

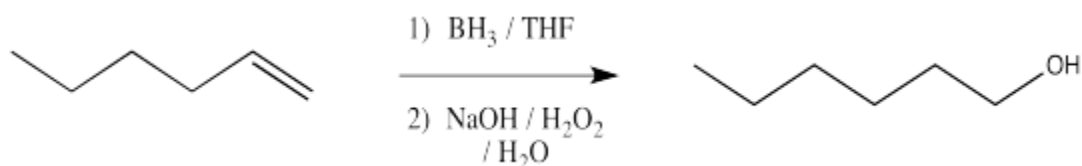
CONCERTED ADDITION TO ALKENES

Alkenes can be treated with aqueous acids or, much more efficiently, with aqueous mercuric salts, followed by sodium borohydride, to produce alcohols. In those cases, the hydroxyl group is found in different places. Treatment with acid often results in a mixture of alcohols in which the OH groups are found in the most substituted positions in the structure, regardless of the position of the original alkene. Oxymercuration - demercuration results in the hydroxyl being fixed at the most substituted end of the former C=C bond.

Those reactions are generally called hydration reactions because they result in the overall addition of H-OH across the double bond.

- Hydration reactions place an OH on one end and a H on the other end of a former double bond.

Hydroboration - oxidation is a two-step sequence of reactions that also results in hydration of a double bond. However, this reaction is complementary to oxymercuration - demercuration.



Instead of leaving an OH group at the most substituted end of the double bond, the hydroxy group is placed at the least substituted end of the double bond.

Let's modify that statement a little bit. In reality, the reaction scheme above just shows the major product. The minor product has the hydroxy group at the more substituted position of the double bond. These two products might be found in different ratios, maybe even as close as 55:45, but the least substituted product always predominates. We will see more efficient hydroboration methods soon, leading to ratios above 95:5, or almost entirely the least substituted product.

The product of non-hydrogen addition (i.e. OH group addition) at the most substituted end of the alkene is called a Markovnikov addition product. The product of non-hydrogen addition at the least substituted end of the alkene is called an anti-Markovnikov addition product.

- Oxymercuration - demercuration results in Markovnikov hydration.
- Hydroboration - oxidation results in anti-Markovnikov hydration.

This selectivity is important in synthetic applications. We use natural products all the time as pharmaceuticals, vitamins and other health and beauty applications, but we can't always obtain these compounds directly from nature, for a number of reasons. It could be that the organism needs to be killed in order to harvest its products, or that there isn't enough of the source in nature to meet demand. Frequently it is more economical to produce commercially useful compounds from convenient chemical feedstocks. Over the last century and a half, those feedstocks have come from coal tar and, later, petroleum. Currently, there is rapid progress underway to develop chemical feedstocks from sources such as vegetable and algal oil (i.e. oil from seaweed).

These feedstocks are just compounds that can be converted synthetically into pharmaceuticals as well as in plastics, paints, coatings and other materials. Frequently, the starting materials for these processes contain C=C bonds that can be functionalized through electrophilic addition. Thus, electrophilic addition and related reactions are among the most important in the world, economically speaking. It's very valuable to be able to control the outcome of these reactions in order to make processes more efficient, producing fewer wasteful by-products.

- Regioselectivity, or control over where a reaction occurs, is very important.
- The Markovnikov versus anti-Markovnikov additions available in hydration are good examples of regiochemical control.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/eladdn/EAborane.htm>