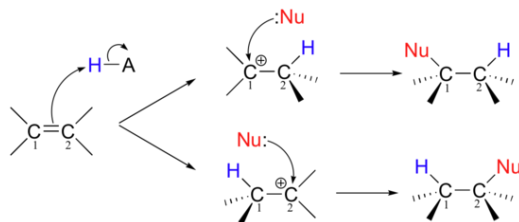


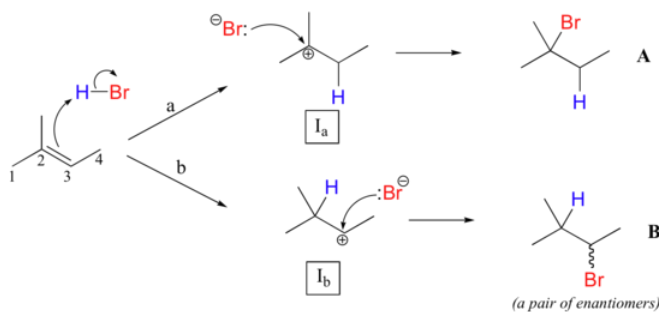
10.10: Markovnikov's Rule

very important regarding electrophilic addition reactions is that if the starting alkene is asymmetrical, there are two possible courses that could be followed, depending on which of the two alkene carbons forms the new sigma bond in the first step.

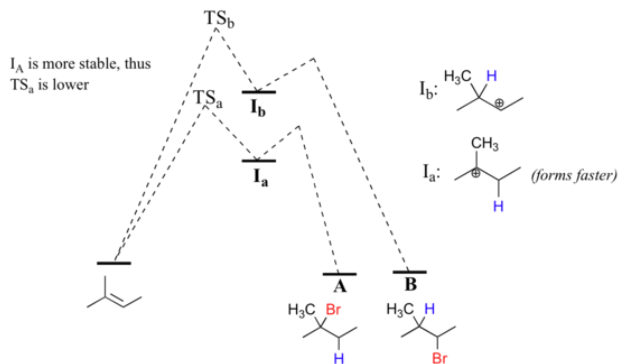


Of course, the two reaction courses involve two different carbocation intermediates, which may have different energy levels. Two different products are possible, and in general *the product which predominates will be the one that is derived from the lower-energy carbocation intermediate.*

This important regiochemical principle is nicely illustrated by a simple electrophilic addition that is commonly carried out in the organic laboratory: the conversion of an alkene to an alkyl bromide by electrophilic addition of HBr to the double bond. Let's look at a hypothetical addition of HBr to 2-methyl-2-butene, pictured below. Two different regiochemical outcomes are possible:

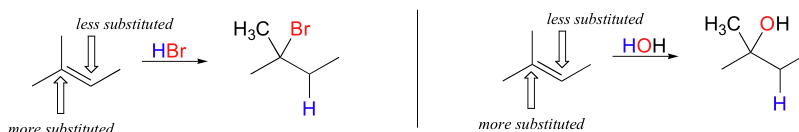


The initial protonation step could follow two different pathways, resulting in two different carbocation intermediates: pathway 'a' gives a tertiary carbocation intermediate (I_a), while pathway 'b' gives a secondary carbocation intermediate (I_b). We know already that the tertiary carbocation is more stable (in other words, lower in energy). According to the Hammond postulate, this implies that the activation energy for pathway **a** is lower than in pathway **b**, meaning in turn that I_a forms *faster*.



Because the protonation step is the rate determining step for the reaction, the tertiary alkyl bromide **A** will form much faster than the secondary alkyl halide **B**, and thus **A** will be the predominant product observed in this reaction. This is a good example of a non-enzymatic organic reaction that is highly regiospecific.

In the example above, the difference in carbocation stability can be accounted for by the electron-donating effects of the extra methyl group on one side of the double bond. It is generally observed that, in electrophilic addition of acids (including water) to asymmetrical alkenes, the *more substituted* carbon is the one that ends up bonded to the heteroatom of the acid, while the less substituted carbon is protonated.

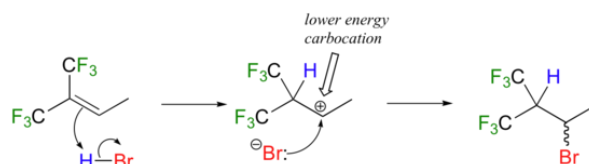


This rule of thumb is known as **Markovnikov's rule**, after the Russian chemist Vladimir Markovnikov who proposed it in 1869.

While it is useful in many cases, Markovnikov's rule does not apply to all possible electrophilic additions. It is more accurate to use the more general principle that has already been stated above:

When an asymmetrical alkene undergoes electrophilic addition, the product that predominates is the one that results from the more stable of the two possible carbocation intermediates.

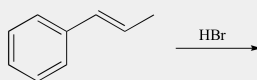
How is this different from Markovnikov's original rule? Consider the following hypothetical reaction, which is similar to the HBr addition shown above except that the six methyl hydrogens on the left side of the double bond have been replaced by highly electron-withdrawing fluorines.



Now when HBr is added, it is the *less* substituted carbocation that forms faster in the rate-determining protonation step, because in this intermediate the carbon bearing the positive charge is located further away from the electron-withdrawing, *cation-destabilizing* fluorines. As a result, the predominant product is the secondary rather than the tertiary bromoalkane. This would be referred to as an 'anti-Markovnikov' addition product, because it 'breaks' Markovnikov's rule.

Example

Predict the product of the following reaction:



Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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