Hydroboration-Oxidation is a two step pathway used to produce alcohols. The reaction proceeds in an Anti-Markovnikov manner, where the hydrogen (from BH\textsubscript{3} or BHR\textsubscript{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 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 Anti-Markovnikov 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.

Introduction

Hydroboration-oxidation of alkenes has been a very valuable laboratory method for the stereoselectivity and regioselectivity of alkenes. An Additional feature of this reaction is that it occurs without rearrangement.

The Borane Complex

First off it is very important to understand little bit about the structure and the properties of the borane molecule. Borane exists naturally as a very toxic gas and it exists as dimer of the general formula B\textsubscript{2}H\textsubscript{6} (diborane). Additionally, the dimer B\textsubscript{2}H\textsubscript{6} ignites spontaneously in air. Borane is commercially available in ether and tetrahydrofuran (THF), in these solutions the borane can exist as a lewis acid-base complex, which allows boron to have an electron octet.

\[
2BH_3 \rightarrow B_2H_6
\]

THF.bmp

The Mechanism

Step #1

- Part #1: Hydroboration of the alkene. In this first step the addition of the borane to the alkene is initiated and proceeds as a concerted reaction because bond breaking and bond formation occurs at the same time. This part consists of the vacant 2p orbital of the boron electrophile pairing with the electron pair of the \( ? \) bond of the nucleophile.
* Note that a carbocation is not formed. Therefore, no rearrangement takes place.

- Part #2: The Anti Markovnikov addition of Boron. 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).
Step #2

- Part #1: the first part of this mechanism deals with the donation of a pair of electrons from the hydrogen peroxide ion. the hydrogen peroxide is the nucleophile in this reaction because it is the electron donor to the newly formed trialkylborane that resulted from hydroboration.

  peorxide 1.bmp

  Epoxidation
  oxidation part 1 (1).bmp

- Part 2: 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 removal of a hydroxide ion.

  1,2, SHIFT.bmp

Two more of these reactions with hydroperoxide will occur in order give a trialkylborate
Part 3: This is the final part of the Oxidation process. In this part the trialkylborate reacts with aqueous NaOH to give the alcohol and sodium borate.

If you need additional visuals to aid you in understanding the mechanism, click on the outside links provided here that will take you to other pages and media that are very helpful as well.

Outside links

- [http://bcs.whfreeman.com/vollhardtsc...2/12010-03.htm](http://bcs.whfreeman.com/vollhardtsc...2/12010-03.htm)
- [http://www.chemhelper.com/hydroboration.html](http://www.chemhelper.com/hydroboration.html)
- [http://www.organic-chemistry.org/nam...roboration.shtm](http://www.organic-chemistry.org/nam...roboration.shtm)

References

Problems

What are the products of these following reactions?

#1.
PROBLEM 1.bmp

#2.
PROBLEM #2.bmp

#3.
PROBLEM #3.bmp

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

#4.
problem 4.bmp

#5. (E)-3-methyl-2-pentene

If you need clarification or a reminder on the nomenclature of alkenes refer to the link below on naming the alkenes.

Answers

#1.
answer #1.bmp

#2.

\[ \text{HO} \]

#3.

Answer #3.bmp

#4.

ANSWER #4.bmp

#5.

Answer 5.bmp

Contributors

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Hydroboration Reactions

Diborane reacts readily with alkynes, but the formation of substituted alkene products leaves open the possibility of a second addition reaction. A clever technique for avoiding this event takes advantage of the fact that alkynes do not generally suffer from steric hindrance near the triple-bond (the configuration of this functional group is linear). Consequently, large or bulky electrophilic reagents add easily to the triple-bond, but the resulting alkene is necessarily more crowded or sterically hindered and resists further additions. The bulky hydroboration reagent needed for this strategy is prepared by reaction of diborane with 2-methyl-2-butene, a highly branched alkene. Because of the alkyl branching, only two alkenes add to a BH₃ moiety (steric hindrance again), leaving one B-H covalent bond available for reaction with an alkyne, as shown below. The resulting dialkyl borane is called disiamylborane, a contraction of di-secondary-isoamylborane (amyl is an old name for pentyl).

\[
2 \text{(CH}_3\text{)}_2\text{C=CHCH}_3 + \text{BH}_3 \rightarrow \text{[(CH}_3\text{)}_2\text{CH-CH(CH}_3\text{) }_2\text{B-H disiamylborane}}
\]

An important application of disiamylborane is its addition reaction to terminal alkynes. As with alkenes, the B-H reagent group adds in an apparently anti-Markovnikov manner, due to the fact that the boron is the electrophile, not the hydrogen. Further addition to the resulting boron-substituted alkene does not occur, and the usual oxidative removal of boron by alkaline hydrogen peroxide gives an enol which rapidly rearranges to the aldehyde tautomer. Thus, by the proper choice of reagents, terminal alkynes may be converted either to methyl ketones (mercuric ion catalyzed hydration) or aldehydes (hydroboration followed by oxidation).

\[
\text{RC=CH} + \text{(C}_5\text{H}_{11})\text{B-H} \rightarrow \text{[RCH=CH-B(C}_5\text{H}_{11})_2 \text{]} + \text{H}_2\text{O}_2 \text{ & NaOH} \rightarrow \text{[RCH=CH-OH]} \rightarrow \text{RCH=CH=O}
\]

Hydroboration of internal alkynes is not a particularly useful procedure because a mixture of products will often be obtained, unless the triple-bond is symmetrically substituted. Mercuric ion catalyzed hydration gives similar results.

Oxidations

Reactions of alkynes with oxidizing agents such as potassium permanganate and ozone usually result in cleavage of the triple-bond to give carboxylic acid products. A general equation for this kind of transformation follows. The symbol \([\text{O}]\) is often used in a general way to denote an oxidation.

\[
\text{RC≡CR’} + [\text{O}] \rightarrow \text{RCO}_2\text{H} + \text{R’CO}_2\text{H}
\]

Contributors


Further Reading

MasterOrganicChemistry