

"Synthesis of a Stereochemically Defined 1,2-Diazetine N,N¹-Dioxide and a Study of Its Thermal Decomposition." Breton, Gary W., Lindsey H. Oliver, and Justine E. Nickerson. *Journal of Organic Chemistry*, 2007. 72: 1412-1416.

Abstract: Diazetine dioxide **1a** has been synthesized in a single step via oxidation of *meso*-2,3-diphenyl-1,2-ethanediamine with dimethyldioxirane, albeit in low yield (7%). Thermal decomposition of **1a** afforded predominantly either *trans*-stilbene or diphenyl glyoxime depending on solvent, temperature, and the presence of an amine catalyst. Reaction in chloroform at 69 °C favored elimination of NO and formation of *trans*-stilbene. The stereospecific formation of *trans*-stilbene suggests a mechanism of decomposition in which C – N bond cleavage leads to a diradical intermediate stabilized by the phenyl group. Bond rotation followed by cleavage of the second C – N bond accounts for the *trans*-stilbene. At 25 °C in chloroform, while *trans*-stilbene was still the major product, some diphenyl glyoxime was also observed (4% yield). However, **1a** as a solution in chloroform in the presence of Et₃N, or **1a** as a solution in DMSO-*d*₆, afforded predominantly diphenyl glyoxime. These results are interpreted in terms of two closely competing reactions subject to the effects of entropic contributions.