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Laser Flash Photolysis Study of Methyl Derivatives of Phenyl Azide

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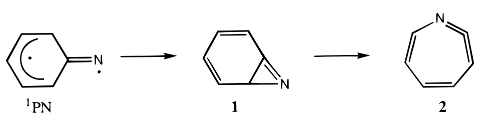
Laser flash photolysis (Nd:YAG, 35 ps, 266 nm, 10 mJ; KrF excimer, 249 nm, 12 ns, 70 mJ; XeCl excimer, 308 nm, 17 ns, 50 mJ) of methyl substituted phenyl azides produces the corresponding singlet nitrenes. The singlet nitrenes were detected directly, and their decay was analyzed to yield the observed rate constant k_{OBS}. The observed rate constant is the sum of $k_R + k_{ISC}$ where k_R is the absolute rate constant of rearrangement to an azirine and k_{ISC} is the absolute rate constant of intersystem crossing. Values of k_{OBS} were measured as a function of temperature and dissected assuming that k_{ISC} is temperature-independent. It was shown that k_{ISC} is independent of temperature for 2,6-dimethyl- and 2,4,6-trimethylphenyl singlet nitrenes. The barriers to rearrangement of singlet phenylnitrene, *p*-methylphenylnitrene, *o*-methylphenylnitrene, 2,6-dimethylphenylnitrene, and 2,4,6-trimethylphenylnitrene in hydrocarbon solvents are found to be 5.6, 5.8, 5.3, 7.0, and 7.3 ± 0.4 kcal/mol, respectively. The data demonstrate that two ortho methyl substituents retard cyclization but that a single ortho or para substituent does not. It is concluded that the rate of retardation provided by the methyl groups has a steric origin, as predicted by Karney and Borden (*J. Am. Chem. Soc.* **1997**, *119*, 3347). These authors predict that ortho methylation raises the barrier to cyclization by 1−2 kcal/mol, in excellent agreement with our results. Our results are also consistent with the work of Sundberg et al. (*J. Am. Chem. Soc.* **1972**, *94*, 513), which demonstrated that singlet 2-methylphenylnitrene cyclizes away from the ortho methyl substituent. Methyl substitution is found to increase the absolute rate constant of intersystem crossing.

I. Introduction

There has recently been substantial progress in understanding the electronic structure,[1] electronic spectra,[2] and reactivity[3,4] of singlet arylnitrenes. Calculations have revealed that singlet phenylnitrene (^{1}PN) has an open-shell electronic configuration similar to that of the lower-energy triplet-state spin isomer (^{3}PN).[1] Theory[1] and experiment[5] agree that singlet phenylnitrene is about 18.5 kcal/mol higher in energy than the triplet state.

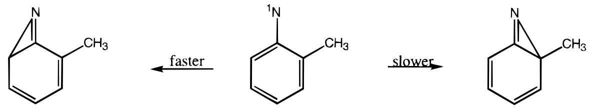
Karney and Borden suggest that ^{1}PN can be thought of as a 1,3-biradical, which explains the ease with which it cyclizes.[4] The calculated barrier to closure of ^{1}PN is about 5.8 kcal/mol after taking into account the tendency of the computational method to overestimate barriers by roughly 3 kcal/mol. Azirine (**1**) is predicted to rapidly open to form a didehydroazepine (**2**, E_a = 3 kcal/mol):



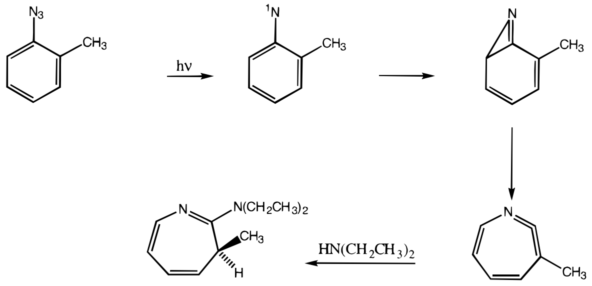
Thus, azirine **1** decays faster than it is formed. It is not surprising, therefore, that it has not yet been detected by spectroscopic methods, although this species has been intercepted by a thiol trap.[6]

Two groups[7,8] have recently reported the direct detection of singlet phenylnitrene by laser flash photolysis of phenyl azide and related precursors. Singlet phenylnitrene absorbs sharply at 350 nm and has a lifetime at ambient temperature of about 1 ns. The activation barrier to cyclization is 5.6 ± 0.3 kcal/mol,[2,8] in excellent agreement with the predictions of theory.[4]

Karney and Borden[9] have also predicted that an ortho methyl substituted arylnitrene will cyclize away from the substituent. The steric effect to cyclization is predicted to be 2 kcal/mol.



Indeed, Sundberg and co-workers[10] established this preference in 1972 by chemical trapping studies.



These reports have stimulated the present study. Herein we are pleased to report the results of our findings with arylmethyl singlet nitrenes, which demonstrate the anticipated steric effect upon nitrene cyclization. The effect of methyl substituents on arylnitrene intersystem crossing rates will be reported as well.

II. Experimental Section

Materials. Azides **3a**−**6a** were prepared by known procedures.[11,12] These compounds were characterized with IR, ^{1}H

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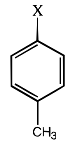

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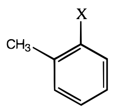

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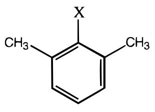

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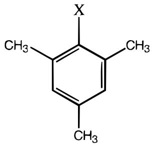

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X = (a) N_3, (b) ^1N, (c) ^3N

NMR, ^{13}C NMR spectroscopies and the spectra compared with those in the literature.

Freon-113 was purified by passage through a column of alumina, whereas pentane and hexane were used as received.

Apparatus. A Nd:YAG laser (Continuum, 35 ps, 10 mJ, 266 nm) was used as the excitation light source. The laser flash photolysis setup has previously been described in detail.[13] The time resolution of the spectrometer was about 1 ns.[13] The kinetics of transient absorption decay and growth were recorded at a temperature range 145−300 K in pentane, in the range 183−330 K in hexane, and in the range 238−315 K in Freon-113. A typical solution was contained in a quartz cuvette, which was placed in a quartz cryostat. The temperature was controlled by passing a thermostabilized nitrogen stream over the sample and kept to within ±1 K. The sample solutions were changed after every laser shot in order to avoid effects due to the accumulation of a photoproduct. Kinetics of long-lived intermediates (longer than 100 ns) were also studied using KrF (249 nm, 12 ns, 70 mJ) or XeCl excimer (308 nm, 17 ns, 50 mJ) lasers. Transient absorption spectra were recorded using a Nd:YAG laser source with detection kinetics in divisions of 0.5−10 nm from 300 to 500 nm. The absorption spectra of long-lived ($\tau \geq 1\ \mu$s) intermediates were measured using an eximer KrF laser in conjunction with EG&G Princeton Applied Research model 1460 optical multichannel analyzer (OMA, minimal time gate of 100 ns). All OMA spectra were averaged for 10−15 experiments.

III. Results

Laser flash photolysis (LFP) of azides **3a**−**6a** produces sharp transient absorptions with maxima in the 340−370 nm region. The transient absorption is formed within the time resolution (1 ns) of the spectrometer and decays between 1 and 300 ns depending upon the sample. In the case of the most short-lived nitrenes (**3b, 4b**) the transient absorption was detected at temperatures well below ambient. The lifetimes of the transients are not affected by the presence of oxygen.

These transient absorption bands are attributed to singlet nitrenes **3b**−**6b**, in accord with experimental[7,8] and theoretical work[1,2] with parent singlet phenylnitrene and with our previous work with singlet perfluorophenyl- and perfluorobiphenylnitrenes.[13]

The decay of the singlet aryl nitrenes is accompanied by the formation of a broad transient absorption with a maximum at about 350 nm of the corresponding ketenimine and the formation of a sharp absorption at about 320 nm and broad absorption between 350 and 450 of the triplet nitrenes. Azirines have not been detected in this study.

The results obtained upon LFP of mesityl azide **6a** are representative. A transient spectrum in pentane at 295 K recorded 50 ns after the laser pulse (Figure 1, spectrum 1) reveals a small amount of triplet nitrene **6c** absorbing at 320 nm and the broad absorption of ketenimine **6d** around 350 nm. For comparison, the spectrum of pure azepine **3d** is shown in Figure 1 (spectrum 3). These assignments rest on the matrix and solution-phase spectroscopy of these species and the parent system.[7,8,13−15]

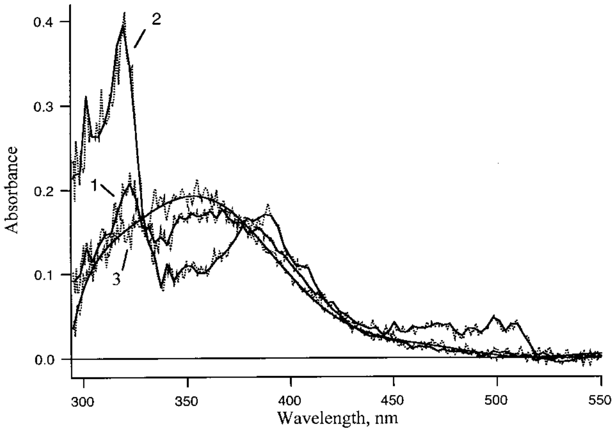
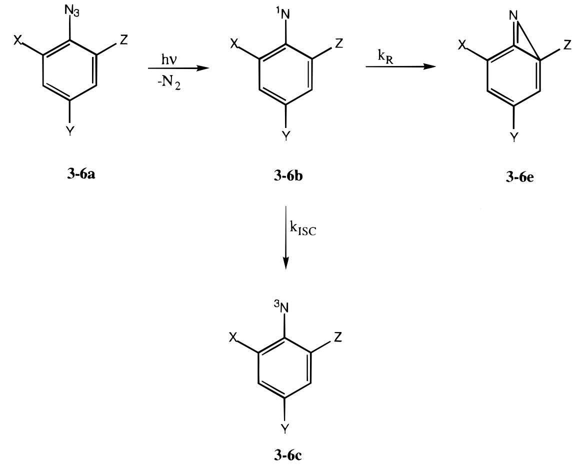
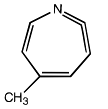


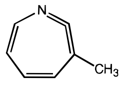
Figure 1. Transient absorption spectra detected after LFP of 2,4,6-trimethylphenyl azide (**6a**) in pentane at 295 K (spectrum 1, 50 ns time delay, 200 ns time window) and at 195 K (spectrum 2, 250 ns time delay, 200 ns time window). Spectrum 3 was recorded after LFP of *p*-methylphenyl azide (**3a**) in pentane at 295 K (50 ns time delay, 200 ns time window).

SCHEME 1

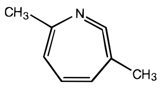




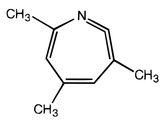
3d



4d



5d



6d

At 295 K ketenimine **6d** is the major species. At 195 K, however, triplet nitrene **6c** (λ_{max} = 320, 380 nm and a low-intensity band tailing out to 550 nm) is the predominant intermediate (Figure 1, spectrum 2). Thus, lower temperature favors relaxation of the singlet to the triplet nitrene ($k_{ISC} > k_R$, Scheme 1), but the opposite is true at ambient temperature. These results are completely consistent with the known temperature-dependent photochemistry of phenyl azide.[14]

Upon LFP of **6a** in $CF_2ClCFCl_2$ at 253 K a structured absorption band between 320 and 380 nm is evident in a spectrum recorded 1 ns after the laser pulse (Figure 2, spectrum 1). This species decays to form triplet nitrene **6c**, which is visible 100 ns after the laser pulse (Figure 2, spectrum 2) and is attributed to singlet nitrene **6b**. The spectrum of **6b** is similar to that of the parent singlet phenylnitrene[2,8] and its fluorinated derivatives.[13] The absorption band is assigned to the promotion

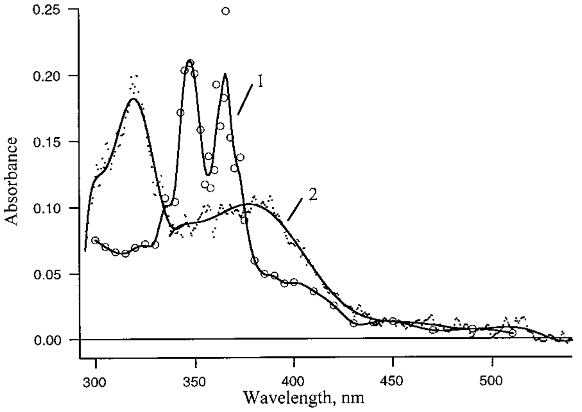


Figure 2. Transient absorption spectra recorded after LFP of azide **6a** in $CF_2ClCFCl_2$ at 253 K. Spectrum 1 was recorded about 1 ns after the laser pulse. Spectrum 2 was recorded 100 ns after the laser pulse over a 100 ns time window.

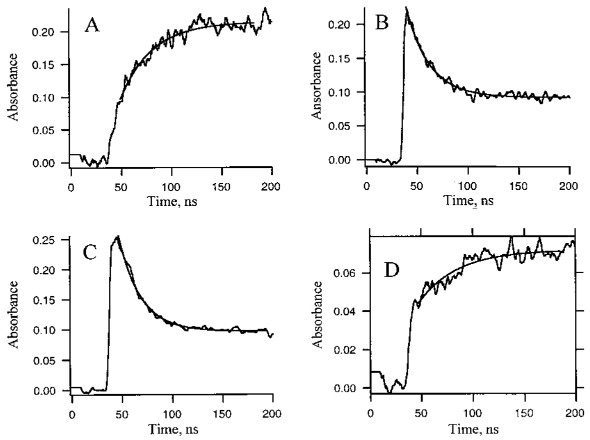
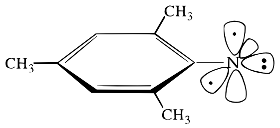


Figure 3. Changes in transient absorption at selective wavelengths after LFP of 2,4,6-trimethylphenyl azide (**6a**) in Freon-113 at 253 K: (A) 320 nm; (B) 345 nm; (C) 366 nm; (D) 400 nm.

of an electron in the nitrogen lone pair to a singly occupied in-plane p orbital of the nitrene nitrogen:[1,2,14]



6b

The vibrational structure at ~1670 cm^{-1} is associated with the C−N stretch. Calculations indicate that there is substantial double bond character between carbon and nitrogen in singlet phenylnitrene but that this is lost in the excited state.[1,2]

Changes in transient absorption (253 K, $CF_2ClCFCl_2$) at selected wavelengths are given in Figure 3. It is possible to measure either the decay of singlet nitrene **6b** (parts B and C) or the formation of triplet nitrene **6c** (part A) or ketenimine **6d** (part D).

The decay of ortho and para methyl substituted singlet phenylnitrenes **3b**−**6b** and the formation of reaction products are described by exponential functions that can be analyzed to yield observed rate constants k_{OBS} (Figure 3). Values of k_{OBS} of singlet nitrenes **3b**−**6b** decrease with decreasing temperature but then remain independent of temperature until 145 K (Figure 4). For singlet nitrenes, **5b**, and **6b** k_{OBS} is temperature-independent over the temperature range 190−145 K.

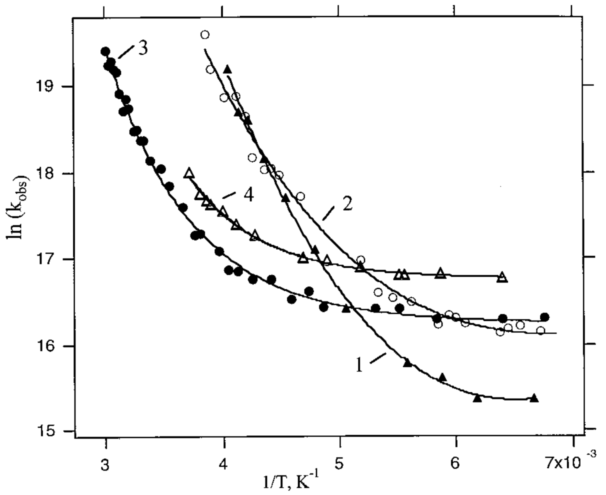


Figure 4. Arrhenius plots for the rate constants (k_{OBS}) of the decay of singlet arylnitrenes **3b** (1), **4b** (2), **5b** (3), and **6b** (4) in hydrocarbon solvents.

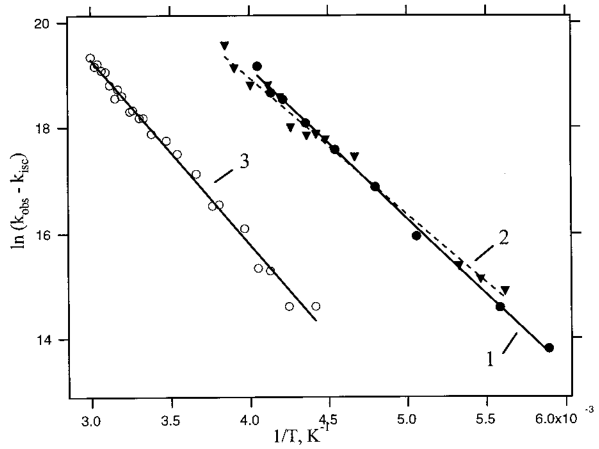


Figure 5. Arrhenius treatment of k_R data for singlet 4-methylphenylnitrene (**3b**, curve 1) and 2-methylphenylnitrene (**4b**, curve 2) in pentane and 2,6-dimethylphenylnitrene (**5b**, curve 3) in hexane.

The observed rate constant (k_{OBS}) of nitrene disappearance is related to the fundamental processes of Scheme 1 by eq 1:

$$k_{OBS} = k_R + k_{ISC} \tag{1}$$

where k_{ISC} is the rate constant of intersystem crossing and k_R is the rate constant of rearrangement. It is seen from Figure 4 (curves 3 and 4) that for nitrenes **5b** and **6b** k_{ISC} is temperature-independent. Upon assuming that k_{ISC} is independent of temperature for all nitrenes **3b**−**6b**,[7,8,13,15] k_{OBS} can be dissected into k_{ISC} and k_R. Figure 5 demonstrates the Arrhenius treatment for the rate constant of rearrangement of singlet nitrenes **3b**−**5b**. It is seen that experimental data can be nicely fit to the Arrhenius type equation, assuming that k_{ISC} is independent of temperature.

IV. Discussion

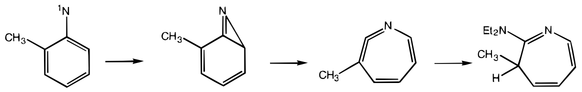
As seen in Table 1, a para methyl or a single ortho methyl substituent has no effect, outside of experimental error, on the barrier to rearrangement of singlet arylnitrenes. These substituents do not have a significant electronic effect on k_R. Two ortho substituents, however, raise the barrier to cyclization by 1−2 kcal/mol. These results are consistent with the report of

TABLE 1: Spectroscopic and Kinetic Parameters of Some Simple Singlet Arylnitrenes

singlet nitrene	solvent	λ_{max} (nm)	k_{ISC} ($\times 10^6$)	τ_{298} (ns)	log A (s^{-1})	E_a (kcal/mol)
phenyl-[2]	pentane	350	3.2 ± 0.3	~1[a]	13.1 ± 0.3	5.6 ± 0.3
4-methylphenyl-	pentane	365	5.0 ± 0.2	~1[a]	13.2 ± 0.2	5.8 ± 0.4
2-methylphenyl-	pentane	350	10 ± 1	~1[a]	12.8 + 0.3	5.3 ± 0.4
2,6-dimethylphenyl-	hexane	350	15 ± 3	12 ± 1	13.0 ± 0.3	7.0 ± 0.3
	Freon-113[b]	350	30 ± 8	13 ± 1	12.9 ± 0.3	7.5 ± 0.5
	pentane	350	12 ± 1			
2,4,6-trimethylphenyl-	Freon-113[b]	366	29 ± 3	8 ± 1	13.4 ± 0.4	7.3 ± 0.4
	pentane	366	20 ± 1			

[a] Estimated. [b] $CF_2ClCFCl_2$.

Sundberg et al.[10] that ortho alkyl substituted singlet arylnitrenes cyclize *away* from the substituent.



Both results are in good agreement with the calculations of Karney and Borden.[9] Following the work of Karney and Borden, we interpret the 2,6-dimethyl effect as steric in origin.[9]

The para methyl substituent has little influence on the rate of intersystem crossing (ISC). However, the rate constant of ISC of 2-methylphenylnitrene, 2,6-dimethylphenylnitrene, and 2,4,6-trimethylphenylnitrene exceeds that of singlet phenylnitrene by a factor of 3−7. Although the effect is real, it is still relatively small. These results are consistent with the findings of Wirz and Adam[16] and the predictions of Michl[17] that the zwitterionic character in the wave function of singlet-state species increases spin−orbit coupling mediated intersystem crossing. It should be noticed that the more polar solvent $CF_2ClCFCl_2$ slightly increases the rate constant of ISC.

Singlet 2,6-dimethyl- and 2,4,6-trimethylphenylnitrenes (**5b** and **6b**) are both relatively long-lived (Table 1). Singlet mesitylnitrene **6b** is known to react with a very electron-deficient alkene (tetracyanoethylene).[12] Thus, the yield of bimolecular chemistry from a singlet arylnitrene requires two ortho substituents to retard azirine formation (the competitive process) and the appropriate electronic influence of the substituent on bimolecular reactions with a specific partner. The latter issue remains to be addressed in quantitative terms by LFP methods.

V. Conclusions

Laser flash photolysis (Nd:YAG, 35 ps, 266 nm, 10 mJ; KrF excimer, 249 nm, 12 ns, 70 mJ; XeCl excimer, 308 nm, 17 ns, 50 mJ) of methyl substituted phenyl azides produces the corresponding singlet nitrenes. The singlet nitrenes were detected directly, and their decay was analyzed to yield the observed rate constant k_{OBS}. The observed rate constant is the sum of $k_R + k_{ISC}$ where k_R is the absolute rate constant of rearrangement to an azirine and k_{ISC} is the absolute rate constant of intersystem crossing. Values of k_{OBS} were measured as a function of temperature and dissected assuming that k_{ISC} is temperature-independent. The barriers to rearrangement of singlet phenylnitrene, *p*-methylphenylnitrene, *o*-methylphenylnitrene, 2,6-dimethylphenylnitrene, and 2,4,6-trimethylphenylnitrene in hydrocarbon solvents are found to be 5.6, 5.8, 5.3, 7.0, and 7.3 ± 0.4 kcal/mol, respectively. The data demonstrate that two ortho methyl substituents retard cyclization but that a single ortho or para substituent does not. It is concluded that the rate of retardation provided by the methyl groups has a steric origin, as predicted by Karney and Borden.[9] These authors predict that ortho methylation raises the barrier to cyclization by 1−2 kcal/mol, in excellent agreement with our results. Our results are also consistent with the work of Sundberg et al.,[10] which demonstrated that singlet 2-methylphenylnitrene cyclizes away from the methylphenyl substituent. Methyl groups are found to increase the absolute rate constant of intersystem crossing.

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