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 a Lewis Anti-Markovnikov 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$_2$H$_6$ (diborane). Additionally, the dimer B$_2$H$_6$ 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 occur 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.

  ![Epoxide.png](peoxide_1.bmp)

  ![Epoxidation.png](Epoxidation_1.bmp)

  ![Oxidation.png](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.png](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://www.organic-chemistry.org/nam...oboration.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.

#3.
Answer #3.bmp

#4.
ANSWER #4.bmp

#5.
Answer 5.bmp

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