

6.8: Radical Addition

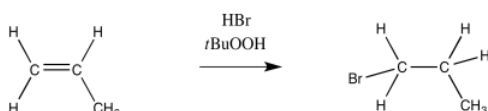
Radical addition to alkenes is another classic example of a radical reaction. Like radical substitution, it illustrates some important elements of radical reactivity.

The most common example of radical addition to alkenes seen in college chemistry textbooks is radical addition of hydrogen bromide, HBr. That's because it complements the usual addition of HBr to an alkene.

In the usual addition, HBr adds in a Markovnikov fashion to place the bromine at the more-substituted end of the alkene and the hydrogen on the less substituted end (remember the adage, "the rich get richer and the poor get poorer").

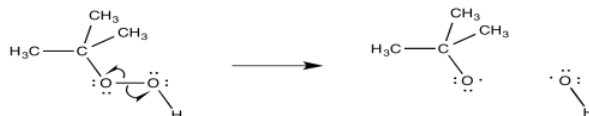


In contrast, addition of HBr under radical conditions leads to the bromine attaching at the least-substituted position, whereas the hydrogen bonds to the most-substituted position. This is a Robin Hood reaction.

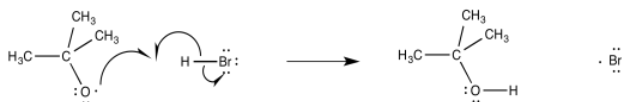


How does that reversal in regiochemistry come about? Consider the mechanism of the reaction.

Radical addition of HBr is almost always done in the presence of peroxides. The peroxide acts as an initiator for the reaction. The O-O bond may break through the simple action of thermal energy (maybe even at room temperature).



The alkoxy or hydroxy radicals that result from this initiation step are left to induce radical propagation. Certainly one of the easiest available targets is the relatively weak H-Br bond. Abstraction of a hydrogen atom from HBr produces a bromine radical.

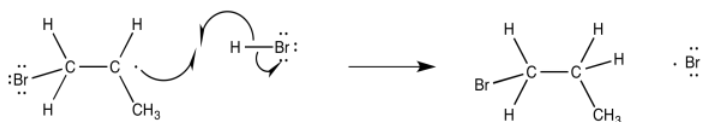


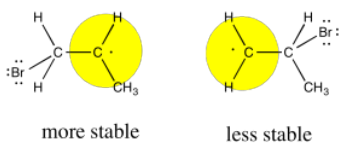
One of the things that the bromine radical could do is add to the double bond of an alkene. When it does so, it will bind to one end or the other of the former double bond. To which end will it go?



Like cations, radicals are considered to be somewhat electron-deficient. They are stabilized by electron-donating factors. That means that, like a cation, the radical will be more favorable on the most-substituted carbon of the former double bond.

Notice that this step is actually governed by almost the exact same factor that governs the polar addition of HBr. The regiochemistry is governed by the stability of the intermediate. Once that event has transpired, the regiochemistry of the product is fixed. It only remains for the alkyl radical to pluck a hydrogen atom from another HBr molecule, forming the final product and generating another bromine radical.





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