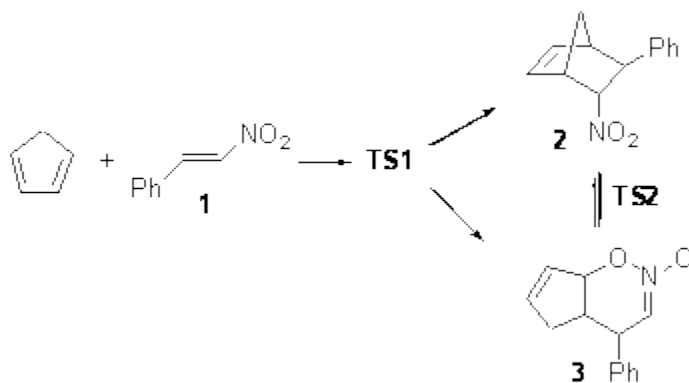


BRANCHING ON THE DIELS-ALDER POTENTIAL ENERGY SURFACE

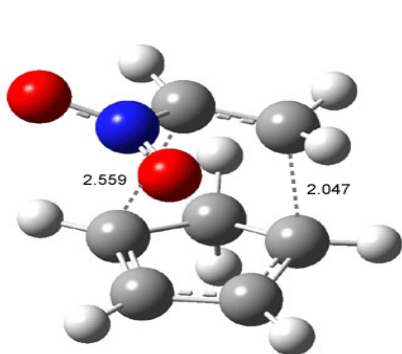
The search for unusual potential energy surface topologies continues. Unusual surfaces can lead to dynamic effects that result in rates and product distributions dramatically divergent from that predicted by statistical theories. I addressed this topic in Chapter 7 of the book.

Houk has found another interesting example in the Diels-Alder reaction of cyclopentadiene with nitrostyrene **1**.¹ The [4+2] adduct is **2**, which can undergo a [3,3] Cope-like rearrangement to give **3**. Product **3** can also result from a [2+4] Diels-Alder cycloaddition where cyclopentadiene acts as the *dienophile*.

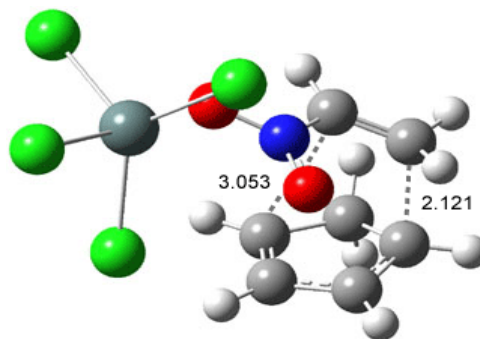


Like some of the examples in Chapter 7, the potential energy surface, computed at B3LYP/6-31+G*, contains a single transition state (**TS1**) from reactants.

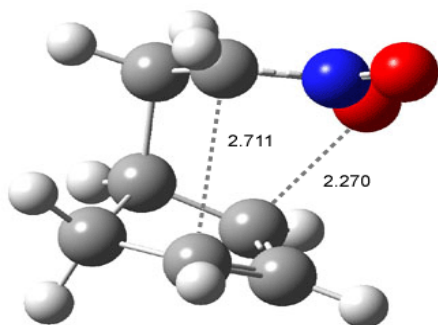
Continuing on the reaction path past the transition state, a valley ridge inflection point (VRI) intervenes, causing the path to bifurcate: one path leads to **2** and the other leads to **3**. In other words, a single transition state leads to *two* different products! **TS1** is geometrically closer to **2** than **3**, while **TS2** lies closer to **3** than **2** (Figure 1). This topology directs most molecules to traverse a path over **TS1** and on to **2**. What is novel in this paper is that the acid-catalyzed reaction, using SnCl₄, shifts **TS1** towards **3** and **TS2** towards **2**, leading to the opposite product distribution. The uncatalyzed reaction favors formation of **2** while the catalyzed reaction favors **3** over **2**. Confirmation of this prediction awaits a molecular dynamics study.



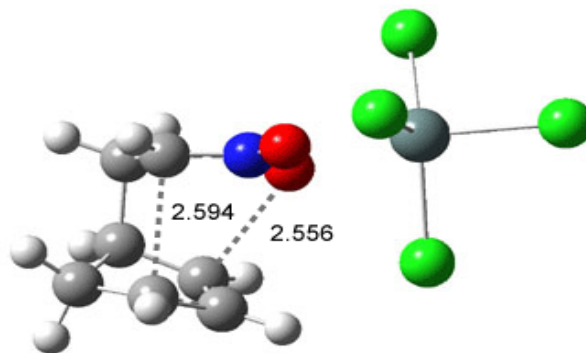
TS1



TS1-Cat



TS2



TS2-Cat

Figure 1. B3LYP/6-31+G(d) optimized structures for **TS1** and **TS2**.¹

Source: <http://comporgchem.com/blog/?p=22>