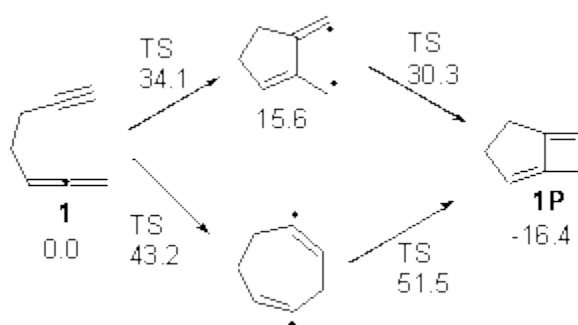


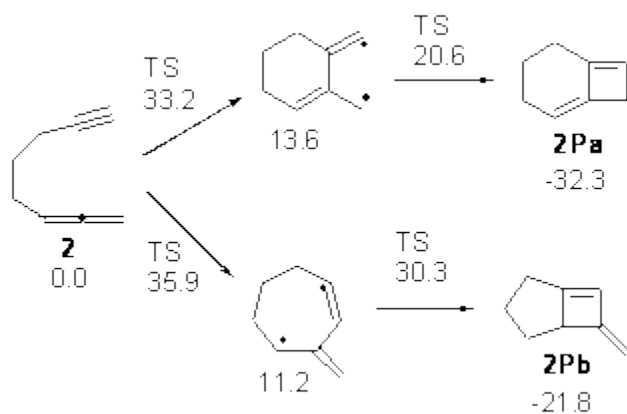
# [2+2] CYCLOADDITION OF TETHERED ALLENE-YNES

Matt Seibert pointed out to me a paper of his related to a previous blog post that also deals with the allene-yne thermal [2+2] cyclization. (My apologies to Matt and Dean for overlooking this paper!) Tantillo and Brummond looked at the system with various saturated tethers between these functional groups.<sup>1</sup> For example, UB3LYP/6-31+G(d,p) study of the cyclization of **1** indicates two possible paths, where the 5-member ring is formed first, or where the 7 member ring is formed first. The relative energies of the TSs and intermediates are shown in Figure 1. (Note that there are actually two intermediates on the first pathway, differing in the orientation terminal methyne hydrogen.) The closure to the smaller ring first is favored due to the allylic stabilization of the radical intermediate on this pathway.



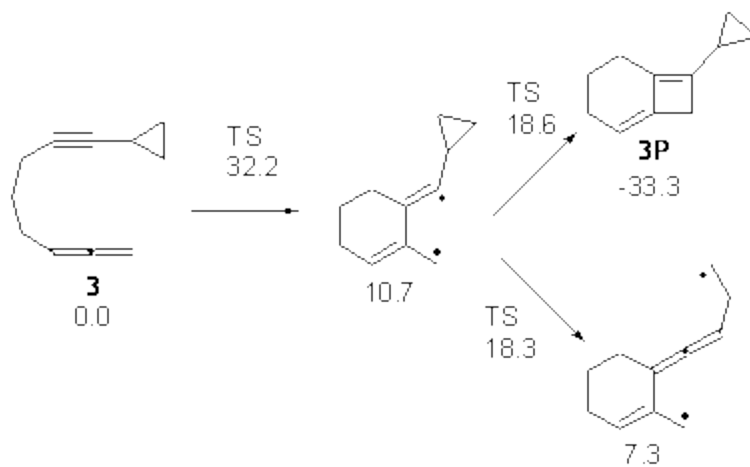
**Figure 1.** Relative energies of TSs and critical point in the cyclization of **1**.

Next, they examined the regioselectivity for the inner or outer double bond of the allene in **2**. For the reaction with the outer double bond, the 6 member ring is formed first. For the reaction with the inner double bond, the 7-member ring is formed first, and this pathway has a higher barrier than the other. The preference for the reaction with the terminal double bond is consistent with experiments.



**Figure 2.** Relative energies of TSs and critical point in the cyclization of **2**.

With potential diradical intermediates, they decided to append a cyclopropyl ring to as a trap. So, for example, the reaction of **3** can lead to the [2+2] product or to a diradical that might be trapped and identified. The computed energies along these two paths are shown in Figure 3. The activation barrier for the closure to the 2+2 product and for ring opening of the cyclopropyl group are nearly identical, so one might expect to observe both processes. Analogues of **3** were prepared and heated; some evidence of the ring opening of the cyclopropyl group was observed.



**Figure 3.** Relative energies of TSs and critical point in the cyclization of **3**.

Source: <http://comporgchem.com/blog/?p=1800>