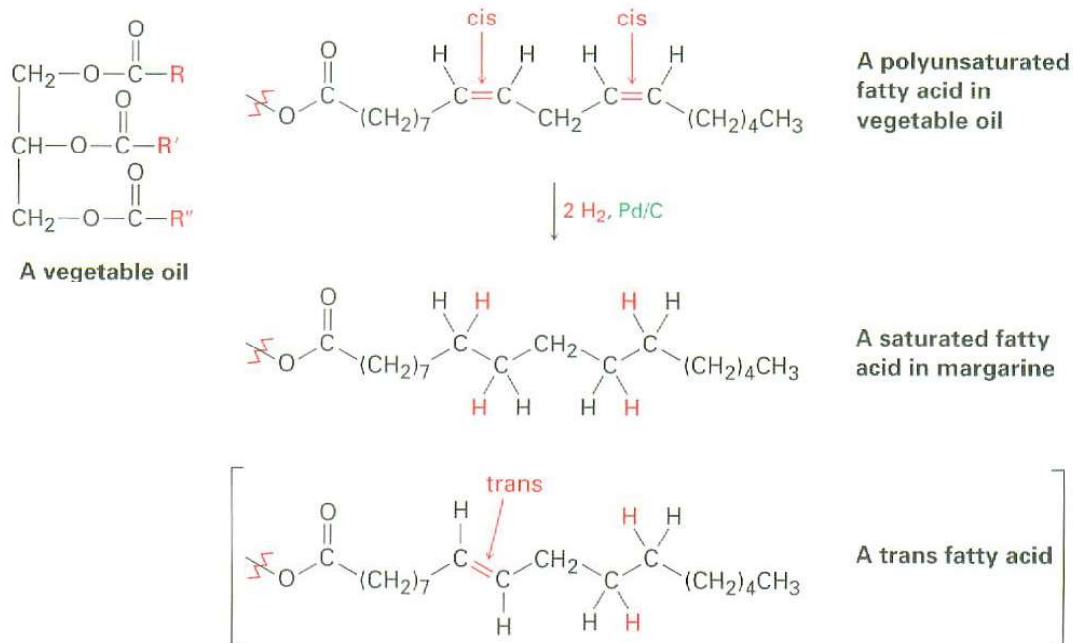Figure 7.8 Catalytic hydrogenation of polyunsaturated fats leads to saturated products, along with a small amount of isomerized trans fats.


7.8 | Oxidation of Alkenes: Epoxidation and Hydroxylation

Like the word *reduction* used in the previous section for 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 by 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

Alkenes are oxidized to give *epoxides* on treatment with a peroxyacid (RCO_3H), such as *meta*-chloroperoxybenzoic acid. An **epoxide**, also called an *oxirane*, is a cyclic ether with an oxygen atom in a three-membered ring. For example:


Cycloheptene   *meta*-Chloroperoxy-benzoic acid   1,2-Epoxy-cycloheptane   *meta*-Chloro-benzoic acid
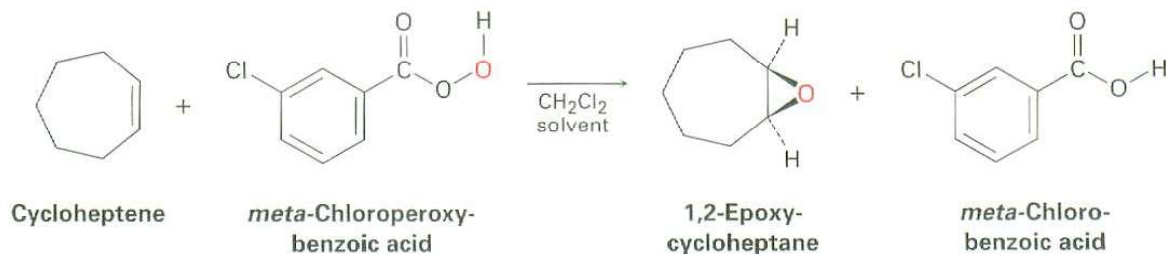
Peroxyacids transfer an oxygen atom to the alkene with syn stereo-chemistry—both C−O bonds form on the same face of the double bond—through a one-step mechanism without intermediates. The oxygen atom farthest from the carbonyl group is the one transferred.

Alkene   **Peroxyacid**   **Epoxide**   **Acid**
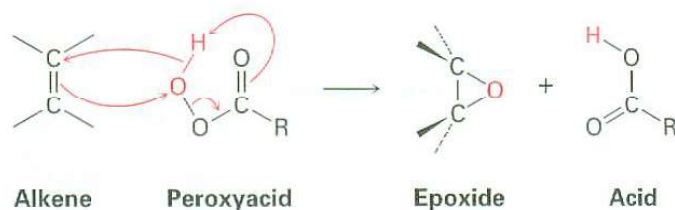
Another method for the synthesis of epoxides is through the use of halo-hydrins, prepared by electrophilic addition of HO−X to alkenes (Section 7.3). When a halohydrin is treated with base, HX is eliminated and an epoxide is produced.
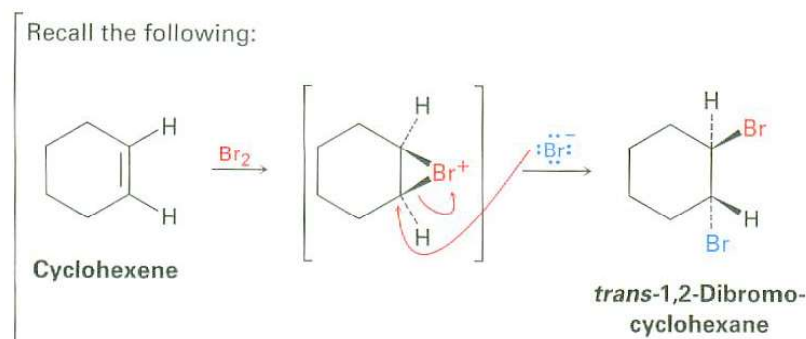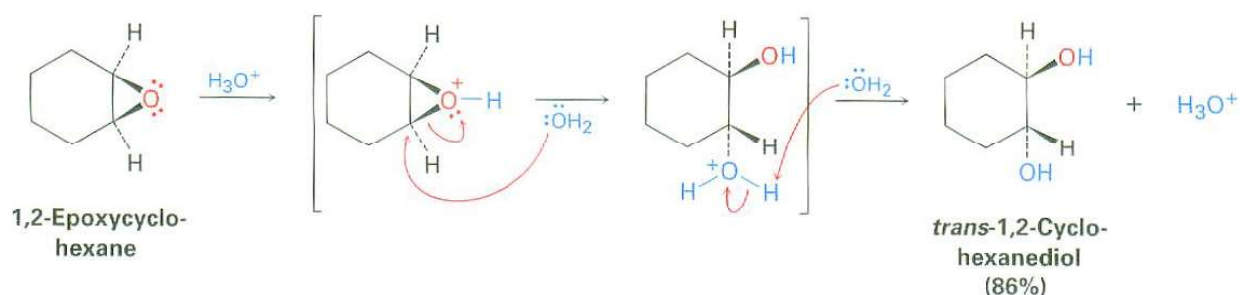

Cyclohexene   ***trans*-2-Chloro-   **1,2-Epoxycyclohexane**
                         cyclohexanol   **(73%)**
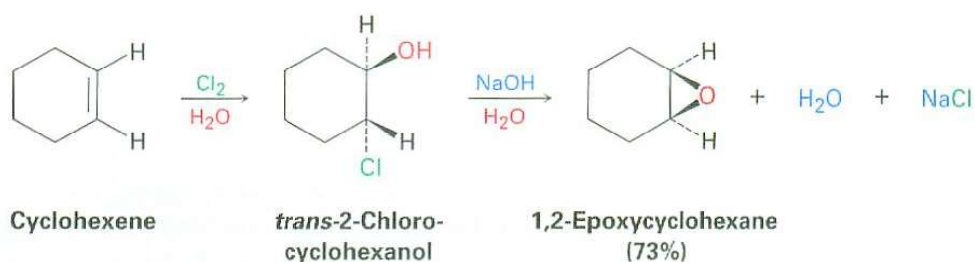
Epoxides undergo an acid-catalyzed ring-opening reaction with water (a *hydrolysis*) to give the corresponding dialcohol *(diol)*, also called a **glycol**. Thus, the net result of the two-step alkene epoxidation/hydrolysis is **hydroxylation**—the addition of an −OH group to each of the two double-bond carbons. In fact, more than 3 million tons of ethylene glycol, $HOCH_2CH_2OH$, most of it used for automobile antifreeze, is produced each year in the United States by epoxida-tion of ethylene followed by hydrolysis.

**An alkene**   **An epoxide**   **A 1,2-diol**
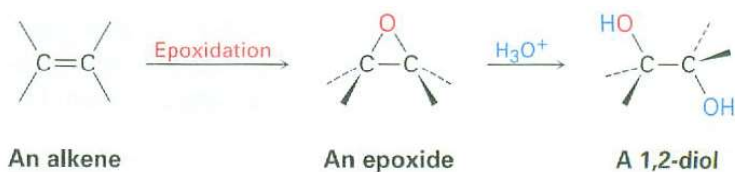
Acid-catalyzed epoxide opening takes place by protonation of the epoxide to increase its reactivity, followed by nucleophilic addition of water. This nucleophilic addition is analogous to the final step of alkene bromination, in which a cyclic bromonium ion is opened by a nucleophile (Section 7.2). That is,

a *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 halogenated. We'll look at epoxide chemistry in more detail in Section 18.6.
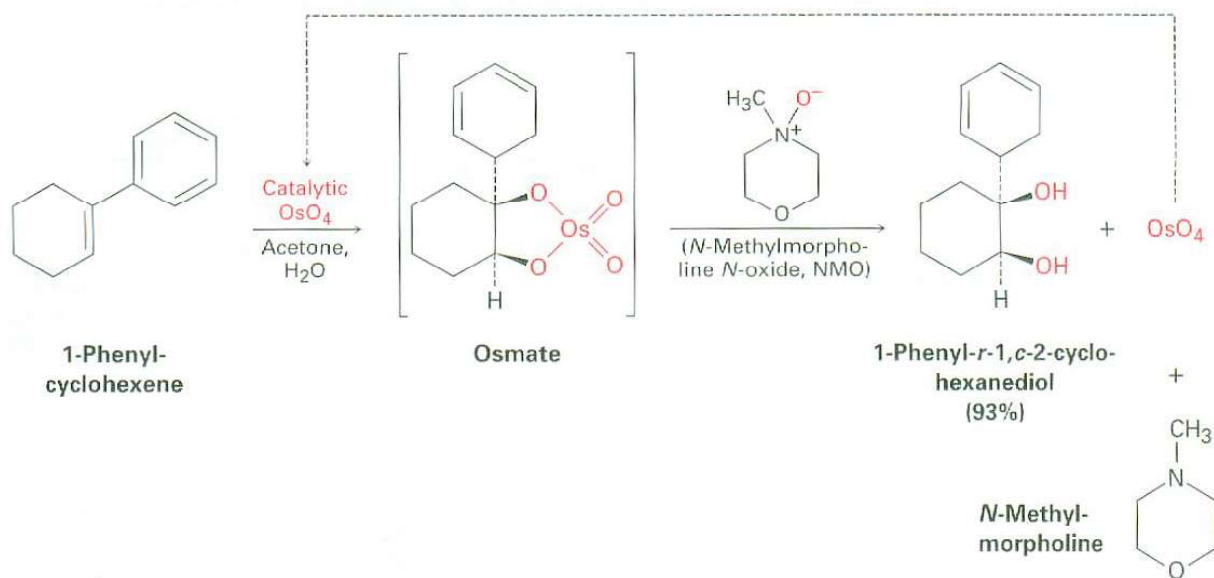
1,2-Epoxycyclo-hexane → **trans-1,2-Cyclo-hexanediol (86%)** + H_3O^+

Recall the following:

Cyclohexene → **trans-1,2-Dibromo-cyclohexane**

Hydroxylation can be carried out directly without going through the intermediate epoxide by treating an alkene with osmium tetroxide, 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 OsO_4 to the alkene. This cyclic osmate is then cleaved using aqueous sodium bisulfite, $NaHSO_3$.

1,2-Dimethylcyclopentene → **A cyclic osmate intermediate** → **cis-1,2-Dimethyl-1,2-cyclo-pentanediol (87%)**
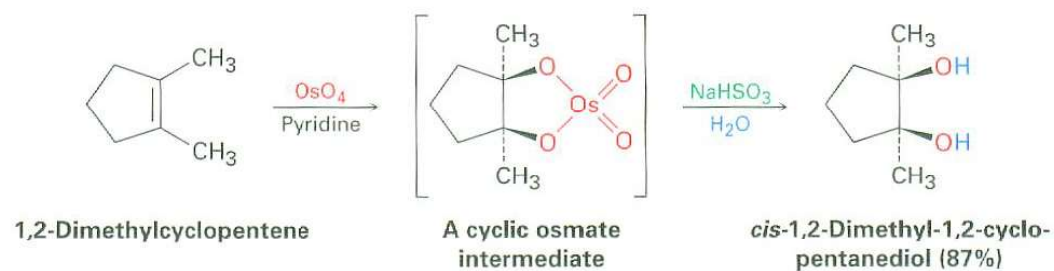
Unfortunately, a serious problem with the osmium tetroxide reaction is that OsO_4 is both very expensive and *very* toxic. As a result, the reaction is usually carried out using only a small, catalytic amount of OsO_4 in the presence of a stoichiometric amount of a safe and inexpensive co-oxidant such as N-methylmorpholine N-oxide, abbreviated NMO. The initially formed osmate intermediate reacts rapidly with NMO to yield the product diol plus

N-methylmorpholine and reoxidized OsO_4. The OsO_4 then reacts with more alkene in a catalytic cycle.

1-Phenyl-cyclohexene   **Osmate**   (N-Methylmorpholine N-oxide, NMO)   **1-Phenyl-r-1,c-2-cyclo-hexanediol** (93%)   + OsO_4

+

N-Methyl-morpholine

Note that a *cis-* or *trans-* prefix would be ambiguous when naming the diol derived from 1-phenylcyclohexene because the ring has three substituents. In such a case, the substituent with the lowest number is taken as the reference substituent, denoted *r*, and the other substituents are identified as being cis *(c)* or trans *(t)* to that reference. When two substituents share the same lowest number, the one with the highest priority by the Cahn–Ingold–Prelog sequence rules (Section 6.5) is taken as the reference. In the case of 1-phenyl-1,2-cyclohexane-diol, the −OH group at C1 is the reference *(r-1)*, and the −OH at C2 is either cis *(c-2)* or trans *(t-2)* to that reference. Thus, the diol resulting from cis hydroxylation is named 1-phenyl-*r*-1,*c*-2-cyclohexanediol, and its isomer resulting from trans hydroxylation would be named 1-phenyl-*r*-1,*t*-2-cyclohexanediol.

Problem 7.14 | What product would you expect from reaction of *cis*-2-butene with *meta*-chloro-peroxybenzoic acid? Show the stereochemistry.

Problem 7.15 | How would you prepare each of the following compounds starting with an alkene?

(a)   (b) $CH_3CH_2CHCCH_3$ (c) $HOCH_2CHCHCH_2OH$
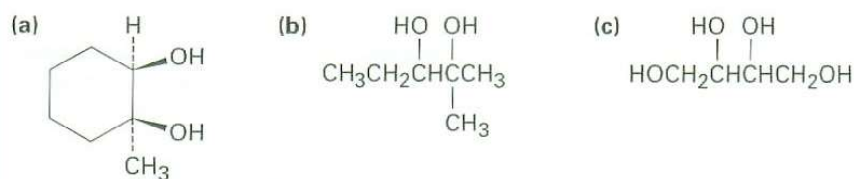
7.9 | Oxidation of Alkenes: Cleavage to Carbonyl Compounds

In all the alkene addition reactions we've seen thus far, the carbon–carbon double bond has been converted into a single bond but the carbon skeleton has been left intact. There are, however, powerful oxidizing reagents that will cleave C=C bonds and produce two carbonyl-containing fragments.