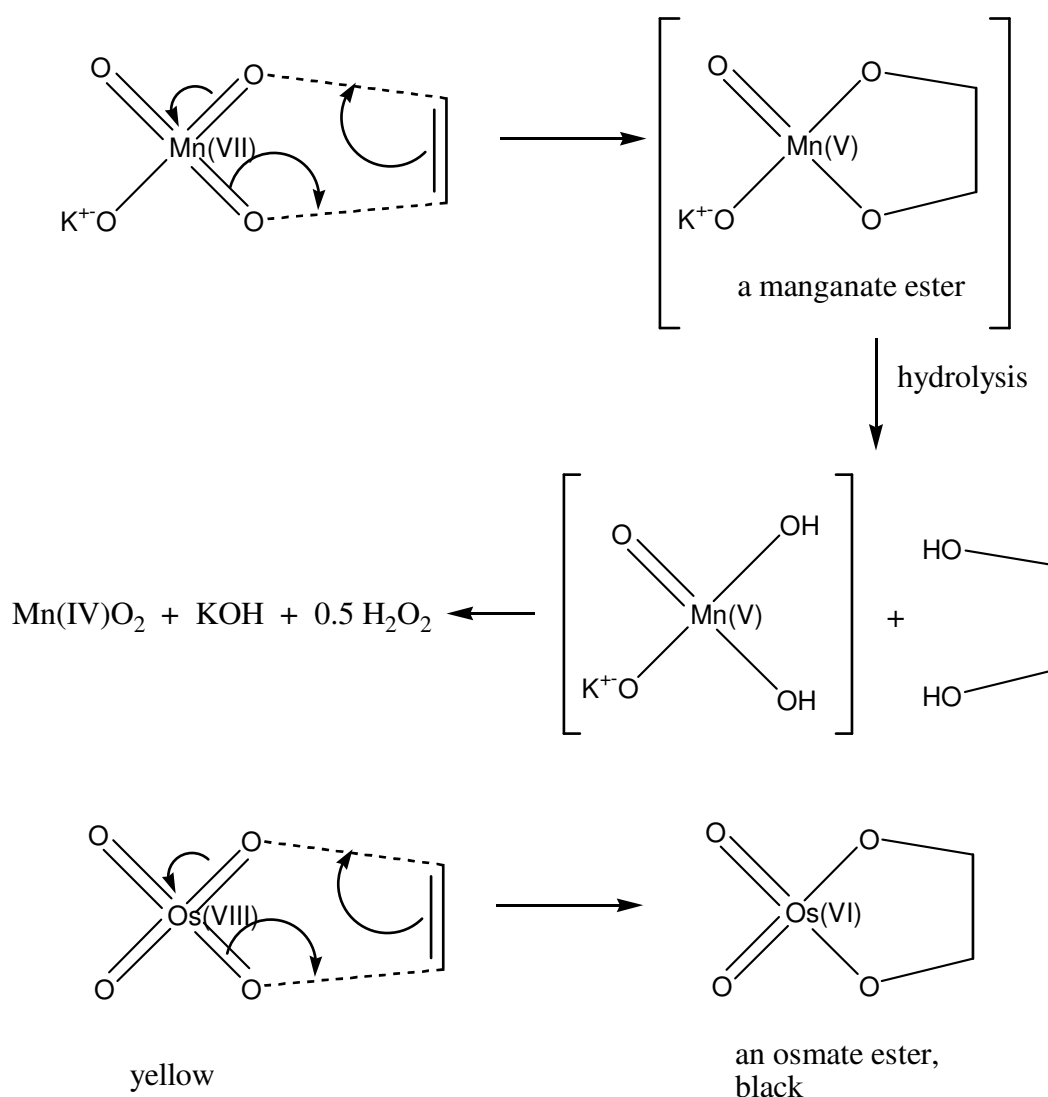


LECTURE 7

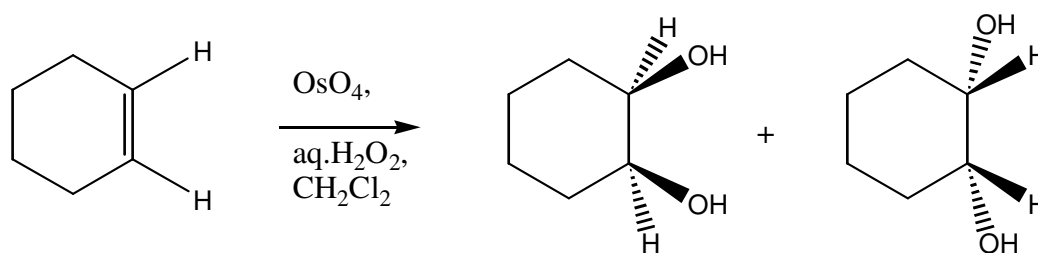
(a) Dihydroxylation ($X = Y = \text{OH}$)

Although dihydroxylation is formally the addition of hydrogen peroxide, in practice the addition of H_2O_2 to alkenes is almost impossible. Two reagents which work especially well for this overall addition are cold, neutral potassium permanganate, KMnO_4 , and osmium tetroxide, OsO_4 . They complement one another in that the first is used in aqueous solution whereas the latter is used in organic solvents. The mechanisms are very similar.

Thus both proceed through a pericyclic mechanism:

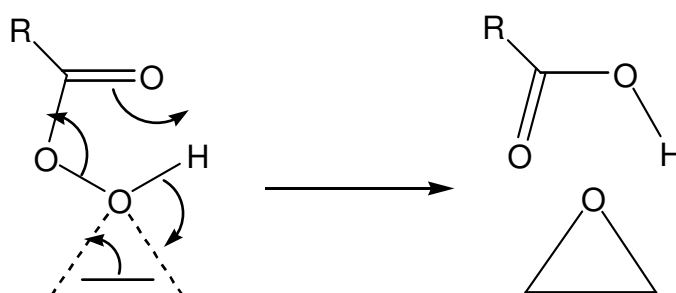


Because osmium tetroxide is expensive and very toxic it is rarely used in stoichiometric amounts. Rather a co-oxidant is added to oxidise the stable osmate ester back to OsO_4 . Since we want to hydrolyse the osmate ester as well, the co-oxidant is often aqueous hydrogen peroxide so the oxidation is two-phase. The alkene and the OsO_4 remain in the organic phase, the H_2O_2 is in the aqueous phase and the osmate ester is at the interface between the two phases:

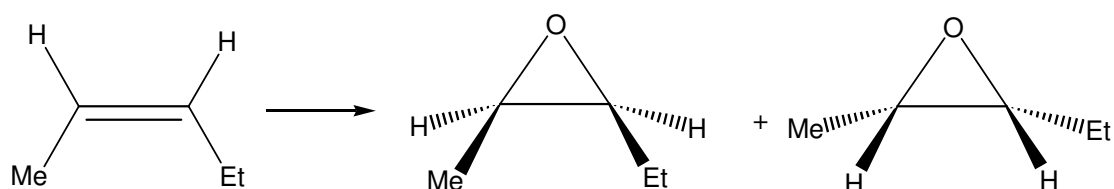


(c) Epoxidation ($X = Y = \text{O}$)

The reaction of alkenes with peroxy acids (RCO_3H) leads to a cyclic ether, known as an epoxide, as follows:

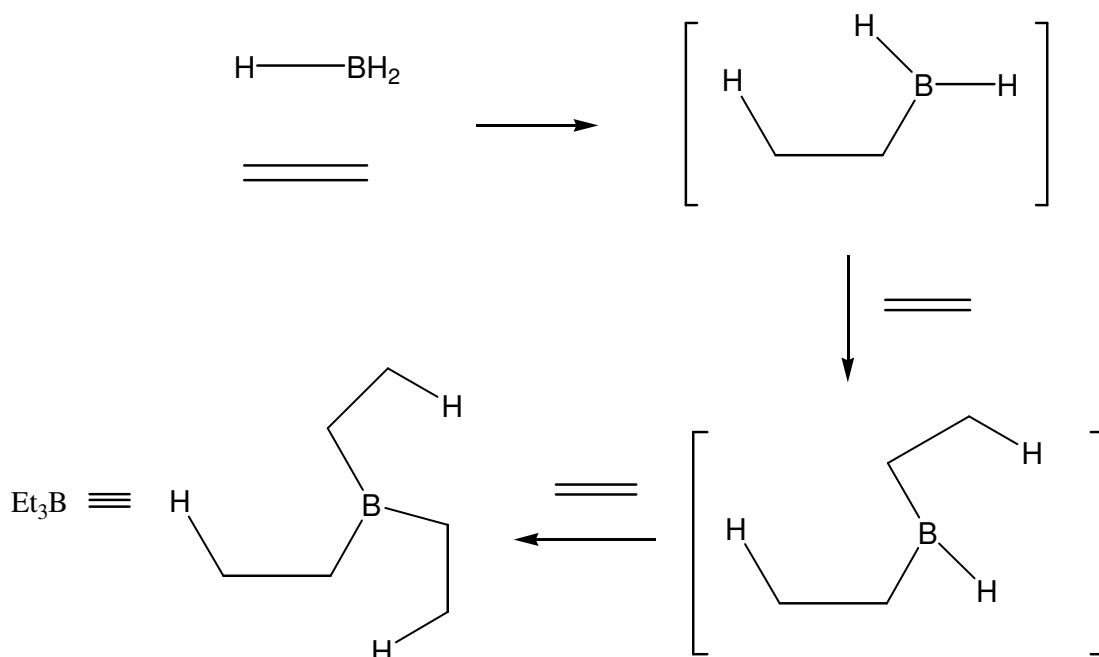
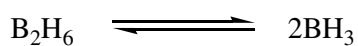


Although the reaction will work with peroxyacetic acid ($\text{R} = \text{Me}$) it works best with peroxy acids bearing electron-withdrawing groups e.g. $\text{R} = \text{CF}_3$, C_6H_5 , $3\text{-ClC}_6\text{H}_4$, $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$. Again the reaction is stereospecific, e.g. a cis-alkene giving a cis-epoxide:

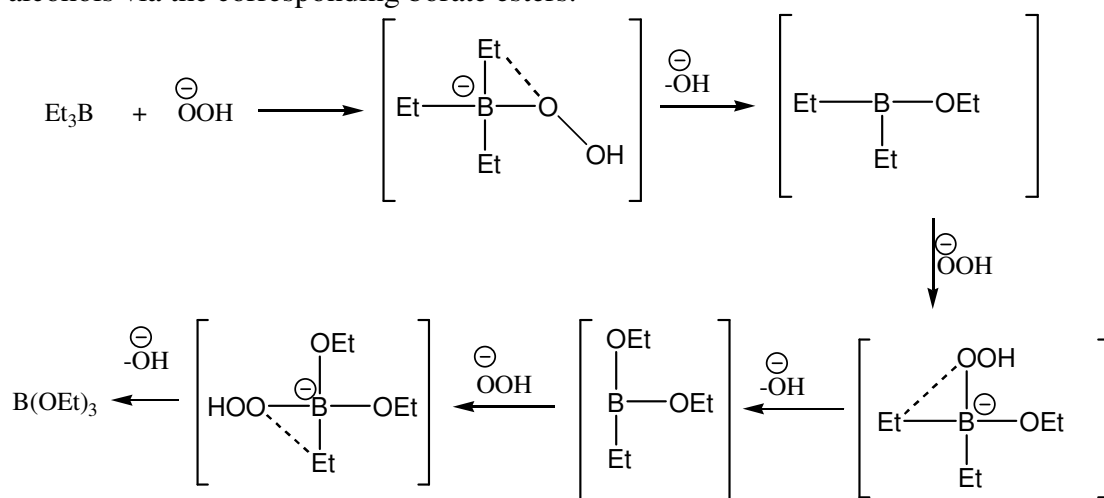


(d) Hydroboration ($X = \text{H}$, $Y = \text{BR}_2$)

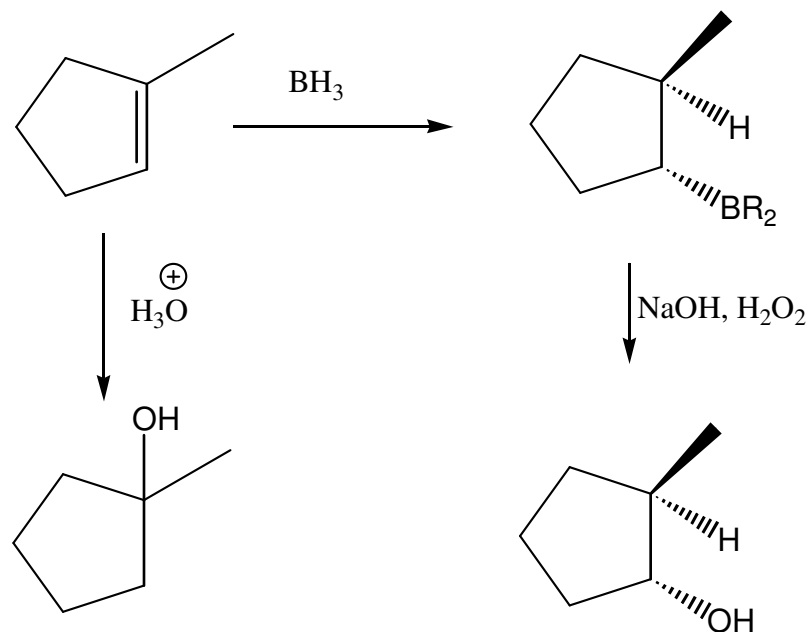
Diborane (B_2H_6) reacts rapidly with alkenes through the intermediacy of borane (BH_3). Each of the three hydrogens of borane are added to the alkene to give a trialkylborane:



The importance of the air-sensitive boranes to organic chemists is that they can easily be converted by alkaline hydrogen peroxide into alcohols via the corresponding borate esters:



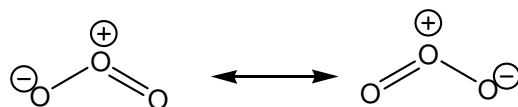
The advantage of making alcohols by this method from alkenes rather than simple electrophilic addition of water (hydration) is that, for steric reasons, the boron always adds to the least hindered carbon of the double bond and hence the alcohol is the product of anti-Markovnikov addition:



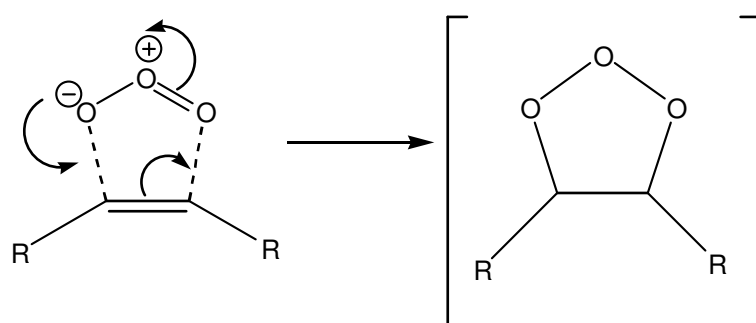
Note the syn-stereospecificity of the borane addition and also that the oxidation to the alcohol proceeds with retention of configuration i.e. the H and the OH groups are also cis.

(e) Ozonolysis (formally $X = Y = O$)

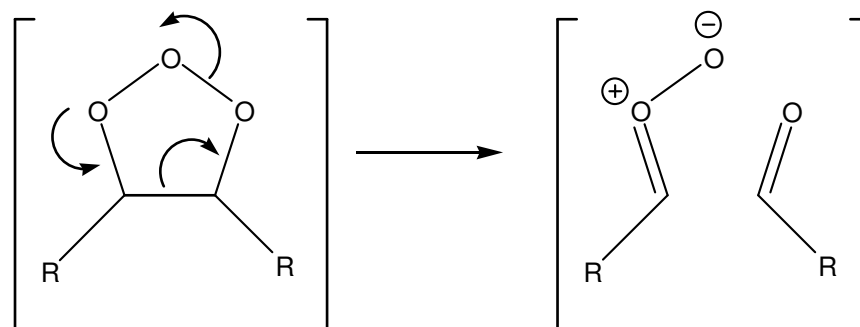
Ozone, O_3 , has the structure:



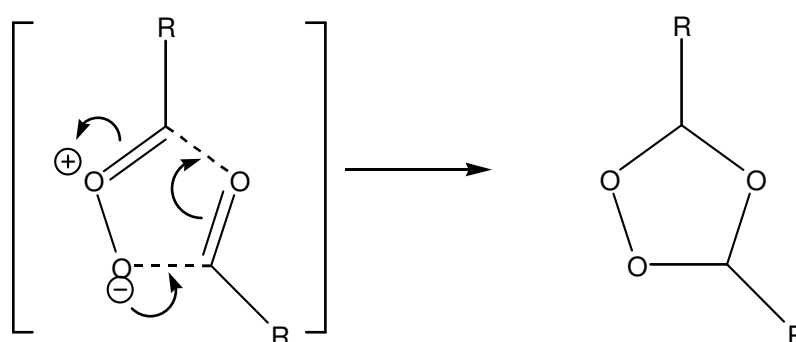
It is a resonance hybrid of the two canonical forms shown. It reacts with alkenes in a pericyclic manner:



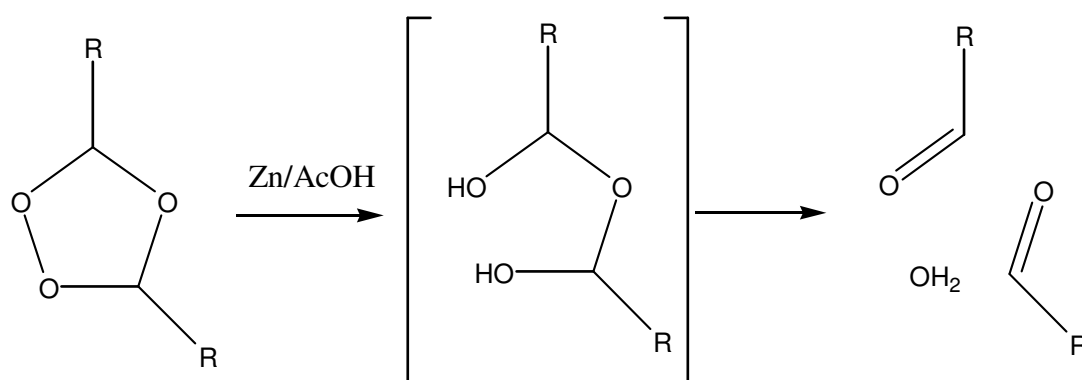
The resultant product is called a primary ozonide or molozonide. Unlike the other reactions which we have seen in this section, this reaction does not stop at this stage because the molozonide is extremely unstable, decomposing as follows:



i.e. into a carbonyl compound and another species known as a carbonyl oxide. The carbonyl oxide is electronically very similar to ozone (it is said to be isoelectronic) and after rotating in space it adds back onto the carbonyl compound:



The resultant product of this second pericyclic reaction is called a secondary ozonide and most of these are sufficiently stable to isolate. However, some are dangerously explosive and so they are generally not isolated but rather reduced by zinc and acetic acid added to the ozonolysis reaction mixture at the end:



Thus the final products (aldehydes or ketones) result from the complete cleavage of the double bond. The reaction is generally high-yielding and used to be used a lot for structure determination before modern spectroscopic techniques were introduced e.g.:

