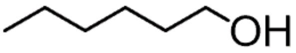
B.Sc Semester – IV MJC – 6(T) Organic Chemistry
Unit – I Alcohols, Phenols , Esters and Epoxides
Diols : Oxidation of diols and Pinacol-Pinacolone Rearrangement

Introduction and Nomenclature of Diols

In an earlier article, we discussed the nomenclature of alcohols and mentioned that the presence of a hydroxyl group is identified by **changing the parent suffix from "*e*" to "*ol*":**

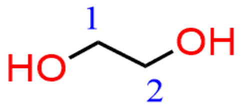
hexane



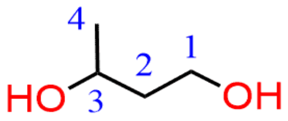
hexan**ol**

Now, compounds with two hydroxy groups are called **diols** in the IUPAC nomenclature. So, to name a diol, the suffix ***-diol*** is added to the name of the parent chain alkane, and the positions of these hydroxyl groups are indicated with numbers just like for any functional group we have seen before.
For example,

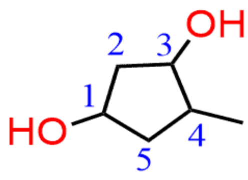
The IUPAC Nomenclature of Diols



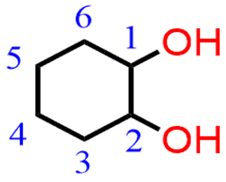
ethane-1,2-diol



butane-1,3-diol

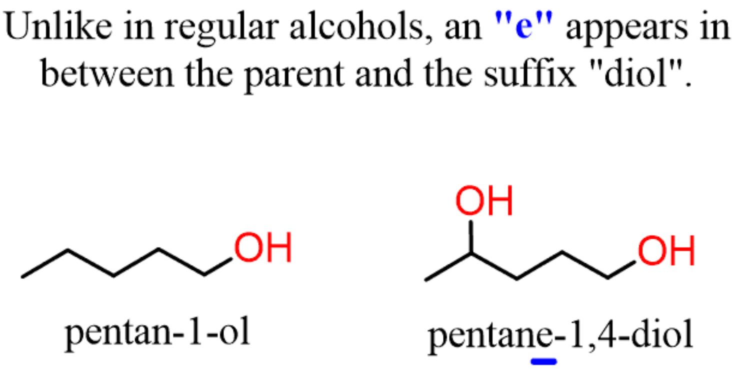


4-methylcyclopentane-1,3-diol



cyclohexane-1,2-diol

Notice that, unlike regular alcohols, an "e" appears in between the parent and the suffix "diol".



Simple diols are also commonly named as **glycols,** which is also accepted by the IUPAC system.

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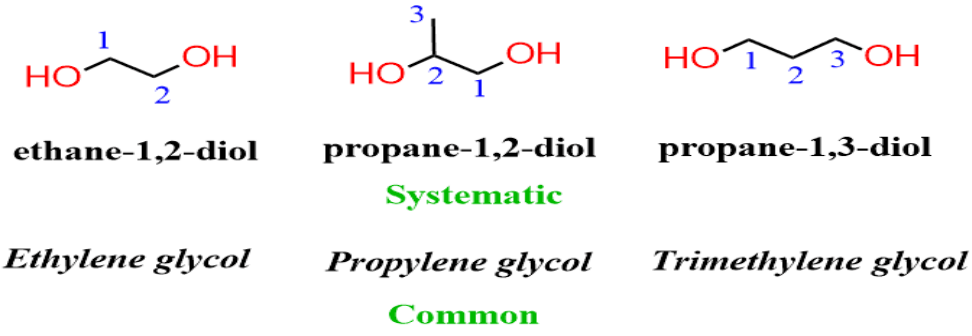
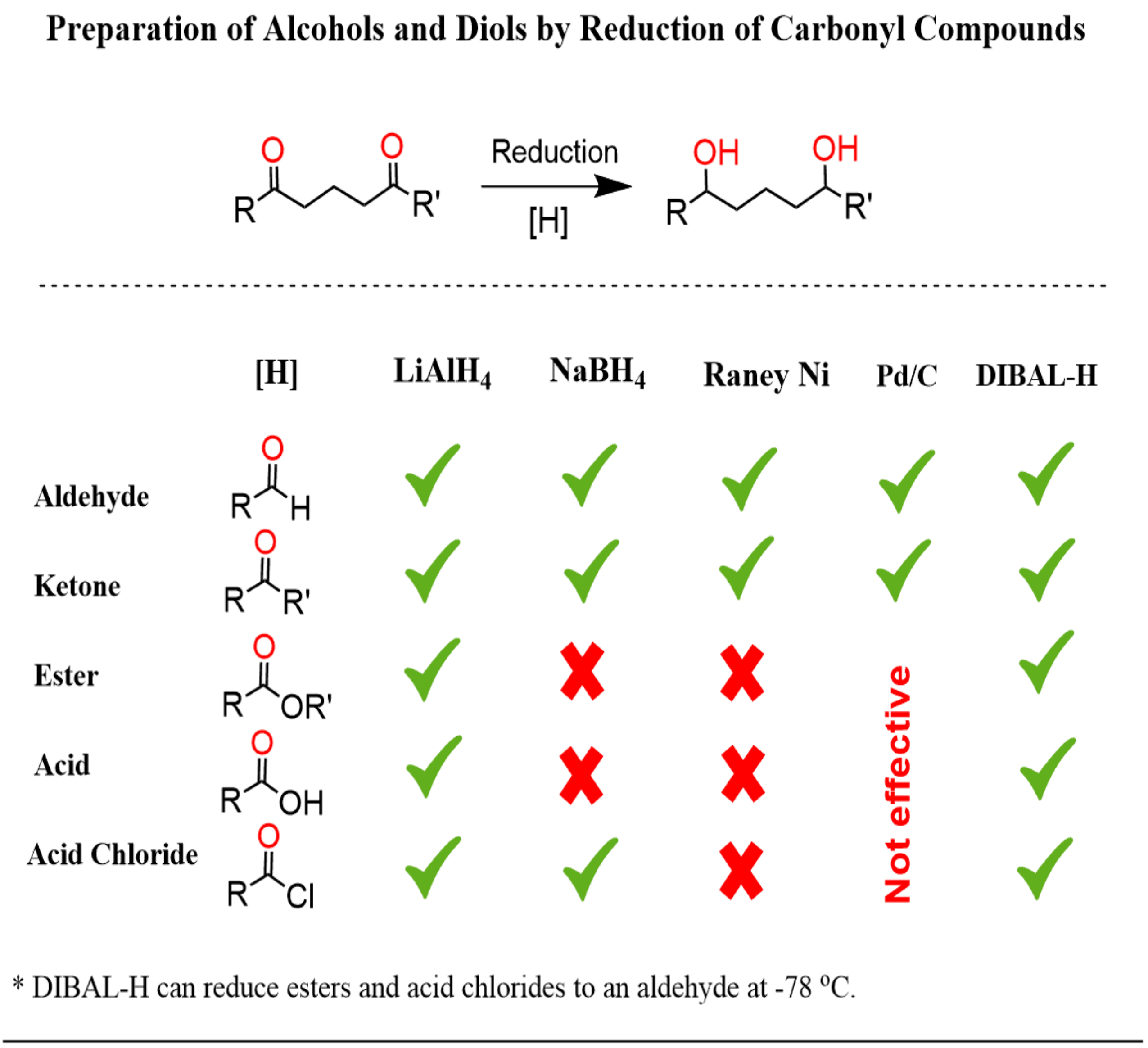


Having two hydroxyl groups brings some changes to the physical properties of diols due to the additional hydrogen bonding. For example, **diols** are used as **antifreeze** to cool down the internal combustion engines of automobiles. And in order to qualify for this application, they need to have a significantly lower freezing point and higher boiling point than water. The combination of **ethylene glycol** (f.p. = -12.9 °C) and **propylene glycol** (f.p. = -59 °C) is most commonly used in **antifreeze** solutions.

Preparation of Diols

Diols can be prepared from diketones by reducing the two carbonyl groups using a variety of reducing agents such as NaBH$_4$, LiAlH$_4$, H$_2$/Pd and etc., that we discussed before.

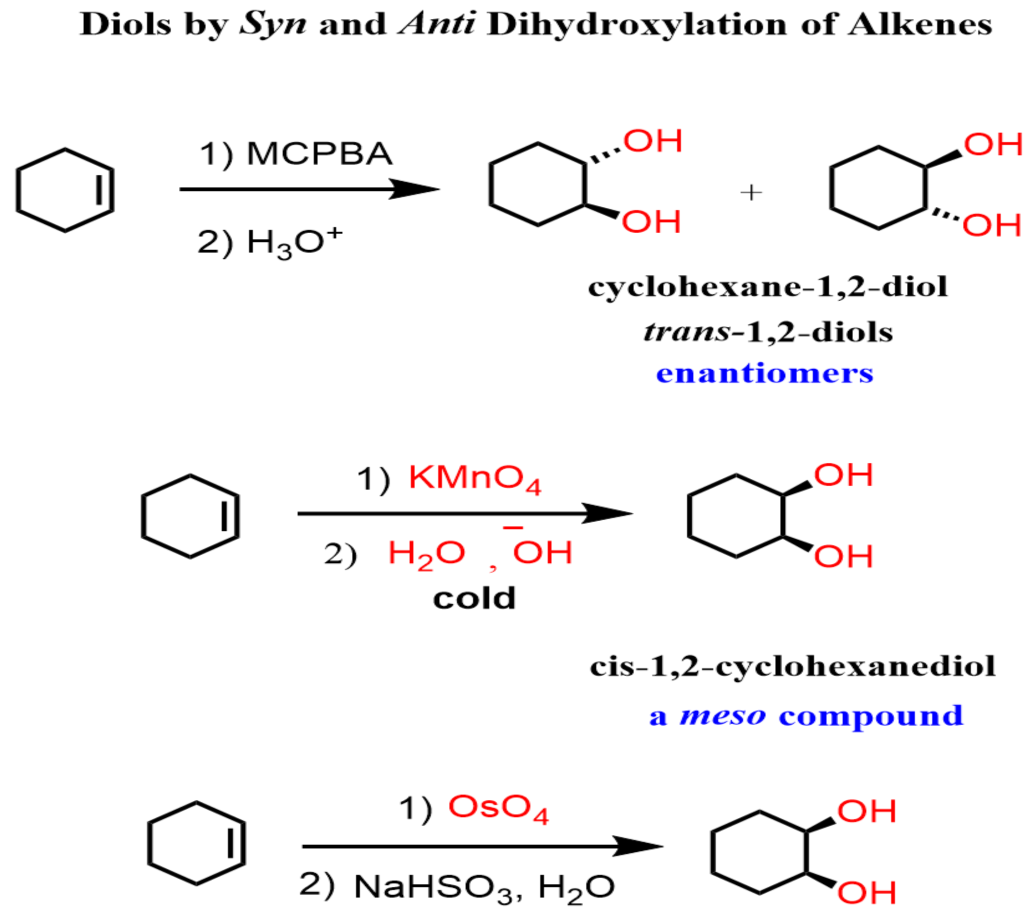


Preparation of Alcohols and Diols by Reduction of Carbonyl Compounds

	[H]	$LiAlH_4$	$NaBH_4$	Raney Ni	Pd/C	DIBAL-H
Aldehyde	$RCHO$	✓	✓	✓	✓	✓
Ketone	$RCOR'$	✓	✓	✓	✓	✓
Ester	$RCOOR'$	✓	✗	✗	Not effective	✓
Acid	$RCOOH$	✓	✗	✗		✓
Acid Chloride	$RCOCl$	✓	✓	✗		✓

* DIBAL-H can reduce esters and acid chlorides to an aldehyde at -78 °C.

Another common approach for preparing diols is the **dihydroxylation of alkenes**. Remember, this can be either a syn or anti-dihydroxylation depending on the reagent:



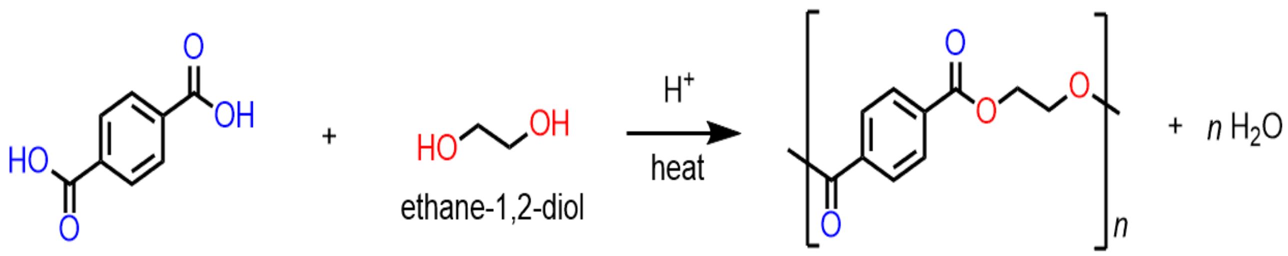
Diols by *Syn* and *Anti* Dihydroxylation of Alkenes

The ***syn* dihydroxylation** is done using **osmium tetroxide,** and 1,2-diols (vic-diols – vicinal diols) are obtained. This can also be achieved with potassium permanganate, although this approach has the risk of cleaving the double bond and over-oxidizing it to a carboxylic acid.
The ***anti*-dihydroxylation** of alkenes is carried out with **MCPBA** and other peroxides.
You can find more about these reactions, including the mechanisms and the stereochemistry, in the corresponding articles linked above.

Reactions of Diols

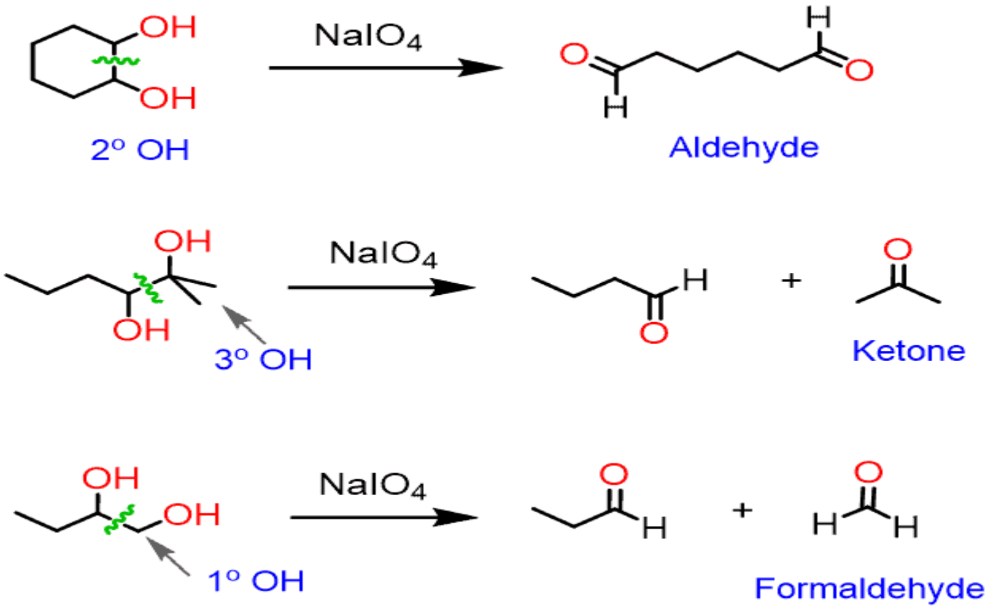
You can expect to observe **all the reactions of alcohols when working with diols**. The OH groups can be converted into halides, can react as nucleophiles, and oxidized to different carbonyl-containing functional groups depending on the structure of the diol and the oxidizing agent.
For example, **ethylene glycol is used for the synthesis of polyeste**rs, which are widely used in clothing, plastics, furniture, tires, and many other products.

The polyester structure shown in the image is polyethylene terephthalate (PET), which is prepared by a condensation reaction between 1,4-benzenedicarboxylic acid (terephthalic acid) and 1,2-ethanediol:



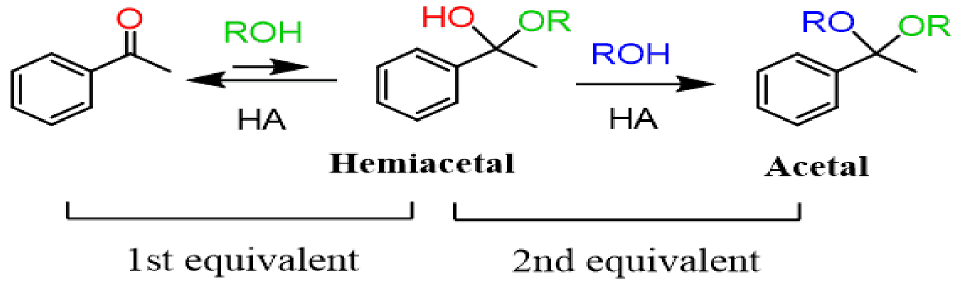
The ethylene glycol in this reaction acts as a nucleophile, adding to the carbonyl group and converting the acid to an ester. Check this article about the Fischer esterification for more details.

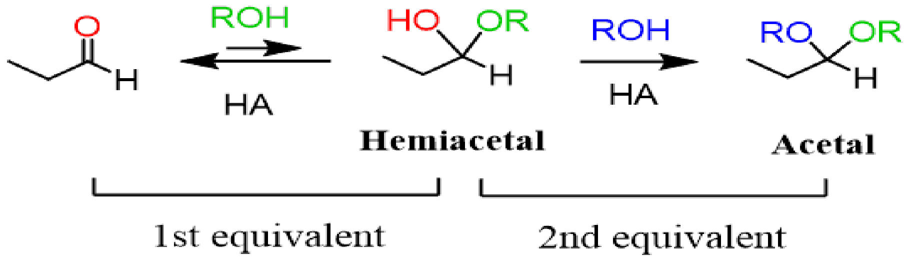
Vicinal diols can be oxidized to aldehydes and ketones depending on the structure of the alcohol with **sodium periodate ($NaIO_4$)**:



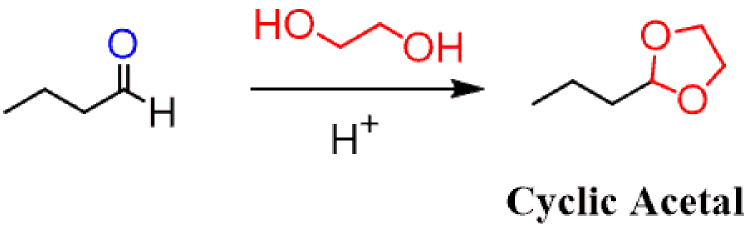
So, there are two things happening here: 1) the OH group is oxidized to a carbonyl, and 2) the C-C bond with the oxygens is cleaved. And the pattern is that a primary OH group gives formaldehyde, secondary OH groups produce a ketone, and a tertiary alcohol results in a ketone. The mechanism of this reaction is covered in a separate article, which you can find here.

An important application of 1,2- and 1,3-diols is their use as a **protective group for aldehydes and ketones**. When aldehydes and ketones are reacted with an excess alcohol, an **acetal** is formed where two alkoxy (OR) groups are connected to the same carbon atom:

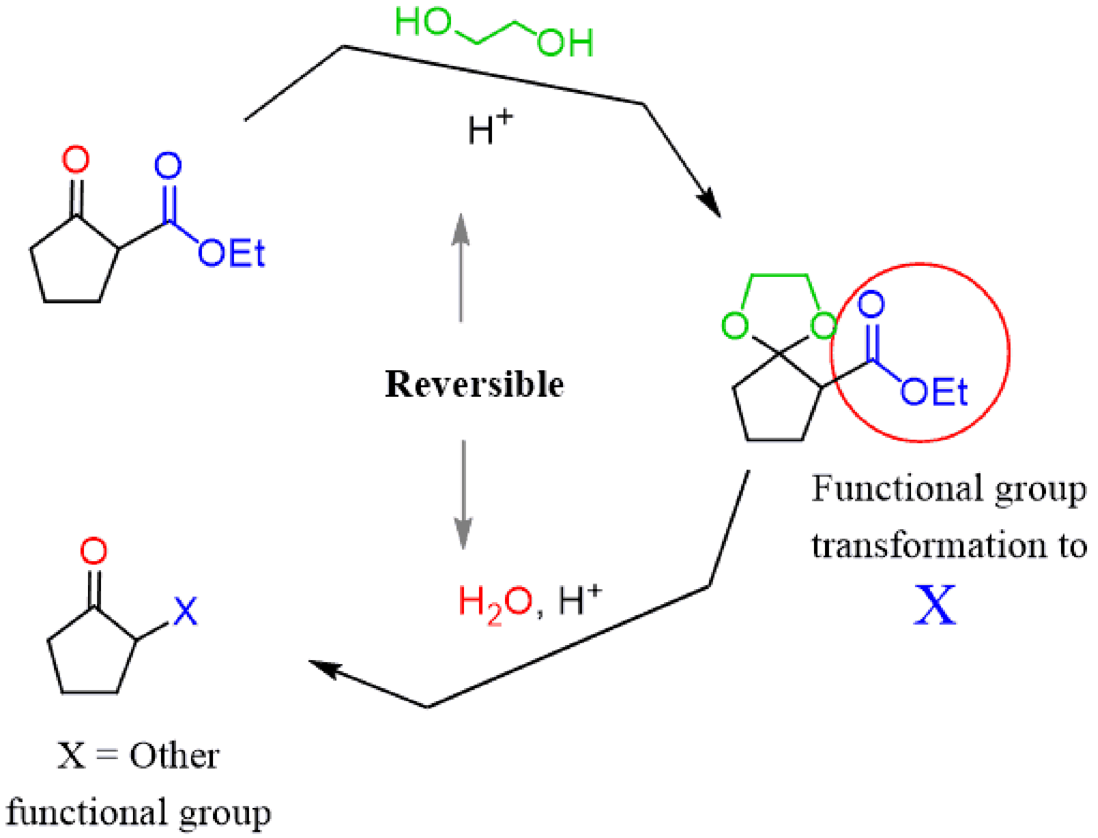




These two equivalents of the OH group can also be incorporated by a **diol,** producing a **cyclic acetal**, which is especially favored when five or six-membered rings are formed:

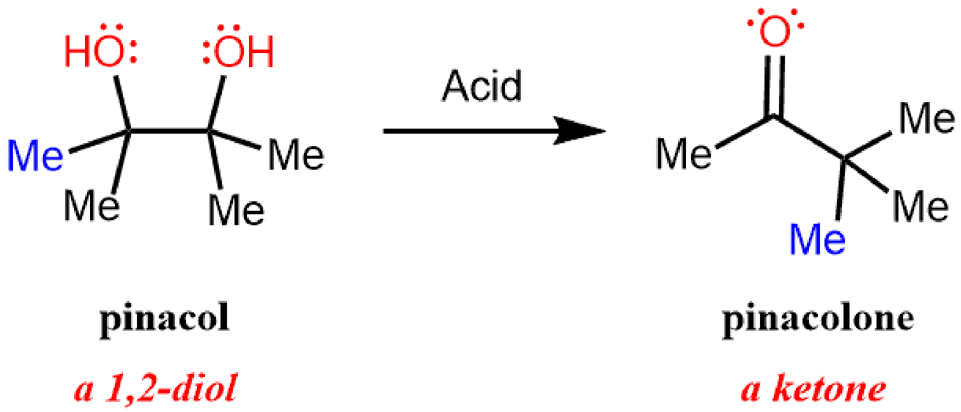


Cyclic acetals are very **stable under basic conditions** but can be removed when treated with acids. Therefore, cyclic acetals are used as protecting groups for aldehydes and ketones:



In the reaction above, ethylene glycol was used to convert the ketone into an acetal and protect it while reducing the ester group.

An important reaction of some **1,2-diols (vicinal diols)** is what is called the **pinacol rearrangement.** Here, the diol is converted into a ketone when treated with an acid.



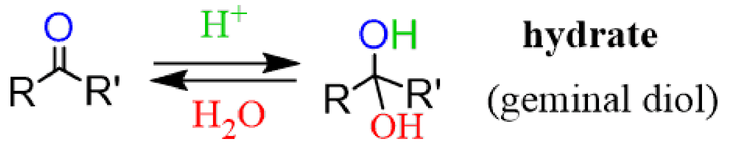
The mechanism and some other details of the pinacol rearrangement are covered in a separate post, which you can find here.

Geminal Diols

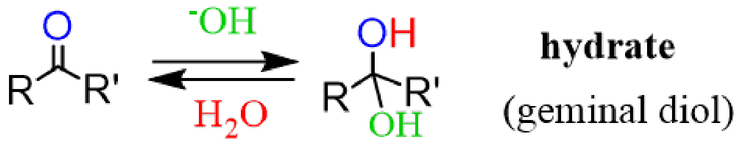
In all the examples above, we had 1,2-diols, which can also be referred to as vicinal diols. When the two **OH groups** are connected to the **same carbon atom**, we now have **geminal diols (*gem*-diols). These are formed when an aldehyde is d**issolved in water. The system establishes an equilibrium between the aldehyde and the **geminal diol,** called a **hydrate** of the aldehyde.

Aldehydes and Ketones:

Reaction with Water produces a Hydrate

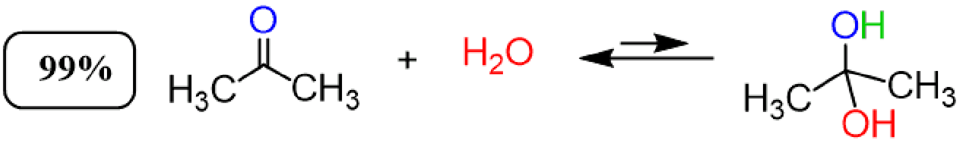


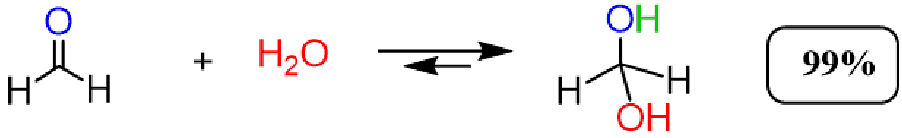
Acid-Catalyzed Addition of water



Base-Catalyzed Addition of water

The addition of water to most aldehydes and ketones is unfavorable, and **the equilibrium is shifted mainly toward the carbonyl compound**.
A few exceptions are the aldehydes with nearby electron-withdrawing groups and the simplest aldehyde, formaldehyde, which exists primarily as the *gem*-diol in aqueous solution:





Because of this, it is **not possible to isolate most *gem*-diols** from the aqueous solutions in which they are formed. If we try to evaporate the water, for example, the equilibrium simply shifts to simply shifts toward the carbonyl compound as expected by Le Chatelier’s principle: