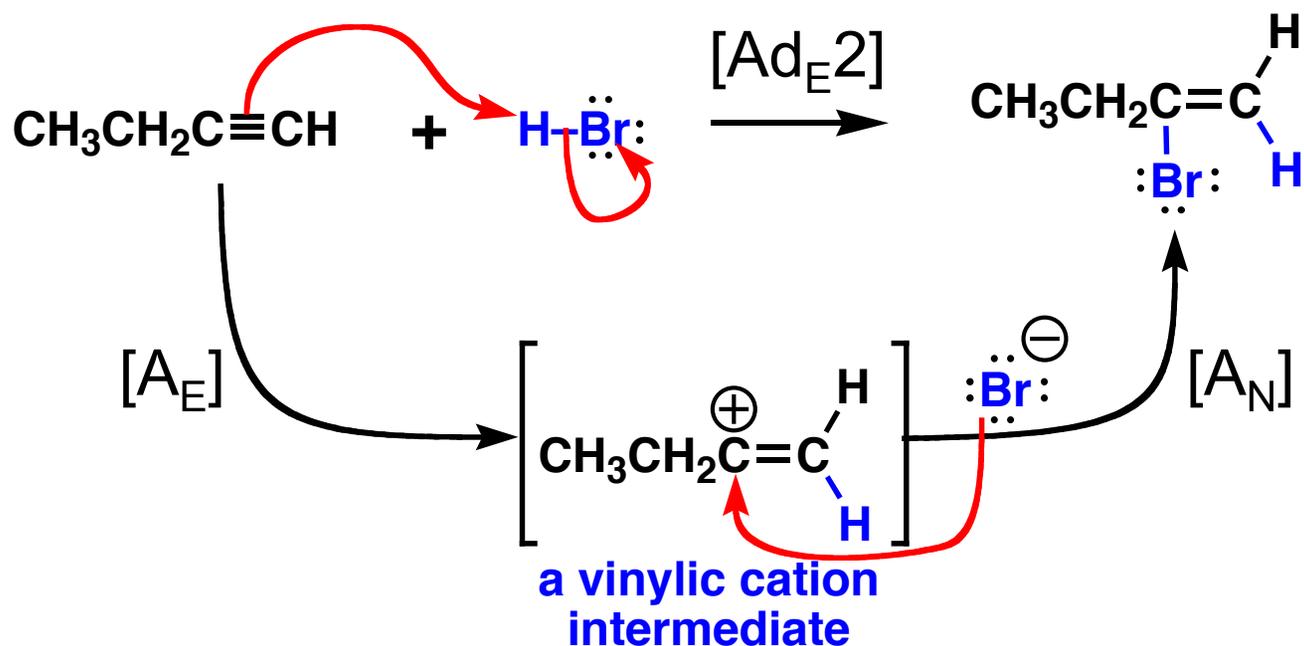
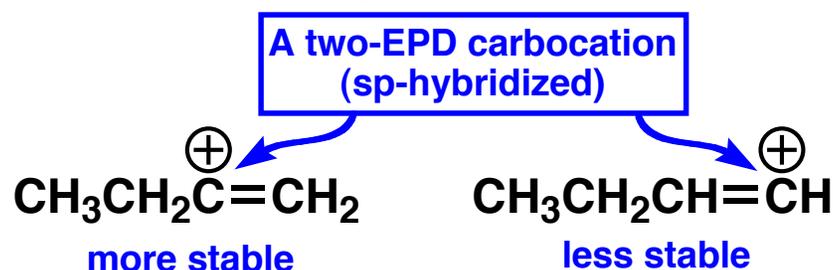


Addition Reactions to Alkynes

Alkynes contain carbon-carbon triple bonds. The triple bond is an electron dense region and it should therefore not be surprising that it has good nucleophilic characteristics. In studying the reactions of alkynes, we will reason-through new transformations by drawing analogies to the mechanisms and concepts that we have previously learned. The success of applying established ways to a new class of compounds illustrates the power of the mechanism-based approach for studying reactivity.

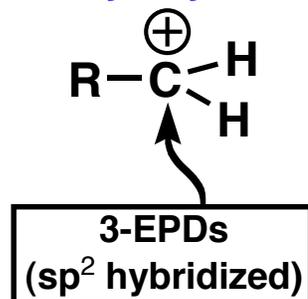


The Vinylic Cation

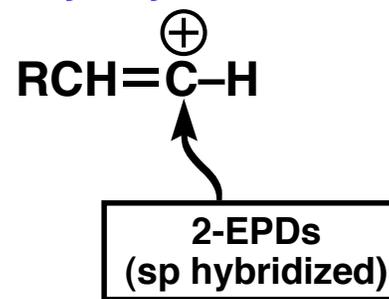


The vinylic cation possesses a positively charged carbon atom having only two electron pair domains (EPDs); the carbon bearing the positive charge is thus sp-hybridized. The addition of the electrophilic H^+ takes place so as to place the positive charge on the most highly substituted carbon, just as for alkenes. As before, the more highly substituted the vinylic cation, the greater its stability. This preference determines the regioselectivity of the addition. As a consequence, the bromide is located on the more highly substituted carbon (i.e., the internal carbon). It turns out that **the vinyl cation is much less stable (i.e., much more reactive) than the corresponding alkyl cation**. One reason is because sp hybrid orbitals, consisting of 50% s character, are less well-suited to stabilize positive charge compared to sp^2 hybrid orbitals that have only 33% s character (the s orbital resides closer to the positively charged nucleus).

primary alkyl cation

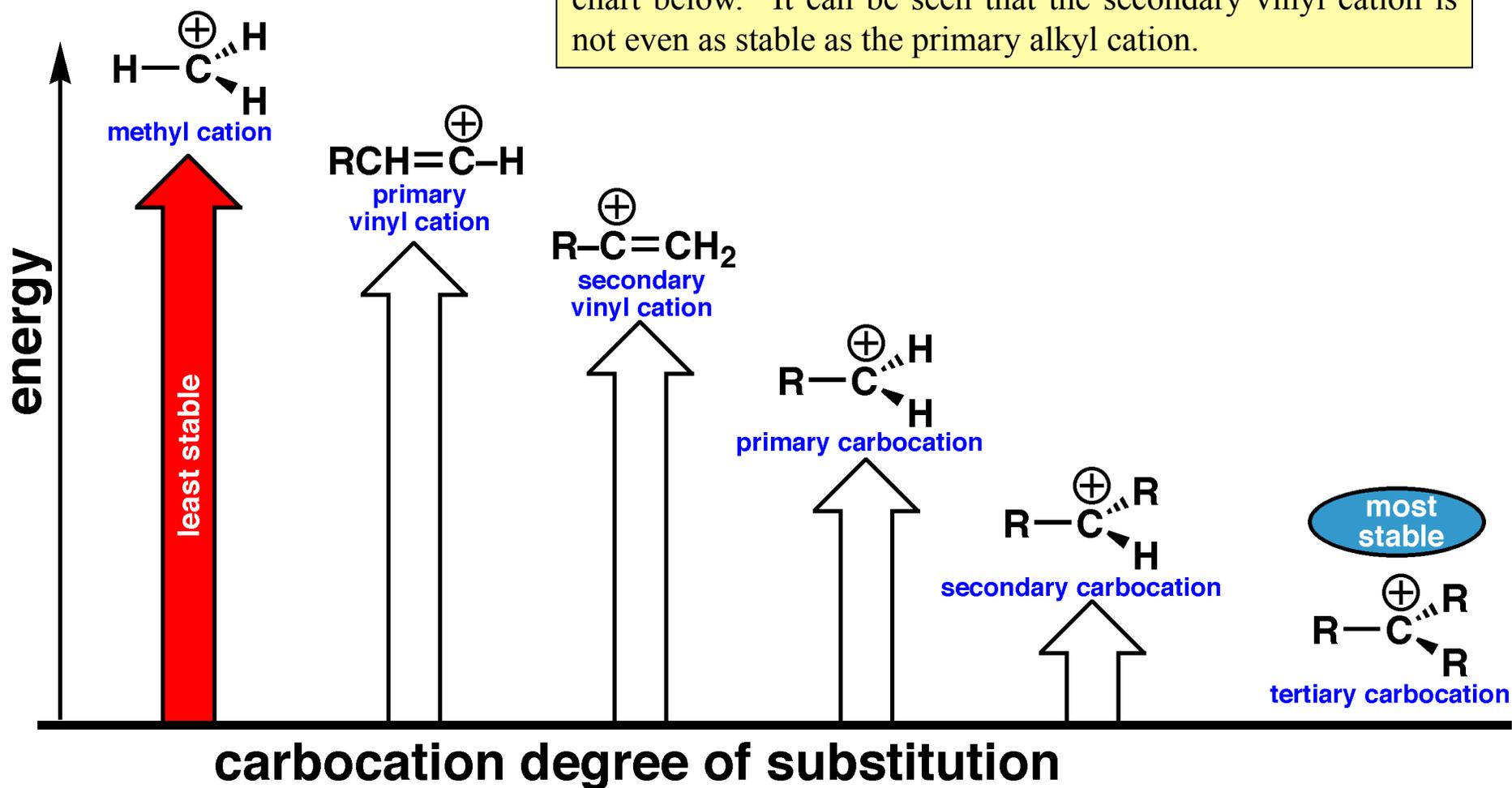


primary vinylic cation



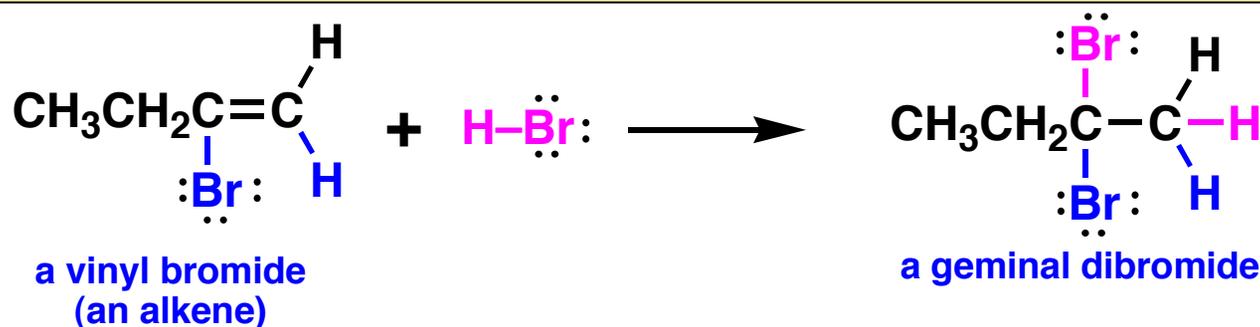
Relative Stability of Various Carbocations

The order of stability for various carbocations is provided in the chart below. It can be seen that the secondary vinyl cation is not even as stable as the primary alkyl cation.



Successive Addition

Since the addition product to an alkyne is a vinyl bromide – a type of alkene – it should not be surprising that subsequent reaction involving further addition is possible. In fact, successive addition tends to be the normal mode of reactivity for alkynes, as addition to the alkene is generally faster than the initial alkyne addition.



One reason why the subsequent reaction is faster is because of the special stability of the carbocation intermediate that results when an electrophile adds to a vinyl bromide. The lone pairs on the bromo group can donate to the electron deficient carbocation. Although this places a positive charge on the electronegative bromo group, all atoms have an octet of electrons making this a very important resonance contributor.

