

Photogenerated Arylnitrenium Ions: Absorption Spectra and Absolute Rate Constants for *tert*-Butyl(4-halo-2-acetylphenyl)nitrenium Ions Measured by Time-Resolved Laser Spectroscopy

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Nitrenium ions ($R-N-R^+$) are short-lived, cationic intermediates which contain a divalent nitrogen atom.¹ Considerable evidence indicates that nitrenium ions are formed from the solvolysis of *N*-chloroamines,² hydroxylamines,³ and *O*-sulfate⁴ and *O*-acyl⁵ esters of hydroxylamines. Arylnitrenium ions are proposed intermediates in chemical carcinogenesis.⁶ Despite their importance, there has been no reported direct observation of an aryl nitrenium ion in solution⁷ nor have their lifetimes in solution been directly measured. Recent work from this laboratory⁸ has shown that photolysis of **1a** gives stable products arising from aryl nitrenium ion **2a**. Herein it is shown that the 5-halogenated derivatives **1b** and **1c** form the corresponding nitrenium ions **2** upon photolysis. These nitrenium ions have been detected by laser flash photolysis, allowing for the characterization of their electronic spectra, lifetimes, and reactivities.

The photochemical behavior of halogenated anthranilium ions **1b** and **1c** is qualitatively similar to that of the unsubstituted ion **1a**. Steady-state irradiation (>320 nm) of **1b** and **1c** gives stable products that originate from the nitrenium ion **2** (Scheme I): parent amine **3**, iminium ion **4**, and nucleophilic adduct **5**. Products **4** and **5** have been shown to arise from reactions of the singlet state nitrenium **2**.¹ Addition of water to the phenyl ring of **2**¹ gives **5**. This is a characteristic reaction of both photochemically⁸ and thermally²⁻⁵ generated aryl nitrenium ions. As expected, the yield of **5** increases with increasing concentration of water (Table I). In contrast with **2a**, addition to **2b** and **2c** occurs predominantly at the position ortho to the nitrenium

Scheme I

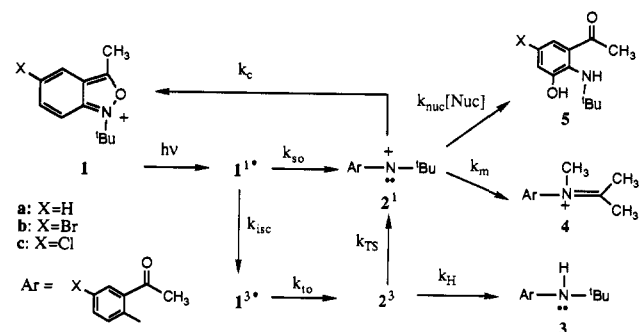


Table I. Percentage Yields of Photoproducts from Direct Irradiation of **1b,c-BF₄** in CH₃CN Containing Various Amounts of H₂O^a

[H ₂ O] ^b /conditions	substrate					
	1b			1c		
	3b	4b	5b	3c	4c	5c
0.0	14	73	8	9	72	10
0.27	23	33	43	11	39	45
3.14	37	<1	55	<1	<1	87 ^c
3.14/quencher ^d	25	<1	70			
3.14/sensitizer ^e	93	<1	trace	96	<1	trace
11.0	28	<1	59	<1	<1	89 ^c
28.0	25	<1	64	<1	<1	85 ^c

^a Yields by ¹H NMR of the photolysates containing an internal standard (ref 8a). ^b 1% HClO₄ added to prevent deprotonation of the anthranilium salts. ^c This product undergoes secondary photolysis, hence the low yields. ^d 0.05 M TMDD added as triplet quencher. ^e Thioxanthene-9-one as triplet sensitizer.

nitrogen rather than para. Apparently, the halogen atoms retard para addition.⁹

Parent amine **3** comes from H-atom transfer from the solvent to the triplet nitrenium ion **2**.³ It has been shown that this product arises from a parallel triplet reaction pathway **1**¹ → **1**³ → **3** (Scheme I).⁸ Triplet-sensitized photolysis results in enhanced yields of **3**, and addition of a triplet quencher (TMDD)¹⁰ suppresses the formation of **3** (Table I). The yield of **3** relative to that for singlet products **4** and **5** depends on k_{so}/k_{isc} as well as the efficiency of each reaction pathway (Scheme I). At nucleophile concentrations >3.14 M, **5** is the only product detected for **1c**. For **1b**, the parent amine **3** is formed in ca. 25% yield even at the highest nucleophile concentrations. This suggests that for the bromo-derivative the ratio k_{isc}/k_{so} is larger than for the chloro-derivative.¹¹

Pulsed laser (308 nm, 20–50 mJ, 10 ns) irradiation of anthranilium ions **1b** and **1c** gives the transient absorption spectra shown in Figure 1. These signals decay rapidly with first-order lifetimes (CH₃CN) of 131 and 137 ns for **1b** and **1c**, respectively. The transients are assigned to the corresponding nitrenium ions **2** on the basis of the following observations.

(1) The transient species react with nucleophiles (CH₃OH and H₂O). Pseudo-first-order rate constants for the decay of the transients, k_{obs} , were obtained at various concentrations of nucleophile. These follow $k_{obs} = k_0 + k_{nuc}[nuc]$. The k_{nuc} values thus derived fall between 10⁶ and 10⁸ M⁻¹ s⁻¹ Table II.

(9) Para addition would most likely result in loss of the halide to give 1,4-benzoquinone imines analogous to those reported earlier: Novak, M.; Pelecanou, M.; Pollack, L. *J. Am. Chem. Soc.* **1986**, *108*, 112. Such products were not detected by ¹H NMR of any of the photolysates.

(10) TMDD is tetramethyldiazatene dioxide, which has a triplet energy of 42 kcal/mol: Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077.

(11) It is important to realize that while the quantum yield of the triplet process (formation of **3**) does not depend on nucleophile concentration, the chemical yield does. This is because the singlet nitrenium ion can revert back to starting material (process k_c , Scheme I). For a more detailed discussion of the general kinetic scheme, see ref 8a.

(1) Reviews of nitrenium ion chemistry: (a) Abramovitch, R. A.; Jeyaraman, R. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 6. (b) Gassman, P. G. *Acc. Chem. Res.* **1970**, *3*, 26.

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(7) Diarylnitrenium ions have been reported as intermediates in anodic oxidations of diarylamines: (a) Svanholm, U.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 1234. (b) Serve, D. *J. Am. Chem. Soc.* **1975**, *97*, 432. (c) Rieker, A.; Speiser, B. *Tetrahedron Lett.* **1990**, *35*, 5013.

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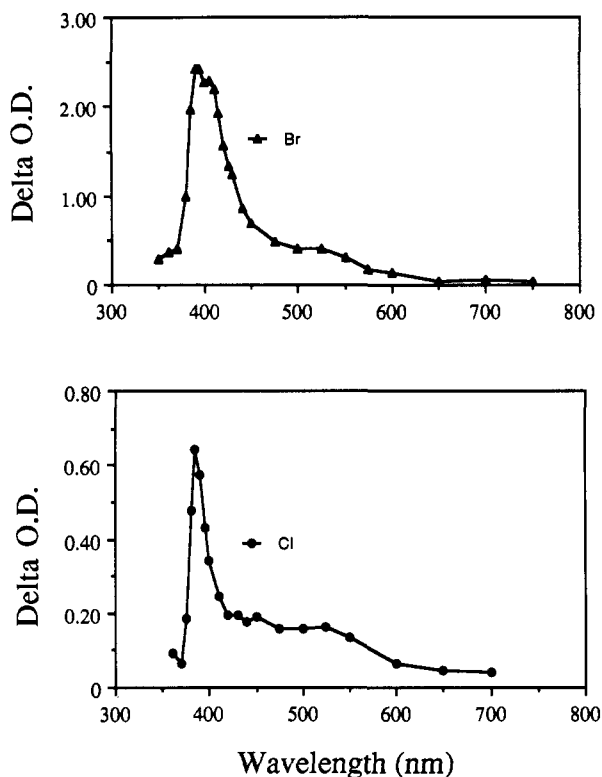


Figure 1. Transient absorption spectra obtained from laser flash photolysis of anthranilium ions **1b**-BF₄ (top panel) and **1c**-BF₄ (bottom panel) in CH₃CN. Spectra are taken 100 and 150 ns after the laser pulse for **1b** and **1c**, respectively. These absorptions are assigned to the corresponding nitrenium ions (see text).

Table II. Second-Order Rate Constants Obtained from Decay of Transient Absorptions at 385 (**1c**) and 395 (**1b**) nm Produced by Laser Flash Photolysis of **1**-BF₄ in CH₃CN with Added Nucleophiles

substrate	nucleophile ^a	k_{nuc} (M ⁻¹ s ⁻¹)
1b	H ₂ O	2.26×10^6
1c	H ₂ O	6.08×10^6
1b	MeOH	6.41×10^7
1c	MeOH	1.54×10^8

^a 1% of HClO₄ was added to the nucleophile to prevent deprotonation of **1**.

(2) The k_{nuc} values are of a similar magnitude to those reported for similar species. Competition experiments by Fishbein and McClelland¹² give an upper limit of 2×10^7 M⁻¹ s⁻¹ for the reaction of 2,6-dimethylnitrenium with H₂O. Similar experiments recently reported by Novak et al.¹³ give an upper limit of 1.6×10^6 M⁻¹ s⁻¹ for reaction of 4-biphenylnitrenium with H₂O. Reactions of arylcarbenium ions with water typically have rate constants of 10^6 – 10^8 M⁻¹ s⁻¹.¹⁴

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(3) The dependence of k_{nuc} on the structure of the nucleophile follows the expected trend. The reactions with CH₃OH are 10–20 times faster than the corresponding H₂O reactions. This follows the same trend as reported for the reactions of arylcarbenium ions with nucleophiles.¹⁴

(4) The lifetimes are not diminished by the addition of excited triplet-state quenchers O₂ (air-saturated sample) or TMDD (10 mM). This excludes the possibility that the spectra are due to excited triplet states of **1**.

(5) The spectra and lifetimes are insensitive to changes in the solvent or the counterion (provided that they are nonnucleophilic). The same transient spectra are observed in CH₃CN, CH₂Cl₂, and CF₃CH₂OH solvents and with both the ClO₄⁻ and BF₄⁻ salts. This excludes any transient species that would be particular to a solvent such as the nitrile ylide-type products that have been detected when arylcarbenes are generated in CH₃CN.¹⁵

Nitrenium ions have two low-energy electronic configurations: the singlet, where the highest energy electrons are paired, and the triplet, where the highest energy electrons are unpaired. Generally, arylnitrenium ions are thought to be ground-state singlets due to electron donation by filled π -orbitals in the phenyl ring. Ab initio¹⁶ and semiempirical¹⁷ calculations on arylnitrenium ions typically predict ground-state singlets with large energy gaps. It has been shown that H-atom donors react rapidly with triplet nitrenium ions to give the parent amines.^{8a} To determine the spin state of **2b** and **2c**, we examined the reactivity of the transient species toward tris(trimethylsilyl)silane, an efficient H-atom donor.¹⁸ The lifetimes of the transient spectra were not decreased when up to 0.10 M of this reagent was added to the CH₃CN solutions. This observation and the rapid reactions observed with nucleophiles provide circumstantial evidence that the observed transient species is a singlet nitrenium ion.

These experiments show that arylnitrenium ions can be generated photochemically and detected using time-resolved techniques. The reactivity of these species toward nucleophiles is qualitatively similar to that of arylcarbenium ions. The approach employed here should prove useful for further explorations of nitrenium ion behavior.

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