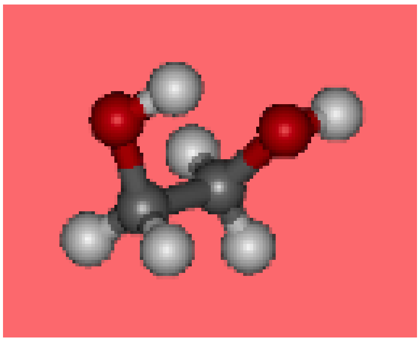
11

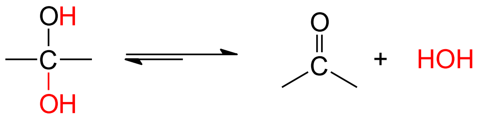


Difunctional Compounds II: Diols

In this topic, molecules with two alcohols that can be synthesized by a method other than those discussed in topic 10 or that have a different reactivity from that discussed in the same topic are studied. Molecules of this type are 1,1-diols; 1,2-diols, 1,4-diols, and 1,5-diols.

1. 1,1-DIOLS. CARBONYL HYDRATES

The hydration products of carbonyls (gem-diol, hydrate, or 1,1-diol) are not stable (except for formaldehyde and aldehydes with electron attractor groups). These compounds are transformed into water and a carbonyl:



These compounds are discussed in more detail in Topic 17.

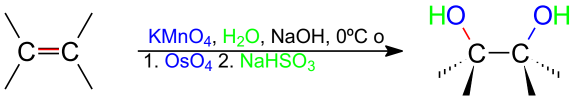
2. 1,2-DIOLS

2.1. SYNTHESIS

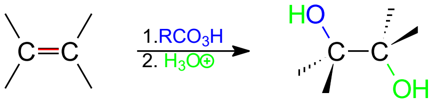
Neighborhood alcohols (*vic-diols*, glycols, or 1,2-diols) are normally synthesized by oxidation of alkenes. It can also be done by a reducing coupling of aldehydes and ketones.

2.1.1. Dihydroxylation of alkenes

The dihydroxylation of alkenes was explained in detail in item 7, section 4.8.1. The following only lists the various methods of accomplishing this transformation. If oxidation is carried out with KMnO4 or OsO4, diol is formed by addition *without*:

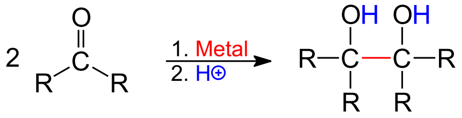


If oxidation is carried out with a peroxyacid, followed by a hydrolysis of the epoxide, diol is formed by an *anti*:



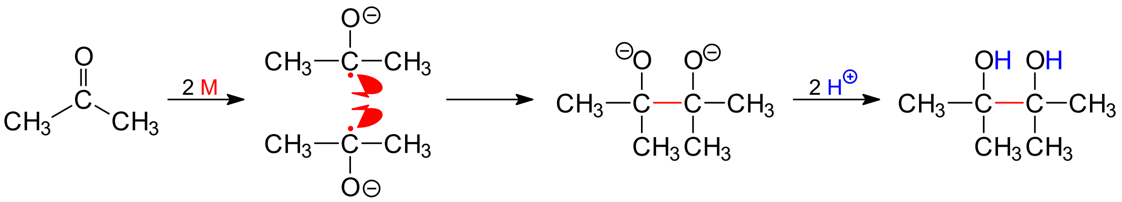
2.1.2. Bimolecular reduction of aldehydes and ketones

1,2-diols can be synthesized by reducing aldehydes and ketones with active metals, such as sodium, magnesium, aluminum, or titanium:



Metal = Na, Mg , Na-Hg, Mg/MgI$_2$, TiCl4/mg.

The mechanism of the reaction begins with the reduction of the carbonyl to form a cetyl anion-radical, which undergoes coupling to form a carbon–carbon bond:

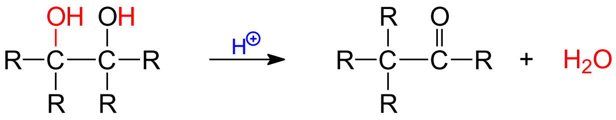


2.2. REACTIVITY

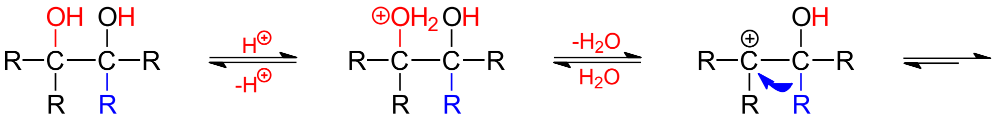
Diols have a similar reactivity to alcohols, in that they react with bases forming alkoxide ions and with strong electrophiles on oxygen, giving the corresponding product depending on the electrophile. Depending on the relative position of the two hydroxyl groups, some different unimolecular transformation than expected for the monohydroxyl compound may take place.

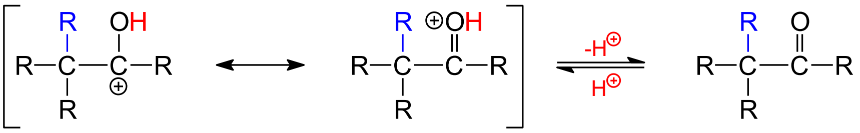
2.2.1. Pinacholic transposition

When 1,2-diols are treated with an acid, they are transformed into aldehydes or ketones by a transposition, known as *the pinacolic transposition*:



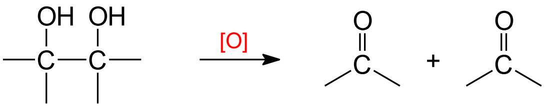
The mechanism begins with the hydronation and dehydration of the alcohol that forms the most stable carbocation, followed by a transposition to form a carbocation stabilized by the hydroxyl, which by dehydronation forms a carbonyl:





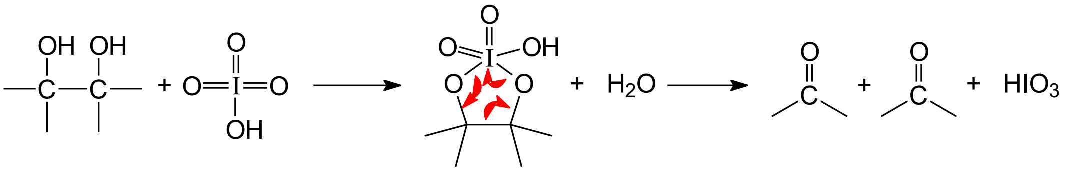
2.2.2. Oxidation

The 1,2-diols are oxidized, with the carbon–carbon bond breaking, giving aldehydes or ketones by treatment with HIO4 or Pb(OAc)4:



[O] = HIO4, Pb(OAc)4.

Below is the proposed mechanism for HIO4. The mechanism with Pb(OAc)4 is similar.

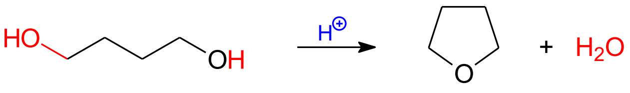


3. 1,4 AND 1,5-DIOLS

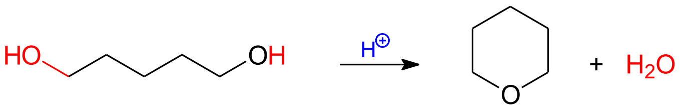
The 1,4 and 1,5-diols have the two hydroxyl groups at the right distance to make intramolecular substitutions to form cyclic ethers.

3.1. DEHYDRATION

When 1,4- and 1,5-diols are treated with an acid, they form cyclic ethers, tetrahydrofuran and tetrahydropyran, respectively, by dehydration:



Tetrahidrofurano



Tetrahidropirano

The mechanism consists of a hydronation of one of the hydroxyls, followed by an intramolecular substitution, which by dehydronation of the dialkyloxonium ion forms an ether: