SYNTHETIC APPLICATION OF THE BERGMAN CYCLIZATION

Synthetic application of the Bergman cyclization is rare. Basak reports a real interesting use of this reaction to create polycyclic aromatics.[1] So, for example, heating up **1** in DMSO leads to the 4helicene **2**. The proposed mechanism is shown in Figure 1. The Bergman cyclization leads to the biradical **3**, which adds to the pendant phenyl group to give **4**. Hydrogen abstraction then gives **5**, which abstracts hydrogens from the solvent to produce **6**. (Use of DMSO-d_6 provides deuterium incorporated products consistent with the diradical shown in **4**.) Oxidation then gives the final product **2**.

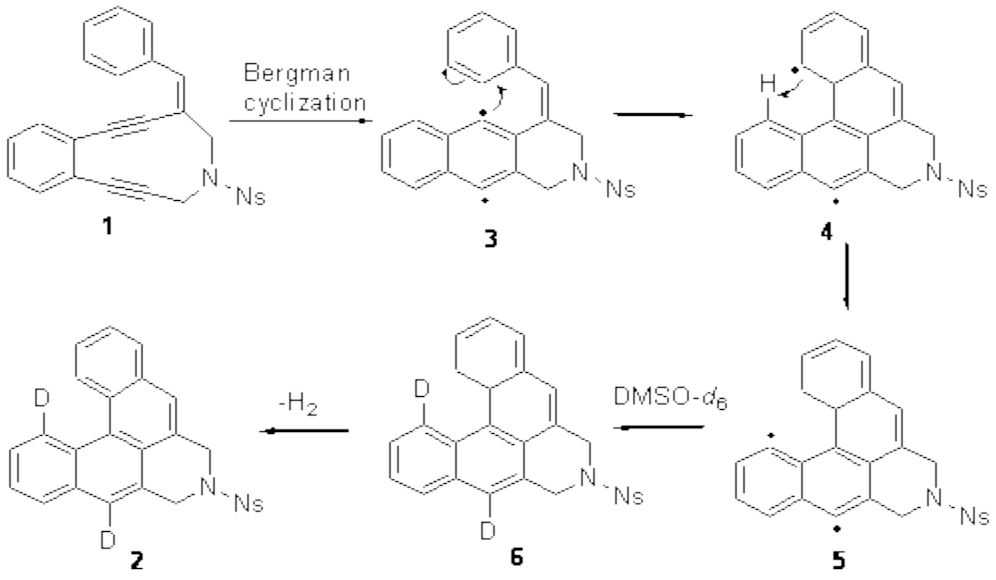

Figure 1. Proposed mechanism for the conversion of **1** to **2**.

B3LYP computations were performed to examine the relative rates with substituents on the phenyl ring. The structure of **1'** (with a methyl group replacing the Ns group – 4-nitrobenzenesulfonyl) and the transition state for the Bergman cyclization are shown in Figure 2. Unfortunately, computations were not used to analyze the complete proposed mechanism – a project that awaits the eager student perhaps?

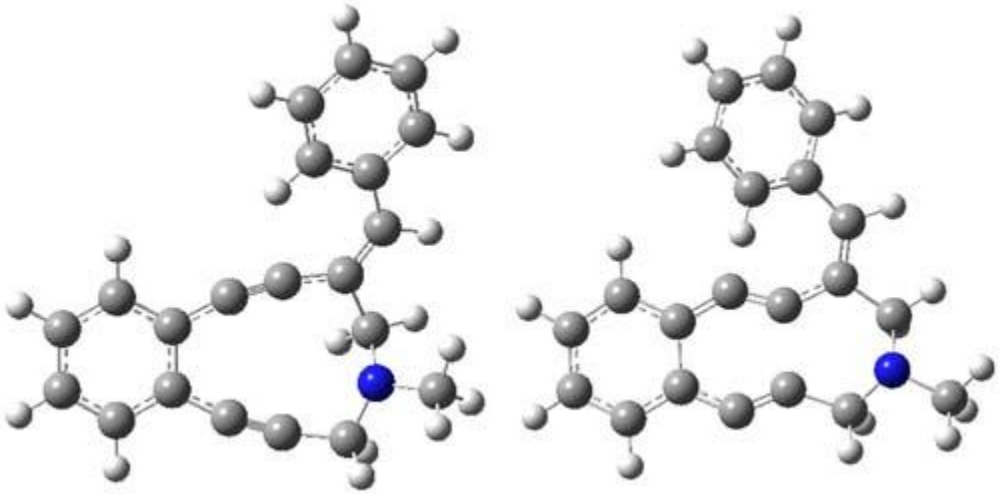

Figure 2. B3LYP/def2-TZVP//BP86/def2-TZVP optimized structures of **1'** and transition state for the Bergman cyclization of **1'**.

Source: http://comporgchem.com/blog/?p=1811