**Reactions of Alkenes**

All alkenes have a common feature: a carbon–carbon double bond. The reactions of

alkenes arise from the reactivity of the carbon–carbon double bond.

Reactivity of the Carbon–Carbon Double Bond

Because single bonds (sigma bonds) are more stable than pi bonds, the most common reactions of double bonds transform the pi bond into a sigma bond. For example, catalytic hydrogenation converts the C = C pi bond and the H ¬ H

sigma bond into two C ¬ H sigma bonds. The reaction is exothermic , showing that the product is more stable than the reactants.



Hydrogenation of an alkene is an example of an **addition,** one of the three major reaction types we have studied: addition, elimination, and substitution

Some reagents react with carbon–carbon double bonds without the aid of a catalyst. To understand what types of reagents react with double bonds, consider the structure of the pi bond. Although the electrons in the sigma bond framework are tightly held, the pi bond is delocalized above and below the sigma bond (Table 8-1).



**Addition of Hydrogen Halides to Alkenes**

The simple mechanism shown for addition of HBr to but-2-ene applies to a large number of electrophilic additions. We can use this mechanism to predict the outcome of some fairly complicated reactions. For example, the addition of HBr to 2-methylbut-2- ene could lead to either of two products, yet only one is observed.



**Markovnikov’s Rule** A Russian chemist, Vladimir Markovnikov, first showed the orientation of addition of HBr to alkenes in 1869. Markovnikov stated:

**MARKOVNIKOV’S RULE: The addition of a proton acid to the double bond of an alkene results in a product with the acid proton bonded to the carbon atom that already holds the greater number of hydrogen atoms.**

An electrophile adds to the less substituted end of the double bond to give the more substituted (and therefore more stable) carbocation



Like HBr, both HCl and HI add to the double bonds of alkenes, and they also follow Markovnikov’s rule; for example,





In 1933, M. S. Kharasch and F. W. Mayo found that some additions of HBr (but not HCl or HI) to alkenes gave products that were opposite to those expected from Markovnikov’s rule. These **anti-Markovnikov** reactions were most likely when the reagents or sol- vents came from old supplies that had accumulated peroxides from exposure to the air. Peroxides give rise to free radicals that initiate the addition, causing it to occur by a radical mechanism. The oxygen–oxygen bond in peroxides is rather weak, so it can break to give two alkoxy radicals.



**Radical Addition of HBr to Unsymmetrical Alkenes** Now we must explain the anti- Markovnikov orientation found in the products of the peroxide-catalyzed reaction. With an unsymmetrical alkene like 2-methylbut-2-ene, adding the bromine radical to the secondary end of the double bond forms a tertiary radical.







Electrophilic Addition to Alkenes

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**Addition of Water: Hydration of Alkenes**

The reaction follows Markovnikov’s rule. The proton has added to the end of the double bond that already had more hydrogens (that is, the less substituted end), and the

¬ OH group has added to the more substituted end.





**Hydration by Oxymercuration– Demercuration**

Oxymercuration–demercuration is another method for converting alkenes to alcohols with Markovnikov orientation. Oxymercuration–demercuration works with many alkenes that do not easily undergo direct hydration, and it takes place under milder conditions



Alkoxymercuration Demercuration

When mercuration takes place in an alcohol solvent, the alcohol serves as a nucleophile to attack the mercurinium ion. The resulting product contains an alkoxy group. In effect, **alkoxymercuration**–demercuration converts alkenes to ethers by adding an alcohol across the double bond of the alkene 



**Hydroboration of Alkenes**

We have seen two methods for hydrating an alkene with Markovnikov orientation.

What if we need to convert an alkene to the anti-Markovnikov alcohol? For example, the following transformation cannot be accomplished using the hydration procedures covered thus far.



**Addition of Halogens to Alkenes**

Halogens add to alkenes to form vicinal dihalides.

Chlorine and bromine commonly add to alkenes by the halonium ion mechanism. Iodination is used less frequently because diiodide products decompose easily

**Formation of Halohydrins**

A **halohydrin** is an alcohol with a halogen on the adjacent carbon atom. In the presence of water, halogens add to alkenes to form halohydrins.

When a water molecule attacks the halonium ion, the final product is a halohydrin, with a halogen on one carbon atom and a hydroxyl group on the adjacent carbon. The product may be a *chlorohydrin*, a *bromohydrin*, or an *iodohydrin*, depending on the halogen.



For example, the addition of bromine water to cyclopentene gives *trans*-2-bromocyclopentanol, the product of anti addition across the double bond.



**Catalytic Hydrogenation of Alkenes**

Hydrogenation of an alkene is formally a reduction, with H2 adding across the double bond to give an alkane. The process usually requires a catalyst containing Pt, Pd, or Ni.



Epoxidation of Alkenes

An **epoxide** is a three-membered cyclic ether, also called an **oxirane.** Epoxides are valuable synthetic intermediates used for converting alkenes to a variety of other func- tional groups. An alkene is converted to an epoxide by a **peroxyacid,** a carboxylic acid that has an extra oxygen atom in a ¬ O ¬ O ¬ (peroxy) linkage.



**Syn Dihydroxylation of Alkenes**

Converting an alkene to a glycol requires adding a hydroxyl group to each end of the double bond. This addition is called **dihydroxylation** (or **hydroxylation**) of the double bond.



**Oxidative Cleavage of Alkenes**

In a potassium permanganate dihydroxylation, if the solution is warm or acidic or too concentrated, **oxidative cleavage** of the glycol may occur. In effect, the double bond is cleaved to two carbonyl groups





**Ozonolysis**

Like permanganate, ozone cleaves double bonds to give ketones and aldehydes. However, ozonolysis is milder, and both ketones and aldehydes can be recovered without further oxidation.

