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A Laser Flash Photolysis Study of Some Simple Para-Substituted Derivatives of Singlet Phenyl Nitrene

Nina P. Gritsan,*,† Dean Tigelaar,‡ and and Matthew S. Platz*,‡

Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia, and Newman and Wolfrom Laboratory of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210

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The photochemistry of several para-substituted aryl azides was studied by laser flash photolysis (LFP) techniques in pentane. Para F, Cl, Br, I, CH_3, CF_3, $COCH_3$, OCH_3, and NO_2 substituted aryl azides were studied. LFP of aryl azides generates singlet aryl nitrenes which were detected in absorption with maxima between 300 and 365 nm in pentane. The nitrene decay can be fit to an exponential function and analyzed to yield observed rate constant, k_{obs}, which was measured as a function of temperature. The value of $k_{obs} = k_R + k_{ISC}$ where k_R and k_{ISC} are the rate constants of nitrene rearrangement to azirine intermediates and intersystem crossing to the lower energy triplet states, respectively. Values of k_{obs} decrease as the temperature is reduced and reach a limiting value attributed to k_{ISC}. Assuming that k_{ISC} is temperature independent allows values of k_R to be deduced along with the Arrhenius parameters to cyclization for para CH_3, CF_3, $COCH_3$, F, Cl, and Br singlet phenyl nitrenes. The Arrhenius parameters to rearrangement closely resemble those of parent singlet phenyl nitrene with the exception of the para bromo compound. For para I and OCH_3, k_{ISC} is large and prevents measurement of k_R. The increased rate of intersystem crossing in these two singlet nitrenes is due to heavy-atom and to electron-donation effects, respectively. No transient absorptions were detected upon LFP of *p*-nitrophenyl azide.

I. Introduction

Photolysis of aryl azides generates singlet aryl nitrenes.[1] This process is of practical value in lithography,[2] in the covalent attachment of small molecules to synthetic and biopolymers,[3] and in cross-linking experiments.[4] The properties of singlet nitrenes are of intrinsic scientific interest.

The direct detection of singlet phenyl nitrene has recently been accomplished using laser flash photolysis (LFP) techniques.[5,6] LFP of phenyl azide (**1a**, Scheme 1) releases singlet phenyl nitrene which absorbs at 350 nm. Singlet phenyl nitrene (**2a**) has a lifetime at ambient temperature of approximately 1ns which is controlled by cyclization to benzazirine (**3a**). The Arrhenius parameters to this process are $E_a = 5.6 \pm 0.3$ kcal/mol and $A = 10^{13.1\pm0.3}$ s^{-1}.[7] The barrier to cyclization is in good agreement with the predictions of Karney and Borden.[8,9]

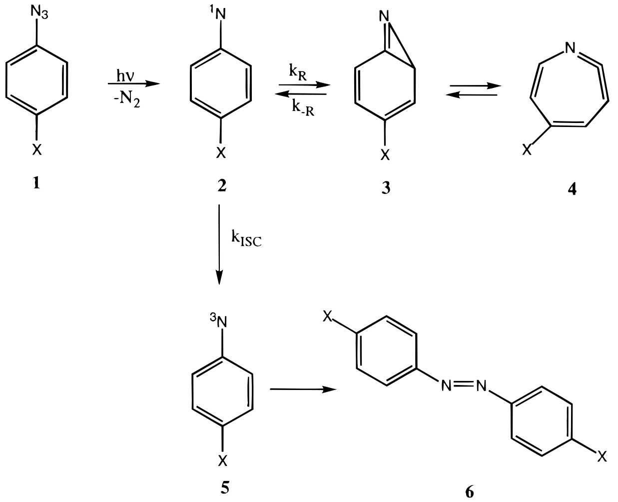
At low temperature the lifetime of singlet phenylnitrene is controlled by intersystem crossing (ISC) to the lower energy triplet state.[10] The absolute rate constant of ISC (k_{ISC}) is $3.2 \pm 0.3 \times 10^6$ s^{-1} which is independent of temperature in solution over the temperature range studied.[7]

These initial studies provide us with the first opportunity to study the effects of substituents on the cyclization and spin relaxation processes. Herein we are pleased to report the effect of para substitution on these two processes. The effects of halogens and electron-donating and -accepting groups will be explored.

II. Experimental Section

Aryl Azides. All azides were prepared according to known procedures from commercially available anilines.[11,12] They were purified on a silica gel column with either pentane or hexane and had IR, NMR, and mass spectra consistent with the literature and with the proposed structures.

SCHEME 1



X = (a) H (b) Cl (c) Br (d) I (e) F (f) CH_3
(g) CF_3 (h) $COCH_3$ (i) OCH_3 (j) $N(CH_3)_2$

Laser Flash Photolysis. Either a Nd:YAG laser (Continuum PY62C-10, 10 mJ, 35 ps 266 nm), KrF Excimer laser (Lumonics, 50 mJ, 12 ns, 249 nm), or XeCl Excimer laser (Lambda Physik 100 mJ, 17 ns, 308 nm) was used as the excitation source. The apparatus has been described previously.[13]

In a typical experiment, samples were placed in quartz cuvettes and allowed to reach the appropriate temperature over a period of at least 10 min. At least two kinetic traces were obtained at each temperature and the observed rate of disap-

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* Authors to whom correspondence should be addressed.
† Institute of Chemical Kinetics and Combustion.
‡ The Ohio State University.

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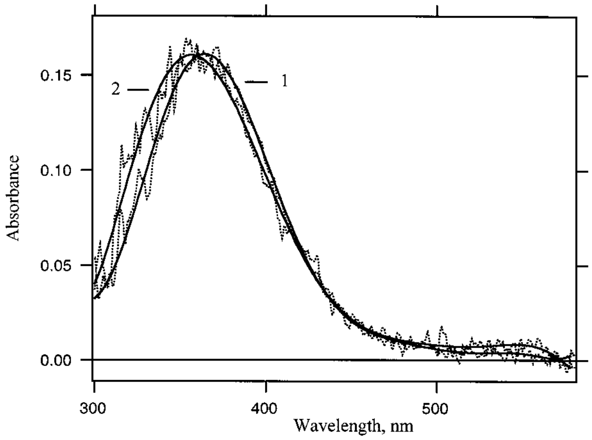


Figure 1. Transient spectra recorded upon LFP (XeCl, 308 nm, 17 ns) of (1) *p*-chlorophenyl azide **1b** and (2) *p*-bromophenyl azide **1c** in pentane at ambient temperature. The bands at 370 and 360 nm are due to the corresponding ketenimines **4b** and **4c**, respectively. LFP of *p*-bromophenyl azide **1c** under these conditions also gives rise to a small amount of triplet nitrene (**5c**) absorption above 500 nm. The spectra were recorded with an OMA over a 100 ns window, immediately after the laser pulse.

pearance of the signal was averaged. The time resolution of the spectrometer was about 1 ns.[13] The kinetics of transient absorption decay and growth were recorded in pentane at a temperature range 150−270 K. A typical solution was contained in a quartz cuvette which was placed in a quartz cryostat. Temperature was controlled by passing a thermostabilized nitrogen stream 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. The absorption spectra of long-lived ($\tau \geq 300$ ns) intermediates were measured using an excimer KrF laser (Lumonics, 12 ns, 50 mJ, 249 nm) in conjunction with EG & G Princeton Applied Research Model 1460 optical multichannel analyzer (OMA, minimal time gate of 100 ns).

III. Results

The results with *p*-chlorophenyl azide **1b** are representative. LFP of this azide in pentane at low temperature produces a species with a sharp transient absorption at 360 nm which is essentially identical to that of singlet phenyl nitrene and its perfluorinated derivitatives.[6,7,13] The lifetime of the transient is not influenced by the presence of oxygen. The transient is attributed to singlet *p*-chlorophenyl nitrene **2b** in analogy with our work on the parent system[6,7] and perfluorophenyl singlet nitrene.[13] A transient spectrum recorded in pentane at 295 K over a 100 ns window (Figure 1, Spectrum 1, see Scheme 1) is that of the corresponding ketenimine **4b**. Cyclization of the singlet nitrene is the dominant relaxation pathway at 295 K. Very similar results were obtained with the para bromo analogue. However, in this case (Figure 1, Spectrum 2) a small amount of triplet nitrene **5c** absorption above 500 nm is evident. Although cyclization is still the major decay route of brominated nitrene **2c** at 295 K, intersystem crossing of singlet *p*-bromophenyl nitrene is clearly more rapid than that of the chloro analogue.

The chlorinated ketenimine intermediate **4b** lifetime is many microseconds, but the eventual product of the photolysis is azo compound **6b** (Figure 2) formed by dimerization of two triplet nitrenes.[1] The ketenimine intermediate **4b** likely reverts to singlet nitrene **2b** at high dilution where polymerization reactions are suppressed[14−17] and an equilibrium may be established.

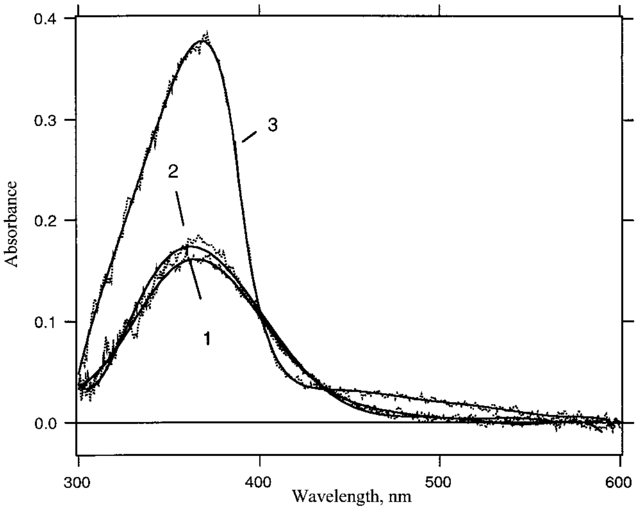


Figure 2. Transient spectra recorded upon LFP (XeCl, 308 nm, 17 ns) of *p*-chlorophenyl azide **1b** in pentane at ambient temperature. Spectrum 1 was recorded with zero delay after the laser pulse (100 ns window). Spectrum 2 was recorded 500 ns after the laser pulse (200 ns window), and spectrum 3 was recorded 30 s after the laser pulse (200 ns window). Spectra 1 and 2 are of the ketenimine, **4b**. Spectrum 3 is of azo compound **6b**.

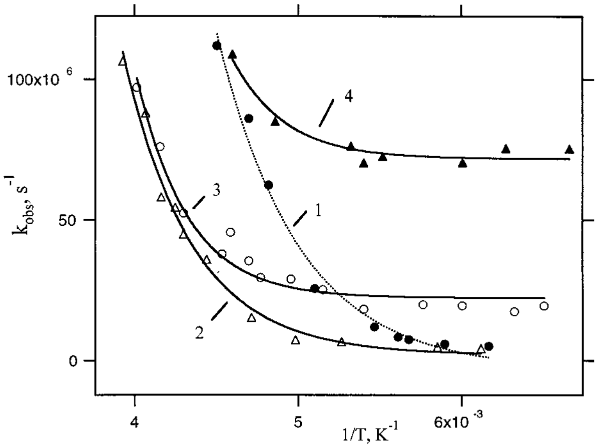


Figure 3. The temperature dependence of k_{obs} values of (1) *p*-fluoro, (2) *p*-chloro, (3) *p*-bromo, and (4) *p*-iodo singlet phenyl nitrene in pentane.

Eventually, the singlet nitrene will relax irreversibly to the lower energy triplet nitrene which then dimerizes to form an azo compound as shown in Scheme 1.

The singlet nitrene decay can be fit to an exponential function and analyzed to yield k_{obs}, which in turn can be related to the absolute rate constants of Scheme 1 via eq 1,

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

where k_R and k_{ISC} are the absolute rate constants of nitrene rearrangement and intersystem crossing, respectively.

Values of k_{obs} were measured as a function of temperature. The magnitude of k_{obs} decreases as the temperature decreases until a limiting value is reached (Figure 3). The temperature-independent rate constant observed at low temperature is associated with k_{ISC}. Values of k_R of para CH_3, CF_3, $COCH_3$, F, Cl, and Br substituted singlet nitrenes were deduced assuming that k_{ISC} is independent of temperature over the entire range of measurement of k_{obs} (Figures 4 and 5). Values of k_{ISC} and the Arrhenius parameters to cyclization for singlet para-substituted phenylnitrenes are given in Table 1.

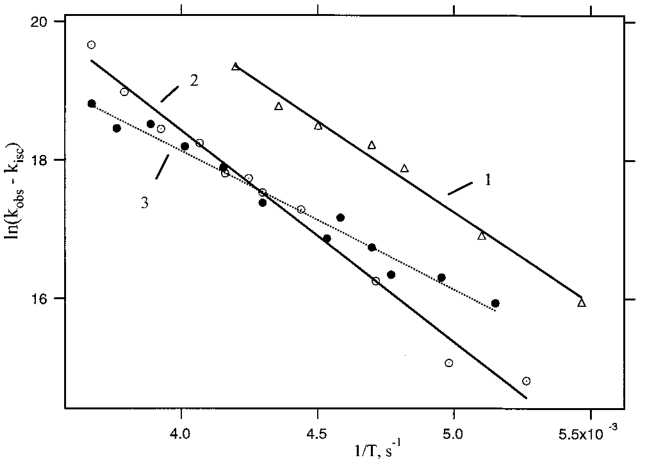


Figure 4. Arrhenius treatment of k_R (= $k_{obs} - k_{ISC}$) of (1) *p*-fluoro, (2) *p*-chloro, and (3) *p*-bromo singlet phenyl nitrene in pentane.

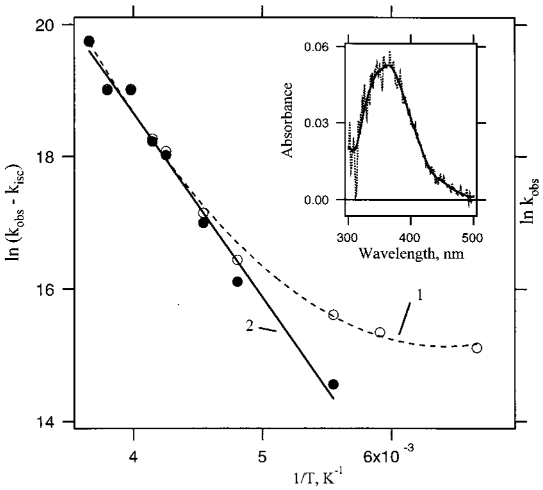
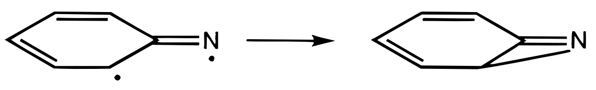


Figure 5. Arrhenius treatment of (1) k_{obs} (right-hand *y*-axis) and (2) k_R (=$k_{OBS} - k_{ISC}$, left-hand *y*-axis) of *p*-trifluoromethyl singlet phenyl nitrene **2g** in pentane. Insert: transient spectrum of the ketenimine intermediate **4g** produced upon LFP (308 nm) of *p*-trifluoromethylphenyl azide **1g** in pentane at ambient temperature. The spectrum was recorded immediately after the laser pulse over a window of 100 ns.

Intersystem crossing of the *p*-iodo- and *p*-methoxyphenyl nitrenes is very rapid which prevents measurement of k_R and its associated Arrhenius parameters. LFP of *p*-nitrophenyl azide fails to produce any transients we can detect.

IV. Discussion

The data of Table 1 are remarkable for the lack of sensitivity of k_R on the electron-donating or -accepting ability of the para substituent. The para CH_3, CF_3, and acetyl group have little influence on the rate of nitrene cyclization. This is consistent with the view of Karney and Borden that the cyclization reaction is best thought of as the cyclization of a 1,3 biradical.[8,9]



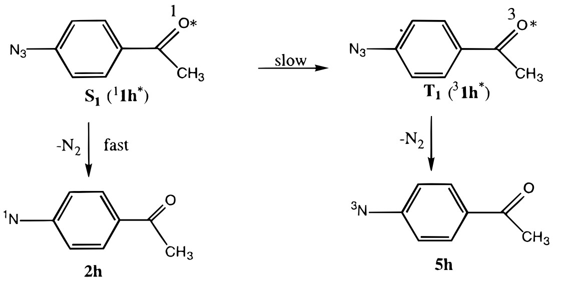
The rate constant of intersystem crossing (ISC) for *p*-bromo singlet phenyl nitrene is about 7 times larger than that of parent ^{1}PN and the para chloro analogue. This is easily attributable to a small heavy-atom effect. The heavy-atom effect of iodine is larger than that of bromine, as expected, and increases the rate of ISC by more than a factor of 20, relative to parent singlet phenyl nitrene.

TABLE 1: Kinetic Parameters of Para-Substituted Singlet Aryl Nitrenes ($X-C_6H_4-N$) in Pentane

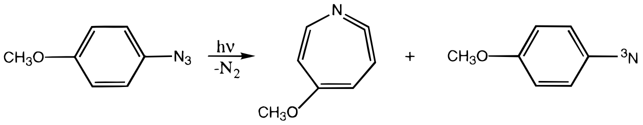
para-X	λ_{max} (nm)	k_{ISC} ($\times 10^6$ s^{-1})	τ_{295K} (ns)	E_a (kcal/mol)	log A (s^{-1})
H[a]	350	3.2 ± 0.3	~1	5.6 ± 0.3	13.1 ± 0.3
CH_3[b]	365	5.0 ± 0.4	~1	5.8 ± 0.4	13.5 ± 0.2
CF_3	320	4.6 ± 0.8	1.5	5.6 ± 0.5	12.9 ± 0.5
$\overset{O}{\overset{\|}{C}}-CH_3$	330	8 ± 3	5.0	5.3 ± 0.3	12.5 ± 0.3
F	365	3.5 ± 1.4	~0.3	5.3 ± 0.3	13.2 ± 0.3
Cl	360	3.9 ± 1.5	~0.6	6.1 ± 0.3	13.3 ± 0.3
Br	361	17 ± 4	~3	4.0 ± 0.2	11.4 ± 0.2
I	328	72 ± 10	*e*	*e*	*e*
OCH_3	330[d]	> 500	<1	*e*	*e*
$N(CH_3)_2$[c]	460	8300 ± 200	0.12	*e*	*e*

[a] Ref 7. [b] Ref 27. [c] Ref 26. [d] Absorption maxima of the triplet nitrene. [e] Not measured.

Acetophenone and benzophenone have n → π* singlet states, S_1, which undergo ISC to the triplet state T_1 with near unit quantum yield. The lifetime of singlet benzophenone is 16−30 ps.[18,19] The singlet energy of phenyl azide is 83 kcal/mol, the triplet energy is ≈70 kcal/mol.[20] The singlet energy of acetophenone is 78.6 kcal/mol, and its triplet energy is 73.8 kcal/mol.[19] Thus, one might predict that photolysis of **1h** might lead efficiently to the formation of a triplet state with the excitation localized on the aryl azide moiety. Fragmentation of this triplet would lead to direct production of triplet nitrene **5h**. However, LFP of para acetyl phenyl azide **1h** produces singlet aryl nitrene **2h** whose transient spectrum is very similar to that of parent phenyl nitrene singlet **2a**.[7] No acetophenone like triplet−triplet absorption was observed upon LFP of **1h**, thus, there is no evidence of internal sensitization. Several explanations of this result can be advanced, however, it is clear that fragmentation of the excited singlet state to form singlet nitrene is faster than ISC to the triplet excited state of the precursor. We wish only to note that if acetephenone **1h** has an n → π* lowest singlet excited state then the fragmentation of singlet azide **1h*** must occur on a time scale shorter than about 30 ps.



LFP of *p*-methoxylphenyl azide **1i** in pentane at ambient temperature produces the transient spectra of the corresponding ketenimine **4i** and triplet nitrene **5i**, (Figure 6.)



1i **4i** **5i**

Li et al. found that upon photolysis of *p*-methoxyphenyl azide in cyclohexane an 80% yield of azo compound (triplet nitrene dimer) was formed.[17] Upon photolysis of the same azide in cyclohexane containing diethylamine, a 27% yield of ketenimine

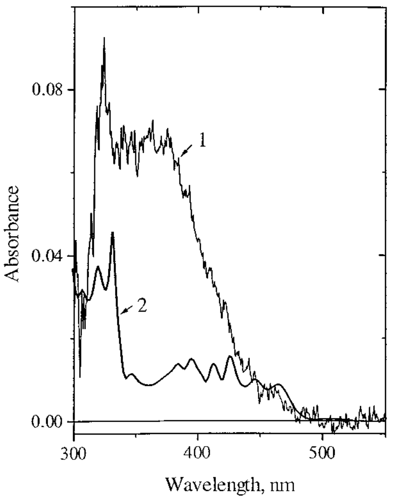
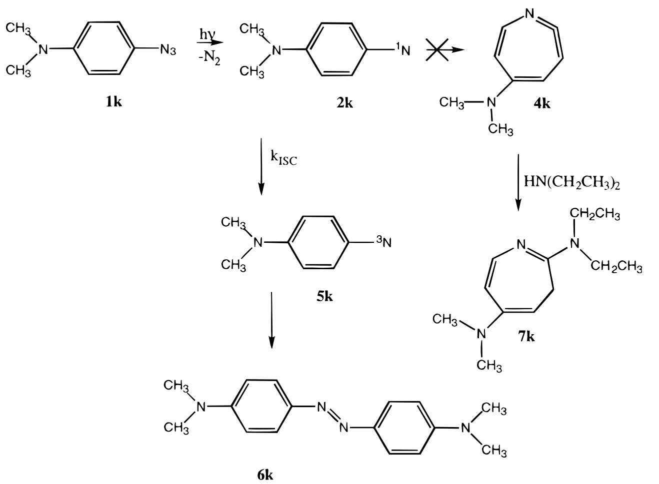


Figure 6. Spectrum 1 is the transient spectrum of ketenimine **4i** and triplet nitrene **5i** produced upon LFP (308 nm) of *p*-methoxyphenyl azide **1i** in pentane at 295 K. The spectrum was recorded immediately after the laser pulse over a window of 100 ns. Spectrum 2 is the persistent spectrum of triplet nitrene **5i** produced by photolysis of *p*-methoxyphenyl azide **1i** in methylcyclohexane at 77 K.

adduct was formed. Thus, product studies indicate that both secondary intermediates **4i** and **5i** are present in solution upon photolysis of this azide.[17]

Calculations predict that the lowest energy configuration of singlet phenylnitrene is open shell.[21] The electronic spectrum of ^{1}PN can be analyzed on this basis.[7] The Salem−Rowland[22] rule for ISC promoted by spin−orbit coupling (SOC) predicts that singlet-to-triplet relaxation will have its maximum rate when the singlet state is closed shell. This is the case with diaryl carbenes where the absolute rate constants of ISC are on the order of 10^{9-10} s^{-1}.[23] Michl[24] has recently pointed out the importance of donor−acceptor interactions in promoting ISC which explains the lifetimes of certain localized singlet biradicals.[25] The CH_3, CF_3, acetyl, fluoro, and chloro substituents are not sufficiently strong π-donors or acceptors to significantly influence the size of k_{ISC} (Table 1). The strong π-donating *p*-methoxy group has a huge influence on k_{ISC}, however. Similar results have been reported with azide **1k**[26] where a very large ISC rate constant has been reported ($k_{ISC} = 8.3 \pm 0.2 \times 10^9$ s^{-1}) for singlet nitrene **2k**. Photolysis of **1k** in cyclohexane produces a 92% yield of azo compound **6k**. Upon photolysis of **1k** in the presence of diethylamine, no adduct with putative ketenimine **7k** is observed,[17] thus $k_{ISC} \gg k_R$ at ambient temperature in this system.



Thus, there is no question that strong π-donors will accelerate ISC in singlet nitrenes, although we are not prepared to speculate on the origin of this effect at this time. We did attempt to study the π-accepting para nitro system. Unfortunately, LFP of *p*-nitrophenyl azide did not product useful transient spectra.

V. Conclusion

The photochemistry of several para-substituted aryl azides was studied by laser flash photolysis (LFP) techniques in pentane. Para F, Cl, Br, I, CH_3, CF_3, $COCH_3$, OCH_3, and NO_2 substituted aryl azides were studied. LFP of aryl azides generates singlet aryl nitrenes which were detected in absorption with maxima between 300 and 365 nm in pentane. The nitrene decay can be fit to an exponential function and analyzed to yield observed rate constant k_{obs}, which was measured as a function of temperature. The value of $k_{obs} = k_R + k_{ISC}$, where k_R and k_{ISC} are the rate constants of nitrene rearrangement to azirine intermediates and intersystem crossing to the lower energy triplet states, respectively. Values of k_{obs} decrease as the temperature is reduced and reach a limiting value attributed to k_{ISC}. Assuming that k_{ISC} is temperature independent allows values of k_R to be deduced along with the Arrhenius parameters to cyclization for para CH_3, CF_3, $COCH_3$, F, Cl, and Br singlet phenyl nitrene. The Arrhenius parameters to rearrangement closely resemble those of parent singlet phenyl nitrene with the exception of the para bromo compound. For para I and OCH_3, k_{ISC} is large and prevents measurement of k_R. The increased rate of intersystem crossing in these two singlet nitrenes is due to heavy-atom and to π-electron donation effects, respectively. No transient absorptions were detected upon LFP of *p*-nitrophenyl azide.

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