

Photochemical and Thermal Reactions of Intermediates in the Phenylnitrene Rearrangement Inside a Hemicarcerand

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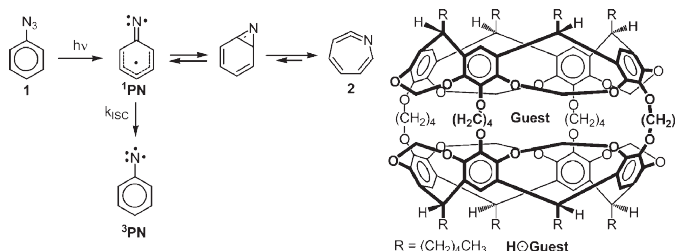
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Abstract: Broadband irradiation ($\lambda > 320$ nm) of hemicarceplex **H**⊙**1** between -74 °C and -84 °C, produces encapsulated didehydroazepine (**2**), triplet phenylnitrene (3 PN), 2-azabicyclo[3.2.0]hepta-1,3,6-triene (**6**), and 4-azaspiro[2.4]hepta-1,4,6-triene (**7**). The highly strained anti-Bredt imine **6** is formed from **2** via a photochemical four-electron electrocyclicization. Under the irradiation conditions, **6** rearranges further to azaspiroene **7**. In addition, **6** thermally rearranges to **7** via a 1,5-sigmatropic shift ($\Delta G_{267K}^\ddagger = 20.0 \pm 0.5$ kcal/mol), yielding a final equilibrium composed of $[7]/[6] = 5$ at room temperature. The observation of a photochemical rearrangement of **2** to **6** contrasts earlier results of narrow band irradiations ($\lambda = 334$ nm) of matrix-isolated **2**, which gave 3 PN (Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879–5881). Encapsulated 3 PN is remarkably stable due to the prevention of its dimerization by the surrounding hemicarcerand. Above 255 K, it slowly decays with a rate constant $k = 10^{7.7 \pm 0.4} \text{ s}^{-1} \times \exp \{-(13300 \pm 500 \text{ cal/mol})/RT\}$. The isolation of substantial amounts of a hemicarcerand lacking one acetal spanner suggests that 3 PN decays preferentially by inserting into an inward-pointing acetal C–H bond of **H**.

Introduction

Aryl azides have important applications in photolithography, polymer chemistry, and photoaffinity labeling of biomolecules.¹ Photolysis of the parent phenyl azide (**1**) produces singlet phenylnitrene (1 PN). Above 165 K, 1 PN ring-expands to didehydroazepine (**2**).² At lower temperature, 1 PN preferentially intersystem crosses to triplet phenylnitrene (3 PN) (Scheme 1). Much of our knowledge about the mechanistic details of the phenylnitrene rearrangement and about the properties and

Scheme 1. Photochemistry of Phenylazide



reactivities of participating intermediates has come from matrix isolation studies,^{3–8} time-resolved spectroscopy,^{9–14} and high level ab initio calculations.^{15,16}

Recently, synthetic host molecules have been applied to investigate arylnitrene rearrangements and their intermediates.^{17–19} Bucher et al. incorporated an aryl azide unit into the molecular

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