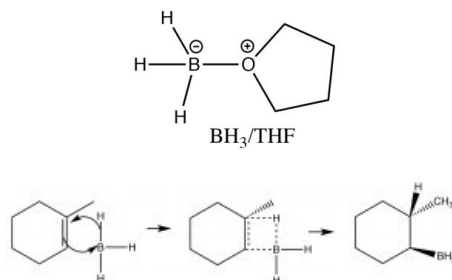


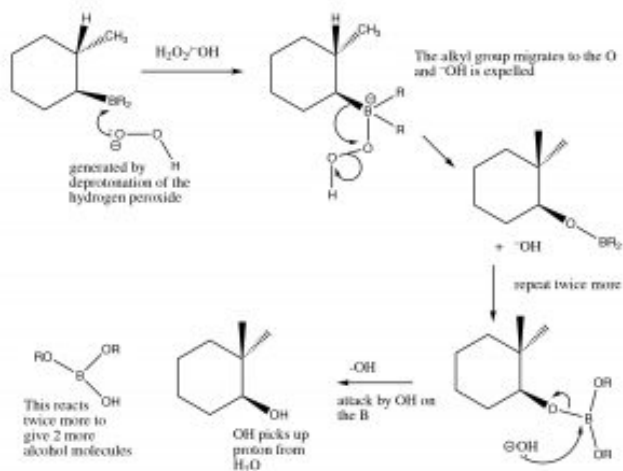
5.2: "Anti-Markovnikov" Addition across Double Bonds

While the heading for this section is called "anti-Markovnikov" addition, this does not mean that the reaction mechanism is actually different. In the two examples we will discuss here, the difference is merely that the first addition to the double bond is not the H, which as we will see makes it appear that we have added a particular reagent the opposite way to the normal addition. For example, if we want to add water across the double bond in to give the anti-Markovnikov product a different set of reagents is used: a Lewis acid-base complex of BH_3 and the ether tetrahydrofuran (THF), followed by a solution of hydrogen peroxide in base. This reagent adds across the double bond in the direction that you would expect, that is the electrophile (Lewis acid) boron adds to the *least* substituted carbon, but *atthesametime*, a hydrogen adds to the *most* substituted carbon from the same side of the molecule.



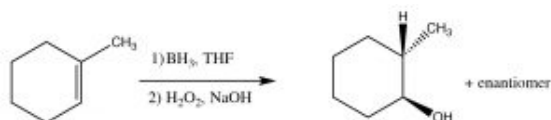
Mechanism of syn addition of BH_3 across the double bond

This process happens twice more, and then the boron species is replaced by reaction with hydrogen peroxide and sodium hydroxide.

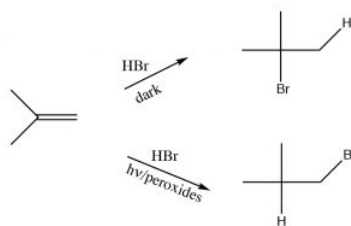


Mechanism of removal of boron moiety from the double bond

The overall reaction appears to have added the elements of water in an anti-Markovnikov direction. This reaction is not only *regiospecific*, but it is also *stereospecific*. The H and OH are added on the same (cis) side of the double bond and it is termed a syn addition.

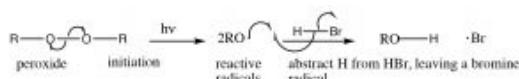


Anti-Markovnikov addition of HBr across a double bond.

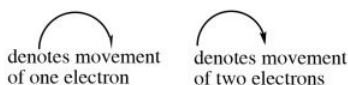


Another reaction which appears to violate what we have learned about the regiochemistry of addition across double bonds is the reaction of an alkene with HBr in the presence of light or peroxides. In contrast to the reaction we discussed previously, under conditions of light and in the presence of peroxides, the HBr adds in the reverse direction. Clearly something different is happening here: the reaction is proceeding by another Br mechanism. The clue is the presence of peroxides, which almost always signify that a reaction is proceeding via a radical mechanism rather than a polar mechanism.

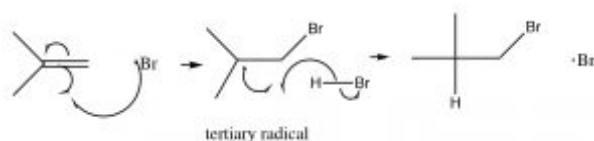
Radicals are species with unpaired electrons, and, as such, are very reactive. The reaction begins with an initiation step in which the peroxide (which contains a weak O–O bond) is broken homolytically to give two oxygen radicals. These react with HBr by abstracting a hydrogen, and leaving a bromine radical. Note that the oxy radical abstracts H and not Br, because Br is a more stable radical than H. Bromine radical is a large polarizable species and which can help stabilize the unpaired electron. A hydrogen radical is actually a hydrogen atom, it is highly unstable and reactive.



Note: when a mechanism involves single electrons moving (as in a homolytic bond cleavage, or any reaction of a radical species) we use what is called a fishhook arrow—with only one head, rather than the typical arrow that denotes movement of two electrons.



The resulting bromine radical now reacts with the alkene double bond to produce the most stable intermediate, which is (just as in the carbocations) the tertiary. Carbon radicals show the same trends in stability as carbocations for the reason that they are also electron deficient and can be stabilized by the same mechanisms as carbocations (induction and hyperconjugation). The resulting carbon radical now abstracts an H from another molecule of HBr, to produce the anti-Markovnikov addition product, plus another bromine radical that can begin the cycle again. This is called a radical chain reaction—because it produces another reactive species that can continue the chain reaction.



Note: Even though this reaction produces a different addition product than the typical addition of HBr across the double bond, the principles guiding the reaction are the same. The first addition produces the most stable intermediate; the difference is that bromine adds first.

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