Photogenerated Arylnitrenium Ions: Photoisomerization of the *N-tert*-Butyl-3-methylanthranilium Ion and Spin-Selective Reactivity of the Isomeric Arylnitrenium Ion

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Received November 16, 1992

Abstract: The photochemical behavior of the *N-tert*-butyl-3-methylanthranilium ion was examined with the goal of understanding the chemical behavior of the intermediate nitrenium ion. Trapping experiments show that the corresponding nitrenium ion is generated through an excited-state, electrocyclic ring-opening reaction. Nucleophiles add to the aromatic ring of the nitrenium ion. In the absence of nucleophiles, two new products are detected, the parent amine and an iminium ion. The latter results from a [1,2]-sigmatropic shift of a methyl group from the *tert*-butyl residue to the nitrenium nitrogen. Yields of the parent amine are increased when triplet sensitization is used as the mode of photolysis. Likewise, its yield is suppressed when triplet quenchers are employed. These experiments show that the reactions of the arylnitrenium ion depend on its electronic spin configuration: the triplet favors formation of the parent amine, and the singlet favors rearrangement and nucleophilic addition.

Nitrenium ions are reactive intermediates which contain a divalent, positively charged nitrogen atom.[1,2] These species are of interest not only because of their open-shell electronic structure but also because of their postulated role in carcinogenesis.[3-5] Aromatic amines are metabolized to form hydroxylamines which, in turn, can be converted to their *O*-sulfate or *O*-acetate esters. It has been shown that these types of esters react with DNA to form covalent adducts with the guanine residues.[6,7] The mechanism of this DNA-damaging step is not known in detail. It has been suggested to involve initial heterolysis of the ester to give the nitrenium ion which, in turn, attacks the DNA. On the other hand, recent work by Novak,[8] Ohta,[9] and Boche[10] has shown that these esters can undergo concerted (S_N2) substitution at nitrogen.

Nitrenium ions are isoelectronic with carbenes. Therefore, these species can possess either a singlet ($S = 0$) or triplet ($S = 1$) lowest energy electronic configuration. The simplest example NH_2^+ is a ground state-triplet.[11-13] In general, phenyl rings act as electron donors and stabilize the singlet state relative to the triplet state.[14] The best available ab initio calculation on phenylnitrenium predicts that the singlet is favored by ca. 10 kcal/mol.[15] We have recently reported semiempirical calculations which predict that nitrenium ions with aromatic substituents are ground-state singlets with substantial energy gaps.[16] These energy gaps are affected by the nature of the substituents. Electron-withdrawing groups on the phenyl ring and sterically demanding substituents are both predicted to stabilize the triplet state relative to the singlet state.

Reports of nitrenium triplet-state chemistry in solution have been controversial. Initially, certain reactions of alkylnitrenium ions were attributed to the triplet on the basis of solvent heavy-atom effects.[17] Subsequent workers questioned this interpretation based on somewhat different experiments.[18-20] The difficulties with interpreting the earlier work can be traced to the inherent instability of the nitrenium precursors. Most of the previous work in this area involved experiments where nitrenium ions were generated by solvolysis of precursors such as *N*-chloroamines, *N*-(sulfonyloxy)amines, and *N*-(acyloxy)amines. Interpretation of data from these experiments is complicated due to competing homolytic/heterolytic modes of bond scission,[18-22] metal ion-induced decomposition of the precursors,[23,24] and concerted decomposition mechanisms not involving free nitrenium ions.[8,10,25,26]

To avoid some of the complications with generating nitrenium ions solvolytically, our approach was to generate these species photochemically. Although there has been considerable recent interest in photogeneration of carbocations,[27-30] few methods exist

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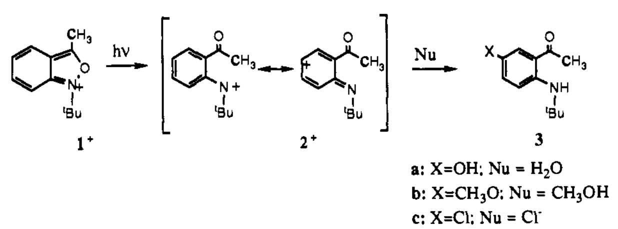
Scheme I



for photogeneration of nitrenium ions. Haley[31] reported that photolysis of *N*-alkylanthranilium (*N*-alkyl-2,1-benzisoxazolium) ions (e.g., **1**$^+$, Scheme I) leads to stable products that were attributed to reactions of the isomeric alkylarylnitrenium ions **2**$^+$. Hansen[32-34] and Giovanni[35,36] have shown that photolysis of the conjugate acids of anthranils gives similar results. In the latter case, the initial photochemical step is isomerization to a primary arylnitrenium ion.

Photochemical generation holds several significant advantages over solvolytic generation. First, if the photoprecursor is thermally stable, ambiguities from competing concerted decomposition reactions (S_N2 vs S_N1) are avoided. Second, photochemical generation allows selective preparation of triplet nitrenium ions through triplet sensitization experiments. Finally, with photochemical generation, nitrenium ions could be generated and spectroscopically characterized using laser flash photolysis or matrix isolation. Before quantitative spectroscopic and kinetic measurements on nitrenium ions can be interpreted, the mechanism of photogeneration and subsequent chemical reactions must be well understood. The experiments reported herein were undertaken with the aim of further characterizing the photoisomerization of anthranilium ions to arylnitrenium ions. Of special interest is the behavior of triplet nitrenium ions and whether they exhibit reactivity different from that of the singlet state.

Nitrenium ion **2**$^+$ was generated by direct and triplet-sensitized photolysis of **1**$^+$. The identity of the photoproducts and their distributions were determined as a function of trapping-agent concentration and triplet-sensitized vs direct irradiation. Nitrenium ion **2**$^+$ is efficiently trapped by nucleophiles, such as chloride ion and alcohols. In the absence of trapping agents, it undergoes rearrangement of a *tert*-butyl methyl group competitively with formation of the parent amine **4**. Yields of the parent amine **4** are increased in the presence of H-atom donors and when **2**$^+$ is generated by triplet sensitization. These results confirm that photolysis of anthranilium ion **1**$^+$ generates the corresponding nitrenium ion **2**$^+$. Significantly, this report shows that the reactivity of the nitrenium ion depends on its electronic spin state: the triplet state favors formation of the parent amine **4**, and the singlet favors nucleophilic addition and rearrangement. This study represents the first unambiguous observation of triplet nitrenium ion chemistry in solution.

Results

Preparative Photolysis. Ultraviolet irradiation of **1**$^+$ in the presence of nucleophiles gives ring-adducts **3a–c** in excellent to reasonable preparative yields. These adducts result from addition to the para position of nitrenium ion **2**$^+$ (Scheme I). In general, these are the exclusive photoproducts provided the nucleophile is present in concentrations greater than 0.1 M. Results of the preparative photolyses are compiled in Table I. The outcome is not noticeably affected by either solvent or counterion. Thus, the methanol adduct **3b** appears to be the sole product in both CH_2Cl_2 and CH_3CN and with both the perchlorate and the tetrafluoroborate counterions (studies of the perchlorate salt in CH_2Cl_2 were precluded by its low solubility). The distribution of photoproducts was sensitive to even trace amounts of water. For example, irradiation of **1**$^+$ in CH_2Cl_2 gives significant amounts of **3a** unless care is taken to remove residual water from the solvent and glassware.

Table I. Isolated Yields from Irradiation of 1^+X^- in the Presence of Nucleophiles

trap (M)	solvent	X^-	product (% yield)
H_2O (5.5)	CH_3CN	ClO_4^-	**3a** (65)
CH_3OH (0.46)	CH_3CN	ClO_4^-	**3b** (81)
Bu_4NCl (0.02)	CH_3CN	ClO_4^-	**3c** (40)
CH_3OH (2.7)	CH_2Cl_2	BF_4^-	**3b** (83)

Scheme II

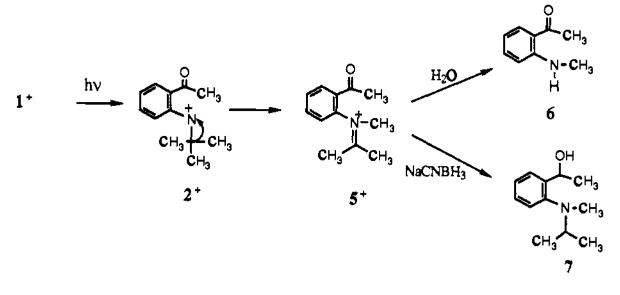
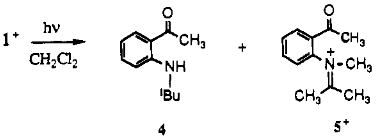


Table II. Quantum Yields for Decomposition of $1^+BF_4^-$

solvent (trap, M)	Φ
CH_2Cl_2	0.028
CH_3CN	0.10
THF	0.11
CH_3CN (H_2O, 3.0)	0.58

In the absence of nucleophiles, two other products are generated. Photolysis in anhydrous CH_2Cl_2 gives iminium ion **5**$^+$ as the major photoproduct (93%) (eq 1). The parent amine **4** is formed in trace (2%) amounts under these conditions. Iminium **5**$^+$ apparently arises from a [1,2]-shift of a methyl group from the *tert*-butyl moiety to the nitrogen of nitrenium ion **2**$^+$. The structure of the iminium salt **5**$^+$ was determined by its resonances in the ^{1}H and ^{13}C NMR spectra of the photolysis mixture. Product **5**$^+$ is hydrolytically unstable and was therefore not isolated. Instead, it was converted to methylamine **6**; the latter was then isolated and fully characterized. Further confirmation of the structure of **5**$^+$ came from its conversion to **7** upon reductive ($NaCNBH_3$) treatment of the photolysis mixture (Scheme II).



(1)

Formation of the parent amine **4** is significant (vide infra). To determine if this product was formed by an H-atom-transfer process, photolyses were carried out in the presence of hydrogen-atom donors. As expected, yields of **4** are enhanced in tetrahydrofuran (THF) solvent. The yield of the rearrangement product **5** is correspondingly reduced (Table II, direct photolysis). THF has a C–H bond dissociation energy of 92 kcal/mol compared with 100.6 kcal/mol for CH_2Cl_2.[37]

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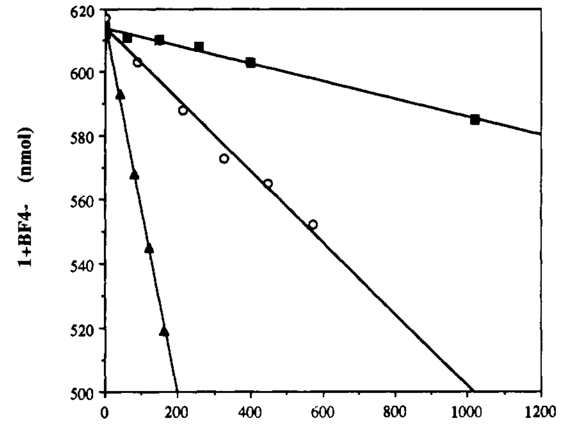
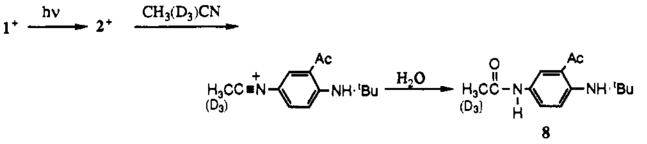
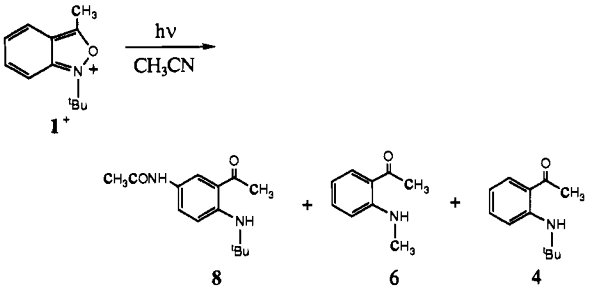


Figure 1. Photolysis rates of $1^+BF_4^-$ in CH_2Cl_2 (squares), THF (circles), and 3 M H_2O/CH_3N (triangles). Solutions were purged with N_2 and irradiated at 312 ± 9 nm. The decomposition of $1^+BF_4^-$ was monitored by UV-vis absorption. The number of photons absorbed were counted using ferrioxalate-calibrated photodiodes. The moles of substrate were normalized to the same initial value.

Scheme III



When photolysis of 1^+ is carried out in acetonitrile, acetamide **8** is formed along with 5^+ and **4** (eq 2). Product **8** is the result of Ritter-like[38] addition of the solvent to the ring position para to the nitrenium group. The nitrilium ion intermediate is not detected under the conditions employed. It is apparently hydrolyzed by traces of water in the solvent. Further confirmation of this mechanism comes from an isotope-labeling experiment. When the photolysis is carried out in CD_3CN, the ^1H NMR spectrum of the crude photolysis mixture shows the resonances for 5^+ and the conjugate acids of **4** and **8**. However, in the deuterated solvent, the resonance assigned to the acetamido methyl group of **8** is absent (see Experimental Section and Scheme III).



(2)

Quantum Yield Studies. In order to assess the reversibility of the photoisomerization of 1^+, the quantum yield for its decomposition, Φ, was measured under various conditions. If nitrenium ion 2^+ forms irreversibly upon photolysis, then the presence of trapping agents would have no effect on the quantum yield of decomposition. On the other hand, if 2^+ is capable of reverting back to 1^+, then Φ would be expected to increase with higher concentration of trapping agents and when photolysis is carried out in more reactive media. Φ depends on the solvent and concentration of trapping agents employed. Figure 1 shows the rates of photodecomposition of 1^+ in CH_2Cl_2, THF, and 3 M H_2O/CH_3CN. Quantum yields derived form these plots are collected in Table II. The photoreactivity of 1^+ is highest when a strong nucleophile is present. Thus, in the presence of 3 M H_2O, $\Phi = 0.58$. THF is a poor nucleophile but is expected to be more reactive toward H-atom transfer. In this solvent, $\Phi = 0.11$. In CH_2Cl_2, which is both non-nucleophilic and a poor H-atom source, the quantum yield is the lowest: $\Phi = 0.028$.

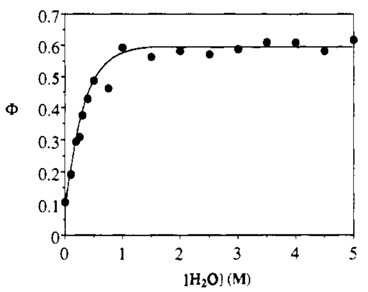


Figure 2. Dependence of the quantum yield of photolysis of $1^+BF_4^-$ on the concentration of H_2O in CH_3CN. Individual quantum yields were determined from the initial photolysis rates, as described in Figure 1.

Table III. Product Distributions from Direct Irradiation and Triplet-Sensitized Irradiation of $1^+BF_4^-$ in Various Solvents

	products (% yield)	
solvent (trap, M)	direct	triplet
CH_2Cl_2	**4** (2), 5^+ (93)[a]	**4** (77), 5^+ (21)
THF	**4** (76), 5^+ (11)	**4** (97)
CH_3CN	**4** (11), 5^+ (48), 8 (29), **3a** (10)	**4** (47), **8** (37), **3a** (10)
CH_2Cl_2(MeOH, 2.7)	**3b** (98)	**4** (51), **3b** (44)
THF (MeOH, 0.118)	**4** (17), 5^+ (trace), **3b** (76)	**4** (86), **3b** (10)

[a] Trace amount of **3a** detected.

The quantum yield for decomposition, Φ, depends on the concentration of the nucleophilic trap. Figure 2 shows the Φ in CH_3CN as a function of added H_2O concentration. This quantity is found to increase with $[H_2O]$, reaching 0.58 at 2.0 M. Increasing the water concentration beyond that point results in no further increase in Φ. The dependence of Φ on water concentration indicates that the intermediate being trapped (singlet nitrenium ion, see the Discussion section) can revert back to ground-state starting material in the absence of the trap. The saturation behavior shows that above ca. 2 M, virtually all of the intermediates thus generated are intercepted by water. If that intermediate were the excited singlet state of the anthranilium ion, then the limiting quantum yield would be 1.0. The fact that it is less than 1.0 indicates that the intermediate being trapped is formed subsequently to the excited singlet state. This intermediate is formed with a quantum yield of 0.58; in the absence of water, it mainly recyclizes back to the ground-state anthranilium ion.

Triplet-Sensitized Photolysis. Reaction of nitrenium ions to form their parent amines has been attributed to the nitrenium triplet state.[17] However, this interpretation, which was based on solvolysis experiments, has proven controversial.[18,19] Triplet energy transfer makes it possible to prepare the excited triplet state of the anthranilium ion without passing through its excited singlet state. The excited triplet anthranilium ion rearranges to initially form the triplet nitrenium ion. Even if the triplet state is not the lowest energy state of the nitrenium ion, it would be possible to observe its chemical reactions provided that they are rapid relative to intersystem crossing. Therefore, it is of interest to determine if the triplet sensitization of 1^+ gives stable products that are different from direct irradiation.

The results of triplet sensitization experiments are listed in Table III along with results from direct irradiations performed under the same conditions. In all cases, triplet sensitization gives higher yields of the parent amine **4** compared with those of direct photolysis. In particular, **4** is generated quantitatively in THF when triplet sensitization is employed. In CH_2Cl_2, the difference

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Table IV. Yields of Addition Product **3a** or **3b** and Reduction Product **4** from Direct and Triplet-Sensitized Photolysis of $\mathbf{1^+BF_4^-}$ in THF Containing Added Water/Methanol and Triplet Quencher TMDD

		direct		triplet	
trap/quencher	[trap]	**3a/b**	**4**	**3a/b**	**4**
none	0.00	<1[a]	76	<1	97
none/TMDD [0.062]	0.00	<1[b]	41		
H_2O	0.27	37	59	trace	96
H_2O/TMDD [0.058]	0.27	78	18		
H_2O/TMDD [0.125]	0.27	88	10		
H_2O	1.35	74	22	2	95
H_2O	5.05	84	12	3	94
MeOH	0.12	76	17	10	86

[a] Rearrangement product 5^+ is formed in 11% yield. [b] Rearrangement product 5^+ is formed in 54% yield.

Table V. Yields of Addition Product **3b**, Rearrangement Product $\mathbf{5^+}$, and Reduction Product **4** from Direct and Triplet-Sensitized Photolysis of $\mathbf{1^+BF_4^-}$ in CH_2Cl_2 Containing Added Methanol

	direct		triplet	
[CH_3OH]	**3b**	$\mathbf{5^+}$	**3b**	**4**
0.00	<1	93	<1	77
0.014	58	39	43	53
0.12	93	5	73	24
1.18	94	4	57	42
2.69	98	<1	44	51
24.7 (neat)	98	<1	32	66

between triplet and direct irradiation is particularly pronounced. Direct irradiation gives 2% of **4** while triplet-sensitized irradiation gives 77% of **4**. With acetonitrile, a similar difference is observed; the yield of **4** is significant only when triplet sensitization is employed.

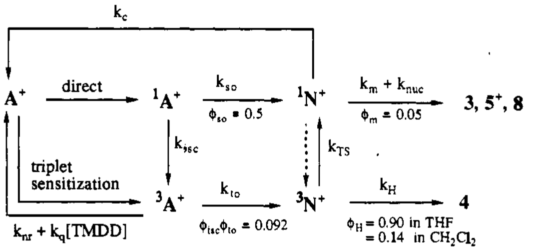
Competitive Trapping Experiments. The above results revealed two modes of nitrenium ion reactivity: nucleophilic addition to give adducts such as **3** and **8** as well as reduction to give the parent amine **4**. Competitive trapping experiments, using both direct irradiation and triplet sensitization, were undertaken with the aim of understanding the factors which control the balance between these two pathways. The results are given in Tables IV and V.

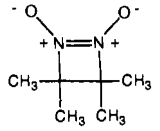
In the first series of experiments, THF is the solvent and varying amounts of water were added (Table IV). Reaction of the nitrenium ion $\mathbf{2^+}$ with the solvent is expected to give the reduction product, and reaction with water is expected to yield the nucleophilic adduct **3a**. Under direct photolysis conditions, this behavior is observed. Increasing water concentration leads to higher yields of the adduct **3a** and correspondingly lower yields of the parent amine **4**. In contrast, triplet sensitization gives **4** almost quantitatively, even with water concentrations as high as 5 M.

A similar study was undertaken using CH_2Cl_2 as the solvent and methanol as the trap (Table V). In the direct irradiation, the nitrenium ion is efficiently trapped by methanol; nearly quantitative yields of the methoxy adduct **3b** are obtained provided the trap concentration is greater than 0.2 M. When triplet sensitization is employed, a rather interesting result is obtained. The yield of **3b** increases with increasing methanol concentration up to 0.12 M. As the methanol concentration is increased beyond this point, the yield of **3b** *decreases*. When neat methanol is employed as the solvent, the yields are 32% for **3b** and 66% for **4**. The implications of these results relative to the reactions of singlet and triplet nitrenium ions are considered in the Discussion section. Here, it is noted that methanol can react with the nitrenium ion through two pathways: one leading to the parent amine **4** and the other leading to the methoxy adduct **3b**. In contrast, water can only react with $\mathbf{2^+}$ by nucleophilic addition.

Triplet-Quenching Experiments. Because of the high yields of **4** obtained upon triplet sensitization, the involvement of triplet pathways in the direct photolysis experiments was considered. Intersystem crossing can occur between anthranilium excited states as well as between the nitrenium ion states. In other words, the excited singlet anthranilium ion $\mathbf{1^+}$ might intersystem cross in competition with ring opening. This would give the excited triplet anthranilium ion which, in turn, would partition between ring opening to the triplet nitrenium and relaxation to the ground-state anthranilium (Scheme IV). Triplet quenchers, such as tetramethyldiazetine dioxide (TMDD),[39] undergo energy transfer from triplet excited states. This has the effect of suppressing any photochemical processes which occur through triplet pathways. Addition of TMDD to a sample containing $\mathbf{1^+}$ and 0.27 M water in THF alters the product distribution. It reduces the yield of the parent amine **4** and leads to an increase in the yield of **3a** (see Table IV). This implies that formation of **4** in the direct photolysis comes from intersystem crossing in the anthranilium ion excited state.

Scheme IV





=TMDD

Discussion

The objective of this study was to determine the mechanistic pathways followed in the photolysis of $\mathbf{1^+}$. Of particular interest was whether the spin state of the nitrenium ion intermediate plays a role in its chemical behavior. In the first part of this section, the stable products and their mechanisms of formation from $\mathbf{2^+}$ are considered. In the second part, a general model for the photochemistry of anthranilium ions is described. This model accounts for the results of the trapping, sensitization, and quenching experiments. A central premise of this model is that the triplet and singlet spin states of $\mathbf{2^+}$ show different reactivity. Below, $^1N^+$ and $^3N^+$ are used to refer specifically to the singlet and triplet states of $\mathbf{2^+}$. Similarly, $^1A^+$ and $^3A^+$ are used to refer to the singlet and triplet excited states of anthranilium ion $\mathbf{1^+}$. In the third section, the quantitative feasibility of the model is assessed by comparing the yields predicted from the quantum yields with those actually measured. Finally, the magnitude of the singlet–triplet energy gap for $\mathbf{2^+}$ is discussed in light of this and previous work.

1. Intermediacy of the Nitrenium Ion. The stable products from the photolysis of **1** can all be understood to arise from the nitrenium ion $\mathbf{2^+}$. The addition of nucleophiles to arylnitrenium ions at the ortho and para ring carbons is a characteristic reaction of aromatic nitrenium ions.[9,23,40–46] Molecular orbital analysis

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predicts that the highest charge density lies on the ring carbons,[15,47] making them susceptible to attack by hard nucleophiles. Many reactions where nucleophiles add at nitrogen now appear to occur through concerted (S_N2) pathways.[8,10,25]

The formation of the solvent-addition product **8** illustrates the highly electrophilic nature of the nitrenium ion 2^+. Nitriles are very poor nucleophiles. For example, acetonitrile reacts with benzhydryl cations ca. 3 orders of magnitude less rapidly than does water.[48] While the reactions of nitriles with nitrenium ions have not been previously documented, the present example can readily be understood by analogy to the carbocationic process. Therefore, product **8** provides further evidence for formation of 2^+.

Iminuim ion 5^+ results from a [1,2]-shift of a methyl group from the alkyl portion of 2^+. Rearrangements of the alkylnitreniums is well documented.[2,20,49-51] In contrast, few examples of Wagner–Meerwein rearrangements of alkylarylnitrenium ions are known. Gassman and Campbell[40,42,44] generated a series of *tert*-butylarylnitrenium ions by solvolysis of *N*-chloroamines. No rearrangement was observed. The major products were from solvent addition and addition of the leaving group to the aryl ring. This is consistent with the results reported here. Rearrangement is rather sluggish compared with nucleophilic addition. Even 0.27 M H_2O is sufficient to cause addition to occur to the exclusion of rearrangement. Competition studies by Fishbein and McClelland[52] show that one particular arylnitrenium ion ((2,6-dimethylphenyl)nitrenium) reacts with water with a rate constant of 2×10^7 M^{-1} s^{-1}. Use of this value as a rough estimate for the rate of methanol addition to 2^+ along with the ratio of 5^+ to **3b** from direct irradiation in the presence of 0.014 M methanol (Table V) suggests that the rearrangement occurs in the nanosecond time regime.

The parent amine **4** is generated in the presence of H-atom donors. Novak and Hoffman have shown that under solvolytic conditions, the analogous product can be generated by pathways not involving free nitrenium ions. For example, in one case, the parent amine was shown to be the result of Fe^{2+} reduction of the starting material (a (sulfonyloxy)amine).[23,24] In other cases, parent amines are created through a homolytic decomposition of the *N*-chloroamine precursor.[18,19,21] Primary nitrenium precursors can undergo an α-elimination, giving the corresponding nitrene, which, in turn, reacts to form the parent amine.[8,53]

None of these alternative pathways appears to be significant under the conditions employed here. Nitrenium 2^+ is generated by a rearrangement rather than a dissociation reaction. Therefore, homolytic dissociation is not possible. (The analogous process would give a singlet diradical cation, which simply corresponds to an excited-state electronic configuration of 2^+.) While it is possible that **4** could arise from reduction of the anthranilium ion by Fe^{2+} (or some other metal ion), the high concentrations of substrate employed in the study make this unlikely. For example, the photolysis of $1^+BF_4^-$ in THF was done with a starting concentration of 2×10^{-3} M. It seems improbable that the millimolar concentrations of Fe^{2+} in THF required for the reduction would escape detection. Moreover, the impurity quenching mechanism does not account for the correlation of the yields of **4** with the presence of H-atom donors, triplet sensitization, and triplet quenching. The α-elimination reaction is unlikely when the proton is replaced with a *tert*-butyl group. In fact, this group is still present in products **4** and **5**.

The parent amine **4** could arise from 2^+ either by a direct hydride abstraction or else by sequential H-atom transfers to 2^+. Hydride abstraction, being a two-electron process, would be characteristic of the singlet-state nitrenium ion. H-atom transfer, being a one-electron process, would be characteristic of the triplet. The triplet sensitization and quenching experiments described below cause us to attribute formation of **4** to a H-atom transfer mechanism to the triplet state of 2^+.[54] The subsequent step is either electron transfer or else a second H-atom transfer.

2. Spin-Selective Reactivity. The evidence for spin-selective reactivity comes primarily from the observation of differing product distributions from triplet-sensitized and direct irradiation. In all cases, triplet-sensitized photolysis gives higher yields of the parent amine **4** at the expense of the rearrangement product 5^+ and the addition products **3** and **8**. These observations exclude any mechanisms where all products originate from a common intermediate (such as $^1N^+$) or from rapidly equilibrating intermediates (such as $^1N^+$ and $^3N^+$). In these cases, the product distribution would be identical regardless of the mode of generation. These observations require that there be at least two intermediates: the first is preferentially generated upon direct photolysis and forms the addition and rearrangement products; the second is preferentially generated by triplet sensitization and leads to the parent amine **4**.

The results from trapping, sensitization, and quenching studies are explained by the spin-selective reactivity model which is diagrammed in Scheme IV. Included in that scheme are estimates for the quantum efficiencies of each reaction step which are derived in part 3, below. Direct photolysis of 1^+ forms the excited singlet anthranilium ion $^1A^+$. The latter partitions between ring opening (k_{so}) to give singlet nitrenium ion $^1N^+$ and intersystem crossing (k_{isc}) to give the excited triplet anthranilium $^3A^+$. The triplet undergoes ring opening (k_{TO}), giving triplet nitrenium ion $^3N^+$. Additionally, $^3A^+$ can be quenched by energy transfer to TMDD (k_q). The singlet nitrenium $^1N^+$ either reacts by rearrangement (k_m) or nucleophilic addition (k_{nuc}) or else it reyclizes back to the ground state of the starting material 1^+ (k_c). In the absence of nucleophiles, recyclization is the predominant process. The triplet nitrenium ion $^3N^+$ either reacts by hydrogen transfer to form the parent amine **4** (k_H) or suffers intersystem crossing to $^1N^+$ (k_{TS}). MO calculations[16] and the analysis described below both indicate that the singlet state of the nitrenium ion is lower in energy. In this case, the triplet nitrenium ion is trapped only if its reactions are rapid compared with those of spin inversion.

Triplet-Sensitized Photolysis. According to Scheme IV, the analysis of the triplet sensitization data is less complicated since only a single reaction pathway is operative. Therefore, these experiments are considered first. Triplet-sensitized irradiation generates $^3A^+$ which undergoes ring opening to $^3N^+$. The latter partitions between H-atom transfer from the solvent (k_H) and intersystem crossing to $^1N^+$ (k_{TS}). In THF, a good H-atom donor, $^3N^+$, is trapped efficiently and **4** is the sole product. In CH_2Cl_2 and CH_3CN, $^3N^+$ is trapped less efficiently and the singlet products 5^+ and **3** are observed. It is important to realize that the chemical yield of **4** is not a direct measure of the efficiency of the triplet reaction. Because $^1N^+$ can recyclize back to starting material, the yield of **4** is also sensitive to the rates of the singlet processes. This can be seen from the following analysis. The chemical yield for **4**, Y_4, is related to the quantum yields Φ for each of the products formed:

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(54) Preliminary laser flash photolysis experiments show that for some derivatives of 2^+ the cation radicals resulting from H-atom transfer to the nitrenium ion are detected when the nitrenium ion is generated in THF. No transient absorption signals were detected when 1^+ was irradiated. This might be due to its low efficiency of triplet formation under direct irradiation.

$$Y^t_4 = \frac{\Phi^t_4}{\Phi^t_3 + \Phi^t_4 + \Phi^t_{5+}} \tag{3}$$

The Φ are the products of quantum efficiencies of each elementary step, ϕ, which leads to that product. The quantum efficiency for a given step is the rate constant for that reaction divided by the sum of the rate constants for all possible reactions undergone by that intermediate. (For example, $\phi_{to} = k_{to}/\{k_{to} + k_{nr} + k_q[\text{TMDD}]\}$.) Under triplet sensitization, all products originate from $^3A^+$:

$$\Phi^t_4 = \phi_{ET}\phi_{to}\phi_H \tag{4}$$

$$\Phi^t_{5+} = \phi_{ET}\phi_{to}\phi_{TS}\phi_m \tag{5}$$

$$\Phi^t_3 = \phi_{ET}\phi_{to}\phi_{TS}\phi_{nuc} \tag{6}$$

where ϕ_{ET} is the efficiency of energy transfer from the sensitizer. Substituting the efficiencies in eqs 4–6 in for the quantum yields in eq 3 and noting that $\phi_{TS} = 1 - \phi_H$ gives the following expression for the yield of **4** as a function of the quantum efficiencies.

$$Y^t_4 = \frac{\phi_H}{\phi_H + (1 - \phi_H)(\phi_{nuc} + \phi_m)} \tag{7}$$

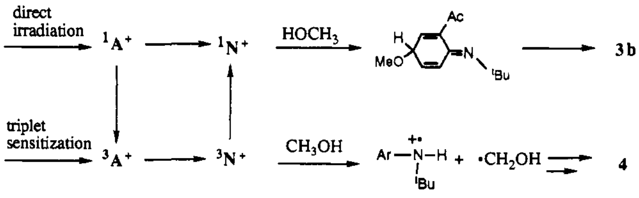
The yield of **4** decreases as the efficiencies of the singlet processes ($\phi_{nuc} + \phi_m$) increase. Only when ($\phi_{nuc} + \phi_m$) = 1 will the yield of **4** give the efficiency of H-atom transfer.

The effect of nucleophiles on the yield of **4** is seen in the THF/H_2O triplet experiments listed in Table IV. Increasing [H_2O] results in a slight, but systematic, decrease of the yield of **4** (from 97 to 94%). Likewise, the yield of **3a** is ca. 3% at 5.05 M H_2O. THF is a good, but not totally efficient, triplet trap. The results with MeOH are similar: a 10% yield of **3b** is detected. The lack of an exact, quantitative agreement for the efficiency of THF trapping in the presence of the two nucleophiles could be caused by greater aggregation of the H_2O in THF compared with that in methanol. Also, the polarity changes caused by the traps may affect the individual rate constants differently.

The triplet-sensitized competitive trapping experiments described in Table IV provide further support for the mechanism in Scheme IV. At moderate [CH_3OH], the methoxy adduct **3b** is the major product. As the [CH_3OH] increases, the yield of **3b** decreases in favor of the parent amine **4**. In contrast, upon direct irradiation, the yield of **3b** increases monotonically with the concentration of methanol. This shows that the turnaround in the yield of **3b** is connected to the spin state of the nitrenium ion. Alternative explanations for the turnaround, such as the aggregation of methanol in acetonitrile, are excluded for this reason.

The turnaround in the yield of **3b** in the triplet sensitization experiments is explained by the mechanism in Scheme V. These observations provide further evidence for the involvement of the triplet state of $\mathbf{2}^+$. At low methanol concentrations, $^3N^+$ is formed and relaxes to $^1N^+$, which, in turn, reacts with methanol via nucleophilic substitution to yield **3b**. At high methanol concentrations, the $^3N^+$ is trapped prior to intersystem crossing, reacting with methanol (and solvent) via H-atom transfer to give **4**. At the very least, these data require that there be two reactive species. For example, if $^1N^+$ were reacting with methanol by both hydride transfer (giving **4**) and nucleophilic addition (giving **3b**), then these processes would occur at the same ratio at all methanol concentrations. As the methanol concentration is reduced, the reaction with the solvent leading to **4** would become more likely. This would lead to a direct correlation of the yield of **3b** with methanol concentration rather than the turnaround actually observed.

Scheme V



Direct Irradiation. Analysis of these experiments is somewhat more complicated by the existence of two parallel reaction pathways. This arises from the possibility of partitioning of $^1A^+$ between ring opening to give $^1N^+$ and intersystem crossing to give $^3A^+$.[55] If intersystem crossing were the exclusive fate of $^1A^+$, then all of the nitrenium ions would follow the same reaction pathway as that obtained from triplet-sensitized photolysis. In that case, the results from direct irradiation would be identical with those from triplet-sensitized photolysis. Because this is not the case, $^1A^+$ either reacts exclusively through ring opening to $^1N^+$ or partitions between ring opening and intersystem crossing with a branching ratio of k_{so}/k_{isc}.

We now consider the origins of the parent amine **4** from the direct photolysis experiment. If this product is formed from triplet nitrenium ion $^3N^+$ as implied in Scheme IV, then some process must connect the singlet and triplet manifolds. This could occur either by intersystem crossing from singlet to triplet nitrenium ion or by intersystem crossing in the excited anthranilium ions. The TMDD quenching experiments implicate the latter pathway. As increasing amounts of TMDD are added, the chemical yield of the parent amine **4** is reduced in favor of the presumed singlet products $\mathbf{5}^+$ and **3**. If **4** were being formed directly from $^1N^+$, then the triplet quencher would have no effect on the product distribution. TMDD quenching also argues against the possibility that **4** arises from a direct hydride abstraction by $^1N^+$. If **4** were being formed from ring opening to $^1N^+$ followed by intersystem crossing to $^3N^+$, again TMDD would have no influence on the product distribution.

The quencher TMDD converts $^3A^+$ back to starting material by energy transfer. It is not anticipated that TMDD would promote the relaxation of $^3N^+$ back to $^1N^+$. This is because the triplet energy of TMDD (42 kcal/mol)[39] is much higher than the expected singlet–triplet gap for $\mathbf{2}^+$.[56] Semiempirical calculations predict an upper limit to the singlet–triplet gap of $\mathbf{2}^+$ of only 15 kcal/mol.[16] The efficiency by which $^3A^+$ is intercepted depends on its lifetime as well as the TMDD concentration. The quantum efficiency of triplet ring opening (ϕ_{to}) is given in eq 8, where k_t is the rate constant for triplet ring opening, k_{nr} is the rate constant for nonradiative decay of $^3A^+$ to ground-state $\mathbf{1}^+$, and k_q is the rate constant for energy transfer.

$$\phi_{to} = \frac{k_{to}}{k_{to} + k_{nr} + k_q[\text{TMDD}]} \tag{8}$$

Only in the limit of infinite TMDD concentration would the triplet reaction be completely suppressed. Therefore, the parent amine **4** is still detected even at the highest TMDD concentrations (the solubility limit of TMDD in THF is ca. 0.15 M). In principle, $^1N^+$ could react directly to form **4** by single-electron transfer, hydride transfer, or some sort of addition/reductive elimination mechanism. While such pathways are not entirely ruled out by our data, they would account for less than $^1/_6$ of the amount of **4** formed.[56] Therefore, **4** is attributed to reactions of $^3N^+$.

The quenching experiments show that *both* the singlet ($^1A^+ \rightarrow {}^1N^+$) and triplet ($^1A^+ \rightarrow {}^3A^+ \rightarrow {}^3N^+ \rightarrow {}^1N^+$) channels are

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[55] The anthranilium ions show no detectable fluorescence at room temperature in fluid solution.

[56] Based on a 59% yield of **4** in the absence of TMDD vs a 10% yield with 0.125 M TMDD, Table IV. Even if TMDD were quenching the triplet nitrenium ion, our assignment of the formation of **4** to the triplet would remain unchanged.

operative in the direct irradiation experiments. Therefore, both singlet and triplet products can be expected; the relative yields of these depend on the rate of intersystem crossing relative to singlet ring opening as well as the reactivity of the traps present. In anhydrous THF, which is an efficient H-atom trap, the triplet channel is clearly more productive than the singlet channel and **4** is the major product. As increasing amounts of the nucleophilic trap are added, the singlet reaction channel begins to compete and **3** becomes the major product. However, even at the highest concentrations of H_2O (5.05 M), a significant amount of $^3N^+$ is formed and trapped by THF.

CH_2Cl_2 and CH_3CN are poorer H-atom donors than THF. It is for this reason that the parent amine **4** is only a minor product when direct irradiation is carried out in these solvents. In CH_3CN, both solvent addition (giving **8**) and rearrangement (giving $\mathbf{5}^+$) can occur through the singlet channel. Consequently, the quantum yield for decomposition, Φ, is higher in this solvent than in CH_2Cl_2 where only rearrangement can occur from $^1N^+$. The low yield of **4** in CH_2Cl_2 is somewhat surprising considering the high yield of that product from triplet sensitization. This may be due to a lower efficiency of $^3N^+$ formation in that solvent. This is further discussed in part 3, below.

3. Quantum Yields. The quantum yields measured can be used to determine the efficiencies of the elementary steps. This allows the model in Scheme IV to be tested for quantitative consistency. Consider photolysis in 3 M H_2O in CH_3CN where the yield of nucleophilic adduct **3a** is nearly quantitative:

$$\Phi^{H_2O} = 0.6 = \Phi_{3a} = \phi_{so}\phi_{nuc} + \phi_{isc}\phi_{to}(1 - \phi_H)\phi_{nuc} \quad (9)$$

(Recall that $\phi_{st} = 1 - \phi_H$.) According to Figure 2, at water concentrations > 2 M, the efficiency of trapping is $\phi_{nuc} = 1$. Because of the negligible yield of **4** under these concentrations, we further approximate the quantum yield for **4** $= \phi_{isc}\phi_{to}\phi_H = 0$. This simplifies eq 9:

$$\Phi^{H_2O} = 0.6 = \phi_{so} + \phi_{isc}\phi_{to} \quad (10)$$

Iminium $\mathbf{5}^+$ is formed nearly quantitatively in CH_2Cl_2. Neglecting $\phi_{isc}\phi_{to}\phi_H$.

$$\Phi^{CH_2Cl_2} = 0.03 = \phi_{so}\phi_m + \phi_{isc}\phi_{to}\phi_m \quad (11)$$

In THF, H-atom transfer cannot be neglected. Therefore, the measured quantum yield is the sum of the quantum yield for both photoproducts:

$$\Phi^{THF} = 0.11 = \Phi_{5+} + \Phi_4 = \phi_{so}\phi_m + \phi_{isc}\phi_{to}(1 - \phi_H{}^{THF})\phi_m + \phi_{isc}\phi_{to}\phi_H{}^{THF} \quad (12)$$

From the triplet sensitization experiments discussed above, $\phi_H{}^{THF}$ is approximated as 0.9 (based on the yield of **4** in 5.05 M H_2O/THF, Table IV). Equations 10–12 can be solved for the three unknowns: $\phi_m = 0.05$, $\phi_{so} = 0.5$, and $\phi_{isc}\phi_{to} = 0.09$. Using eq 7, the yield of **4** from the triplet sensitization experiment in CH_2Cl_2, and the value for ϕ_m, the value for the efficiency of H-atom abstraction from that solvent can be estimated to be $\phi_H{}^{CH2Cl2} = 0.14$.

The quantum efficiencies determined from the quantum yield experiments can be used to predict the chemical yields of the photoproducts and compared with the observed product yields. The yield of the parent amine **4** under direct photolysis, $Y^d{}_4$, is a function of the quantum efficiencies, using reasoning similar to that for the triplet case (eqs 4–6). The singlet reactions can occur through both the singlet channel and the triplet channel. Therefore, the quantum yield for migration plus nucleophilic addition is:

$$\Phi^d{}_m = \Phi^d{}_{nuc} = \phi_{so}(\phi_{nuc} + \phi_m) + \phi_{isc}\phi_{to}(1 - \phi_H)(\phi_{nuc} + \phi_m) \quad (13)$$

Substitution into eq 7 gives the following expression for the yield of **4**:

$$Y^d{}_4 = \frac{\phi_{isc}\phi_{to}\phi_H}{\phi_{isc}\phi_{to}\phi_H + \phi_{so}(\phi_{nuc} + \phi_m) + \phi_{isc}\phi_{to}(1 - \phi_H)(\phi_{nuc} + \phi_m)} \quad (14)$$

In general, reasonable quantitative agreement is found between the chemical yields calculated from the quantum efficiencies and the measured chemical yields. Direct irradiation of $\mathbf{1}^+$ in anhydrous THF produces 76% of the parent amine **4**; eq 14 predicts a yield of 77%. In THF/5.05 M H_2O (assuming $\phi_{nuc} + \phi_m = 1$), a yield of 14% is calculated from eq 14; 12% is observed (Table III). Similarly, triplet sensitized yields can be compared with those calculated from eq 10. In anhydrous THF, a yield of 97% is observed; a yield of 99% is calculated.

The only deviation comes from direct irradiation in CH_2Cl_2. Here, the yield of **4** is lower than that predicted (2 vs 27%). Generally, however, the consistency is reasonable considering the approximations made. For example, there is an implicit assumption in this analysis that the ϕs are invariant with solvent and at all concentrations of the traps. This is probably not true. The polarity of the medium undoubtedly exerts an influence on the various rate constants. Heavy-atoms solvents such as CH_2Cl_2 are known to catalyze spin inversion processes.[57] This might have the effect of increasing nonradiative relaxation from $^3A^+$, which, in turn, would reduce the magnitude of $\phi_{isc}\phi_{to}$ in that particular solvent.

4. Singlet–Triplet Energy Gap. In the absence of direct spectroscopic data, it is difficult to infer an accurate singlet–triplet energy gap. However, some observations from this work are relevant. By triplet sensitization experiments, it is demonstrated that the singlet nitrenium ion can be formed from its triplet state. Thus, it can be concluded with reasonable certainty that either the singlet is the lower energy state or the two spin states are energetically close enough to be in equilibrium. No evidence is found for the reverse singlet to triplet intersystem crossing in the nitrenium ion. The triplet-quenching experiments suggest that in direct irradiation, the triplet product **4** occurs from intersystem crossing of the excited anthranilium ion rather than the nitrenium ion. Therefore, the simplest and most probable explanation is that the singlet is the ground state for the nitrenium ion $\mathbf{2}^+$. However, a triplet ground state in equilibrium with a much more reactive singlet cannot entirely be ruled out.

A singlet ground state would agree with earlier experiments and semiempirical calculations on structurally similar arylnitrenium ions. For the most part, the stable products found in the solvolysis experiments were nucleophilic adducts analogous to **3**. Thermal reactions are expected to initially generate the singlet nitrenium ion. Assuming that this is the ground state addition products analogous to **3** would be expected from these reactions. Results from thermal (solvolysis) reactions, are largely consistent with this. Nucleophilic addition to the ring carbons is reported for most[58] of these experiments.[22,41,42,44,45,52,59–61]

It should be noted that the singlet–triplet energy gaps depend on the structure of the nitrenium ion. Most simple aromatic nitrenium ions seem to have singlet ground states, on the basis of these results and previous work. However, it should be possible

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to manipulate the energy gap by varying ring substituents as well as the alkyl group on nitrogen.[16,62] For example, electron-withdrawing groups on the aromatic ring are predicted to attenuate its ability to donate electrons and thus favor the triplet. Therefore, it should not be assumed that all arylnitrenium ions will be ground-state singlets.

Conclusions

There are two major conclusions from this work. First, further evidence is provided showing that photolysis of anthranilium **1**$^+$ produces the isomeric nitrenium ion **2**$^+$. In the presence of nucleophiles, the anticipated adducts **3** are generated. In the absence of nucleophiles, a previously unreported methyl rearrangement to give iminium **5**$^+$ is observed. The second conclusion is that the spin state of the nitrenium ion controls its chemical reactivity. The parent amine **4** is produced mainly from the triplet state. Its yield is increased when triplet sensitization is employed and diminished when a triplet quencher is added to the direct photolysis mixture. Likewise, formation of the nucleophilic adducts **3** and the rearrangement product **5**$^+$ is characteristic of the singlet nitrenium ion. These observations provide a paradigm which will be useful in interpreting further mechanistic and spectroscopic studies on these systems.

Experimental Section

General. Ethyl ether, benzene, and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. Anhydrous acetonitrile was distilled from CaH_2 through a vacuum-sealed column (30 cm) packed with glass helices. Methylene chloride was distilled from P_2O_5. ^1H NMR spectra were run at 200 MHz and ^{13}C NMR spectra at 55.1 MHz, unless otherwise noted. All ^1H NMR J values are reported in hertz. Mass spectra were performed using electron-impact ionization (70 eV). Photolysis reactions were performed in quartz or Pyrex vessels. The vessels were treated with a 5% v/v solution of Me_2SiCl_2 in CH_2Cl_2 and oven dried overnight before use. The solutions were purged of O_2 by passing N_2 through the solutions. Two light sources were used, a medium pressure 450-W Hg lamp or a 400-W Xe lamp. The light was filtered as described. Tetramethyldiazetine dioxide (TMDD) was prepared according to the method of Ullman.[39] 3-Methyl-*N*-*tert*-butylanthranilium perchlorate, **1**$^+$**ClO**$_4^-$, was prepared according to the method of Haley.[31]

Caution! *Perchlorate salts can be explosive. Although we have not experienced any difficuties with the materials described here, all perchlorate salts should be handled with care.*

^{1}H NMR Product Yields. Yields in Tables III–V were determined by ^1H NMR integration vs an added internal standard. Photolysis reactions were performed on 6–25 mM solutions in anthranilium salt. After photolysis, the solvent was removed under reduced pressure and products were observed by ^1H NMR in a measured volume of CD_3CN with a known amount of hexamethyldisiloxane (HMDS) as the internal standard. The relaxation delay was set to 2 s, and product peaks were integrated relative to the HMDS peak. The observed peaks corresponded to the amine conjugate acids (except product **5**$^+$), and yields were based on converted starting material.

Triplet-Sensitized Irradiation. The triplet sensitization experiments were performed on 6.0–9.0 mM solutions in anthranilium salt. Thioxanthen-9-one (0.135–0.170 mmol) was added as the triplet sensitizer (E_t = 65 kcal/mol, τ = 95 μs).[39] The solutions were analyzed by UV to ensure that the sensitizer was absorbing ca. 95–98% of the light at 400 nm. The solution and head volume were thoroughly purged with N_2 and irradiated for 1–2 h with the Xe lamp through a 385-nm cut-off filter. (A solution of anthranilium salt was irradiated without sensitizer under the same conditions for 17 h, with only a 20% loss of starting material.)

Quantum Yield Determinations. **1**$^+$**BF**$_4^-$ solutions (0.08–0.20 mM in specified solvents, typically 3 mL) were purged with N_2 in quartz cuvettes and irradiated at 312 nm (slit width of 9 nm) while being continually stirred. The light from a 200-W Hg lamp (Illumination Industries, Inc.) passed through a monochromator and was focused on the sample. The integrated incident and transmitted light intensities were measured using photodiodes which were calibrated by ferrioxalate actinometry.[63] The extent of reaction was measured by steady-state UV absorption spectroscopy. Quantum yields were determined from the initial slopes (10–20% conversion) from plots of mole of starting material vs mole of photons absorbed.

3-Methyl-*N*-*tert*-butylanthranilium Tetrafluoroborate (1$^+$BF$_4^-$). 3-Methylanthranil (283 mg, 1.33 mmol) was alkylated following Haley's general procedure.[31] Tetrafluoroboric acid (48%, 400 mg) was added to a solution of 3-methylanthranil, and *tert*-butyl alcohol (108 mg, 1.47 mmol) in 10 mL of nitromethane, and the solution was stirred for 48 h. The product was precipitated by addition of ethyl ether, and then the solution was filtered. The solid was taken up in acetone and was reprecipitated with ethyl ether. The yellow solid, mp 174 °C dec, was recrystallized from methanol to give 3-methyl-*N*-*tert*-butylanthranilium tetrafluroborate (280 mg, 59%), mp 180 ∞C dec, as white needles: IR (CD_3CN) 2990 (w), 1637 (s), 1537 (s), 1472 (s), 1431 (m), 1378 (m), 1190 (m), 1084 (vs), 1073 (vs); ^1H NMR (CD_3CN) 8.03 (m, 2 H), 7.88 (m, 1 H), 7.52 (m, 1 H), 3.03 (s, 3 H), 1.85 (s, 9 H); ^{13}C NMR (CD_3CN) 175.7, 147.5, 141.8, 127.7, 124.6, 120.3, 112.3, 70.9, 28.7, 13.5; mass spectrum m/z (relative intensity) 190 ($M - BF_4$, 3), 189 (17), 174 (3), 134 (9), 133 (98), 132 (8), 105 (23), 104 (100); high resolution mass spectrum m/z 189.1151 ($M^+ - HBF_4$), calcd for $C_{12}H_{15}NO$ m/z 189.1153; UV (CH_3CN) λ_{max} (log ϵ) 209 (4.22), 269 (3.49), 339 (3.61).

2-Acetyl-4-hydroxy-*N*-*tert*-butylaniline (3a). Salt **1**$^+$**ClO**$_4^-$ (20 mg) in 5 mL of 10% aqueous CH_3CN was irradiated with the Hg lamp through Pyrex for 15 m. The resulting solution was neutralized, extracted with ether, and concentrated in vacuo. The resulting oil was subjected to radial chromatography to give **3a** (9 mg, 64%) as a yellow liquid: R_f = 0.10 (5:1 hexanes/ethyl acetate); IR ($CDCl_3$) 3601 (m), 3295 (br w), 2978 (s), 2931 (m), 2860 (w), 1637 (vs), 1619 (s), 1578 (s), 1519 (vs), 1437 (m), 1361 (s), 1249 (m), 1196 (vs), 1173 (s); ^1H NMR (CD_3CN) 7.23 (m, 1 H), 6.90 (m, 2 H), 3.24 (br s, 1 H), 2.48 (s, 3 H), 1.36 (s, 9 H); ^{13}C NMR (CD_3CN) 201.4, 146.1, 145.6, 124.3, 119.6, 118.8, 117.0, 51.2, 30.1, 28.6; mass spectrum m/z (relative intensity) 207 (M^+, 33), 192 (64), 174 (51), 151 (55), 150 (19), 137 (13), 136 (100); high resolution mass spectrum m/z 207.1266 (M^+), calcd for $C_{12}H_{17}NO_2$ m/z 207.1259.

Preparative Irradiation of 1$^+$ClO$_4^-$ in Anhydrous CH$_3$CN. Salt **1**$^+$**ClO**$_4^-$ (60 mg, 0.21 mmol) was irradiated in 10 mL of acetonitrile for 2 h with a Hg lamp through a 300-nm filter. The mixture was neutralized, extracted with ether, concentrated in vacuo, and subjected to radial chromatography. The crude solid was recrystallized from ethanol to give 2-acetyl-4-acetamido-*N*-*tert*-butylaniline (**8**) (12 mg, 23%), mp 143 °C, as yellow plates: R_f = 0.39 (ethyl acetate); IR ($CDCl_3$) 3436 (m), 3285 (br w), 2975 (m), 2938 (w), 1679 (s), 1641 (vs), 1585 (m), 1538 (vs), 1510 (s), 1430 (m), 1411 (m), 1369 (m), 1336 (w), 1261 (m), 1214 (s), 1200 (vs); ^1H NMR (CD_3CN) 7.98 (d, J = 2.6, 1 H), 7.41 (dd, J = 9.2, 2.6, 1 H), 6.94 (d, J = 9.2, 1 H), 2.48 (s, 3 H), 2.01 (s, 3 H), 1.23 (s, 9 H); ^{13}C NMR (CD_3CN) 201.7, 169.7, 148.3, 129.0, 126.8, 125.9, 118.8, 115.6, 51.4, 30.0, 28.6, 24.0; mass spectrum m/z (relative intensity) 248 (M^+, 39), 233 (52), 215 (22), 209 (11), 192 (19), 191 (39), 176 (54), 150 (55), 135 (100); high resolution mass spectrum m/z 248.1520 (M^+), calcd for $C_{14}H_{20}N_2O_2$ m/z 248.1525. This mixture also provided 6 mg (18%) of **3a** and 2-acetyl-*N*-methylaniline (**6**) (5 mg, 16%) as a yellow liquid: R_f = 0.39 (5:1 hexanes/ethyl acetate); IR ($CDCl_3$) 3331 (br w), 2975 (s), 2875 (m), 1630 (s), 1568 (w), 1513 (m), 1100 (vs); ^1H NMR (CD_3CN) 8.68 (br s, 1 H), 7.79 (dd, J = 8.0, 1.5, 1 H), 7.38 (m, 1 H), 6.72 (m, 1 H), 6.58 (m, 1 H), 2.86 (d, J = 5.1, 3 H), 2.51 (s, 3 H); ^{13}C NMR ($CDCl_3$) 200.6, 162.7, 160.6, 135.0, 132.6, 113.9, 111.3, 29.2, 27.7; mass spectrum m/z (relative intensity) 150 (M + 1, 13), 149 (M^+, 100), 134 (3), 104 (6), 91 (5), 85 (14); high resolution mass spectrum m/z 149.0838 (M^+), calcd for $C_9H_{11}NO$ m/z 149.0840. This mixture also provided 2-acetyl-*N*-*tert*-butylaniline (**4**) (2 mg, 5%) as a yellow liquid: R_f = 0.46 (5:1 hexanes/ethyl acetate); IR ($CDCl_3$) 3281 (br w), 2956 (s), 2931 (m), 2875 (w), 1729 (s), 1633 (vs), 1584 (s), 1523 (s), 1456 (m), 1424 (m), 1368 (m), 1251 (s), 1213 (s), 1164 (s); ^1H NMR (CD_3CN) 9.20 (br s, 1 H), 7.80 (dd, J = 8.1, 1.6, 1 H), 7.30 (m, 1 H), 7.00 (dd, J = 8.8, 1.0, 1 H), 6.54 (m, 1 H), 2.51 (s, 3 H), 1.41 (s, 9 H); ^{13}C NMR (CD_3CN) 202.1, 151.4, 135.2, 134.6, 119.5, 115.5, 114.6, 51.5, 30.1, 28.5; mass spectrum m/z (relative intensity) 191 (M^+, 38), 176 (83), 158 (95), 134 (24), 120 (100), 92 (32); high resolution mass spectrum m/z 191.1306 (M^+), calcd for $C_{12}H_{17}NO$ m/z 191.1310. Compound **4** was also synthesized by reduction of **1**$^+$**ClO**$_4^-$ with Sn and HCl in HOAc in 56% yield.

Photolysis To Produce the Iminium Salt 5$^+$BF$_4^-$. Salt **1**$^+$**BF**$_4^-$ (15 mg, 0.35 mmol) was irradiated in 10 mL of freshly distilled CH_2Cl_2 for 0.5 h with a 320-nm filtered Xe lamp. The solvent was evaporated, and the

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(62) Glover, S. A.; Scott, A. P. *Tetrahedron* **1989**, *45*, 1763–1776.

(63) Murov, S. L. In *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; pp 119.

residue was dissolved in CD_3CN and observed by ^{1}H NMR. A trace amount of **3a**, 2% of **4**, and 93% yield of **5** was detected. A crude analysis of **5** is as follows: IR (CD_3CN) 3060 (m), 2994 (w), 2966 (w), 2928 (w), 1693 (vs), 1636 (s), 1599 (m), 1486 (w), 1449 (m), 1425 (m), 1364 (m), 1275 (vs), 1261 (vs), 1110 (s), 1073 (vs); ^{1}H NMR 400 MHz (CD_3CN) 8.21 (dd, *J* = 7.7, 1.5, 1 H), 7.84 (td, *J* = 7.7, 1.5, 1 H), 7.77 (td, *J* = 7.7, 1.3, 1 H), 7.44 (dd, *J* = 7.7, 1.3, 1 H), 3.70 (m, 3 H), 2.62 (s, 3 H), 2.39 (br s, 6 H); ^{13}C NMR (110.2 MHz, CD_3CN) 199.0, 194.7, 141.2, 136.2, 133.8, 132.4, 130.4, 126.5, 46.9, 28.7, 26.2, 26.1.

2-(1-Hydroxyethyl)-*N*-methyl-*N*-(1-methylethyl)aniline (7). Salt $\mathbf{1^+ClO_4^-}$ (100 mg, 0.35 mmol) was irradiated in 25 mL of anhydrous acetonitrile for 5 h with a Hg lamp through a 300-nm cut-off filter. The mixture was then treated with 100 mg of $NaCNBH_3$ with stirring for 5 min and quenched with water. The mixture was extracted with ether, concentrated in vacuo, and purified by radial chromatography to give 2-(1-hydroxyethyl)-*N*-methyl-*N*-(1-methylethyl)aniline (**7**) (12 mg, 18%) as a yellow liquid: R_f = 0.46 (5:1 hexanes/ethyl acetate); IR ($CDCl_3$) 3605 (s), 3200 (br w), 2962 (s), 2931 (s), 2855 (m), 1633 (w), 1462 (m), 1419 (w), 1381 (w), 1367 (w), 1263 (vs), 1096 (s), 1077 (s), 1015 (s); ^{1}H NMR (CD_3CN) 7.34–7.06 (m, 4 H), 5.12 (q, *J* = 6.5, 1 H), 3.18 (q, *J* = 6.4, 1 H), 2.59 (s, 3 H), 1.38 (d, *J* = 6.5, 3 H), 1.06 (d, *J* = 6.4, 6 H); ^{13}C NMR (CD_3CN) 151.9, 143.6, 128.4, 127.7, 125.8, 124.7, 67.6, 55.6, 38.4, 25.2, 20.5, 20.4; mass spectrum *m/z* (relative intensity) 193 (M^+, 23), 178 (45), 160 (16), 150 (100), 132 (70), 118 (29); high resolution mass spectrum *m/z* 193.1453 (M^+), calcd for $C_{12}H_{19}NO$ *m/z* 193.1466. Products **3a**, **4**, and **8** were also isolated from this reaction.

2-Acetyl-4-chloro-*N*-*tert*-butylaniline (3c). Photolysis of $\mathbf{1^+ClO_4^-}$ (246 mg, 0.85 mmol) in 50 mL of freshly distilled MeCN with 260 mg (0.94 mmol) of Bu_4NCl added, for 2 h with a Hg lamp (320-nm, cut-off), produces a dark solution. The mixture was worked up as described above and eluted on a preparative TLC plate to give 2-acetyl-4-chloro-*N*-*tert*-butylaniline (**3c**) (76.2 mg, 40%) as a yellow oil: R_f = 0.48 (5:1 hexanes/ethyl acetate); IR (neat) 3276 (br m), 2970 (s), 2937 (m), 2871 (w), 1641 (vs), 1580 (vs), 1510 (vs), 1422 (m), 1397 (w), 1364 (m), 1246 (m), 1213 (s), 1190 (vs); ^{1}H NMR (CD_3CN) 7.76 (d, *J* = 2.6, 1 H), 7.25 (dd, *J* = 9.2, 2.6, 1 H), 6.97 (d, *J* = 9.2, 1 H), 2.50 (s, 3 H), 1.39 (s, 9 H); ^{13}C NMR (CD_3CN) 201.5, 150.1, 135.2, 134.9, 133.7, 120.0, 117.3, 51.8, 30.1, 28.9; mass spectrum *m/z* (relative intensity) 227 (M + 2, 16), 225 (M^+, 45), 212 (30), 210 (98), 194 (22), 192 (62), 169 (57), 156 (32), 154 (100); high resolution mass spectrum *m/z* 225.0906 (M^+), calcd for $C_{12}H_{16}NOCl$ *m/z* 225.0920.

2-Acetyl-4-methoxy-*N*-*tert*-butylaniline (3b). Salt $\mathbf{1^+ClO_4^-}$ (72.7 mg, 0.252 mmol) was irradiated with 20 μL of MeOH in 1.0 mL of MeCN for 1.25 h with a Xe lamp through a 320-nm cut-off filter. The resulting solution was worked up as described above and subjected to radial chromatography to give 2-acetyl-4-methoxy-*N*-*tert*-butylaniline (**3b**) (45.2 mg, 81%) as a yellow liquid: R_f = 0.10 (5:1 hexanes/ethyl acetate); IR ($CDCl_3$) 3304 (br w), 2975 (s), 2929 (m), 2871 (w), 1641 (s), 1601 (m), 1521 (vs), 1430 (m), 1369 (m), 1209 (vs), 1195 (vs); ^{1}H NMR (CD_3CN) 7.29 (dd, *J* = 2.7, 0.6, 1 H), 7.01 (dd, *J* = 8.9, 2.7, 1 H), 6.98 (dd, *J* = 8.9, 0.6, 1 H), 3.74 (s, 3 H), 2.52 (s, 3 H), 1.38 (s, 9 H); ^{13}C NMR (CD_3CN) 202.2, 150.1, 147.0, 124.4, 120.0, 118.0, 117.6, 57.2, 51.9, 30.8, 29.4; mass spectrum *m/z* (relative intensity) 221 (M^+, 68), 206 (85), 188 (33), 165 (41), 150 (100), 149 (70), 134 (33); high resolution mass spectrum *m/z* 221.1415 (M^+), calcd for $C_{13}H_{19}NO_2$ *m/z* 221.1415.

Acknowledgment. We thank Ms. Christina J. Olson for assistance in the preparation of $\mathbf{1^+BF_4^-}$ and Dr. Sunny Lee for useful advice on the trapping of $\mathbf{5^+}$. This work was supported by the NSF (CHE-9119998) and the Maryland Cancer Program (MCP-IRG 147J-DEF).