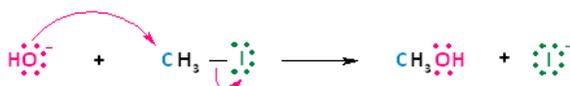


13.6: SYNTHESIS OF ALCOHOLS - REVIEW

ALCOHOLS ARE PREPARED BY S_N2 & S_N1 (SOLVOLYSIS) REACTIONS

Alkyl halides can be converted to alcohols by using S_N2 reactions with OH⁻ as a nucleophile. Substrates that undergo substitution by S_N1 reaction can be converted to alcohols using water as the nucleophile (and it can even be the solvent). Recall that S_N1 reactions are promoted in polar, protic solvents.

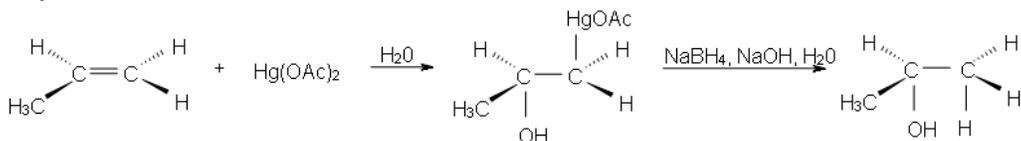
Example #1



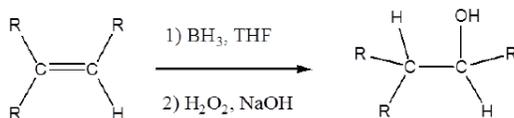
ALCOHOLS FROM ALKENES

Oxymercuration is a special electrophilic addition. It is anti-stereospecific and regioselective. Regioselectivity is a process in which the substituents choose one direction it prefers to be attached to over all the other possible directions. The good thing about this reaction is that there are no carbocation rearrangement due to stabilization of the reactive intermediate. Similar stabilization is also seen in bromination addition to alkenes.

Carbocation rearrangement is a process in which the carbocation intermediate can form a more stable ion. With carbocation rearrangement, the reaction would not be able to hydrate quickly under mild conditions and be produced in high yields. This reaction is very fast and proceeds with 90% yield.

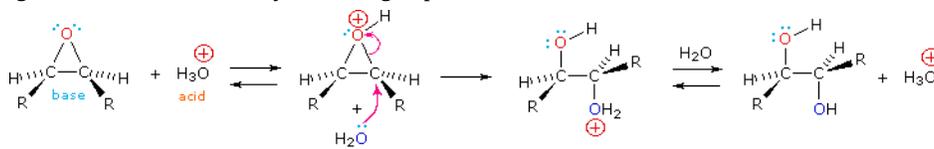


Hydroboration-Oxidation is a two step pathway used to produce alcohols. The reaction proceeds in an Anti-Markovnikov manner, where the hydrogen (from BH₃ or BHR₂) attaches to the more substituted carbon and the boron attaches to the least substituted carbon in the alkene double bond. Furthermore, the borane acts as a Lewis acid by accepting two electrons in its empty p orbital from an alkene that is electron rich. This process allows boron to have an electron octet. A very interesting characteristic of this process is that it does not require any activation by a catalyst. The Hydroboration mechanism has the elements of both hydrogenation and electrophilic addition and it is stereospecific (*syn addition*), meaning that the hydroboration takes place on the same face of the double bond, this leads *cis* stereochemistry.

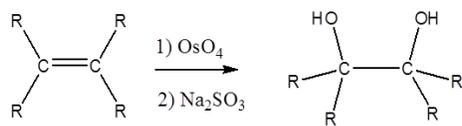


DIOLS FROM ALKENES

Epoxides may be cleaved by aqueous acid to give glycols that are often diastereomeric with those prepared by the *syn*-hydroxylation reaction described above. Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by nucleophiles such as water in the same way that the cyclic bromonium ion described above undergoes reaction. The result is **anti-hydroxylation** of the double bond, in contrast to the *syn*-stereoselectivity of the earlier method. In the following equation this procedure is illustrated for a *cis*-disubstituted epoxide, which, of course, could be prepared from the corresponding *cis*-alkene. This hydration of an epoxide does not change the oxidation state of any atoms or groups.



Osmium tetroxide oxidizes alkenes to give glycols through *syn* addition. A glycol, also known as a vicinal diol, is a compound with two -OH groups on adjacent carbons.



The reaction with OsO_4 is a concerted process that has a cyclic intermediate and no rearrangements. Vicinal syn dihydroxylation complements the epoxide-hydrolysis sequence which constitutes an *anti* dihydroxylation of an alkene. When an alkene reacts with osmium tetroxide, stereocenters can form in the glycol product. Cis alkenes give **meso** products and trans alkenes give **racemic mixtures**.

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- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
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