

9.6: HYDRATION - HYDROBORATION-OXIDATION

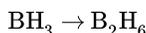
Learning Objectives

- apply the principles of regioselectivity and stereoselectivity to the addition reactions of alkenes
- predict the products, specify the reagents, and discern most efficient reaction for hydration of alkenes (acid catalyzed hydration; or oxymercuration/demercuration; or hydroboration/oxidation)

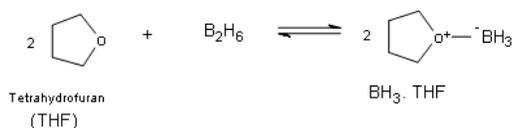
Hydroboration-Oxidation is a two step pathway used to produce alcohols. The reaction proceeds in an anti-Markovnikov manner, where the hydrogen (from BH_3 or BHR_2) attaches to the more substituted carbon and the boron attaches to the least substituted carbon in the alkene double bond. Furthermore, the borane acts as the electrophile 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 a stereospecific (syn addition), meaning that the hydroboration takes place on the same face of the double bond, this leads cis stereochemistry.

THE BORANE COMPLEX

It is very important to understand the structure and properties of the borane molecule. Borane exists naturally as a very toxic gas and it exists as dimer of the general formula B_2H_6 (diborane).



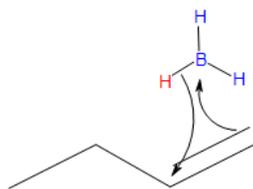
Since diborane dimer ignites spontaneously in air, it commercially distributed in ether or tetrahydrofuran (THF) solutions. In these solutions, the borane can exist as a Lewis acid-base complex which allows boron to have an octet of electrons.



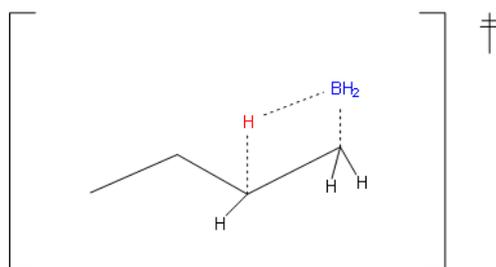
THE MECHANISM

STEP #1: HYDROBORATION OF THE ALKENE

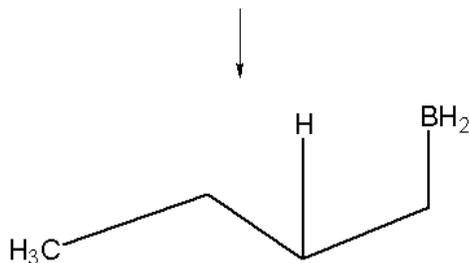
The addition of the borane to the alkene is initiated and proceeds as a concerted reaction because bond breaking and bond formation occur at the same time. The vacant 2p orbital of the boron takes the role of electrophile and accepts the pi electrons from the nucleophilic alkene. The boron adds to the less substituted carbon of the alkene, which then places the hydrogen on the more substituted carbon. Both, the boron and the hydrogen add simultaneously on the same face of the double bond (syn addition). With a concerted mechanism, there is no carbocation formation.



Transition state



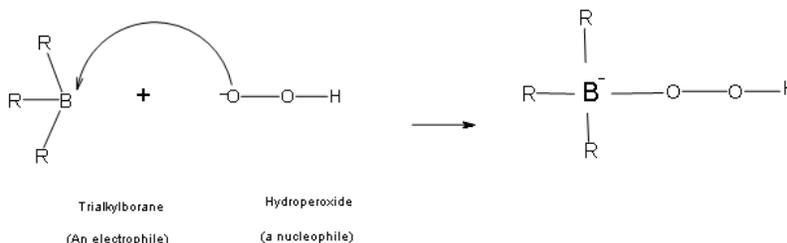
* Note that a carbocation is not formed. Therefore, no rearrangement takes place.



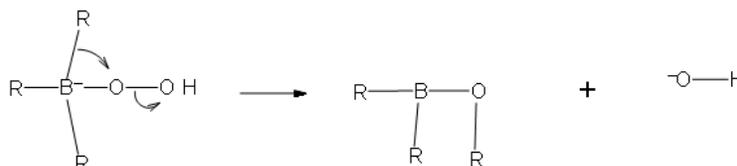
It is important to note that reaction continues two more times until all three hydrogens on the borane have reacted with alkenes to create the trialkylborane intermediate R₃B.

STEP #2: OXIDATION OF THE TRIALKYLBORANE BY HYDROGEN PEROXIDE

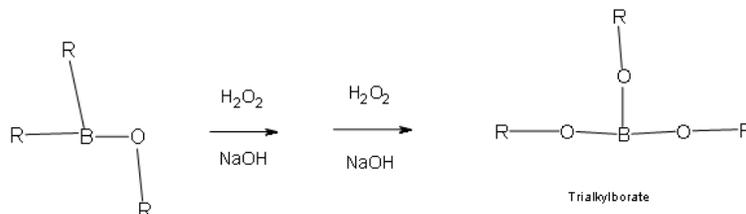
The hydrogen peroxide (HOOH) is the nucleophile in this reaction because it is the electron donor to the newly formed trialkylborane that resulted from the previous hydroboration.



In this second part of the mechanism, a rearrangement of an R group with its pair of bonding electrons to an adjacent oxygen results in the loss of a hydroxide ion.



Two more of these reactions with hydroperoxide will occur in order give a trialkylborate



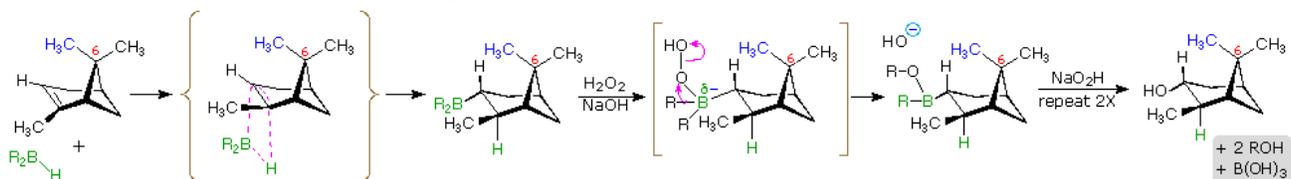
In the final step of the oxidation process, the trialkylborate reacts with aqueous NaOH to give the alcohol and sodium borate (Na_3BO_3).



If you need additional visuals to aid you in understanding the mechanism, click on the outside links provided at the end of this section.

STEREOCHEMISTRY OF THE HYDROBORATION STEP

The hydroboration reaction is among the few simple addition reactions that proceed cleanly in a syn fashion. As noted above, this is a single-step reaction. Since the bonding of the double bond carbons to boron and hydrogen is concerted, it follows that the geometry of this addition must be syn. Furthermore, rearrangements are unlikely inasmuch as a discrete carbocation intermediate is never formed. These features are illustrated for the hydroboration of α -pinene.



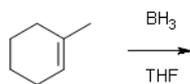
Since the hydroboration procedure is most commonly used to hydrate alkenes in an anti-Markovnikov fashion, we also need to know the stereoselectivity of the second oxidation reaction, which substitutes a hydroxyl group for the boron atom. Independent study has shown this reaction takes place with retention of configuration so the overall addition of water is also syn.

The hydroboration of α -pinene also provides a nice example of steric hindrance control in a chemical reaction. In the less complex alkenes used in earlier examples the plane of the double bond was often a plane of symmetry, and addition reagents could approach with equal ease from either side. In this case, one of the methyl groups bonded to C-6 (colored blue in the equation) covers one face of the double bond, blocking any approach from that side. All reagents that add to this double bond must therefore approach from the side opposite this methyl.

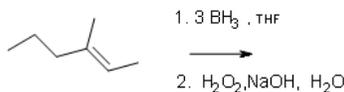
EXERCISES

1. Draw the bond-line structure of the product(s) for these following reactions?

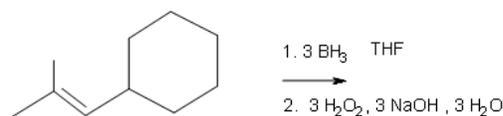
a)



b)

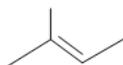


c)



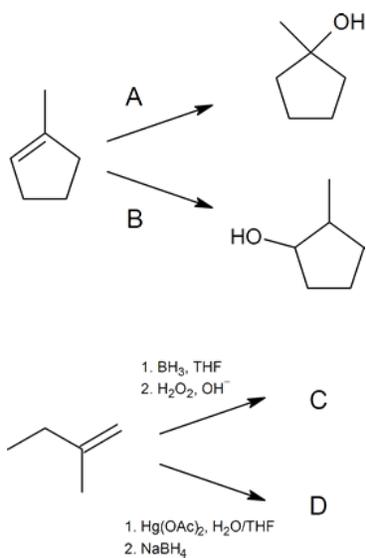
2. Draw the structural formulas for the alcohols that result from hydroboration-oxidation of the alkenes shown.

a)



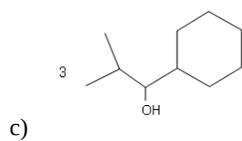
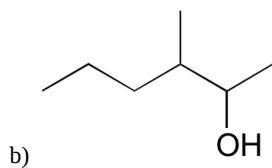
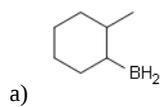
b) (E)-3-methyl-2-pentene

3. Write out the reagents or products (A–D) shown in the following reaction schemes.

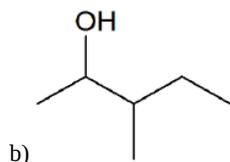
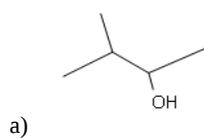


Answer

1.



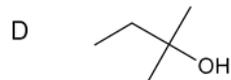
2.



3.

A 1. $\text{Hg}(\text{OAc})_2$, $\text{H}_2\text{O}/\text{THF}$
2. NaBH_4

B 1. BH_3 , THF
2. H_2O_2 , OH^-



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4. Bergbreiter E. David, and David P. Rainville. Stereochemistry of hydroboration-oxidation of terminal alkenes. *J. Org. Chem.*, 1976, 41 (18), pp 3031–3033
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