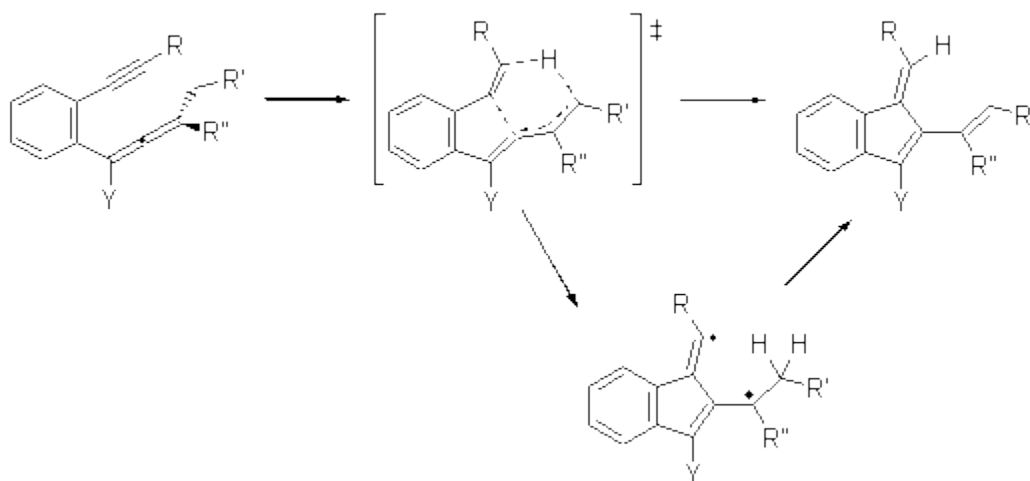


CYCLIZATION OF ENYNE ALLENES

I discuss the computational and experimental results of Singleton¹ regarding C₂-C₆ enyne allene cyclization. The reaction is shown below, and though Singleton could locate no transition state that connects the reactant to the diradical, molecular dynamics trajectory calculations show that the diradical is sampled, though the dominant pathway is the concerted route.



Schmittl has expanded on this work by determining the kinetic isotope effects for four more analogues.

The results are summarized in Table 1. Depending on the substituent, the predominant pathway can be concerted or stepwise or even a mixture of these two (termed “boundary”). Schmittl argues that the region about the single transition state, the one that directly connect reactant to product through a concerted path, is

actually quite flat. This is a “broad transition state zone”. Trajectories can traverse through various regions of the zone, some that go on to diradical, some that go on to product.

Substituents can alter the shape of the TS zone and thereby shift the set of trajectories in one direction or the other. The upshot is further support for the importance on non-statistical dynamics in dictating the course of reactions.

Table 1. Kinetic isotope effects for C2-C6 enyne allene cyclizations

Compound	KIE	Prevailing mechanism
R=TMS, R'=H, R''=TMS, Y=OAc	1.43 ¹	concerted
R=TMS, R'=iPr, R''=TMS, Y=H	1.60	concerted
R= <i>t</i> Bu, R'=iPr, R''=TMS, Y=H	1.24	Boundary
R=TIPS, R'=iPr, R''= <i>p</i> -An, Y=H	1.17	stepwise
R=TMS, R'=iPr, R''= <i>p</i> -An, Y=H	1.08	stepwise

Source: <http://comporgchem.com/blog/?p=49>