# 5.4: Oxidation of Alkenes

There are a variety of reagents that can result in the oxidation (i.e. the addition of oxygen to both carbons) of an alkene.[3] These reactions are synthetically useful because they enable us to place functional groups on adjacent carbons and these groups can subsequently be modified. The reagents used in these transformation reactions are highly reactive, and most include species in a high oxidation states, such as permanganate (MnO_4^-) and or Osmium tetroxide (OsO_4), or contain unstable oxygen-oxygen bonds (e.g. Ozone O_3) or a peroxy-acid (see below). The common factor in these reagents is that they are able to add oxygen in various ways to the $C = C$ bond. Many of resulting reactions are quite complex, and we will not delve into their mechanistic details except where necessary: for example, to explain why a particular stereochemistry is produced.
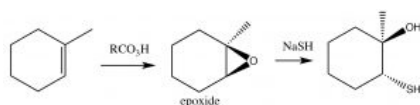
Epoxidation:
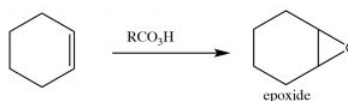
Epoxides (also known as oxiranes) ($\rightarrow$) are three-membered ring ethers, and can be formed by the reaction of an alkene with a per-acid, that is, a carboxylic acid with an extra oxygen ($\leftarrow$). The reaction occurs via a concerted (coordinated) movement of electrons. The result is that both of the carbons in the original double bond end up linked to the same O atom.
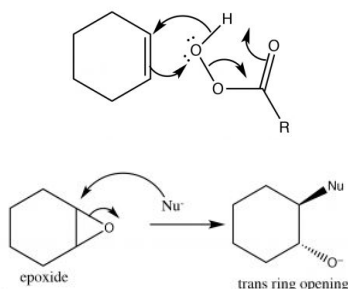

Recall that earlier we looked at relative stabilities of rings, and found that their stability depends on the ring size and the torsional (eclipsing) strain. A three membered carbon ring is highly strained because the bond angles are distorted away from the $109°$ angle that sp^3 hybridization calls for; moreover, all of the bonds are eclipsed. The result is that epoxides are susceptible to nucleophilic attack at a ring carbon ($\rightarrow$). An S_N2 reaction that proceeds via attack from the back side of the ring, leading to the production of the *trans product*. Such ring opening reactions can be accomplished by a range of nucleophiles, including water. The reaction with water results in a trans diol. In general, *under* S_N2 *conditions* the ring opening is also stereospecific—that is the nucleophile will attack the least hindered carbon ($\downarrow$).

Epoxides tend to be reactive and for this reason can be useful as synthetic intermediates. Within biological systems, their reactivity can lead to chemical modification of DNA, leading to mutations (for that reason, many are known as genoxic or toxic to the genome). As a defense against such epoxides, organisms encode enzymes known as epoxide hydrolyzes.[4]
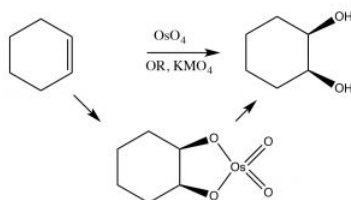
Cis-diols:

Alkenes can be oxidized to produce cis-diols using a different type of reagent that adds atoms across the double bond via a cyclic intermediate. For example permanganate (MnO_4^-) and osmium tetroxide (OsO_4), both of which contain transition metals in high-

oxidation states, can accomplish this transformation ($\rightarrow$). It is worth noting that by controlling the reaction conditions, we can choose to produce either cis or trans diols. As we move into more complex organic chemistry we will see that the ability to choose and predict outcomes is a major component of organic chemistry.

Ozonlysis:

Another type of alkene double-bond oxidation involves a reaction with ozone (O_3), the highly reactive allotrope of oxygen.[5] The mechanism is quite complex as shown below (no need to memorize it!).

Molozonide

reductive workup Zn/H⁺

oxidative workup H₂O₂

Ozonide
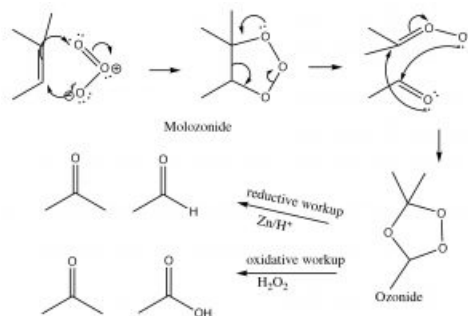
Typically, ozone cleaves the double bond and the reaction is treated with a mild reducing agent such as tin (Sn)[6], leading to the production of the corresponding aldehydes or ketones ($\downarrow$).

the alkene is cleaved at the double bond
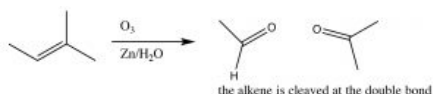
As we will see later, the ozonolysis reaction can be useful in identifying the position of a double bond within a molecule, as well as in the synthesis of aldehydes and ketones.

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