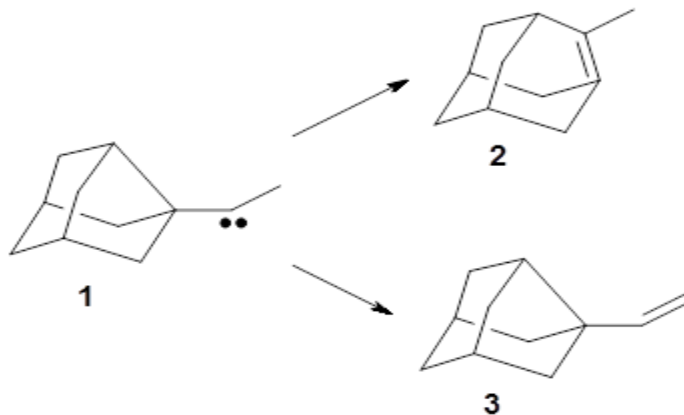


CALCULATIONS ON TUNNELING IN THE REACTIONS OF NORADAMANTYL CARBENES

The notion of tunneling control has been a topic of interest within this blog a number of times. As developed by Schreiner and Allen,^{1,2} tunneling control is a third means for predicting (or directing) the outcome of a reaction, alongside the more traditionally recognized kinetic and thermodynamic control. Tunneling control occurs when tunneling through a higher barrier is preferred over tunneling through a lower barrier.

Kozuch and Borden propose another example of tunneling control, this time in the rearrangement of the noradamantyl carbene **1**.³ This carbene can undergo a 1,2-carbon shift, driven by strain relief to form the alkene **2**. The alternative as a 1,2-hydrogen shift that produces the alkene **3**.



These two reaction pathways were explored using B3LYP/6-31G(d,p) computations coupled with canonical variational theory and small curvature tunneling corrections. Structures of the reactant **1** and the two transition states leading to the two products **2** and **3** are shown in Figure 1. The activation barrier at 300 K is 5.4 kcal mol⁻¹ leading to **2** and 8.6 kcal mol⁻¹ leading to **3**. Tunneling is expected to be much more important for the hydrogen shift than for the carbon shift, but even including tunneling, the rate to form **2** is much faster than the rate to form **3** at 300 K.

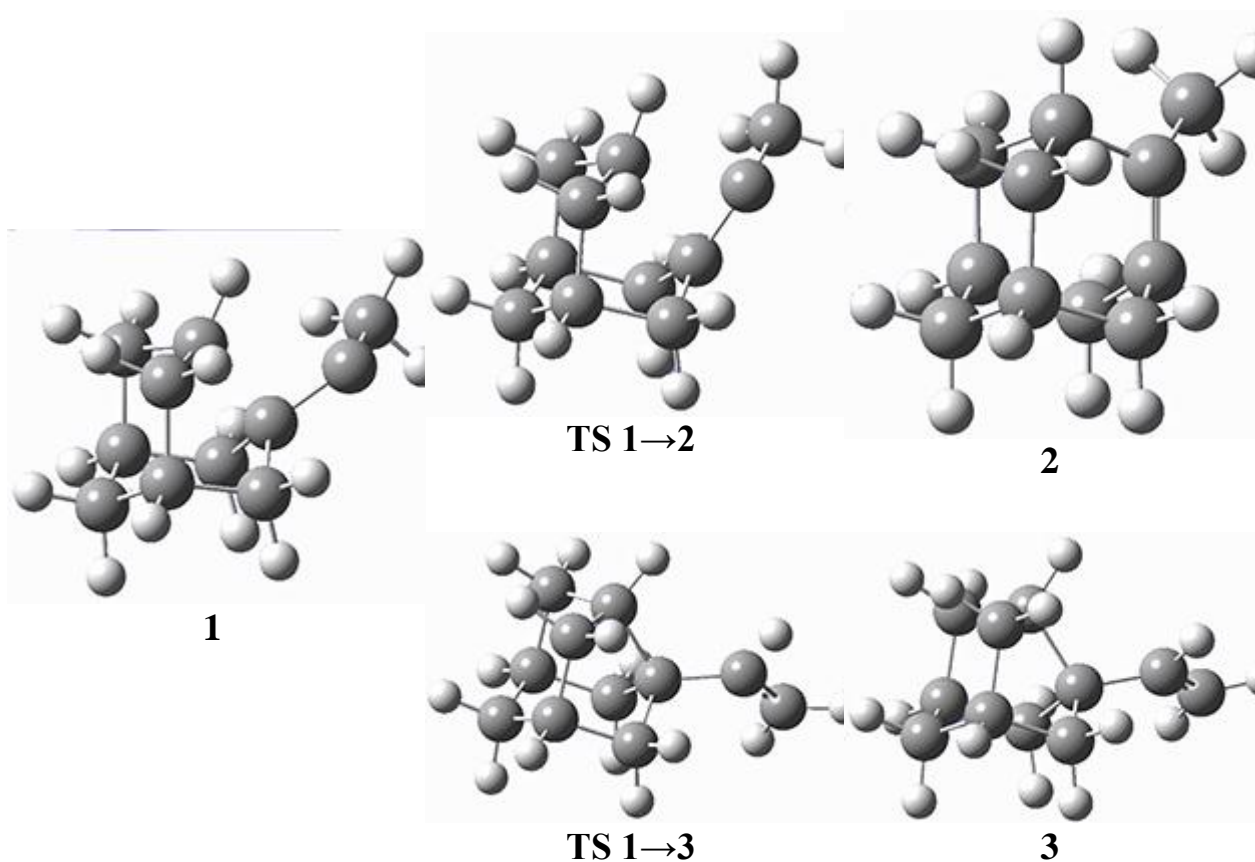


Figure 1. B3LYP/6 optimized structures of **1-3** and the transition states leading to **2** and **3**.

The situation is reversed however at cryogenic temperatures (< 20 K). Tunneling is now the only route for the reactions to occur, and the rate for formation of **3** is dramatically greater than the rate of formation of **2**, which is inhibited by the movement of the much heavier carbon atom. Perdeuteration of the methyl group of **1**, which drastically slows the rate of tunneling in the path to **3**, nonetheless still favors this pathway (forming d_3 -**3**) over formation of d_3 -**2**. Thus, at low temperatures the formation of **3** is the preferred product, a manifestation of tunneling control.

Source: <http://www.compchemhighlights.org/2014/02/calculations-on-tunneling-in-reactions.html>