Evidence for Stepwise Nitrogen Extrusion and Ring Expansion upon Photolysis of Phenyl Azide

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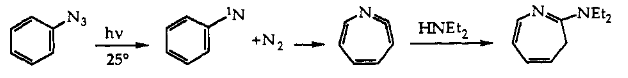
Abstract: The temperature dependence of the products formed on photolysis of two independent precursors of phenylnitrene has been studied. The identity of the product-forming intermediates (triplet phenylnitrene versus ketene imine) produced on photolysis of phenyl azide and benzenesulfoximine in the presence of diethylamine show the same qualitative variation with temperature. An excited state of the nitrene precursor is not responsible for the known temperature dependence of the distribution of stable products. The data are consistent with stepwise formation of singlet phenylnitrene and subsequent expansion to azacycloheptatetraene. The singlet and triplet energies of phenyl azide have been determined by energy transfer.

Introduction

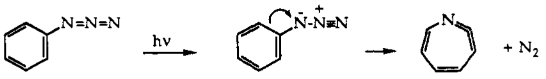
It is impossible to trap singlet phenylnitrene (**2S**) with an external reagent in appreciable yields upon photolysis of phenyl azide (**1**) at ambient temperature.[1] It is clear that the *trappable* species produced upon photolysis of **1** at 25 °C is didehydroazepine (**3**). In the presence of amines, ketene imine **3** is intercepted to produce azepine **4**.[2] In the absence of an amine trap, ketene imine **3** polymerizes or reacts with azide **1** to form a black tar. Unfortunately, the yields of volatile products which can be obtained on decomposition of phenyl azide are generally poor.[3] Upon photolysis of **1** at high dilution in an inert solvent, a species is generated which slowly (hours) forms azobenzene.[4] However, the mechanistic details of this transformation are not known with certainty.

Thus, one can ask the question of whether singlet nitrene **2S** is a precursor to **3**



1 **2S** **3** **4**

or whether nitrogen extrusion and ring expansion are concerted processes.



1 **^{1}1*** **3**

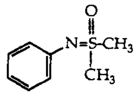
Consideration of the latter mechanism is stimulated by reports of carbon and hydrogen migration concerted with nitrogen extrusion in the photochemistry of diazirines and diazo compounds[5] and by the inability to chemically intercept singlet phenylnitrene in better than trivial yields or to spectroscopically observe singlet phenylnitrene.[1]

It is clear that photolysis of aryl azides substituted with electron-withdrawing groups must produce singlet nitrenes because they are trapped with amines to form hydrazines.[1]

In 1986, we reported that the photochemistry of phenyl azide in the presence of diethylamine is temperature dependent.[6] We proposed the mechanism of Scheme I to explain the available chemical and spectroscopic data. Singlet phenylnitrene was identified as the temperature-dependent branching point. A differential activation barrier to ring expansion and intersystem crossing (ISC) of 3 ± 1 kcal/mol was deduced.

Another mechanistic possibility is depicted in Scheme II. In this scenario, the excited singlet state of phenyl azide is proposed to be the temperature-dependent branching point. Ring expansion and nitrogen extrusion are concerted, and singlet phenylnitrene is never generated and thus can not be trapped.

To distinguish these possibilities, we have studied the temperature-dependent photochemistry of a second nitrene precursor, sulfoximine **6**,[7] in the presence of amine.



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Scheme I predicts that the isokinetic temperature will remain at ~150–160 K whereas Scheme II predicts that this temperature will vary with precursor. The results are consistent with the mechanism of Scheme I.

Results

Temperature-Dependent Photochemistry. Sulfoximine **6** absorbs strongly below 300 nm (λ_{max} = 210, 224, 242, and 278 nm in CH_2Cl_2) with a tailing absorption which extends to 330 nm. It is possible to excite **6** in CH_2Cl_2 with a 308-nm laser pulse. Laser flash photolysis (LFP) of **6** produces the transient spectrum of ketene imine **3** in CH_2Cl_2 at ambient temperature. The

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(1) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, *17*, 69.

(2) Doering, W. von E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.

(3) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092.

(4) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228.

(5) (a) Eaton, P. E.; Hoffmann, K. L. *J. Am. Chem. Soc.* **1987**, *109*, 5825. (b) Eaton, P. E.; Appell, R. B. *J. Am. Chem. Soc.* **1990**, *112*, 4053. (c) Chen, N.; Jones, M. B., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305. (d) Chen, N.; Jones, M. B., Jr. *Tetrahedron Lett.* **1989**, *30*, 6969. (e) Chen, N.; Jones, M. B., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981. (f) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (g) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (h) Kirmse, W.; Buschoff, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 692. (i) Frey, H. M.; Scaplehorn, W. *J. Chem. Soc. A* **1966**, 968. (j) Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (k) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 1700. (l) Figuera, J. M.; Perez, J. M.; Tobar, A. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 809. (m) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512. (n) Frey, H. M. *Adv. Photochem.* **1966**, *4*, 225. (o) White, W. R., III; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841.

(6) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *100*, 3783.

(7) Heintzelman, R. W.; Baily, R. B. *J. Org. Chem.* **1976**, *41*, 2207.

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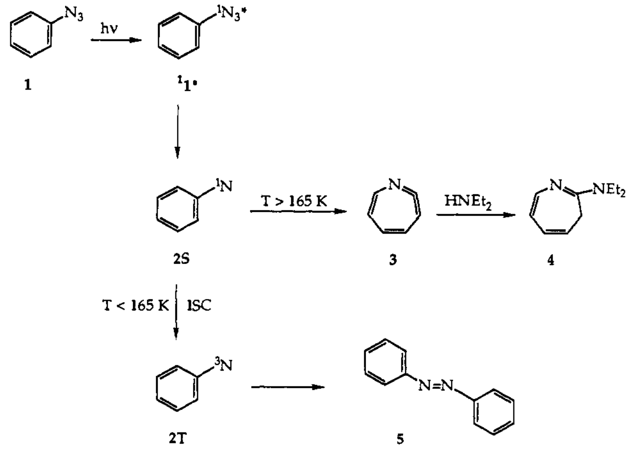
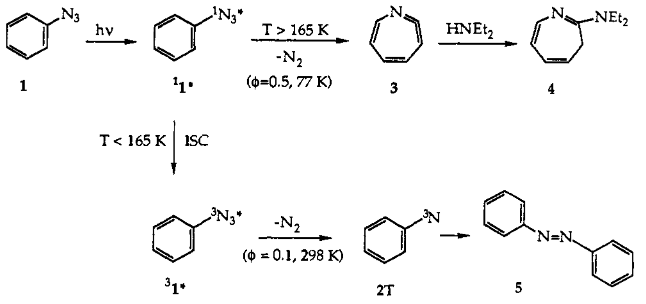
Scheme I



Scheme II



transient spectrum produced by LFP of **6** is identical to that obtained by LFP of phenyl azide under the same conditions. No fluorescence of **6** was observed at ambient temperature. Exposure of **6**, immobilized in a rigid glass at 77 K, to unfiltered UV light produces triplet phenylnitrene which is detected by its characteristic triplet EPR spectrum. Thus, the temperature-dependent photochemistry of **6** and phenyl azide, in regard to the direct detection of intermediates, is identical.

Photolysis of either azide **1** or sulfoximine **6** in 2-methyltetrahydrofuran (2MTHF) containing 1.0 M diethylamine (DEA) leads to the consumption of **1** or **6** and the formation of azepine **4** and azobenzene (**5**).

The material balances obtained in these photolyses show wide variation. It is common to find poor material balances upon decomposition of phenyl azide.[1] With phenyl azide, the material balance is poor at 193 K and improves substantially upon cooling to 165–175 K. Unfortunately, the polymerization of phenyl azide is easily initiated by reactive intermediates generated upon decomposition of phenyl azide.[3] Ketene imine **3** reacts rapidly with phenyl azide at room temperature.[3] We speculate that the reaction of **3** with phenyl azide slows at low temperatures which allows for more efficient trapping of the ketene imine with diethylamine at 165 and 175 K.

The distribution of products is given as a function of temperature in Table I. At temperatures above 175 K, trapping of ketene imine **3**, which produces azepine **4**, predominates with both precursors. Below 153 K, however, azobenzene (**5**), a product derived from dimerization of triplet phenylnitrene, is the only volatile product detected with either precursor. Thus, the temperature at which the nature of the trappable intermediate changes from ketene imine to triplet phenylnitrene is the same for both precursors.

The material balance obtained when triplet phenylnitrene is the product-forming intermediate derived from phenyl azide ($T \leq 153$ K), again, is fairly low. This may be due to diversion of triplet phenylnitrene to aniline or by reaction of the triplet nitrene with precursor.

Table I. Distribution of Stable Products Formed upon Photolysis of Nitrene/Ketene Imine Precursors in the Presence of 1.0 M Diethylamine in 2MTHF[a]

precursor	T (K)	additive	**4**	**5**
1	193	none	29	4
1	193	1.0, M isoprene	27	4
1	175	none	81	11
1	175	1.0, M hexatriene	74	6
1	165	none	43	18
1	165	1.0, M hexatriene	65	8
1	153	none	3	34
1	153	1.0, M isoprene	3	37
1	150	none	4	22
1	150	1.0, M hexatriene	7	22
1	100	none	trace	16
1	100	1.0, M hexatrene	trace	13
6	175	none	16	trace
6	175	1.0, M hexatriene	15	0
6	165	none	4	24
6	165	1.0, M hexatriene	8	13
6	150	none	trace	19
6	150	1.0, M hexatriene	trace	20
6	100	none	0	26

[a] All yields are absolute and are ±5%, based on the disappearance of precursor; all temperatures are ±2 K.

Effect of Isoprene and Hexatriene. The hypothetical mechanism of Scheme II predicts that triplet phenyl azide (^{3}**1**) is formed on direct photolysis of **1** at subambient temperatures. To test this possibility, the temperature-dependent photochemistry of **1** was examined in the presence of both diethylamine and either isoprene or hexatriene. We reasoned that if ^{3}**1*** was formed, it would be quenched immediately by isoprene or hexatriene and the yield of azobenzene (**5**) would be suppressed.

However, as shown in Table I, neither isoprene nor hexatriene quenches the yield of azobenzene in the critical temperature regime below 153 K. One could argue that the failure of isoprene and hexatriene to quench putative triplet phenyl azide is the result of a medium with very high viscosity and low diffusion rates. However, it is important to note that the solvent is still fluid in the critical temperature region between 150 and 175 K. The change in the distribution of products is not due to a change in phase from a fluid liquid to a rigid glass. Greenspan and Fischer[8] have measured the viscosity of 2MTHF as a function of temperature. The viscosity of 2-methyltetrahydrofuran (2MTHF) increases rapidly as the glass is cooled from 95 to 113 K. At the highest temperature of their study (113 K), the viscosity η of 2MTHF was 10^{-6} poise and $k_{\mathrm{DIFF}} = 6 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. Thus, at the higher temperatures utilized in this work, k_{DIFF} will be $\gg 10^6\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and sufficient for 1 M polyene to efficiently quench higher energy triplet-state species if energy transfer is favorable.

One could also argue that polyene fails to quench triplet phenyl azide because the azide has a triplet energy significantly below that of isoprene[9] (E_T = 60.1 kcal/mol) and hexatriene[9] (E_T = 49 kcal/mol).

This possibility appears unlikely, however, because Lewis and Saunders[9] and Leyshon and Reiser[10] in separate experiments found that the triplet energy of phenyl azide is about 75 kcal/mol. These studies relied on the variation of the quantum yield to decomposition of phenyl azide upon triplet sensitization. To verify their conclusions, we remeasured the triplet energy of phenyl azide by standard laser flash photolysis techniques.

A series of triplet states[11] of known energies was produced by LFP of the appropriate aromatic substrate in benzene. The triplet states were detected in absorption and their lifetimes measured.

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[8] Greenspan, H.; Fischer, E. *J. Phys. Chem.* **1965**, *69*, 2466.

[9] Lewis, F. D.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 7033.

[10] Leyshon, L. J.; Reiser, A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1918.

[11] (a) Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973. (b) Malkin, J. *Photophysical and Photochemical Properties of Aromatic Compounds*; CRC Press: Boca Raton, FL 1992.

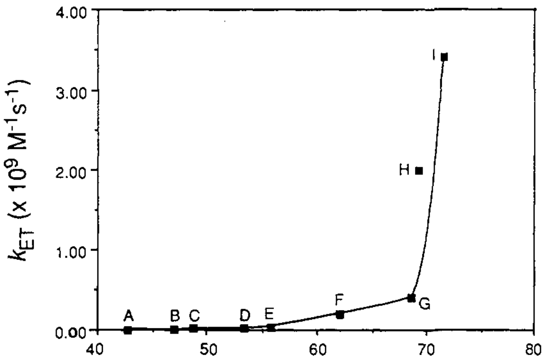


Figure 1. Plot of k_{ET} versus E_T for the quenching of triplet-state absorptions with phenyl azide. E_T values are taken from refs 11a and 11b: (A) anthracene; (B) benzanthrone; (C) pyrene; (D) fluorenone; (E) coronene; (F) phenanthrene; (G) benzophenone, this work; (H) benzophenone, ref 4; (I) 4-methoxyacetophenone.

Table II. Stern–Volmer Quenching of Fluorescence by Phenyl Azide in Benzene at Ambient Temperature

donor	E_S[11a] (kcal/mol)	$k_q\tau$	τ[11b] (ns)	k_q ($\times 10^9$ M^{-1} s^{-1})
perylene	65.8	4.92	4.8	1.03
9,10-dimethylanthracene	71.8	69.08	13.5	5.12
anthracene	76.3	23.69	4.1	5.78
phenanthrene	82.8	465.8	60	7.76
naphthalene	92	871.3	96	9.08
fluorene	94.9	82.84	10	8.28

The absolute rate constant of reaction of the triplet states with phenyl azide was determined by standard methods[12] by noting the decrease in triplet-state lifetime with increasing concentration of phenyl azide. No transient absorption attributable to triplet phenyl azide was observed in these experiments.

A plot of the rate constant of energy transfer k_{ET} versus triplet energy E_T is given in Figure 1. It is clear that the triplet energy of phenyl azide is $\sim$70 kcal/mol, in good agreement with the earlier studies and far above that of isoprene and hexatriene. Thus, any triplet phenyl azide formed upon direct photolysis will be quenched by the diene and triene. Thus, we conclude that triplet phenyl azide is not formed appreciably upon direct photolysis of phenyl azide at low temperature and that Scheme II is invalid. The mechanism of Scheme II can only be valid if the lifetime of triplet phenyl azide is so short at low temperature that it can not be quenched by energy transfer.

For the sake of completeness, the singlet energy of phenyl azide was determined via the quenching of the fluorescence of various aromatic energy donors. Stern–Volmer plots were linear and yielded the $k_q\tau$ values given in Table II.

A plot of k_{ET} versus E_S is given in Figure 2; the singlet energy of phenyl azide is $\sim$83 kcal/mol. The variation of k_{ET} with E_S is smaller than that observed by Lewis and Dalton[13] with hexyl azide. Perhaps there is a contribution of electron transfer to the overall rate of quenching of phenyl azide with polycyclic aromatic hydrocarbons.

Discussion

The data of Table I demonstrate that, barring an unlikely coincidence, the temperature-dependent branching point observed on photolysis of phenyl azide can not be an excited state of the precursor. Thus, the mechanism of Scheme II is excluded. The temperature-dependent branching point in the photolysis of azide **1** or sulfoximine **6** is C_6H_5N, either singlet or triplet phenylnitrene (**2S** or **2T**, respectively), or ketene imine **3**. Triplet nitrene **2T** is quickly dismissed as a candidate because when it is generated directly by photosensitization, in the presence of amine, it does not produce ketene imine-derived product[4] (e.g., **4**, Scheme III) nor does it produce ketene imine-derived polymer in the absence of amine.[14]

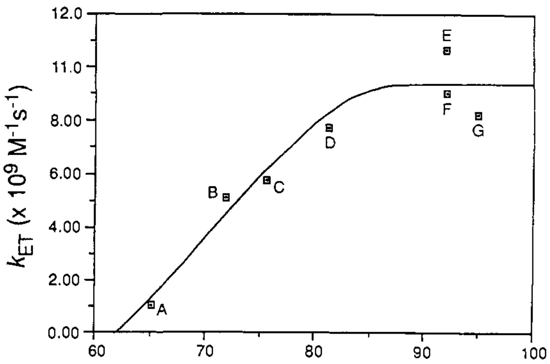
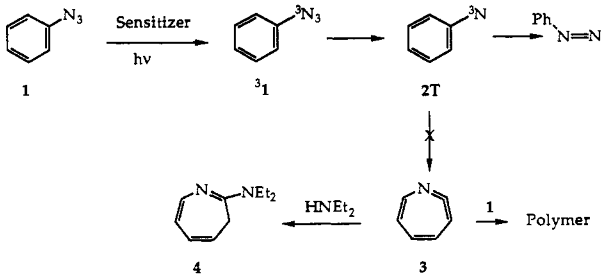
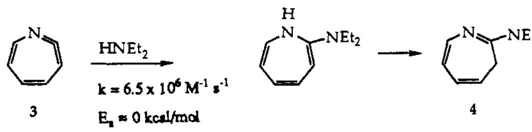


Figure 2. Plot of k_{ET} versus E_S determined by Stern–Volmer analysis of the quenching of fluorescence of singlet energy donors. E_S values are taken from refs 11a and 11b: (A) perylene; (B) 9,10-dimethylanthracene; (C) anthracene; (D) phenanthrene; (E) naphthalene, uncorrected; (F) naphthalene, corrected for the competitive absorption of phenyl azide at the excitation wavelength; (G) fluorene.

Scheme III



Ketene imine **3** can also be excluded as the branching point (Scheme IV). While it is true that azobenzene is formed at long times (hours) *after* photolysis of highly dilute solutions of phenyl azide in *inert* solvents, it is not clear that **2T** is in any way involved in this transformation. In amine-containing solutions, the lifetime of **3** is very short (microseconds) at ambient temperature and triplet nitrene reaction products are not formed. The amine-trapping reaction rate constant does not decrease with temperature[6,15] (E_a = 0 kcal/mol). Thus, **3** will still be scavenged rapidly (microseconds) at low temperature in the presence of 1.0 M amine and will not have the time (hours) necessary to relax to triplet phenylnitrene.



The most economical interpretation of the data remains that of Scheme I, that singlet phenylnitrene is the temperature-dependent branching point and that the photochemical conversion of phenyl azide to ketene imine **3** is a stepwise process.

With hindsight, it is clear that azide excited states are unlikely candidates for the temperature-dependent product distribution. The product data requires that the branching intermediate must surmount a barrier[6] of at least 2–4 kcal/mol to ultimately form

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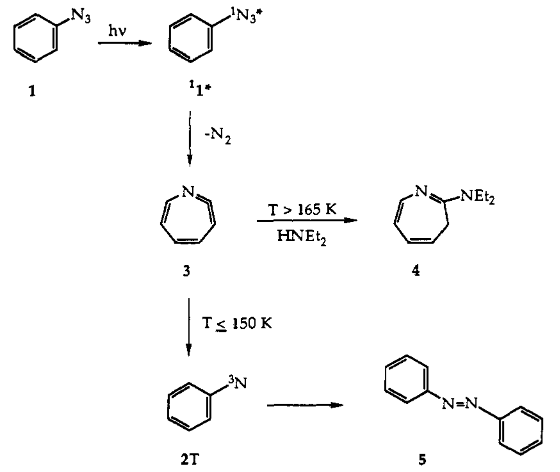
[12] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; Chapter 6.

[13] Lewis, F.; Dalton, C. *J. Am. Chem. Soc.* **1969**, *91*, 5260.

[14] Reiser, A.; Leyshon, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 4051.

[15] DeGraff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7491.

Scheme IV



3. Singlet phenyl azide decomposes with a quantum yield of 0.5 at both 77 and 298 K.[16] The decay of the excited state of singlet phenyl azide does not surmount an enthalpic barrier; thus, it can not be the temperature-dependent branching point.

If triplet phenyl azide was indeed formed at low temperature, as required by Scheme II, it might be possible to detect this species by either EPR or phosphorescence spectroscopy. However, there is no evidence for the formation of ^{3}**1*** upon direct photolysis of phenyl azide at 77 K.[1] Apparently, the high quantum efficiency of nitrogen extrusion in ^{1}**1** ($\phi \approx 0.5$, 77 and 298 K)[16] precludes either fluorescence or intersystem crossing in this excited state, or triplet phenyl azide is too short lived, even at 77 K, to permit its detection.

It is important to note that the lack of concert of nitrogen extrusion and bond migration in phenyl azide does not demonstrate generality. These results should not be taken as evidence that concerted mechanisms are not present in alkyl or even other aryl azides.

Conclusion

The identity of product-forming intermediates (ketene imine versus triplet phenylnitrene) produced on photolysis of two independent precursors to C_6H_5N as a function of temperature is identical. The results demonstrate that photochemical conversion of phenyl azide to 1,2,3,6-azacycloheptatetraene proceeds in steps via singlet phenylnitrene. Light-induced nitrogen extrusion and bond migration in phenyl azide are not concerted. The triplet energy of phenyl azide is ~70 kcal/mol, and the singlet state of **1** is ~83 kcal/mol above the ground state.

Experimental Section

2-Methyltetrahydrofuran was distilled over sodium, and diethylamine was distilled over BaO before use. Hexatriene (Aldrich) was passed through either an alumina or a silica gel column and used immediately.

Gas chromatographic analyses were performed on a Perkin-Elmer 8500 capillary gas chromatograph equipped with a split/splitless injector, a flame ionization detector, and a 30-m × 0.254-mm L&W Scientific fused silica capillary column (5% DB-1701, 0.25 mm). The yields of products were determined by using an internal standard (1-chloronaphthalene). Response factors were determined by injecting calibrated mixtures of standard and reaction products.

Samples for product studies were prepared in 5-mm Pyrex tubes. The solutions were then degassed using two to three freeze–pump–thaw cycles and then sealed under vacuum.

Photolyses were performed in an Oxford cryostat using a water- and Pyrex-filtered output of a 150-W Xe–Hg arc lamp.

In the LFP experiment, a Lumonics Model TE-861 M-4 Excimer laser (351 mm) was used to excite aromatics ($A_{351} = 0.7–1.0$) in benzene. Samples were degassed by purging with argon for 2–3 min in 1 cm^2 cylindrical quartz cells. Transient spectra were recorded with a Princeton EG and G optical multichannel analyzer. Transient decays were measured at the transient absorption maxima, and the output of a IP28 photomultiplier tube detector was digitized with a Tektronic 7912 analog to digital converter. The digitized output was transferred to a Macintosh IIci computer for storage and processing. Decays were fit to a single exponential decay using the Marquadt algorithm.

Fluorescence measurements were made on a Perkin-Elmer LS-5 fluorescence spectrophotometer. Samples were prepared in benzene such that their absorbance was ~1 at the excitation wavelength, which was typically about 351 nm. The intensity of the known fluorescence of the polycyclic aromatics was measured as a function of concentration of phenyl azide.

Acknowledgment. Support of this work by the National Institutes of Health (GM 34823) is gratefully acknowledged. The authors are indebted to Professor Peter Gaspar for suggesting this experiment and Professor Gary Schuster for stimulating discussions.

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[16] Reiser, A.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 1806.