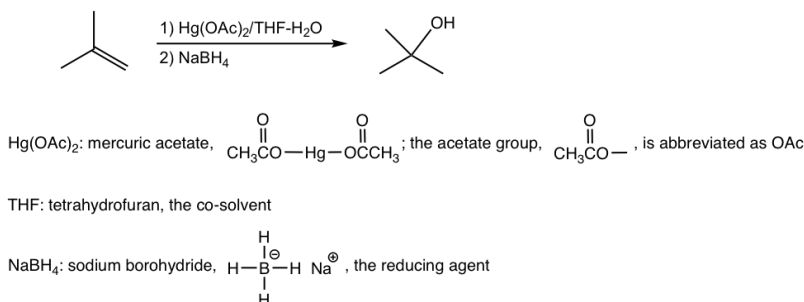


10.6: Two Other Hydration Reactions of Alkenes

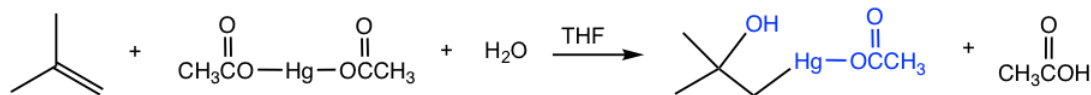
As we learned in section 10.2.2, the acid-catalyzed hydration (addition of water) to alkene produces alcohol that follow Markovnikov's regioselectivity. Here we will investigate two other methods for hydration of alkene, via different reaction conditions and mechanism, and produce either Markovnikov or anti-Markovnikov alcohol product respectively.

10.6.1 Oxymercuration–Demercuration of Alkenes The oxymercuration–demercuration of alkenes provides an alternative way to synthesize Markovnikov's alcohol from alkene. It is a fast reaction with lots application in laboratories, and the yield is usually greater than 90%. Comparing to acid-catalyzed hydration, the benefits of oxymercuration–demercuration are: no strong acids required and no carbocation rearrangements involved. The only reason that limits the wide application of this method is the environment concern since mercury (Hg) waste produced.

Oxymercuration–demercuration is a two-step procedure, as shown explicitly below:



Step 1 Oxymercuration: mercuric acetate and water add to the double bond



Step 2 Demercuration: the mercuric group is reduced and replaced with hydrogen

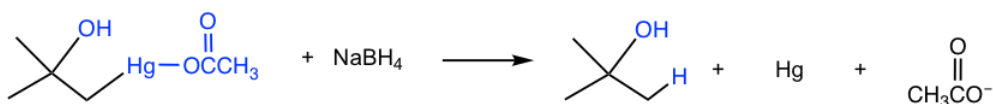


Figure 10.6a 1. Oxymercuration & 2. Demercuration

The mechanism in the oxymercuration step involves a mercury acting as a reagent attacking the alkene double bond to form a cyclic *mercurinium ion* intermediate. Because no carbocation intermediate involved, rearrangements are not observed in such reaction. Then a water molecule attacks the *most substituted* carbon to open the mercurinium ion bridge, followed by proton transfer to solvent water molecule. For the same reasoning that water molecule attacks the more substituted carbon of the cyclic halonium ion in halohydrin formation (section 10.2.4), the water molecule in this mechanism also attacks the more substituted carbon preferentially, as the partial positive charge is better accommodated on a tertiary carbon than on a primary carbon (if attack occurs on the other carbon).

Mechanism of Oxymercuration:

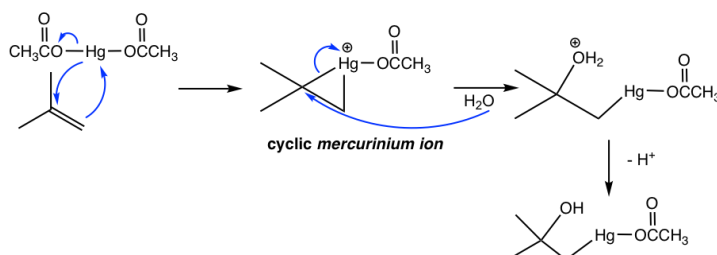


Figure 10.6b Mechanism of Oxymercuration

The organomercury intermediate is then reduced by sodium borohydride, the mechanism for this final step is beyond the scope of our discussions here. Notice that the overall oxymercuration–demercuration mechanism follows Markovnikov's rule with the OH

group is attached to the most substituted carbon and the hydrogen atom adds to the less substituted carbon.

10.6.2 Hydroboration –Oxidation of Alkenes

Hydroboration-oxidation is another method to convert alkene to alcohol, however, in **anti-Markovnikov** regioselectivity, that is OH is bonded to the carbon with greater number of hydrogens and hydrogen atom bonded to the carbon with less hydrogens.

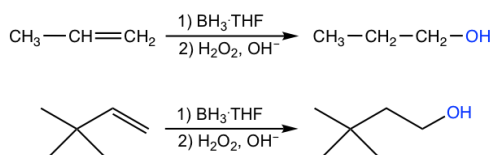


Figure 10.6c Hydroboration-Oxidation of Alkenes

The overall reaction is also a two-step process:

- First step is hydroboration, that is the addition of boron atom and hydrogen atom to the alkene.
- Second step is oxidation and hydrolysis of the alkylborane formed in step 1, to produce alcohol.

The borane reagent used in the first step is usually available as the solution containing $\text{BH}_3 \cdot \text{THF}$ complex. Borane, BH_3 , is an electron-deficient species because the boron atom has incomplete octet with only six electrons. When BH_3 is introduced to THF, they react to form a Lewis acid-Lewis base adduct (Chapter 3.??), which is more stable and relatively easy to be handled and stored. The solution containing $\text{BH}_3 \cdot \text{THF}$ is still rather sensitive and must be used in an inert atmosphere (nitrogen or argon) and with care.

Because of the incomplete octet of the boron atom in BH_3 , it is a good electrophile that reacts with alkene. The mechanism of the hydroboration step is illustrated below with propene as the example.

Mechanism of Hydroboration

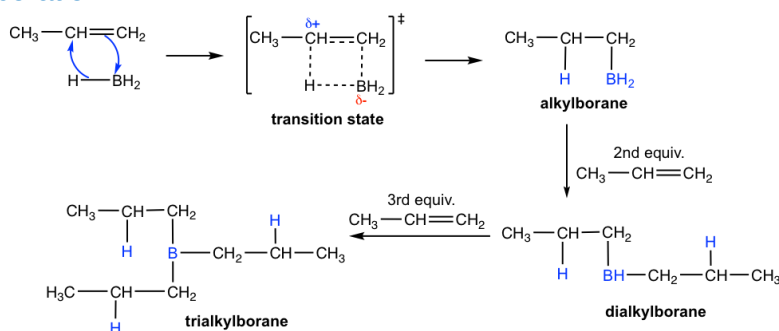


Figure 10.6d Mechanism of Hydroboration

When a terminal alkene, for example propene, is treated with $\text{BH}_3 \cdot \text{THF}$, the BH_3 molecule adds successively to the $\text{C}=\text{C}$ double bond of three alkene molecules to form an trialkylborane. In each addition step, the boron atom becomes attached to the *less substituted* double bond carbon, and a hydrogen atom transferred from the BH_3 to the more substituted carbon. In the second step (oxidation and hydrolysis) of the whole process, the borane is oxidized and hydrolyzed to OH group. So **the regioselectivity of the hydroboration step defines the anti-Markovnikov regioselectivity of the overall reaction.**

Such regioselectivity of the hydroboration step can be explained by both electronic and steric effects. In terms of steric factor, the boron-containing group is more bulky than hydrogen atom, so they can approach the less substituted carbon more easily. The electronic effect lies in the transition state structure for the formation of alkylborane. As shown above, the π electrons from the double bond is donated to the π orbital of boron and a four-atom ringcyclic transition state is approached. In the transition state, electrons shift in the direction of the boron atom and away from the carbon that is not connected to the boron. This make the carbon not connected to the boron bears a partial positive charge, that is better accommodated on the more substituted carbon. As a result the electronic effect also favors the addition of boron on the less substituted carbon.

Stereochemistry of Hydroboration

Hydroboration-oxidation takes place with **syn** stereochemistry, that the OH group and the hydrogen atom add to the same side of the double bond, as shown in the following example.

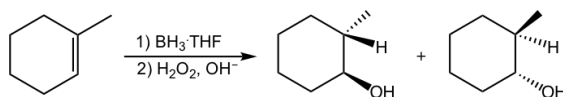


Figure 10.6e Stereochemistry of Hydroboration

This can be explained by the mechanism of the hydroboration step. The four-membered ring transition state requires that the boron atom and the hydrogen atom approach to the same surface of the alkene double bond, so they are added in the **syn** position to the double bond. Since the boron part is converted to OH group in the second step, that results in the syn addition of OH and H in the product.

Oxidation and Hydrolysis of trialkylboranes

With the hydroboration reaction is over, the trialkylboranes are usually *not* isolated, they are oxidized and hydrolyzed with the addition of hydrogen peroxide (H_2O_2) in basic aqueous solution. The mechanism for the oxidation and hydrolysis of trialkylboranes is rather complicated and could be an optional topic, the net result is the boron that initially bonded on the carbon is replaced by the hydroxy OH group.

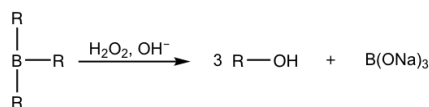


Figure 10.6f Oxidation and Hydrolysis of trialkylboranes

Mechanism: Oxidation and Hydrolysis of trialkylboranes

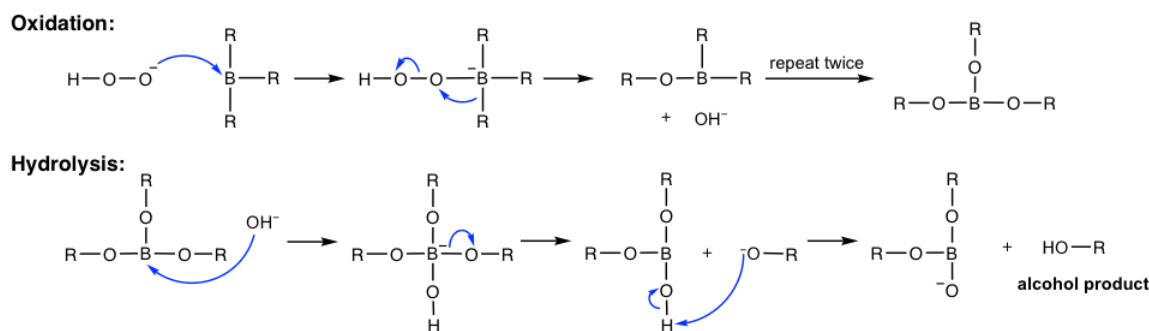


Figure 10.6g Mechanism: Oxidation and Hydrolysis of trialkylboranes

Summary: Hydration Methods of Alkene

Overall there are three methods for converting alkene to alcohol via addition, they are acid-catalyzed hydration, oxymercuration-demercuration and hydroboration-oxidation. Each method has its own character with benefit and disadvantage. The proper method could be picked up based on the need.

	Acid-catalyzed hydration	Oxymercuration-demercuration	Hydroboration-oxidation
Reaction Conditions	cat. $\text{H}^+/\text{H}_2\text{O}$	1) $\text{Hg}(\text{OAc})_2/\text{THF} \cdot \text{H}_2\text{O}$ 2) NaBH_4	1) $\text{BH}_3 \cdot \text{THF}$ 2) NaBH_4
Regioselectivity	Markovnikov	Markovnikov	Anti-Markovnikov
Stereochemistry	Not controlled	Not controlled	syn-addition

Rearrangement	Yes	No	No
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