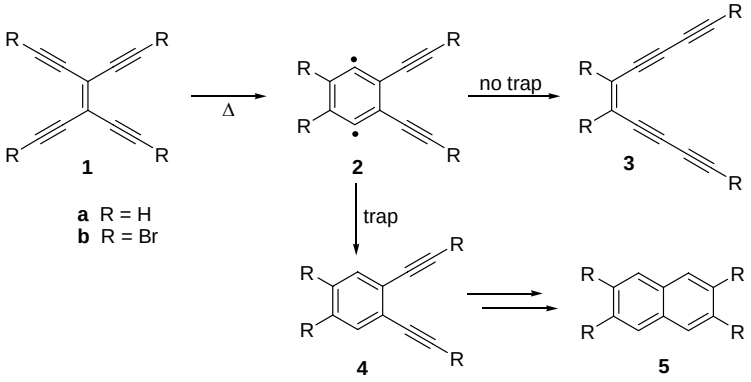
Studies on the Bergman Cyclization and Cyclobutadienes

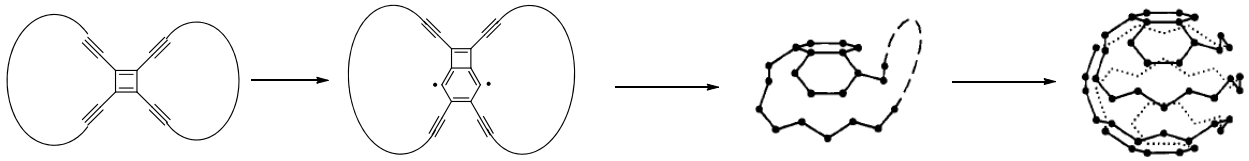
Jessica L. Menke, Alex M. Nolan, Katherine Windsor, Brian J. Esselman, Robert J. McMahon*

Department of Chemistry, University of Wisconsin, 1101 University Ave., Madison, WI 53706

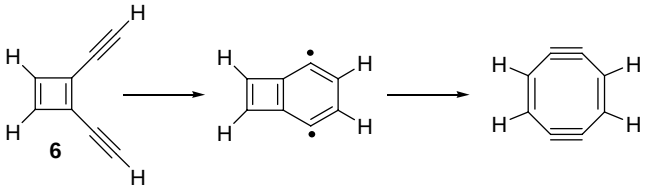
We are investigating the reactivity of $C_{10}H_4$ enediyne isomers **1a** and **3a**, and select derivatives, such as **1b**. The observed reactions of the enediynes may represent important phenomena in the chemistry of carbon-rich compounds under high temperature and/or pressure, conditions often employed in the production of fullerenes and carbon nanotubes.



We have shown that heating a solution of **1a** in the presence of a trapping agent affords naphthalene via two consecutive cycloaromatization reactions. To the best of our knowledge, there have been no documented Bergman cyclizations of a tetraethynylethene, such as **1**.



In a related project, we are studying the possible Bergman cyclization of 1,2-diethynylcyclobutadiene, **6**. This type of reaction has been proposed as the first step in a pathway leading to fullerene formation. The cyclization of **6** has been explored computationally. Several pathways leading to interesting carbenes and diradicals have been discovered. Additionally, the singlet-triplet gaps of each of the ethynyl derivatives of cyclobutadiene have been computed. Work is being done to produce ethynyl-substituted cyclobutadienes under matrix isolation conditions.



In a similar fashion, cyano-substituted cyclobutadienes have been explored. These molecules are of particular interest because cyanocarbons are known to be abundant in the interstellar medium (ISM) and in the atmosphere of Titan. It is possible that mixtures of acetylenes and cyano-acetylenes can dimerize to give various derivatives of cyanocyclobutadienes. This system has been studied computationally at various levels of theory to determine the effects of increasing number of cyano-substituents on the energy of the ring as well as on the singlet-triplet gaps. Cyanocyclobutadienes are also being sought through the use of matrix isolation. Diazotetracyanocyclopentadiene (**7**) is a potential precursor for tetracyanocyclobutadiene (**8**) and 2-oxo-2*H*-pyran-5-carbonitrile (**9**) is a promising precursor for monocyanocyclobutadiene (**10**).