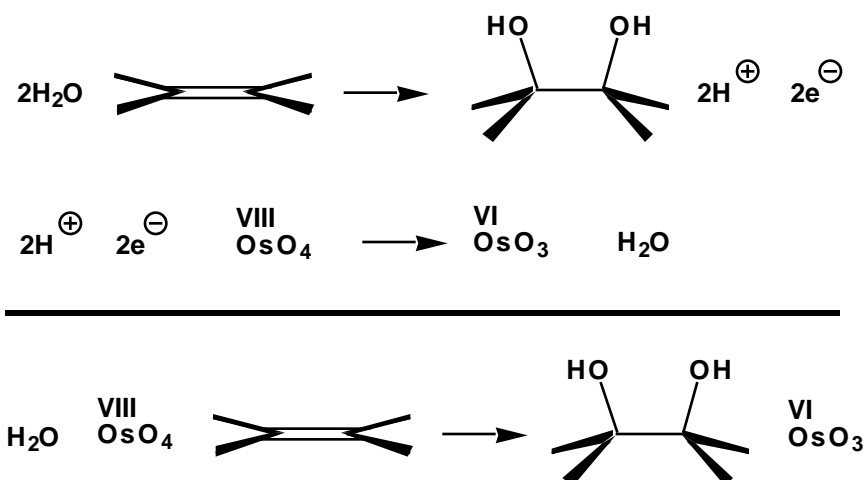
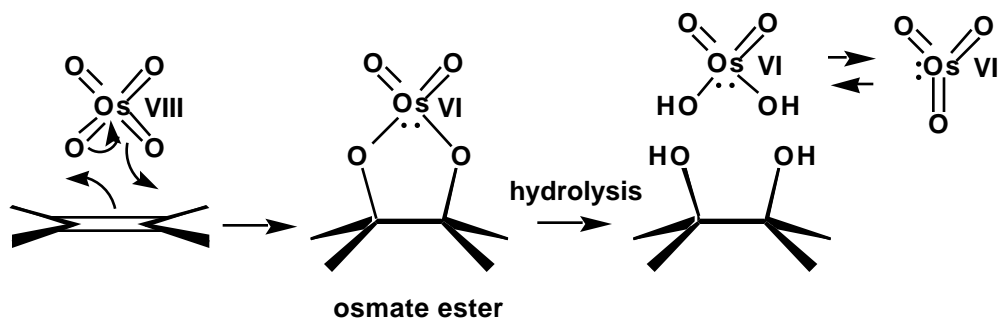


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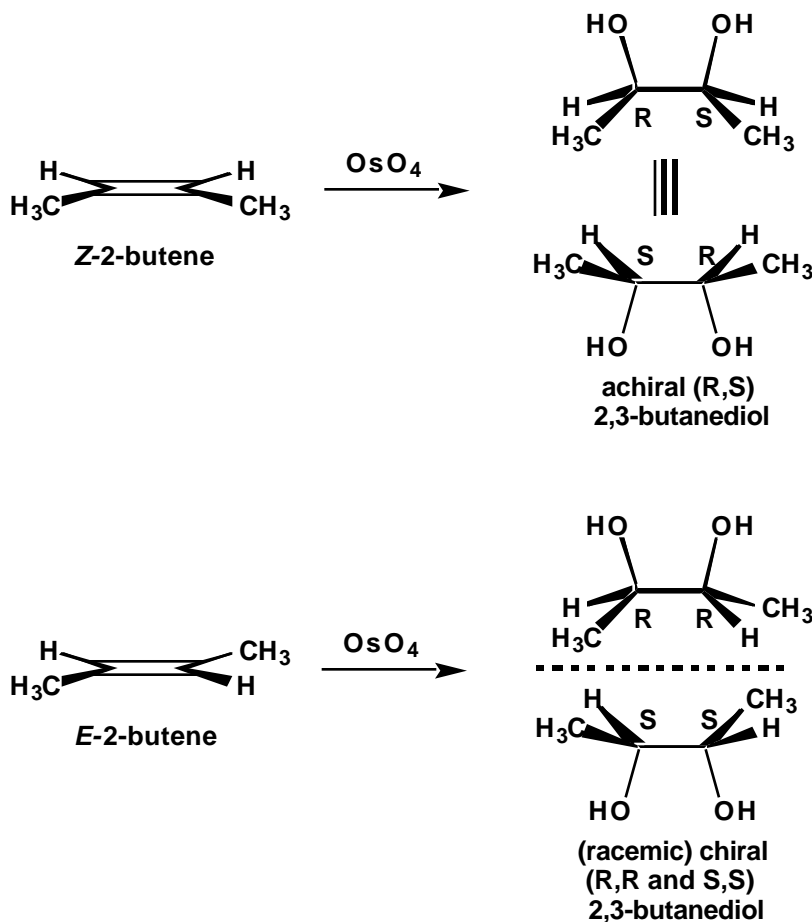
Here we introduce another example of oxidation, one with a stereospecific outcome. An alkene can be oxidized to a 1,2-diol (also called a *vicinal* — neighboring — diol). A reagent that generally will accomplish this change with great dependability, although it is both expensive and very toxic, is osmium tetroxide. (Dilute, neutral potassium permanganate is far more economical, but also may be less reliable for the purpose, as we shall discuss briefly below.) The balanced half-reactions and their sum are as follows:



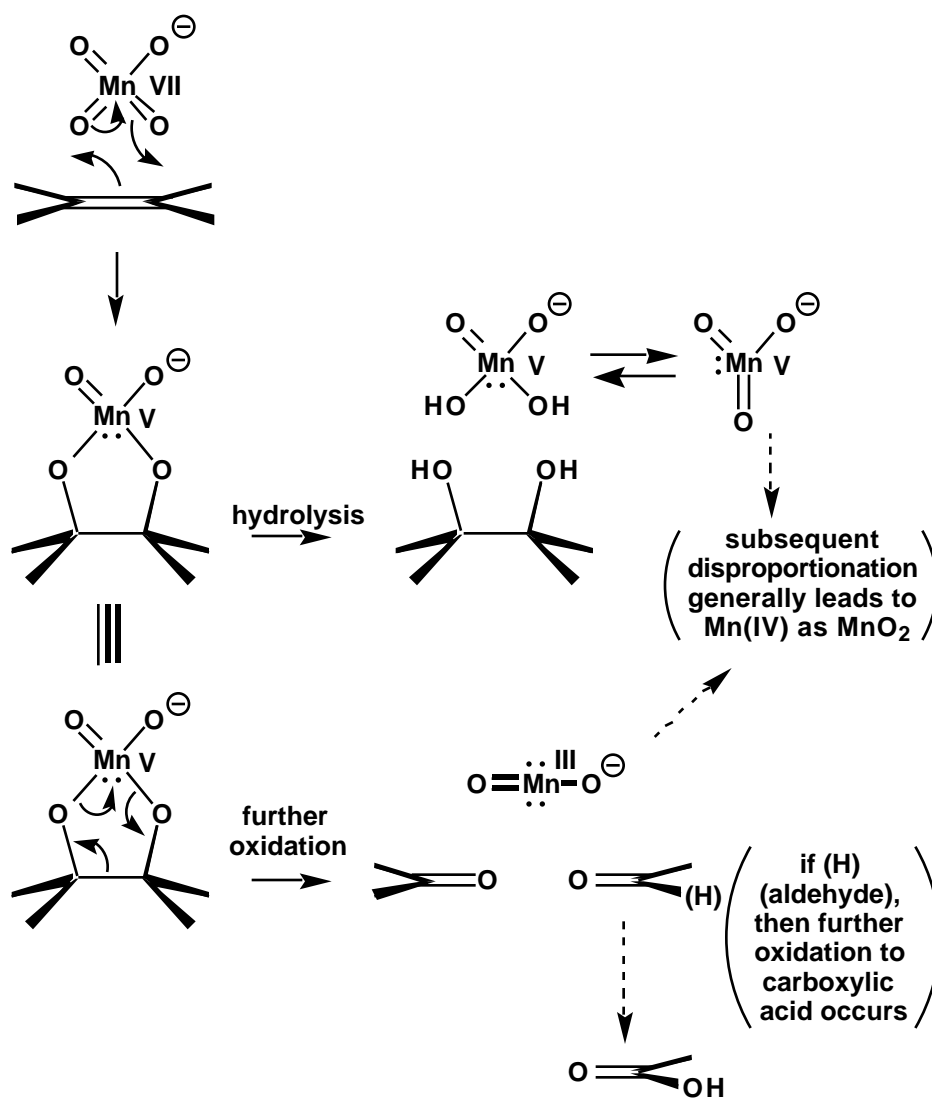
Because the transformation takes place through the intermediacy of a constraining 5-membered cyclic osmate ester, ultimate *cis* placement of the hydroxyl groups relative to the plane of the starting double bond is assured:



The observed stereochemical course of the osmium tetroxide reaction for the cases of *Z*- and *E*-2-butene is in full agreement with this mechanism. Thus, from *Z*-2-butene only an achiral (R,S) osmate ester, and hence only achiral (R,S) 2,3-butanediol are obtained, regardless of which face of the olefin is attacked by the osmium reagent. On the other hand, when one starts with *E*-2-butene, enantiomeric (R,R and S,S) chiral osmate esters result, depending on which face is attacked. There is no factor that favors reaction on one face or on the other. Occurring in equal measure, the two approaches of the reagent yield a racemic mixture of osmate esters and hence, after hydrolysis, both enantiomers of the chiral form of (so, racemic — R,R and S,S) 2,3-butanediol:



If dilute, neutral potassium permanganate is used as the oxidant, then the same results can be obtained, and via a corresponding intermediate. However, as is sketched in the figure, over-oxidation can occur, yielding carbonyl compounds: ketones and aldehydes, with the latter certain to suffer further oxidation to carboxylic acids. Of course, such more vigorous oxidative outcomes can be deemed useful, rather than unwanted — clearly, this depends on where it is one may be headed in the first place! — and we shall find need to return to them.



permanganate oxidation of alkenes

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