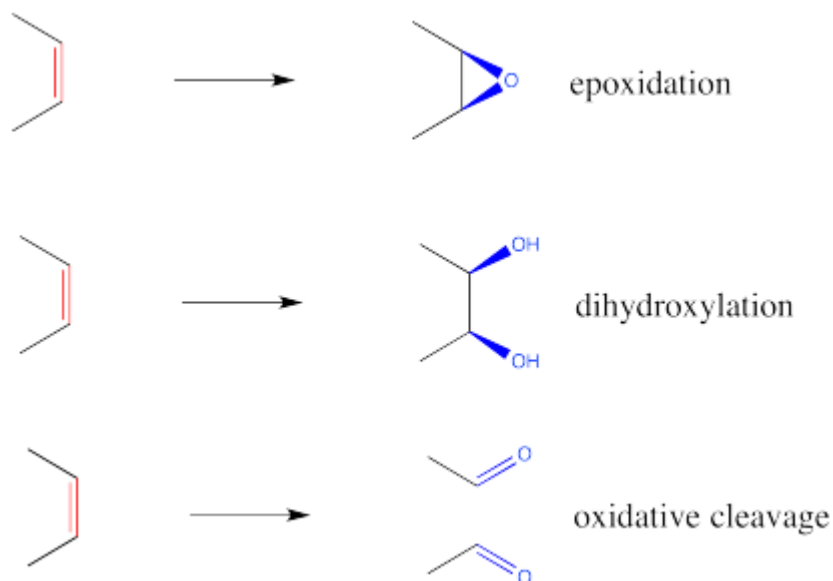


# ALKENE OXIDATIONS

There are a number of other additions to alkenes that occur via concerted mechanisms. Alkene oxidations are among the most synthetically useful of these reactions because they are able to convert simple hydrocarbon starting materials into oxygen-containing compounds. The resulting heteroatomic functional groups may open up new avenues of synthetic utility or they may reflect aspects of a target natural product.

The three most common alkene oxidations are epoxidation, dihydroxylation and oxidative cleavage.

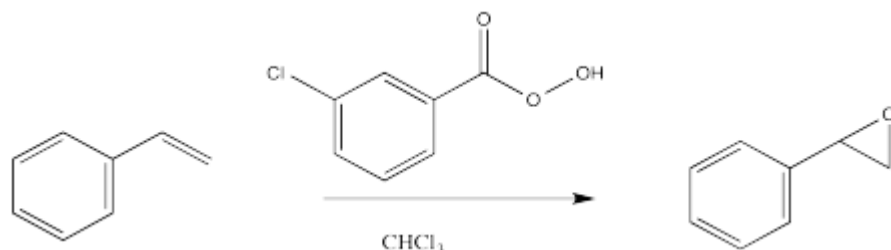


## *Epoxidation*

Epoxidation is a method for converting an alkene into an epoxide. The reagent required is always a peroxy species. A peroxy species looks very much like a normal oxygen-containing compound, but with an extra oxygen in it. Historically, the most common such reagent was *m*-chloroperbenzoic acid (*m*CPBA).

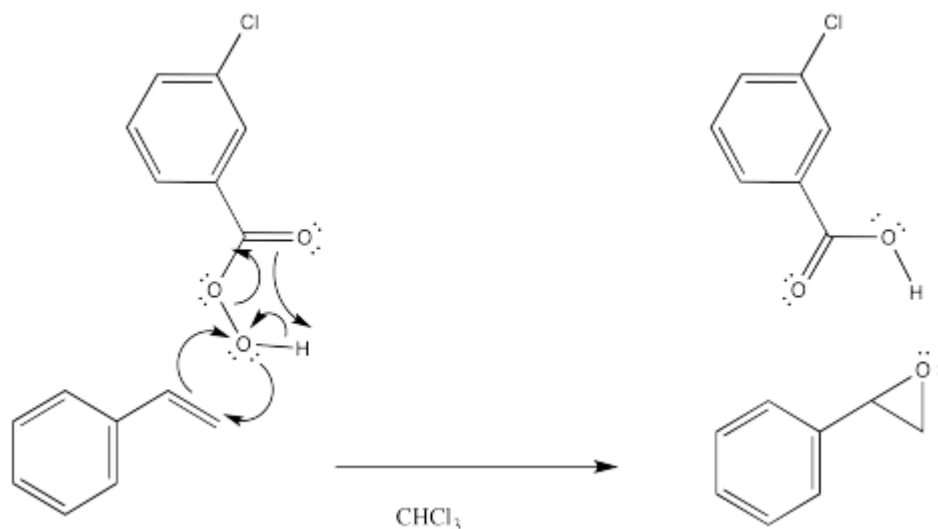
However, other reagents can also be used, such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or potassium hydrogen persulfate ( $\text{KHSO}_5$ ), marketed under the trade name Oxone. The latter methods are considered "greener" or more environmentally friendly, because the side products (water or sulfate, respectively) are pretty innocuous. These methods are generally slower and are often used with a catalyst. Catalysts used with hydrogen peroxide include Lewis acidic species

such as sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) needed to activate the peroxide. A similar reaction using titanium (IV) and chiral ligands leads to an enantiomerically pure epoxide; this reaction is called "[Sharpless](#) epoxidation". With oxone, ketones are used as oxygen transfer catalysts in a method referred to as "[Shi](#) oxidation".



The electrophilicity of peroxy compounds continues a theme seen in halogens such as chlorine and bromine. When two oxygen atoms are connected to each other, one of them can act as an electrophile, just as when two halogens are connected together.

During the epoxidation, the peroxy compound simply delivers its extra oxygen to the double bond. The oxygen atom both accepts a pair of electrons from the double bond and donates an electron pair to the double bond at the same time.



The reaction has something in common with [pericyclic reactions](#). In pericyclic reactions and other reactions that take place under control of orbital symmetry, it is common to see six electrons circulating in a ring as a central feature of the mechanism. This picture is reminiscent of the aromatic structure of benzene. In fact, that aromatic stabilization is thought to play a

role in stabilizing the transition states of various reactions. In this case, the three electron pairs involve delivery of the oxygen, proton transfer and  $\pi$  donation to the carbonyl in mCPBA. However, a similar set of arrows might not be found in the reaction of hydrogen peroxide.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/eladdn/EAoxidation.htm>