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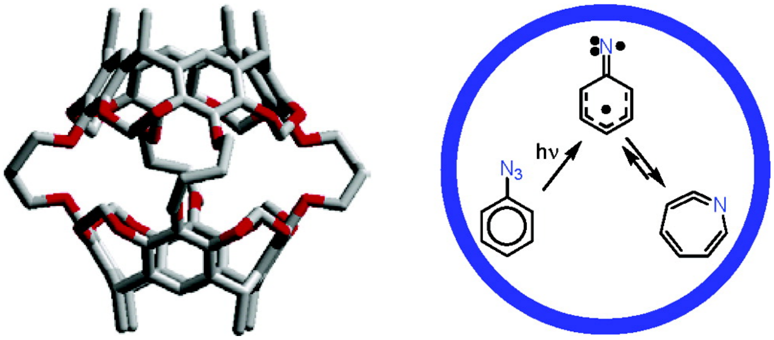

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# The Phenylnitrene Rearrangement in the Inner Phase of a Hemicarcerand

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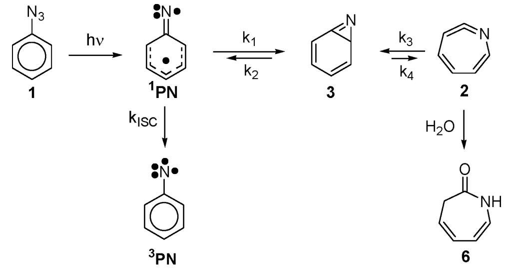
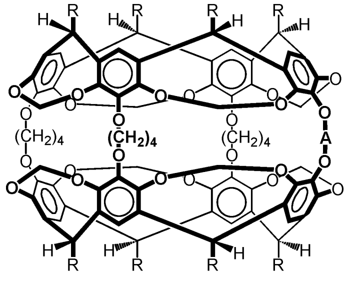
The photolysis of aryl azides has found important applications in lithography, polymer chemistry, and affinity labeling of biomolecules.[1] UV irradition of phenyl azide (**1**) yields singlet phenylnitrene ($^1$**PN**), which above 165 K rapidly ring-expands to 1-azacyclohepta-1,2,4,6-tetraene **2**.[2,3] 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**.



R = (CH$_2$)$_4$CH$_3$ **4**: A = (CH$_2$)$_4$
**5**: A = H H

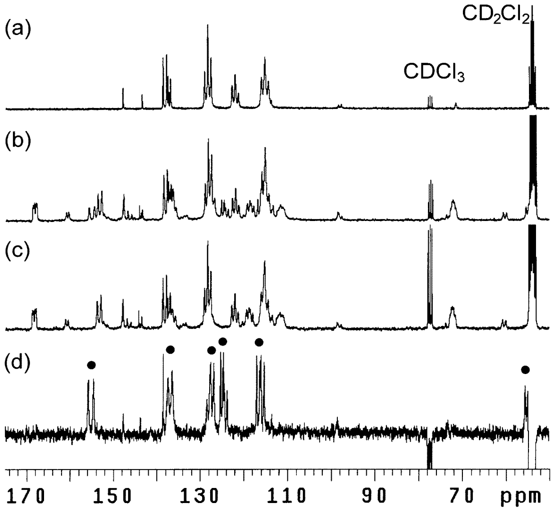


***Figure 1.*** Partial $^{13}$C NMR spectra of **4**$\odot^{13}C_6$-**1** (75 MHz; degassed $CD_2Cl_2/CDCl_3$ 6:1; −86 °C). (a) Before, (b) immediately, and (c) 5 h after photolysis (>320 nm; 12 min; −82 to −83 °C; 50% conv.). (d) Difference spectrum (b−c). $^{13}$C-Signals of incarcerated $^{13}C_6$-**2** 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**$\odot^{13}C_6$-**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**$\odot^{13}C_6$-**1** revealed at least three photoproducts together with unphotolyzed **4**$\odot^{13}C_6$-**1** (50%). Only one product (formed in 18% yield) decayed within 5 h at −86 °C and was assigned to **4**$\odot^{13}C_6$-**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 $\delta$ 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, $\delta_{corr}$, 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**$\odot^{13}C_6$-**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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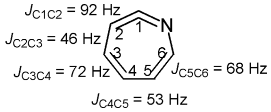
*Table 1.* $^{13}$C Chemical Shifts of **2**



| carbon | $\delta_{exp}$ | $\delta_{corr}$[a] | $\delta_{calc}$[b] | $\Delta\delta$[c] |
|---|---|---|---|---|
| 1 | 155.2 | 156.5 | 153.4 | −3.1 |
| 2 | 54.7 | 56 | 55.3 | −0.7 |
| 3 | 124.6 | 125.9 | 127 | 1.1 |
| 4 | 127.7 | 129 | 132.5 | 3.5 |
| 5 | 116.2 | 117.5 | 120.1 | 2.6 |
| 6 | 137 | 138.3 | 141.7 | 3.4 |

[a] $\delta_{corr} = \delta_{exp} - [\delta_{benzene}(\text{free}) - \delta_{benzene}(\text{incarcerated})]$.[17b] [b] GIAO shielding tensors (PBE1PBE/6-311G++(2d,2p)//6-311G*) relative to TMS.[22] [c] $\Delta\delta = \delta_{calc} - \delta_{corr}$.

a broad triplet at $\delta$ 3.02 ppm (see Supporting Information). This signal decayed with a rate constant $k_{obs} = 3.2 \times 10^{-4}$ s$^{-1}$, identical to $k_{obs}$ measured by FT-IR. The remaining guest signals were covered by host signals.

From the decay of the characteristic ketenimine stretch of incarcerated **2**, we determined the rate constant $k_{obs}$ for the thermal decomposition of **2** between 198.3 and 174.3 K. To calculate the *effective* ring-contraction rate constant $k' = k_2k_3/k_4$ from $k_{obs}$, we made the following assumptions: (1) **2** does not react with **4**. (2) $^{\mathbf{1}}$**PN** does not react with **4** within its lifetime but rather ring-expands to **2** or irreversibly intersystem crosses to $^{\mathbf{3}}$**PN**. $^{\mathbf{3}}$**PN** subsequently reacts with **4** at a rate much faster than it is formed as supported by our NMR experiments. (3) The ring-expansion rate constant $k_1$ and intersystem-crossing rate constant $k_{ISC}$ of **2** in the inner phase of **4** are identical to those measured in pentane.[3b] The following observations suggest the reasonability of these assumptions. (a) We are able to ring-expand $^{\mathbf{1}}$**PN** in the inner phase of **4**. If **4** had been a powerful "trapping reagent" for $^{\mathbf{1}}$**PN**, we would have never observed **2**.[18] (b) When we photolyzed **4**⊙**2** in degassed $CD_2Cl_2$ at −82 ± 0.5 °C for 8 min (37% conv.), the low-temperature $^1$H NMR showed 59% ring expansion of $^{\mathbf{1}}$**PN**. From $k_{ISC}$ and $k_1$ in pentane,[3b] we calculate 61%. The almost identical yields in both phases are strong support for our assumptions.

It is interesting to note that ring expansion of an arylnitrene, which was covalently fixed to the cavity of a calix[6]arene-based reaction bowl, failed and instead led to its addition to an aryl unit of the calix[6]arene.[18b] We suggest that the loss of rotational degrees of freedom raises the activation barrier for a similar addition of incarcerated $^{\mathbf{1}}$**PN** such that ring expansion and ISC become the only reaction channels.[17c]

Under the above assumptions, $k'$ is given by eq 1:[23]

$$k' = k_{obs} + k_{obs}k_1/k_{ISC} \qquad (1)$$

An Arrhenius plot provided $E_a = 12.3 \pm 0.6$ kcal mol$^{-1}$ and log $A = 11.0 \pm 0.7$ (Figure 2). These activation parameters might change slightly, if experimental $k_{ISC}$ and $k_1$ in the inner phase of **4** will become available. Nevertheless, $E_a$ is in very good agreement with the most recent ab initio calculations, which predict $E_a = 10.8$ kcal mol$^{-1}$ (CASPT2N/6-311G(2d,p))[14a] and 14.7 kcal mol$^{-1}$ (B3LYP/6-311+G(2d,p))[14b] Considering the tendency of CASPT2N to overestimate the stability of open-shell relative to closed-shell electronic states, the CASPT2N and measured barriers are also in the correct order.[14a]

In summary, we have demonstrated that singlet phenylnitrene thermally ring-expands in the inner phase of a hemicarcerand to the cyclic ketenimine **2**, whose polymerization is prevented by the surrounding host. This allowed us to measure the activation parameters for the ring contraction of **2**, which complements earlier LFP studies.[3,8] The successful inner-phase ring expansion of $^{\mathbf{1}}$**PN** and the fact that photolysis of **4**⊙**1** at 77 K yields small amounts of **4**⊙**2**[7,9] suggest that many other substituted arylnitrenes can be ring-expanded inside suitable hemicarcerands, limited only by the ability to incarcerate the corresponding azides. An even better understanding of this important rearrangement can be expected from such studies.

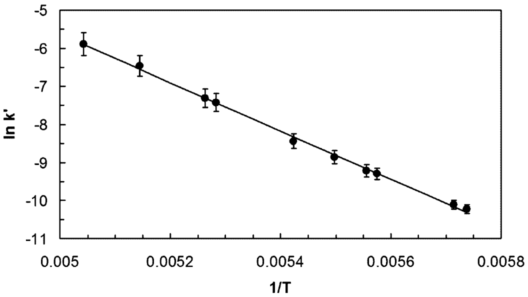


*Figure 2.* Arrhenius plot for the 1-azacyclohepta-1,2,4,6-tetraene to singlet phenylnitrene rearrangement inside hemicarcerand **4**.

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**Supporting Information Available:** Experimental procedures, compound characterization, FT-IR and $^1$H NMR spectra of photolyzed solutions of **4**⊙**1**, rate constants $k_{obs}$, derivation of eq 1, and computed IR stretches of **2** and $^{13}C_6$-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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