

Hydroboration: atom and hydrogen peroxide assignment



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This reaction is anti-Markovnikov, which leads to the hydroxyl group attaching to the less-substituted carbon. In a regular Markovnikov reaction, the electrophile prefers the more stable carbocation, which is the more highly substituted carbon, while the hydrogen prefers the carbon that contains more hydrogens. In hydroboration, though, there are no intermediates but rather transition states. The hydroboration reaction occurs all at once and the mechanism is concerted. The new bonds to carbon are forming at the same time as the initial double bond is breaking.

The result is that the stereochemistry is syn. When BH₃ is mixed with an alkene, the boron molecule acts as a Lewis acid because it has a vacant 2p orbital and is trying to accept electrons. The partially negatively charged boron forms a quick triangle transition state with electrons from both carbons of the double bond. As the carbon-carbon pi bond from the alkene breaks further, any partial positive charge from the alkene carbons will most favor the carbon best able to accept it, which is frequently the most substituted carbon.

In the box-like transition state, the partially positive carbon would be best stabilized by interacting with the atom of BH₃ that bears a negative charge. Because hydrogen is more electronegative than boron, the partially positive charged atom attracts one of the hydrogen atoms from BH₃ via a hydride shift. Boron is also not as favorable to the positively charged carbon because boron is a relatively large molecule and would create too much steric hindrance to form a stable compound at that position. Thus one of the hydrogen atoms from BH₃ now bears a partial negative charge, and hence becomes more nucleophilic.

The breaking pi bond transfers its free electrons to form a bond between the partially positively charged boron atom and negatively charged oxygen between the partially positive carbon and negatively charged hydrogen. This whole process occurs two more times, resulting in a boron atom attached to three of the same alkyl groups along with its vacant 2p orbital. After hydroboration, treatment of the alkylborane with hydrogen peroxide in a base leads to the replacement of the borane atom with a hydroxyl group. Note that the stereochemistry is preserved.

The first step is the deprotonation of hydrogen peroxide to give HOO^- because HOO^- is a better nucleophile and will speed up the rate of reaction for the next step. The nucleophilic HOO^- will then attack the trialkylborane compound and cause an alkyl shift where one of the alkyl groups bonds to the attacking oxygen. The hydroxyl group leaves at the same time this occurs, and this happens two more times. The end result is a trialkoxyborane compound. The trialkoxyborane is then attacked by a nucleophilic hydroxide and induces a negative charge on boron.

This leads to the breakage of one of the B-O bonds and a deprotonated alcohol is now free. The deprotonated alcohol is protonated by a hydrogen from water, which creates the terminal alcohol alkane. The reason to add hydrogen peroxide and NaOH simultaneously during the lab is to keep the pH around 8 so that boric acid is not formed. Boric acid acts to destroy hydroxides in the solution that are necessary to deprotonate hydrogen peroxide. A lack of HOO^- ions ultimately results in less product formed.

Lastly the organic product was extracted with sodium bicarbonate once and then dried with magnesium sulfate to extract as much remaining NaOH and water as possible from the organic layer. From the gas chromatography graph of the hydroboration-oxidation of 1-octene, 34.3% of the product was 1-octanol and 5.7% was 2-octanol. This preference for 1-octanol is due because of the high preference of anti-Markovnikov addition in hydroboration reactions from the electronegativities of boron and hydrogen as well as the large size of boron.