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The Phenylnitrene Rearrangement in the Inner Phase of a Hemicarcerand

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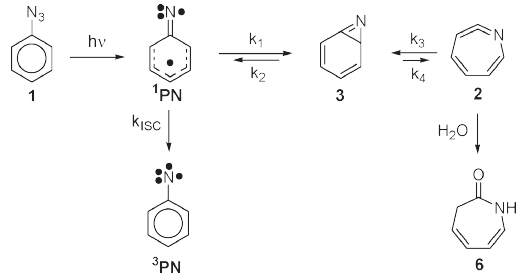
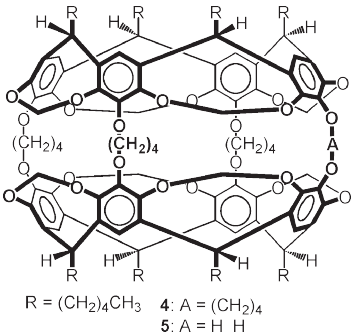
The photolysis of aryl azides has found important applications in lithography, polymer chemistry, and affinity labeling of biomolecules.[1] UV irradition of phenyl azide (**1**) yields singlet phenylnitrene (**^{1}PN**), which above 165 K rapidly ring-expands to 1-azacyclohepta-1,2,4,6-tetraene **2**.[2,3] Below 165 K, intersystem crossing (ISC) to triplet phenylnitrene (**^{3}PN**) dominates. The characterization of intermediates on the C_6H_5N potential energy surface and the mechanism of their interconversion have created great challenges for experimentalists and theoreticians.[2] Spectroscopic evidence exists for **^{1}PN**,[3] **^{3}PN**,[4−6] and **2**.[7−9] Secured also are the singlet−triplet gap E_{ST},[10,11] ISC rate constant k_{ISC},[3b] and ring-expansion barrier of **^{1}PN**.[3b] Missing are spectroscopic evidence for benzazirine (**3**)[12−14] and the barrier of the **2**-to-**^{1}PN** rearrangement,[15] which combined with the known ring-expansion barrier[3b] would provide the energy difference between **2** and **^{1}PN**, which is difficult to calculate accurately.[14,15] This barrier can be obtained from the lifetime of **2**, if bimolecular decay pathways (polymerization or addition to **1**) are excluded, e.g. at low concentration. Under these conditions, the room-temperature ring-contraction rate of the parent,[8] and the ring-contraction barrier of 5-methyl-substituted **2** have been measured.[16]



Encapsulation provides an alternative approach, which we and others have used to prevent bimolecular reactions of strained intermediates allowing for their NMR spectroscopic observation and quantification of their intramolecular rearrangements.[17] The successful investigation of arylcarbenes inside hemicarcerands suggested to us that similar experiments could be possible for **^{1}PN**.[17d,e] Here, we report the successful ring expansion of **^{1}PN** inside hemicarcerand **4**,[18] the first NMR spectroscopic characterization of **2** and the barrier for its rearrangement to **^{1}PN**.



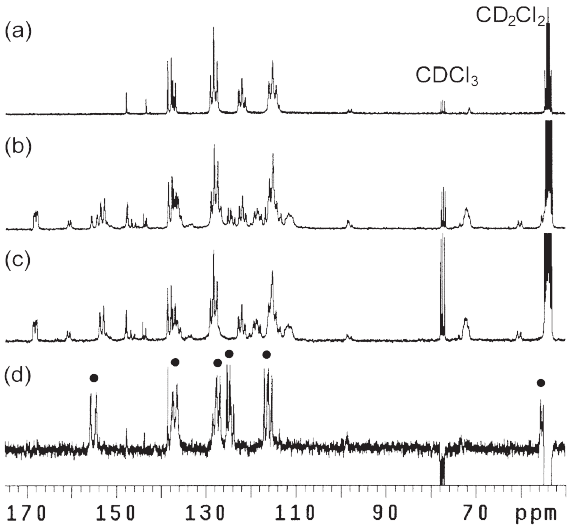


Figure 1. Partial ^{13}C NMR spectra of **4**⊙$^{13}C_6$-**1** (75 MHz; degassed $CD_2Cl_2/CDCl_3$ 6:1; −86 °C). (a) Before, (b) immediately, and (c) 5 h after photolysis (>320 nm; 12 min; −82 to −83 °C; 50% conv.). (d) Difference spectrum (b−c). ^{13}C-Signals of incarcerated $^{13}C_6$-**2** are marked (●).

We incarcerated **1** and fully ^{13}C-labeled $^{13}C_6$-**1** inside **4** by reacting **5** with butane-1,4-dimesylate, Cs_2CO_3, and excess **1** or $^{13}C_6$-**1** in HMPA for 3 days (91% and 70% yield, respectively). Brief irradiation of **4**⊙**1** in Ar-saturated CH_2Cl_2 at 194.4 K yielded a new compound with a characteristic IR absorption at 1886 cm^{-1}, which shifts to 1830 cm^{-1} if **4**⊙$^{13}C_6$-**1** is irradiated.[19] We assigned the new compound to hemicarceplex **4**⊙**2** and the band at 1886 cm^{-1} to the ketenimine stretch of **2** based on the similar frequency of free **2** (1895 cm^{-1}, Ar, 10 K;[7] 1887 cm^{-1}, heptane, 295 K[8]), the isotopic shift,[19] and the thermal instability of this compound, whose lifetime is 32 min at 194.4 K.[20] Furthermore, photolysis of **4**⊙**1** in degassed THF/H_2O (8:1) at −78 °C gave the H_2O-trapping product **4**⊙**6** (20% yield).[21]

The low-temperature ^{13}C NMR spectrum of a photolyzed solution of **4**⊙$^{13}C_6$-**1** revealed at least three photoproducts together with unphotolyzed **4**⊙$^{13}C_6$-**1** (50%). Only one product (formed in 18% yield) decayed within 5 h at −86 °C and was assigned to **4**⊙$^{13}C_6$-**2**. A difference spectrum shows the six multiplets of incarcerated $^{13}C_6$-**2** (Figure 1d). From a ^{1}H-coupled ^{13}C NMR spectrum we assigned the doublet at δ 155.2 to the quaternary carbon of $^{13}C_6$-**2**. The direct J-coupling constants $^1J_{CC}$ allowed assignment of the remaining multiplets and were found to be consistent with the bond order alteration and carbon hybridization in **2**. Furthermore, the guest's ^{13}C chemical shifts, δ_{corr}, after correction for the effect of **4** by adding the host-induced upfield shift of benzene, $\Delta\delta$ = 1.3 ppm,[17b] compare very well with those calculated by the DFT approach, leaving no doubt that the new hemicarceplex is **4**⊙$^{13}C_6$-**2** (Table 1).[22]

The other two products are secondary photoproducts formed on irradiation of $^{13}C_6$-**2**.[7] Elucidation of their structures is in progress.

Low-temperature ^{1}H NMR spectroscopy (degassed CD_2Cl_2; 191 K) allowed us to identify only one proton of **2**, which gives rise to

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