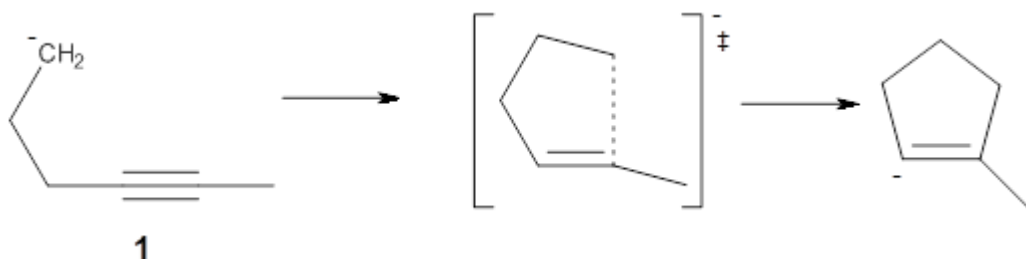


AROMATIC TRANSITION STATES IN NONPERICYCLIC REACTIONS

Anionic 5-Endo Cyclizations Are Aborted Sigmatropic Shifts

The activation energy for the 5-endo-dig reaction of the anion **1** is anomalously low compared to its 4-endo-dig and 6-endo-dig analogues. Furthermore, the TS is quite early, earlier than might be expected based on the Hammond Postulate.

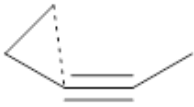


Alabugin and Schleyer have examined this reaction and found some interesting results.¹



First, NICS(0) values for a series of related intermolecular anionic attack at alkynes show some interesting trends (Table 1). Two of the transition states look like they might be aromatic: the TSs for the 3-exo-dig and the 5-endo-dig reaction have NICS(0) values that are quite negative. However, given the geometry of these TSs, particularly the close proximity of the σ bonds to the ring center, one might be concerned about contamination of these orbitals.

So, $\text{NICS}(0)_{\text{MOZZ}}$ computations, which look at the tensor component perpendicular to the ring using just the π -MOs, shows that the 3-exo-dig is likely non-aromatic ($\text{NICS}(0)_{\text{MOZZ}}$ is near zero), the TS for the 4-endo-dig reaction is antiaromatic ($\text{NICS}(0)_{\text{MOZZ}}$ very positive) and the TS for the 5-endo-dig reaction is aromatic ($\text{NICS}(0)_{\text{MOZZ}}$ is very negative). So this last reaction is the first example of an aromatic transition that is *not* for a pericyclic reaction!

Table 1. $\text{NICS}(0)$ and $\text{NICS}(0)_{\text{MOZZ}}$ for the TS of some anionic alkyne cyclizations.

	$\text{NICS}(0)$	$\text{NICS}(0)_{\text{MOZZ}}$
 3-exo-dig	-19.3	-1.6
 4-endo-dig	1.8	23.9
 5-endo-dig (1)	-15.2	-20.5

These authors argue that the reaction of **1** is an “aborted” sigmatropic shift. A normal pericyclic reaction is a single step with a single (concerted) transition state. An interrupted sigmatropic shift has an intermediate that lies higher in energy than the reactants, such as in the Bergman cyclization of an enediyne. The aborted sigmatropic shift has an intermediate that lies lower in energy than the reactants, such as in the cyclization of **1**.

Source: <http://www.compchemhighlights.org/2012/07/aromatic-transition-states-in.html>