

"Thermal Decomposition of a Series of 1,2-Diazetines." Breton, Gary W., and John H. Shugart. *Journal of Organic Chemistry*, 2003, 68: 8643-8649.

Abstract: A homologous series of tricyclic diazetines (**6a--c**), differing by the number of methylene groups in the saturated bridges of the fused carbon bicycles, was synthesized. The ΔH^\ddagger of decomposition for each of the diazetines to afford N_2 and the corresponding alkene was determined experimentally: **6a**, 31.7; **6b**, 39.3; **6c**, 38.8 kcal/mol. The ground-state strain energy of each diazetine was estimated utilizing computationally obtained ΔH_f^\ddagger 's for each of the experimentally investigated diazetines as well as several other diazetines whose ΔH_f^\ddagger 's had been previously reported in the literature. The sum of the ground-state strain energies and ΔH^\ddagger 's of decomposition for all of the diazetines was nearly constant, with an average value of 59 kcal/mol, suggesting that all the diazetines decompose via the same mechanism. Generally, the higher the ground-state strain energy of the diazetine, the less the ΔH^\ddagger for decomposition. The decomposition transition states for **6a--c** and **7** were modeled computationally at the RB3LYP/6-311+G(3df,2p)//UB3LYP/6-31+G(d,p) level. The agreement of the experimentally determined ΔH^\ddagger values with transition-state energies obtained computationally supports the reaction mechanism originally proposed by Yamabe that the elimination process occurs by an unsymmetrical, yet concerted, transition state with strong biradical character.