Some oxidation reactions of alkenes give cyclic ethers in which both carbons of a double bond become bonded to the same oxygen atom. These products are called epoxides or oxiranes. An important method for preparing epoxides is by reaction with peracids, RCO$_3$H. The oxygen-oxygen bond of such peroxide derivatives is not only weak (ca. 35 kcal/mole), but in this case is polarized so that the acyloxy group is negative and the hydroxyl group is positive (recall that the acidity of water is about ten powers of ten weaker than that of a carboxylic acid). If we assume electrophilic character for the OH moiety, the following equation may be written.

It is unlikely that a dipolar intermediate, as shown above, is actually formed. The epoxidation reaction is believed to occur in a single step with a transition state incorporating all of the bonding events shown in the equation. Consequently, epoxidations by peracids always have syn-stereoselectivity, and seldom give structural rearrangement. You may see the transition state by clicking the Change Equation button. Presumably the electron shifts indicated by the blue arrows induce a charge separation that is immediately neutralized by the green arrow electron shifts.

The previous few reactions have been classified as reductions or oxidations, depending on the change in oxidation state of the functional carbons. It is important to remember that whenever an atom or group is reduced, some other atom or group is oxidized, and a balanced equation must balance the electron gain in the reduced species with the electron loss in the oxidized moiety, as well as numbers and kinds of atoms. Starting from an alkene (drawn in the box), the following diagram shows a hydrogenation reaction on the left (the catalyst is not shown) and an epoxidation reaction on the right. Examine these reactions, and for each identify which atoms are reduced and which are oxidized.

Epoxides may be cleaved by aqueous acid to give glycols that are often diastereomeric with those prepared by the syn-hydroxylation reaction described above. Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by nucleophiles such as water in the same way that the cyclic bromonium ion described above undergoes reaction. The result is anti-hydroxylation of the double bond, in contrast to the syn-stereoselectivity of the earlier method. In the following equation this procedure is illustrated for a cis-disubstituted epoxide, which, of course, could be prepared from the corresponding cis-alkene. This hydration of an epoxide does not change the oxidation state of any atoms or groups.
Contributors