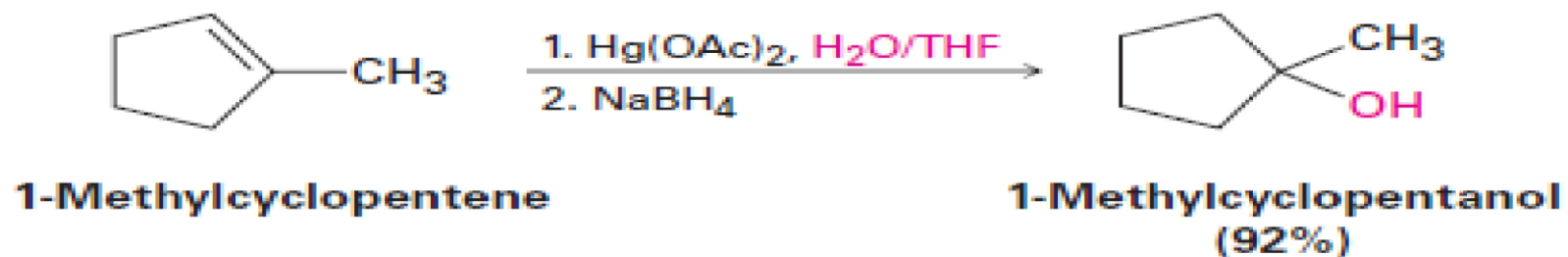
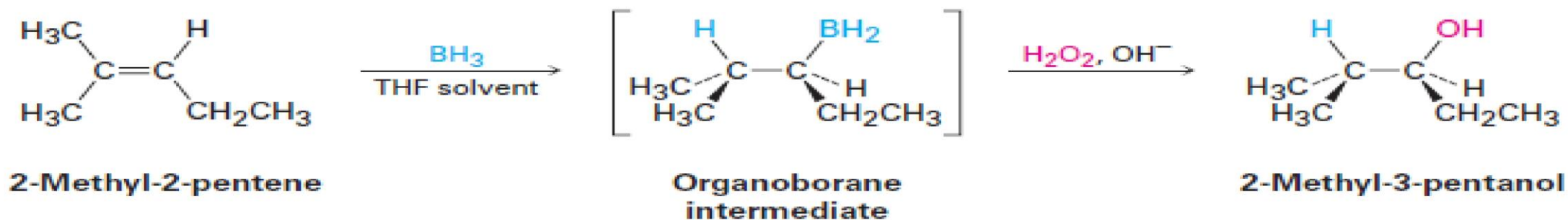


In the laboratory, alkenes are often hydrated by the **oxymercuration–demercuration** procedure. **Oxymercuration** involves electrophilic addition of  $\text{Hg}^{+2}$  to the alkene on reaction with mercury (II) acetate  $[(\text{CH}_3\text{CO}_2)_2\text{Hg}]$ , often abbreviated  $\text{Hg}(\text{OAc})_2$  in aqueous tetrahydrofuran (THF) solvent. The intermediate organomercury compound is then treated with sodium borohydride,  $\text{NaBH}_4$ , and demercuration occurs to produce an alcohol. For example:



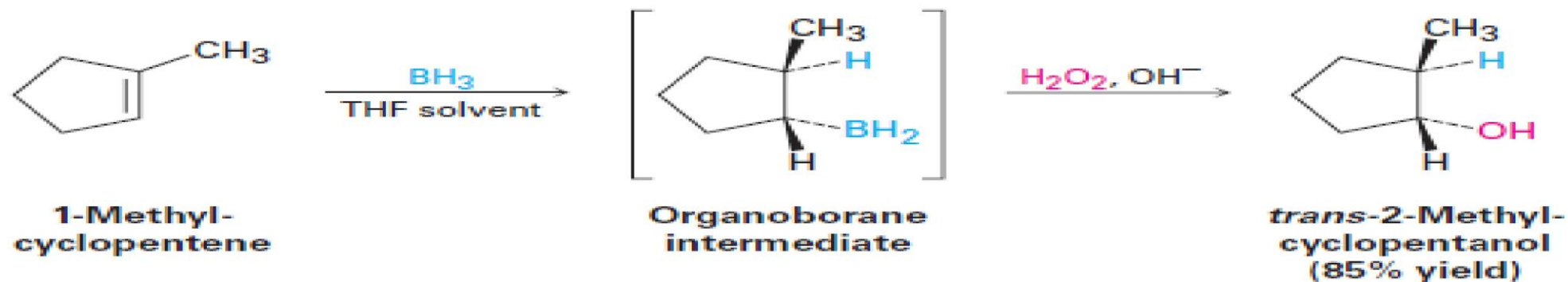
## Hydration of Alkenes: Addition of $\text{H}_2\text{O}$ by Hydroboration

In addition to the oxymercuration–demercuration method, which yields the Markovnikov product, a complementary method that yields the non-Markovnikov product is also useful. Discovered by H.C. Brown and called **hydroboration**, the reaction involves addition of a B-H bond of borane,  $\text{BH}_3$ , to an alkene to yield an organoborane intermediate,  $\text{RBH}_2$ . Oxidation of the organoborane by reaction with basic hydrogen peroxide,  $\text{H}_2\text{O}_2$ , then gives an alcohol. For example:



One of the features that makes the hydroboration reaction so useful is the regiochemistry that results when an unsymmetrical alkene is hydroborated. For example, hydroboration–oxidation of 1-methylcyclopentene yields *trans*-2-methylcyclopentanol. In this process, boron and hydrogen add to the alkene from the same face of the double bond—that is, with **syn stereochemistry**, the opposite of anti—with boron attaching to the less highly substituted carbon.

During the oxidation step, the boron is replaced by an -OH with the same stereochemistry, resulting in an overall syn non-Markovnikov addition of water. This stereochemical result is particularly useful because it is complementary to the Markovnikov regiochemistry observed for oxymercuration–demercuration.



## Reduction of Alkenes: Hydrogenation

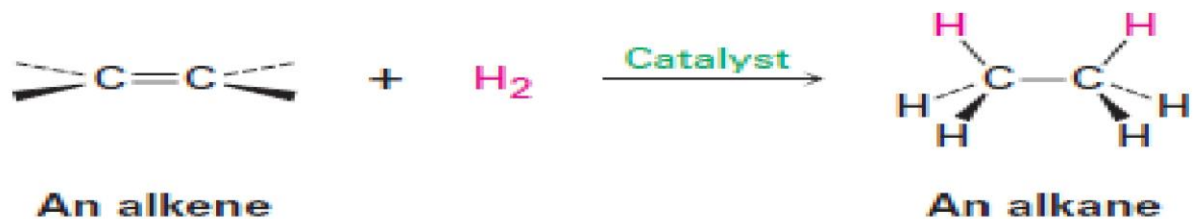
Alkenes react with  $\text{H}_2$  in the presence of a metal catalyst such as palladium or platinum to yield the corresponding saturated alkane addition products. We describe the result by saying that the double bond has been **hydrogenated**, or *reduced*. Note that the word *reduction* is used somewhat differently in organic chemistry from what you might have learned previously. In general chemistry, a reduction is defined as the gain of one or more electrons by an atom. In organic chemistry, however, a **reduction** is a reaction that results in a gain of electron density for carbon, caused either by bond formation between carbon and a less electronegative atom—usually hydrogen—or by bond-breaking between carbon and a more electronegative atom—usually oxygen, nitrogen, or a halogen.

**Reduction** Increases electron density on carbon by:

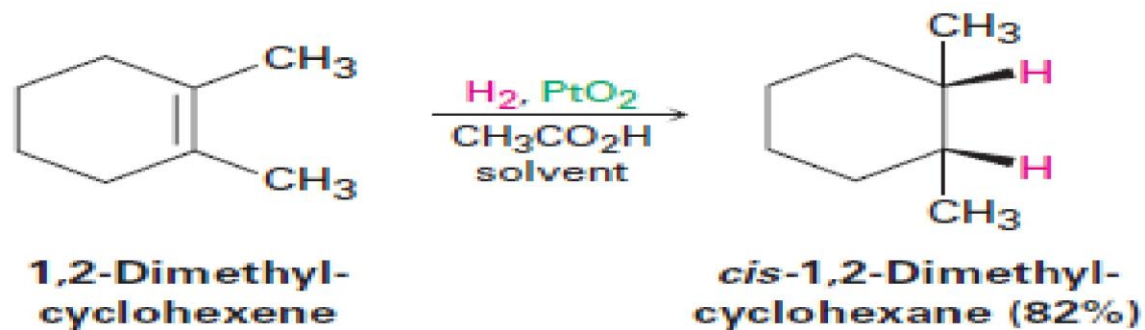
- forming this: C-H
- or breaking one of these: C-O C-N C-X



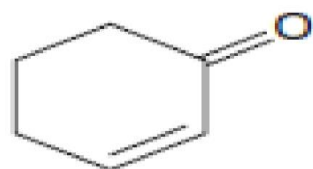
A reduction:



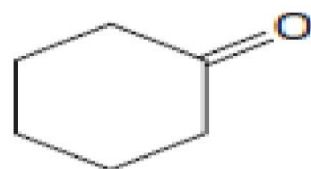
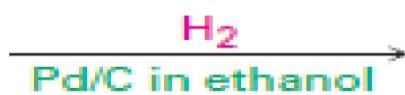
Platinum and palladium are the most common laboratory catalysts for alkene hydrogenations. Palladium is normally used as a very fine powder “supported” on an inert material such as charcoal (Pd/C) to maximize surface area. Platinum is normally used as PtO<sub>2</sub>, a reagent known as *Adams’ catalyst* after its discoverer, Roger Adams. Catalytic hydrogenation, unlike most other organic reactions, is a *heterogeneous* process rather than a homogeneous one. That is, the hydrogenation reaction does not occur in a homogeneous solution but instead takes place on the surface of solid catalyst particles. Hydrogenation usually occurs with *syn* stereochemistry: both hydrogens add to the double bond from the same face.



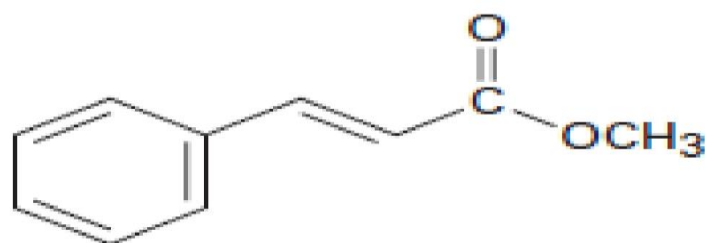
Alkenes are much more reactive toward catalytic hydrogenation than most other unsaturated functional groups, and the reaction is therefore quite selective. Other functional groups, such as aldehydes, ketones, esters, and nitriles, often survive alkene hydrogenation conditions unchanged, although reaction with these groups does occur under more vigorous conditions. Note that, particularly in the hydrogenation of methyl 3-phenylpropenoate shown below, the aromatic ring is not reduced by hydrogen and palladium even though it contains apparent double bonds.



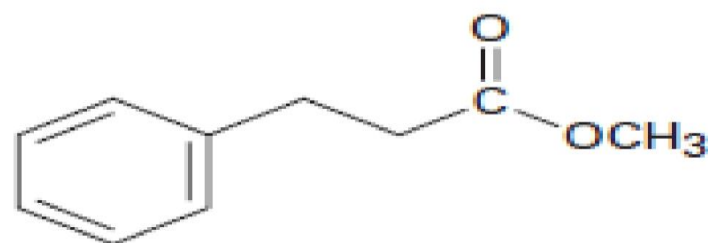
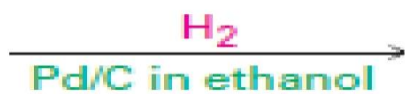
**Cyclohex-2-enone**



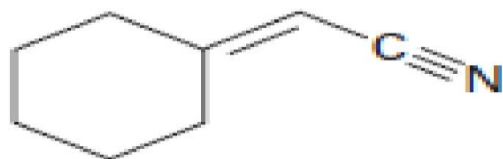
**Cyclohexanone**  
(ketone not reduced)



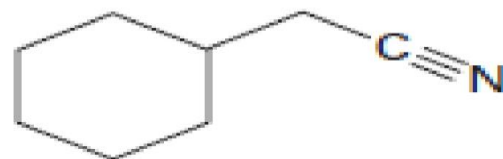
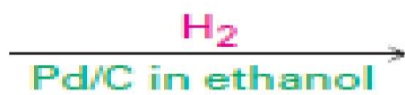
**Methyl 3-phenylpropenoate**



**Methyl 3-phenylpropanoate**  
(aromatic ring not reduced)



**Cyclohexylidenemalonitrile**



**Cyclohexylmalonitrile**  
(nitrile not reduced)

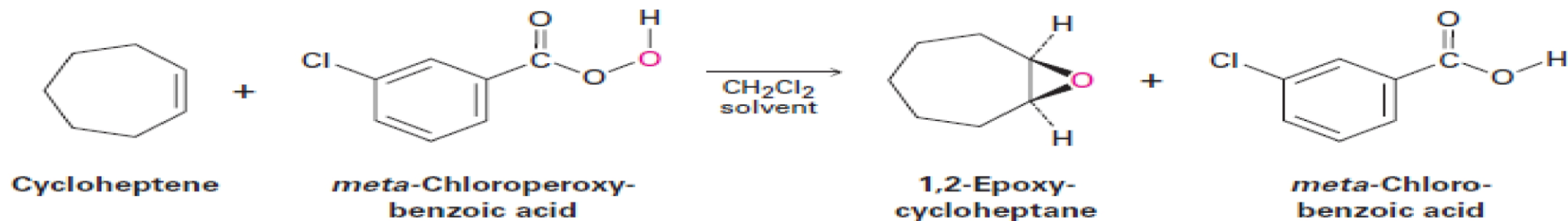
## Oxidation of Alkenes: Epoxidation and Hydroxylation

Like the word *reduction* used in the previous section for the addition of hydrogen to a double bond, the word *oxidation* has a slightly different meaning in organic chemistry from what you might have previously learned. In general chemistry, an oxidation is defined as the loss of one or more electrons by an atom. In organic chemistry, however, an **oxidation** is a reaction that results in a loss of electron density for carbon, caused either by bond formation between carbon and a more electronegative atom-usually oxygen, nitrogen, or a halogen-or by bond-breaking between carbon and a less electronegative atom-usually hydrogen. Note that an *oxidation* often adds oxygen, while a *reduction* often adds hydrogen.

**Oxidation** Decreases electron density on carbon by:

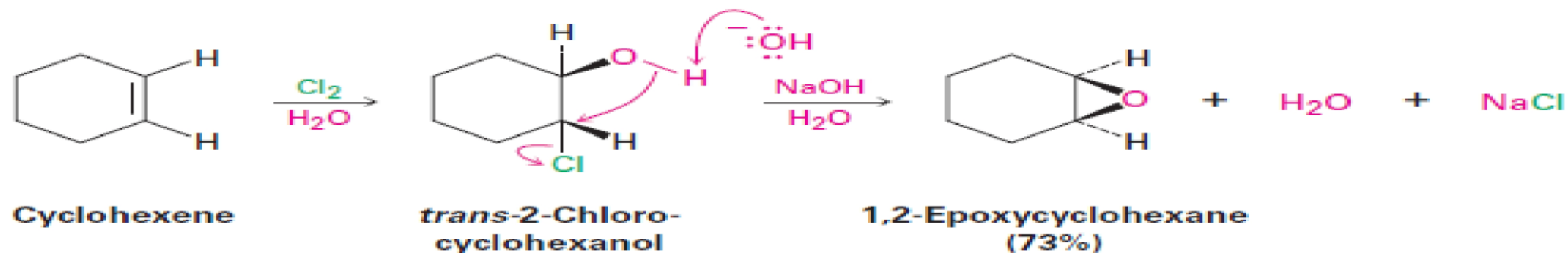
- forming one of these: C-O C-N C-X
- or breaking this: C-H

In the laboratory, alkenes are oxidized to give *epoxides* on treatment with a peroxy acid,  $\text{RCO}_3\text{H}$ , such as *meta*-chloroperoxy benzoic acid. An **epoxide**, also called an *oxirane*, is cyclic ether with an oxygen atom in a three-membered ring. For example:

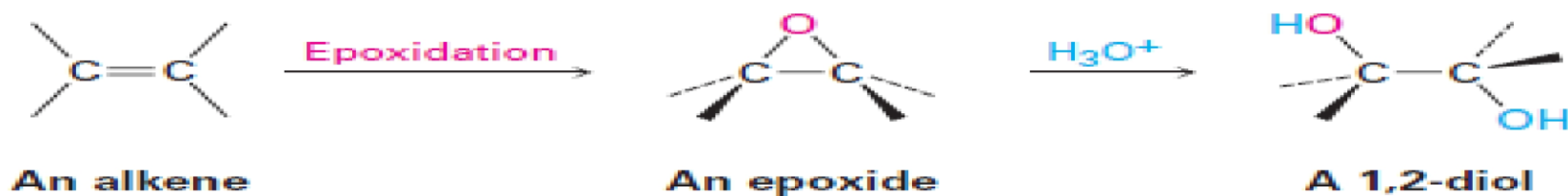


Another method for the synthesis of epoxides involves the use of halohydrins, prepared by electrophilic addition of HO-X to alkenes.

When a halohydrin is treated with base, HX is eliminated and an epoxide is produced.

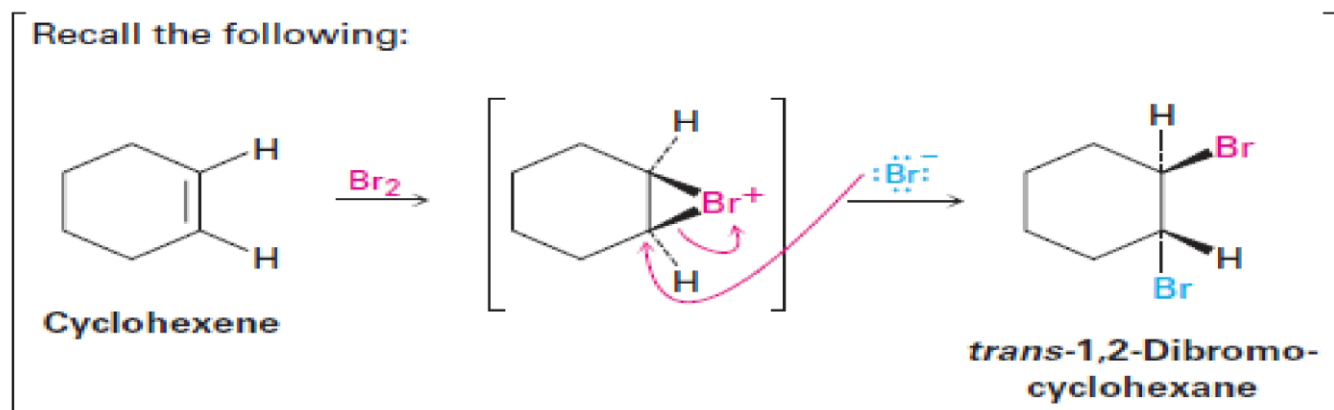
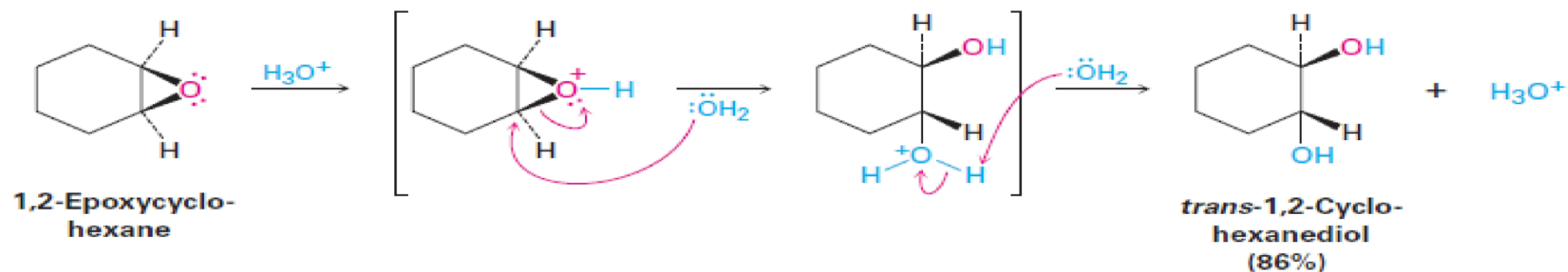


Epoxides undergo an acid-catalyzed ring-opening reaction with water (a *hydrolysis*) to give the corresponding 1,2-dialcohol, or *diol*, also called a **glycol**. Thus, the net result of the two-step alkene epoxidation/hydrolysis is **hydroxylation**—the addition of an -OH group to each of the two double bond carbons. In fact, approximately 18 million metric tons of ethylene glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , most of it used for automobile antifreeze, are produced worldwide each year by the epoxidation of ethylene and subsequent hydrolysis.

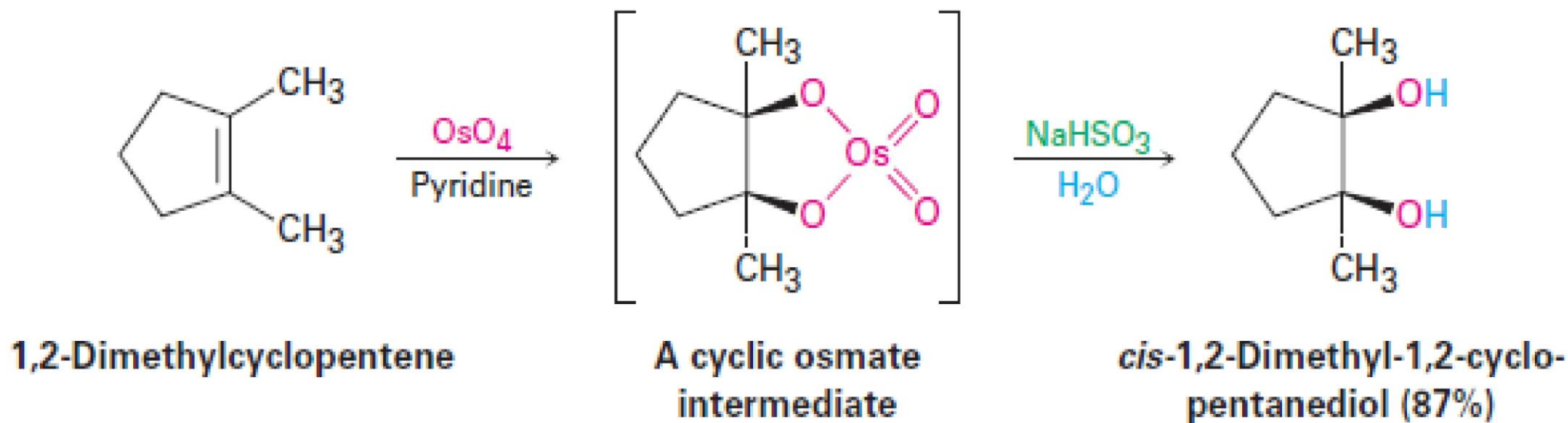




Acid-catalyzed epoxide opening begins with protonation of the epoxide to increase its reactivity, followed by nucleophilic addition of water. This nucleophilic addition is analogous to the final step of alkene bromination, in which a cyclic bromonium ion is opened by a nucleophile. That is, a *trans*-1,2-diol results when an epoxy cycloalkane is opened by aqueous acid, just as a *trans*-1,2-dibromide results when a cycloalkene is brominated.

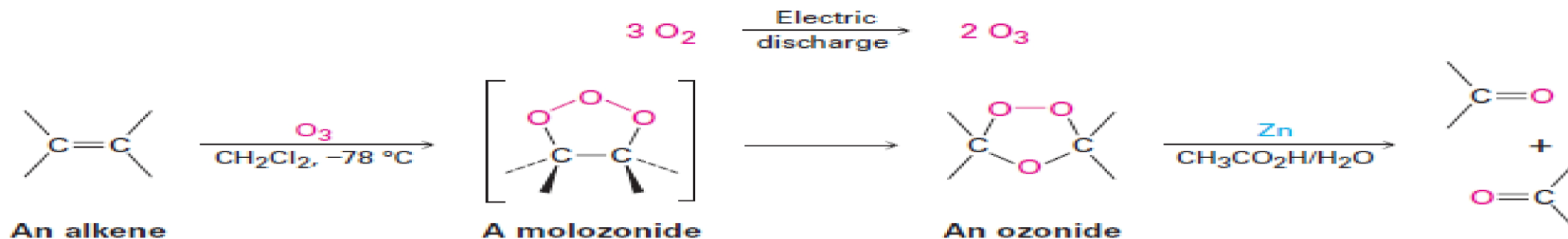


Hydroxylation can be carried out directly (without going through an intermediate epoxide) by treating an alkene with osmium tetroxide,  $\text{OsO}_4$ . The reaction occurs with syn stereochemistry and does not involve a carbocation intermediate. Instead, it takes place through an intermediate cyclic *osmate*, which is formed in a single step by addition of  $\text{OsO}_4$  to the alkene. This cyclic osmate is then cleaved using aqueous sodium bisulfite,  $\text{NaHSO}_3$ .

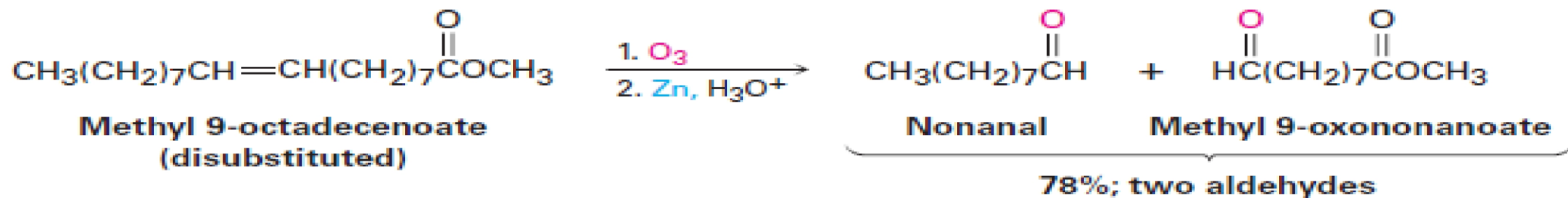
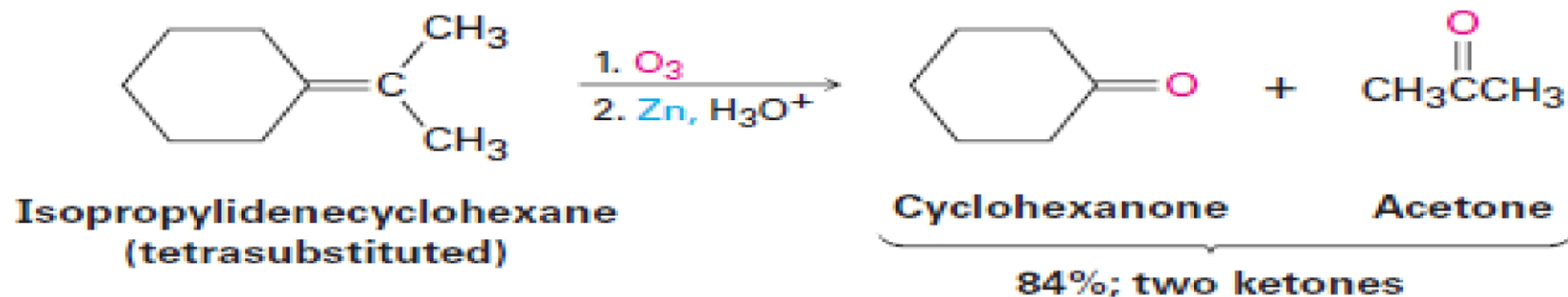


## Oxidation of Alkenes: Cleavage to Carbonyl Compounds

In all the alkene addition reactions the carbon–carbon double bond was converted into a single bond but the carbon skeleton was unchanged. There are, however, powerful oxidizing reagents that will cleave C=C bonds and produce two carbonyl-containing fragments. Ozone ( $\text{O}_3$ ) is perhaps the most useful double-bond cleavage reagent. Prepared by passing a stream of oxygen through a high-voltage electrical discharge, ozone adds rapidly to a C=C bond at low temperature to give a cyclic intermediate called a *molozonide*. Once formed, the molozonide spontaneously rearranges to form an **ozonide**. Although we won't study the mechanism of this rearrangement in detail, it involves the molozonide coming apart into two fragments that then recombine in a different way.



Low-molecular-weight ozonides are explosive and are therefore not isolated. Instead, the ozonide is immediately treated with a reducing agent, such as zinc metal in acetic acid, to produce carbonyl compounds. The net result of the ozonolysis/reduction sequence is that the C=C bond is cleaved and an oxygen atom becomes doubly bonded to each of the original alkene carbons. If an alkene with a tetrasubstituted double bond is ozonized, two ketone fragments result; if an alkene with a trisubstituted double bond is ozonized, one ketone and one aldehyde result; and so on.



Several oxidizing reagents other than ozone also cause double-bond cleavage, although such reactions are not often used. For example, potassium permanganate ( $\text{KMnO}_4$ ) in neutral or acidic solution cleaves alkenes to give carbonyl-containing products. If hydrogens are present on the double bond, carboxylic acids are produced; if two hydrogens are present on one carbon,  $\text{CO}_2$  is formed.

