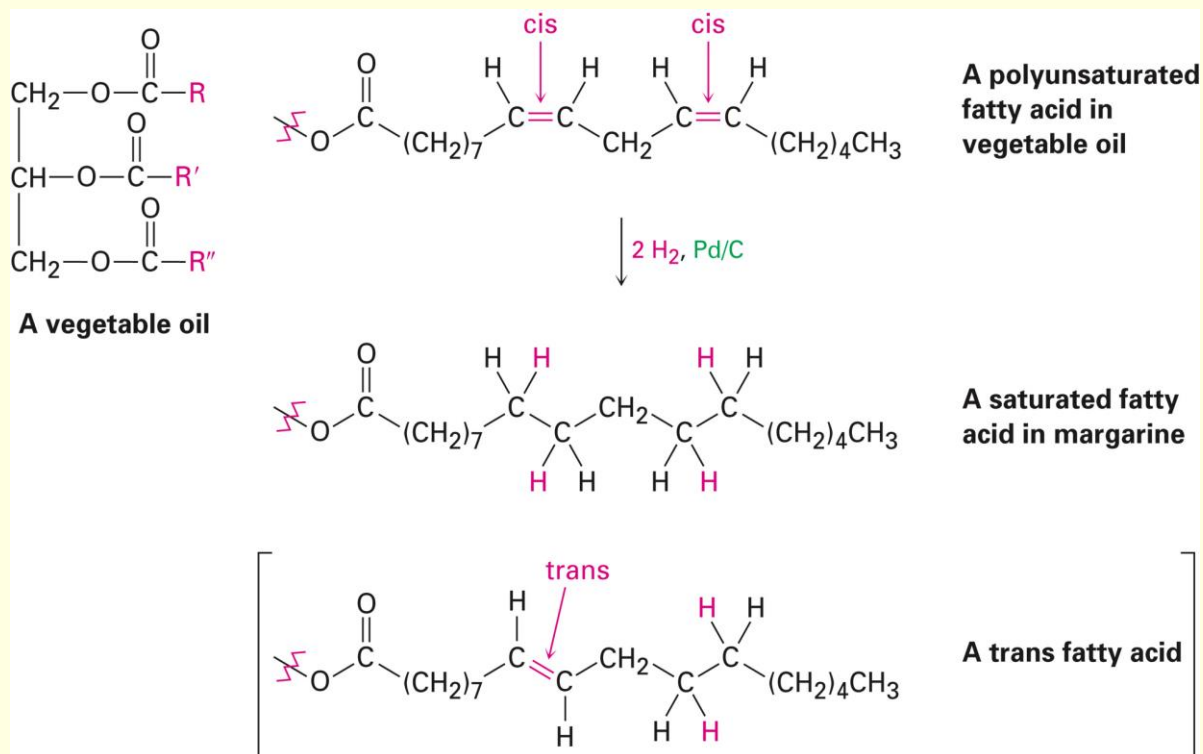
1 Molecular hydrogen adsorbs to the catalyst surface and dissociates into hydrogen atoms.

2 The alkene adsorbs to the catalyst surface, using its π bond to complex to the metal atoms.

3 A hydrogen atom is transferred from the metal to one of the alkene carbon atoms, forming a partially reduced intermediate with a C-H bond and carbon-metal σ bond.

4 A second hydrogen is transferred from the metal to the second carbon, giving the alkane product and regenerating the catalyst. Because both hydrogens are transferred to the same face of the alkene, the reduction has syn stereochemistry.

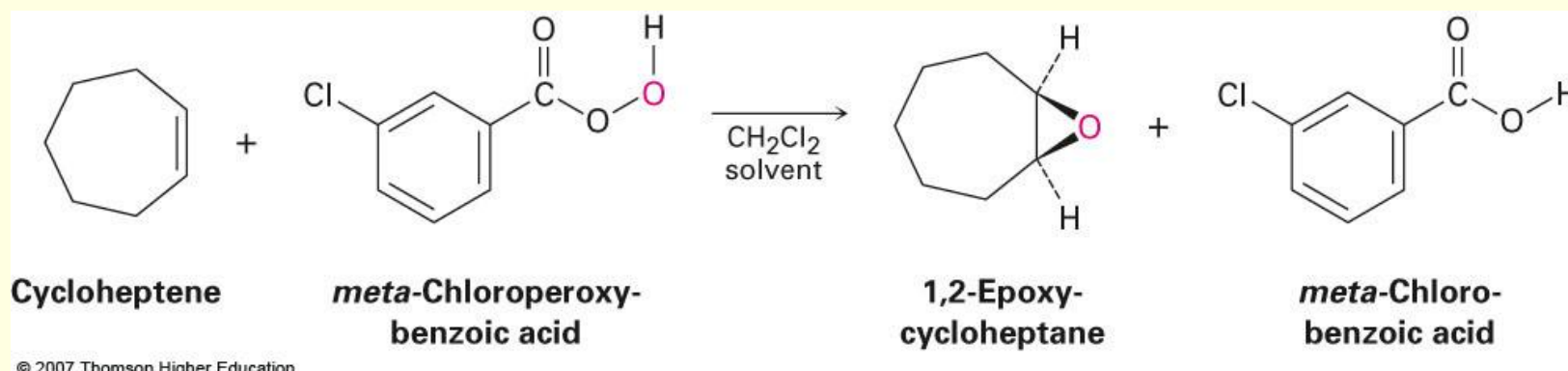




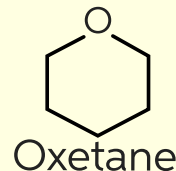
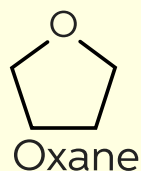
- In addition to its usefulness in the laboratory, catalytic hydrogenation is also important in the **food industry**, where unsaturated vegetable oils are reduced to produce the **saturated fats used in margarine and cooking products.**
- Vegetable oils are triesters of glycerol, $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, with three long-chain carboxylic acids called *fatty acids*. The fatty acids are generally polyunsaturated, and their double bonds have cis stereochemistry.
- **Complete hydrogenation** yields the corresponding saturated fatty acids, but incomplete hydrogenation often results in **partial cis–trans isomerization of a remaining double bond.**
- When eaten and digested, the free trans fatty acids are released, raising blood cholesterol levels and contributing to potential coronary problems.

4.6 Oxidation of Alkenes: Epoxidation, Hydroxylation and Cleavage

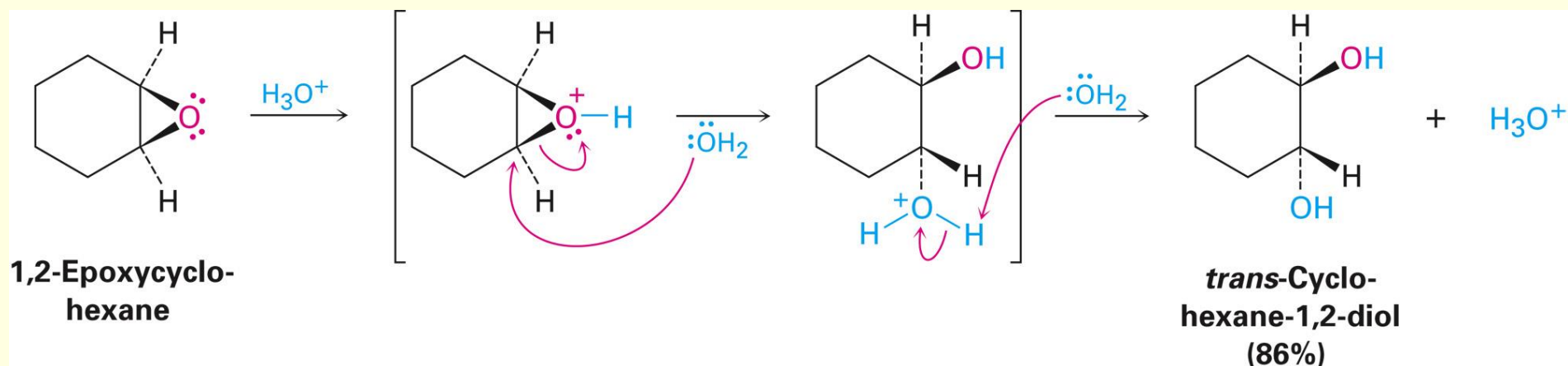
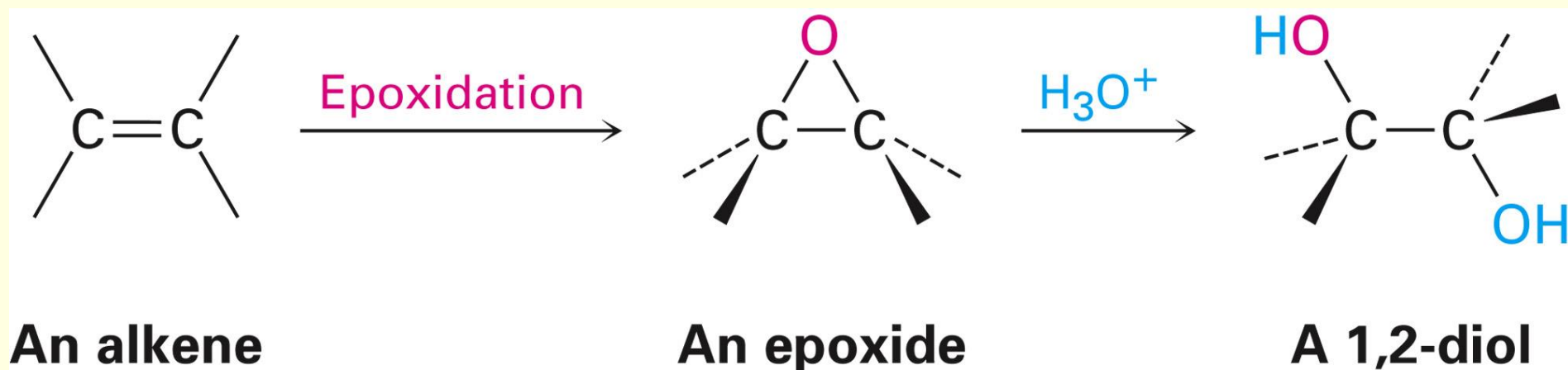
- Reduction usually refers to the addition of hydrogen to a molecule, the word oxidation usually means the addition of oxygen.
- Epoxidation results in a cyclic ether with an oxygen atom
- An epoxide, also called an oxirane, is a cyclic ether with an oxygen atom in a three-membered ring.
- Stereochemistry of addition is syn



cyclic ether



Acid catalyzed ring-opening reaction with water

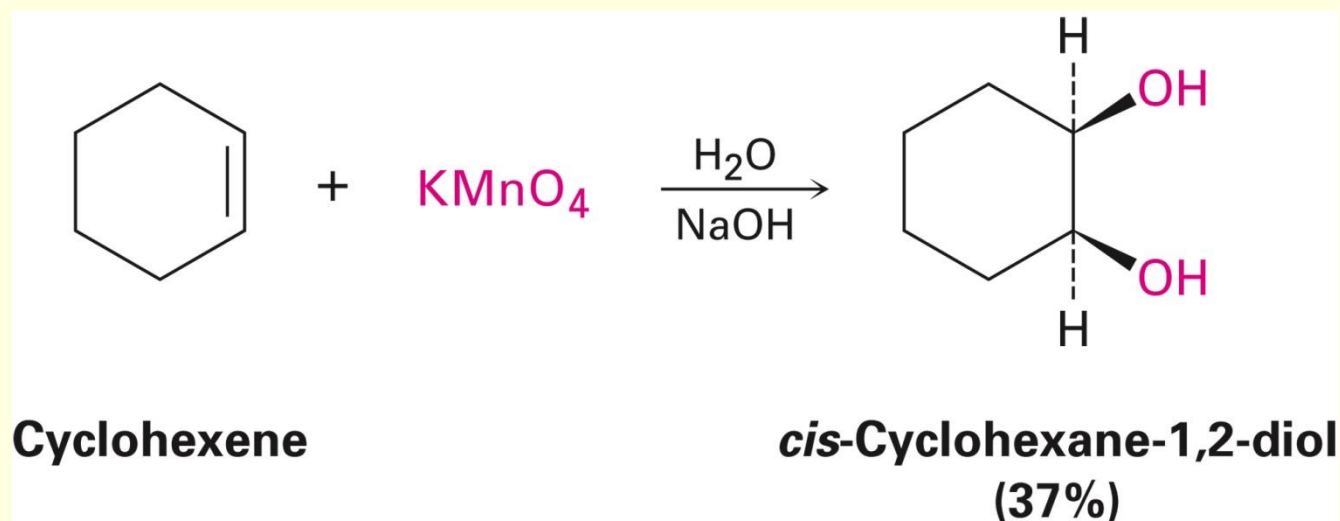


trans-1,2-diol results when an epoxycycloalkane is opened by aqueous acid, just as a *trans*-1,2-dibromide results when a cycloalkene is brominated.

Reaction of the alkene with KMnO_4

Most commonly, **hydroxylation** describes a chemical process that introduces a hydroxyl group ($-\text{OH}$) into an organic compound.

with potassium permanganate, KMnO_4 , in **basic** solution.



Reaction of the alkene with KMnO_4

with potassium permanganate, KMnO_4 , in **acidic** solution.

Cleavage is a word for a kind of splitting or separation:

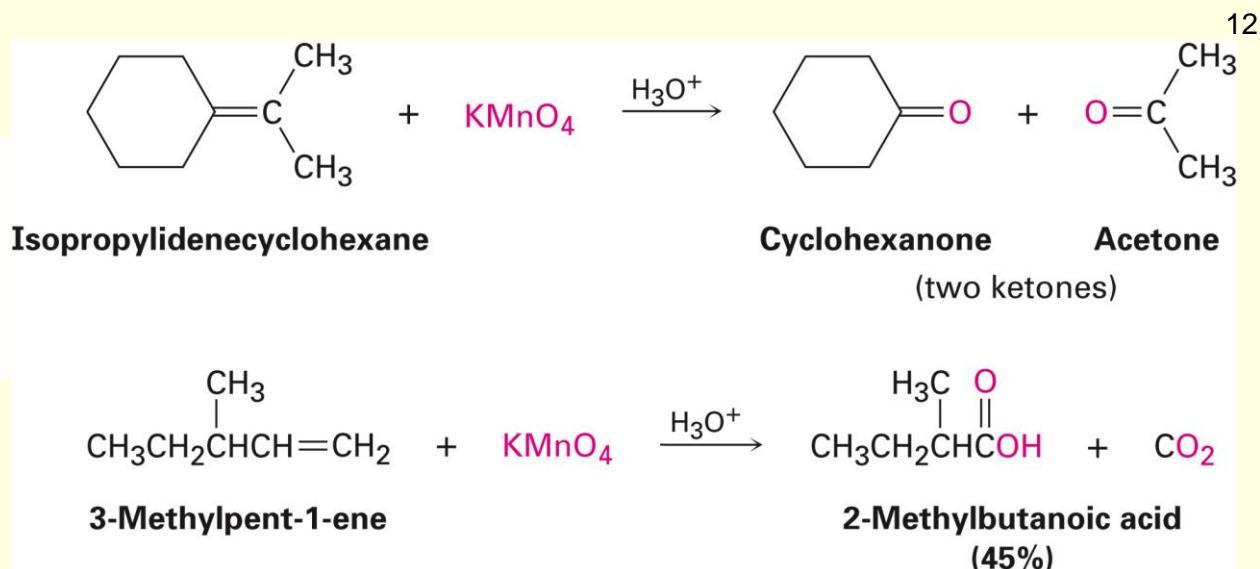
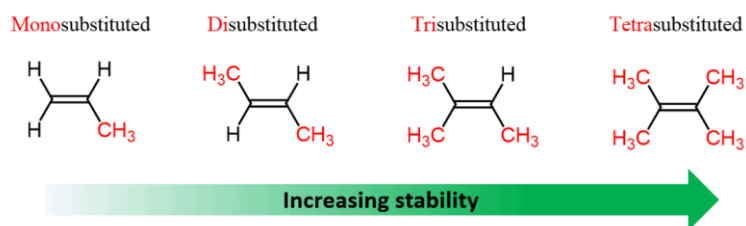
cleavage of the double bond occurs and carbonyl containing products are obtained.

If the double bond is tetrasubstituted, the two carbonyl-containing products are ketones;

if a hydrogen is present on the double bond, one of the carbonyl-containing products is a carboxylic acid;

and

if two hydrogens are present on one carbon, CO_2 is formed.



Worked Example 4.3

Predicting the Structure of a Reactant Given the Products

What alkene gives a mixture of acetone and propanoic acid on reaction with acidic KMnO_4 ?



Strategy

When solving a problem that asks how to prepare a given product, *always work backward*. Look at the product, identify the functional group(s) it contains, and ask yourself, “How can I prepare that functional group?” In the present instance, the products are a ketone and a carboxylic acid, which can be prepared by reaction of an alkene with acidic KMnO_4 . To find the starting alkene that gives the cleavage products shown, remove the oxygen atoms from the two products, join the fragments with a double bond, and replace the $-\text{OH}$ by $-\text{H}$.

Solution

