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Photochemical Generation of Nitrenium Ions from Protonated 1,1-Diarylhydrazines

Arthur H. Winter, Selina I. Thomas, Andrew C. Kung, and Daniel E. Falvey*

Department of Chemistry and Biochemistry, University of Maryland,
College Park, Maryland 20742

falvey@umd.edu

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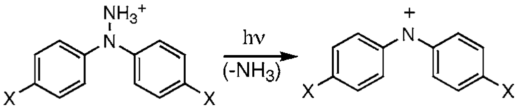
ABSTRACT



Laser flash photolysis experiments, chemical trapping studies, and time-dependent density functional theory calculations demonstrate that photolysis of protonated 1,1-diarylhydrazines generates *N*,*N*-diarylnitrenium ions.

The development of photochemical methods for generating nitrenium ions[1,2] led to renewed interest in these short-lived species. The early 1990s saw the first laser flash photolysis (LFP) studies applied to these reactive intermediates. The initial experiments used photoisomerization of anthranilium ions to generate nitrenium ions (**1**).[3] This route is inherently limited to producing *N*-alkyl-*N*-arylnitrenium ions having a carbonyl group on the aromatic ring (**2**). McClelland et al. developed a more general method. These workers photolyzed aryl azides (**3**) in water or other protic media and obtained a monosubstituted nitrenium ion (i.e., $R{-}N{-}H^+$) through rapid protonation of the singlet arylnitrene[4] (**4**). This route, though more general, is limited to monosubstituted nitrenium ions. More recently our group and others have used *N*-aminopyridinium ions **6** as photochemical precursors to nitrenium ions.[5,6] In principle, this route allows for the generation of any nitrenium ion in any solvent system. Unfortunately, *N*-aminopyridinium ions are available only from multistep syntheses.

To expand the available routes to nitrenium ions, we examined the photochemistry of protonated 1,1-diarylhydrazines. Through a combination of LFP experiments, product analysis, and time-dependent density functional theory (TD-DFT) calculations, it is demonstrated that photolysis of protonated 1,1-diarylhydrazines generates the corresponding nitrenium ions in high yields.

Three 1,1-diarylhydrazine derivatives were studied: 1,1-diphenylhydrazine **8a**, 1,1-di(4-chlorophenyl)hydrazine **8b**, and 1,1-di(4-bromophenyl)hydrazine **8c**. Protonation of the hydrazines using HBF_4 to make the hydrazinium ions was followed by UV spectroscopy. In each case the free bases have strong absorption bands with maxima in the 295−305 nm region. Upon addition of a stoichiometric amount of HBF_4, this highest wavelength absorption band is replaced with a long absorption tail that extends from 240 to ca. 300 nm. Consequently, compounds **8**a, **8b**, and **8c** require lower wavelength light for excitation than do the corresponding *N*-aminopyridinium ions **6**. The latter can generally be excited with wavelengths as high as 400 nm. The protonated hydrazines show only weak fluorescence ($\Phi_{fl} < 0.03$) in CH_3CN.

Photolysis of **8** (BF_4^- salts) in CH_3CN produces stable products that are characteristic of the nitrenium ions **9**.[8] The

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[1] Falvey, D. E. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Maitland Jones, J., Eds.; Wiley-Interscience: Hoboken, NJ, 2004; Vol. 1, pp 593−650.

[2] Novak, M.; Rajagopal, S. *Adv. Phys. Org. Chem.* **2001**, *36*, 167−254.

[3] Anderson, G. B.; Falvey, D. E. *J. Am. Chem. Soc.* **1993**, *115*, 9870−9871.

[4] McClelland, R. A.; Kahley, M. J.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1996**, *118*, 4794−4803.

[5] Abramovitch, R. A.; Shi, Q. *Heterocycles.* **1994**, *37*, 1463−1466.

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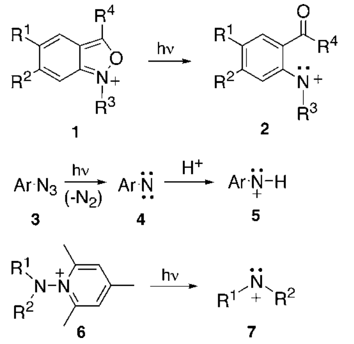
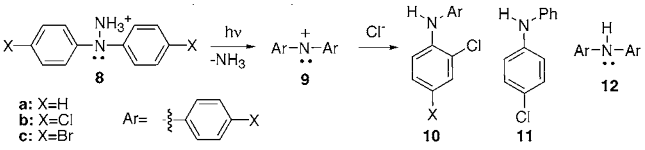
10.1021/ol048250y CCC: $27.50

Scheme 1. Photochemical Generation of Nitrenium Ions



product mixtures were analyzed by GC, and the products were identified by co-injection with authentic samples.[7] Photolysis of diphenylhydrazinium ion (**8a**) in CH_3CN with added Cl^- (as $^nBu_4N^+Cl^-$) gives a mixture of 4-chloro-*N*-phenylaniline **11** and diphenylamine **12**. Likewise, the para-substituted examples **8b** and **8c** each give a mixture of chloride adduct **10** and the reduction product. For the para-substituted diaryl hydrazinium precursors **8b** and **8c**, addition occurs at the unsubstituted ortho-position on the benzene ring. Laser flash photolysis (266 nm, 4 ns, 10−25 mJ/pulse) shows that the corresponding nitrenium ions **9** are formed following photolysis. Figure 1 shows the transient UV−vis spectra generated from pulsed laser photolysis of protonated 1,1-diphenlyhydrazine **8a** in CH_3CN. The spectrum immediately following the laser pulse, having bands at 650 and 410 nm, is experimentally indistinguishable from the spectrum generated from the corresponding *N*-aminopyridinium ion **6a**.[8−10] In previous work the identity of this intermediate was established as the diarylnitrenium ion **9a** by a variety of experiments, including trapping studies and time-resolved infrared[6] and resonance Raman spectroscopy.[11]

Scheme 2. Photolysis of Hydrazinium Ions



The other two hydrazinium ions, **8b** and **8c**, give similar transient spectra upon laser flash photolysis (Figure 1). Both of these initial intermediates decay within 5−7 μs to give a second, longer-lived intermediate. For reasons discussed below, this secondary transient is attributed to the radical cation, deriving from an electron-transfer reaction between **9** and **8**.

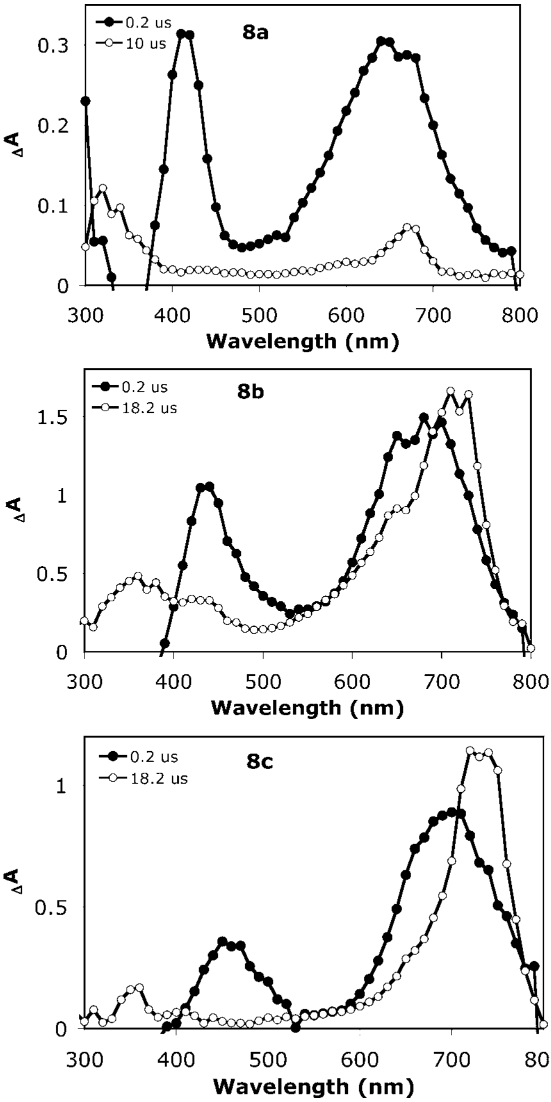


Figure 1. Transient UV−vis spectra derived from LFP (266 nm excitation) of **8a**−**c** in CH_3CN solutions. The spectra at early times (filled circles) are assigned to the corresponding diarylnitrenium ions **9**; those at later times (open circles) are assigned to the corresponding cation radicals $\mathbf{12}^{+\bullet}$.

Two experiments confirm that the absorptions seen immediately after the laser pulse correspond to the nitrenium ions. First, laser flash photolysis (355 nm, 20−30 mJ, 6 ns) of the corresponding *N*-aminopyridinium ions (**6b** and **6c**) give transient absorption peaks at the same maxima as those observed for the corresponding hydrazinium ions (Table 1). With the NAP-generated transients, however, no long-lived intermediate was detected following the decay of the arylnitrenium ion. In fact, the lifetimes of the NAP-generated transients were significantly longer (>100 μs) than the initial intermediates generated from **8b** and **8c**.

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(7) The identities of the products determined by the GC studies were further corroborated by separating the components of the photolysate of **6b** (0.0012 M **6b** with 1 equiv of HBF_4 with 0.015 M $Bu_4N^+Cl^-$, in CH_3CN) by flash chromatography and confirming the identity of the chloro adducts **10** and **11** by ^1H NMR.

(8) Moran, R. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1996**, *118*, 8965−8966.

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Table 1. Calculated and Experimental Absorption Maxima (nm) [Lifetimes (μs)] of **9**[a]

	9a	**9b**	**9c**
8	420, 640 [1.3]	440, 680 [6.1]	450, 690 [4.5]
6	420, 640 [1.2][b]	440, 670 [159]	440, 690 [125]
DFT	645	637	647

[a] Derived from LFP of **6** and **8**. [b] Reference 8.

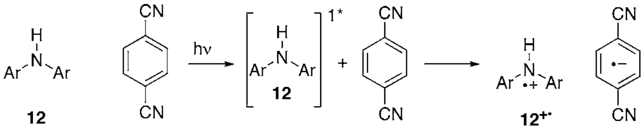
The assignment of **9** was further verified by kinetic quenching studies. In each case, addition of Cl^- was found to diminish the lifetime of the initially formed transient species. A pseudo-first-order analysis of the decay rates with varying concentrations of the trap provides second-order rate constants that are near the diffusion limit. In these experiments, we note that the trapping rate constants are slightly smaller when the nitrenium ions are generated from **8** than those from the *N*-aminopyridinium ions **6**. This difference can be traced to the acid (HBF_4) that is added to the solutions of **8** in order to protonate the hydrazine. It is likely that the acid protonates some of the Cl^- ions as well (which are much more basic in CH_3CN than in H_2O), reducing their reactivity. This was supported by repeating the experiment with **8a** in the presence of a 40-fold excess of HBF_4, which reduced the trapping rate constant by a factor of 10.

As a final confirmation of the assignments, TD-DFT calculations were performed to predict the absorption spectra for nitrenium ions **9a**−**c**.[12] TD-DFT calculations[13] have been shown to reasonably predict the UV spectra of organic compounds[14−16] including organic free radicals.[17,18] Structures for the singlet states of each example were optimized at the RB3LYP/6-31G level. Analytical force field calculations verified that the optimized structures corresponded to minima on their respective potential energy surface. In each example, the TD-DFT calculations predict a strong absorption band in the 600−700 nm region. As shown in Table 1, theoretical−experimental agreement is excellent for the unsubstituted system **9a** and reasonable for the cases of **9b** and **9c**, given the approximations inherent in the formalism. The long-lived intermediates detected in the LFP experiments on **8b** and **8c** are assigned to the cation radicals of the corresponding amines **12**. Two experiments confirm this assignment. First, we generated the same cation radicals by LFP using an alternative route. Specifically, both **12b** and **12c** were photolyzed in the presence of an electron acceptor, 1.4-dicyanobenzene (DCB).[8] It was expected that the excited singlet states of these amines would transfer an electron to DCB, following Scheme 3. The resulting radical ion pair can then be detected by LFP. The results from this experiment with **12c** are illustrated in Figure 2. The two other amines, **12a** and **12b**, both give very similar results. A sharp absorption band is seen at 720 nm for **12b** and at 730 nm for **12c**.

Table 2. Rate Constants for Reaction of **9** with Chloride Ion

precursor	k_{Cl} (M^{-1} s^{-1})
6a	1.0×10^{10}
8a	5×10^9
6b	1.1×10^{10}
8b	4.7×10^9
6c	9.8×10^9
8c	5.5×10^9

Scheme 3. Photogeneration of Amine Radical Cations



The mechanism by which $\mathbf{12}^{+\bullet}$ is formed is shown in Scheme 3. It is postulated that nitrenium ion **9** abstracts an electron from unreacted hydrazinium ion **8**. Under the acidic

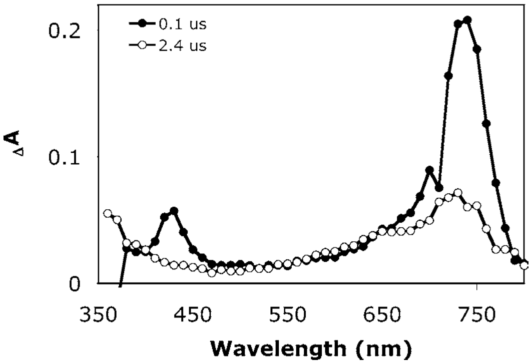


Figure 2. Transient spectra derived from LFP (355 nm excitation) of a mixture of **12c** and 1,4-dicyanobenzene (50 mM) in CH_3CN.

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(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

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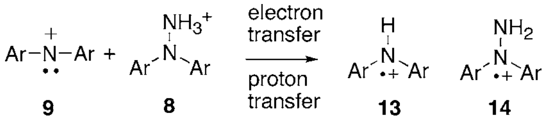
Scheme 4. Generation of Amine Radical Cation



conditions required to protonate the hydrazine, the resulting aminyl radical **13** is also protonated to give $\mathbf{12}^{+\bullet}$. This mechanism is supported by additional LFP experiments. In this case the *N*-aminopyridinium ions **6b** and **6c** were excited in the presence of the corresponding hydrazinium ions using 355 nm excitation. At this wavelength, the fomer but not the latter absorb light. In both cases long-lived absorption bands at 720 and 730 nm, attributed to **12b** and **12c**, respectively, were detected following the laser pulse. This result confirms that the postulated electron-transfer reaction (Scheme 4) occurs rapidly. It should be noted that the same intermediates could also form from a direct H atom abstraction; further experiments would be necessary to rigorously distinguish these pathways.

The unsubstituted system, **8a**, shows only a very weak signal for the cation radical **12a** following the decay of the nitrenium ion **9a**. This can be traced to the short lifetime of the latter intermediate in the absence of hydrazine. Previous studies have shown that this diarylnitrenium ion undergoes a unimolecular cyclization reaction, eventually forming carbazole.[9] This apparently competes with the reaction shown in Scheme 4.

In conclusion, photolysis of 1,1-diarylhydrazinium ions generates diarylnitrenium ions via N−N bond heterolysis.[19] The chief advantage to this method is these photolytic precursors are easier to obtain than the NAPs that have been used previously. On the other hand, these hydrazinium precursors **8** require the use of lower wavelength UV light (<300 nm) than NAPs **6**. An additional limitation is the rapid reaction of the photogenerated nitrenium ion intermediate with unconverted hydrazinium ion.

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Supporting Information Available: Procedures for precursor synthesis, product studies, laser flash photolysis, and computational studies; Cartesian coordinates for DFT-optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] On the other hand, laser flash photolysis of diphenylcarbamoyl chloride (Ph_2NCOCl) at 266 nm in CH_3CN showed no transients that corresponded to the diphenylnitrenium ion. Instead a sharp peak at 680 nm was observed. This absorption could correspond to a six-electron cyclization intermediate, which has been observed for diphenylamine in this region of the spectrum.