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Photogenerated Arylnitrenium Ions: Reactions of *N-tert*-Butyl (2-Acetyl-4-substituted)phenyl Nitrenium Ions with Alcohols and Water Studied by Laser Flash Photolysis

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Abstract: Photolysis of *N-tert*-butyl-3-methylanthranilium ion as well as its 5-halo and methyl derivatives produces transient nitrenium ions via an electrocyclic ring-opening process. This is confirmed by identification of the stable products and transient absorption experiments. Laser flash photolysis of the substituted anthranilium ions gives short-lived (80−200 ns) species which absorb in the UV and visible region of the spectrum. These transient species react with nucleophiles such as alcohols and water with rate constants ranging from 10^6-10^9 M^{-1} s^{-1}. Reactivity of the nucleophiles follows the trend MeOH > EtOH > *i*-PrOH ~ H_2O > *t*-BuOH. This is the same trend that has been observed by others for diarylcarbenium ions and styrene cation radical cations and provides further confirmation for the assignment of the spectra to the singlet state arylnitrenium ions.

Cationic reactive intermediates such as carbenium ions, radical cations, and nitrenium ions have been the focus of research for many years. Such species are interesting both for fundamental reasons and because of the roles they play in biochemical and synthetic processes. Typically carbenium and nitrenium ions undergo decay more rapidly than their generation. Consequently, classical experimental studies have either had to rely on indirect methods, such as competitive trapping,[1−7] or else have focused on highly stabilized cations whose reaction rates could be monitored directly.[8]

The development of laser flash photolysis (LFP) methods has renewed interest in reactive cations. Short laser pulses make it possible to generate reactive intermediates on time scales much shorter than their lifetimes. In this way it is possible to directly measure their spectra and rates of reactions with nucleophiles. All laser flash photolysis experiments depend on reliable and efficient photochemical methods for generating the transient species of interest. Although nanosecond hardware has been available for over two decades, many interesting reactive intermediates have been neglected because of the lack of good photochemical methods for their generation. Over the last several years a number of such procedures have been reported for carbenium ions. Of particular relevance are the LFP studies of McClelland,[9−11] Steenken,[12] and Bartl.[13,14] These investigators examined the reaction of di- and triarylcarbenium ions with a wide variety of nucleophiles. Important advances in the area of carbenium ions have also been reported by several other groups.[15−23]

The focus of the present work is on arylnitrenium ions.[24−26] These species are considered to be chemical carcinogens.[27−29] Enzymatic oxidation of aromatic amines converts them to hydroxylamines. Subsequent acylation or sulfonylation gives hyroxylamine esters that undergo heterolytic cleavage to give the corresponding arylnitrenium ion. The latter is proposed to damage DNA by adding to the 8-position of guanine residues.[30−32]

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

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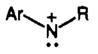
Scheme 1

$$\begin{tikzcd}
\mathbf{1(a\text{-}d)} \arrow[r, "h\nu"] & {}^{1}\mathbf{1}^{*} \arrow[r, "k_{so}"] \arrow[d, "k_{ISC}"] & {}^{1}\mathbf{2}^{+} \arrow[r, "k_{NUC}\text{ or }k_{M}"] \arrow[ll, bend right, "k_{c}"'] & \text{Singlet Products} \\
 & {}^{3}\mathbf{1}^{*} \arrow[r, "k_{to}"] & {}^{3}\mathbf{2}^{+} \arrow[r, "k_{H}"] \arrow[u, "k_{TS}"'] & \text{Triplet Products}
\end{tikzcd}$$

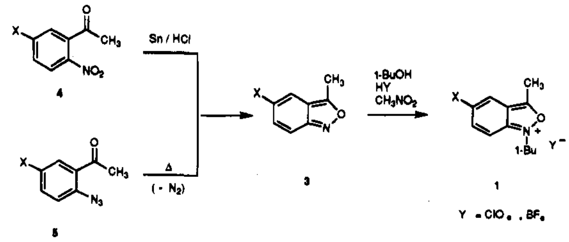
A critical issue in evaluating this model is the selectivity and lifetime of the arylnitrenium ion. The latter species must survive long enough in the largely aqueous cellular environment to diffuse to and react with the DNA target. In the case where the nitrenium ion is extremely reactive, it would be immediately intercepted by water. On the other hand, the nitrenium ion must be sufficiently electrophilic to react with DNA.



Arylnitrenium Ion

As with the carbenium ions, the application of fast laser methods to the nitrenium ions has been limited by the lack of photochemical methods for their generation. Recently some exploratory studies have been reported.[33,34] We have previously shown that 2-acetylphenyl nitrenium ions can be generated by photolysis of anthranilium ions (**1**).[35-41] The latter undergo an excited state electrocyclic ring opening giving nitrenium ions of general structure **2**. A mechanistic study of **1a** showed that both the singlet and triplet excited state anthranilium ions (^{1}**1*** and ^{3}**1***) as well as the singlet and triplet nitrenium ions (^{1}**2** and ^{3}**2**) were formed.[35] A general photochemical mechanism derived from the earlier study is shown in Scheme 1. Theoretical calculations at both semiempirical[42-44] and ab initio levels[45-48] as well as our own experiments[35,49] indicate that arylnitrenium ions have singlet ground states. Consequently most of the observed chemistry originates from the singlet manifold. Triplet products (generally the parent amine) can arise from rapid capture of the triplet nitrenium ion prior to its relaxation to the singlet state.

Scheme 2



In order to provide some insight into the stability and reactivity of nitrenium ions, we have sought to develop LFP methods for their detection and characterization. We have communicated some preliminary results showing the first detection of singlet nitrenium ions by LFP.[36] Subsequently McClelland and Novak[50] have also reported LFP characterization of arylnitrenium ions using an alternative type of photoprecursor. Herein is provided the first full account of our work. The study has also been expanded to explore the effect of solvent and nucleophile structure on the reactivity of the arylnitrenium ions. Furthermore an additional example of the arylnitrenium ions (the 4-methyl derivative) is examined. LFP trapping data along with product studies further confirm the assignment of the observed transient to the singlet state arylnitrenium ions. The arylnitrenium ions react with alcohols with rate constants that follow the order MeOH > EtOH > iPrOH ~ H_2O > tBuOH.

Results

1. Synthesis and Ground State Chemistry. The *N-tert*-butyl anthranilium salts **1** are prepared from acid-catalyzed alkylation of the corresponding anthranil (2,1-benzisoxazole) free base **3** (Scheme 2). The latter can be formed by tin metal reduction of the appropriate *o*-nitroacetophenone derivative **4**. Cyclization apparently occurs from the the *N*-hydroxylamine with loss of water. Alternatively, the anthranil can be formed from thermolysis of the appropriate *o*-azidoacetophenone **5**. The counterion of the salt depends on which acid is used to promote the alkylation reaction. Thus, $HClO_4$ provides the perchlorate salt and HBF_4 provides the tetrafluoroborate salt.

The 3-methylanthranilium ions are electron-poor aromatic rings and can be attacked at the 3-methyl position by nucleophiles as shown in eq 1.[51] Even relatively weak nucleophiles such as alcohols and water are sufficient to effect this reaction. Ground state addition can be detected by a shift in the UV spectrum of the starting material as nucleophiles are added. For example, addition of 2.0 M H_2O to a solution of **1c** acetonitrile is sufficient to cause this reaction. In this case the absorption maximum shifts from 273 to 260 nm upon addition of the water to the solution. All four anthranilium ions (**1a**–**d**) show similar behavior. UV absorption data for compounds **1a**–**d** and their 3-adducts are shown in Table 1. This process is immediately and quantitatively reversed when a small amount of a strong acid is added (Figure 1).

To avoid complications associated with photochemistry of the C3 adducts, all of the laser kinetic studies, trapping

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Table 1. UV Absorption Maxima for Anthranilium Salts **1a−d** and the Corresponding C3 Adducts **6a−d** in CH_3CN

	UV absorption maxima[a] (nm), [molar absorptivity (M^{-1} cm^{-1})]	
	anthranilium ion (**1**)	adduct (**6**)
a	219 [4700]; 269 [3900]; 342 [4700]	218 [5100]; 248 [4300]; 338 [2600]
b	225 [8700]; 277 [3300]; 351 [4700]	211 [7900]; 257 [7900]; 300s [1300]
c	274 [3000]; 350 [5000]	260 [7900]; 300s [1400];350s [1200]
d	272 [4200]; 349 [5700]	242 [6900]; 292 [1400]

[a] s designates a shoulder.

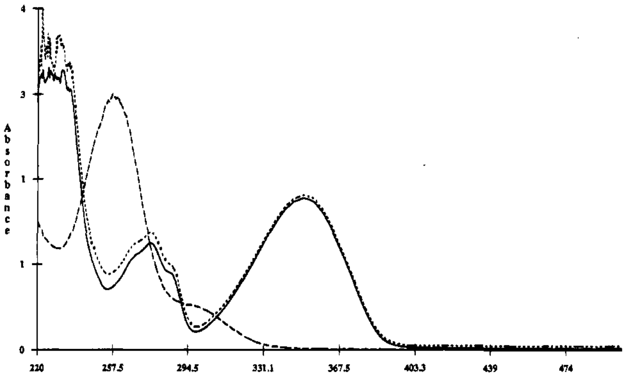
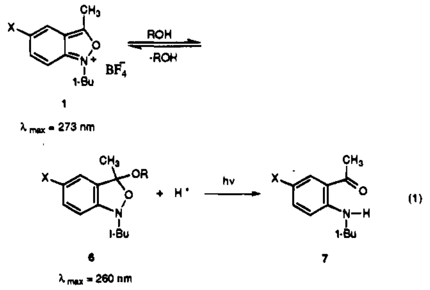


Figure 1. UV absorption spectra of **1b** in (a) CH_3CN [3.8×10^{-4} M] (solid line); (b) in 50/50 acetonitrile/water at the same concentration (long dashes); (c) UV of solution (b) with 20 μL of concentrated $HClO_4$ added (small dashes).



(1)

experiments, and quantum yield determinations were done in the presence of a strong acid (typically 10% $HClO_4$ added to the nucleophile). This shifts the equilibrium in favor of the anthranilium ion. Anionic nucleophiles such as N_3^- and Cl^- also cause a similar UV-shift. Elsewhere it has been shown that photolysis of the 3-adducts produces the corresponding parent amines **7**.[36] The mechanism of the latter reaction is still under investigation, but it is presumed to involve formation of a diradical intermediate which abstracts H-atoms from the solvent.

For the halogenated derivatives **1b** and **1c**, acid was necessary in all experiments where nucleophiles were added. Methyl derivative **1d** was somewhat less reactive. No significant addition was observed with the alcohols <12 M. Experiments with this derivative could be carried out with or without added acid.

2. Characterization of the Stable Photoproducts. UV irradiation of solutions of the anthranilium salts result in three types of products: (1) the parent amine **7**; (2) an iminium ion, **8**; and (3) products derived from addition of nucleophiles to the aromatic ring **9−13** (Chart 1). Yields of these products under various conditions and with each of the four substrates are compiled in Table 2. Several of these experiments have been described in our preliminary communications.[49]

Products **9−13**, despite their variety, all derive from either ortho or para ring addition to the singlet nitrenium ion ^{1}**2** (Scheme 3). The simplest case is the unsubstituted system **1a**.

Chart 1

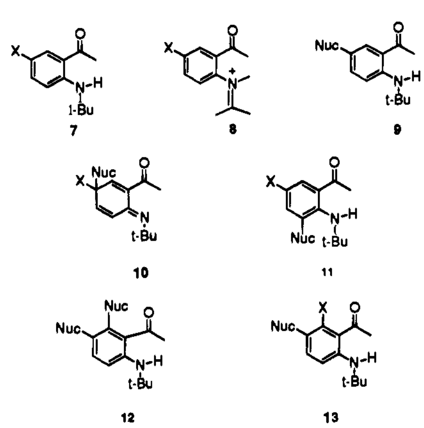
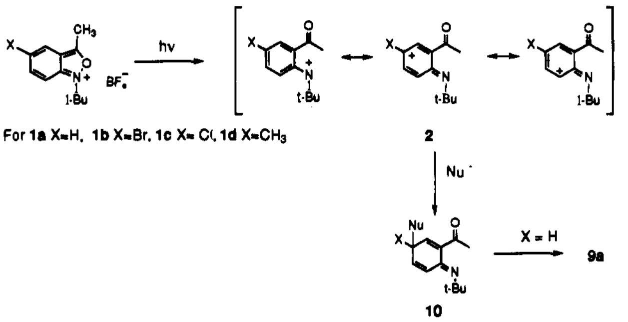


Table 2. Product Yields from Photolysis of Anthranilium Ion 1^+BF_4 in CH_3CN with Various Traps

ion	trap (conc)	**7**	**8**	**9**	**10**	**11**	**12**
1a	H_2O (5.5 M)			92			
	MeOH (0.46 M)			81			
	no trap	11	48	10			
1b	H_2O (28 M)	25				64	
	MeOH (2.4 M)	27		49		24	
	no trap	14	73			8	
1c	H_2O (28 M)					85	
	MeOH (2.4 M)			21		27	23
	no trap	9	72			10	
1d	H_2O (9.3 M)	12			64	11	
	MeOH (4.0 M)				87	8	
	no trap				88		

Scheme 3



For this substrate all nucleophiles add to the para position to ultimately give adduct **9**. It seems reasonable to assume that this comes from initial formation of **10a**, followed by a net 1,5-hydrogen shift.

The methyl derivative **2d** shows similar behavior. Addition occurs at the position para to the nitrenium center. However the methyl group does not undergo a spontaneous 1,5-shift as in the case of the hydrogen in **2a**. Instead, stable quinone imine ethers such as **10d** are formed. This is true regardless of which nucleophile is employed. Compounds **10d** can be characterized spectroscopically or converted to 1,2,3,4-tetrasubstituted arenes of structure **13** upon treatment with acid. The mechanism of the latter process can be envisioned as protonation of the nitrogen followed by a 1,2-sigmatropic shift of the methyl group followed by deprotonation (Scheme 4). Similar behavior has been reported by others.[5,52−54]

The chemistry of the halogenated derivatives, **2b** and **2c**, appears to be more complex. With water, which is a relatively

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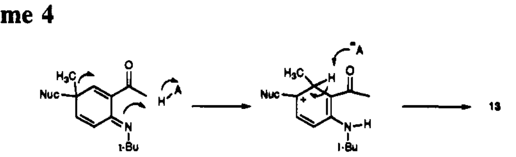
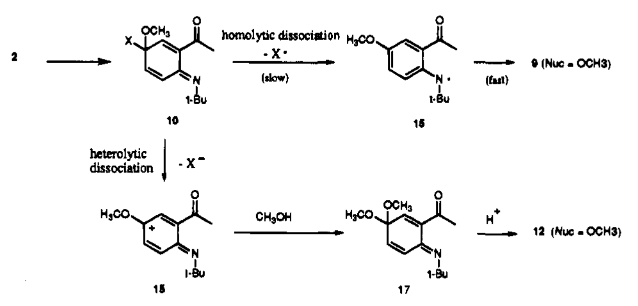
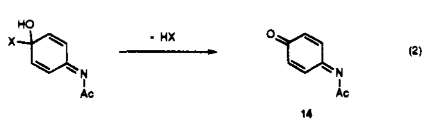
Scheme 4



Scheme 5



weak and sterically undemanding nucleophile, the addition occurs mainly in the position ortho to nitrenium group, giving adducts of structure **11** as the major products. It was somewhat surprising that products of para addition were not detected—especially in light of the work of Novak et al.[55] These workers found that water adds to the para position of *p*-haloarylnitrenium ions, ultimately giving imine quinones **14** in significant yields (eq 2). Similar products were not detected in our studies.



(2)

We note that the mass balances in these experiments were 85 and 89% for **1b** and **1c**, respectively. Signals for additional products were observed in the ^{1}H NMR spectra of the photolysis mixtures. These products were not formed in sufficient quantities to permit their isolation and characterization. It is possible that the unaccounted products are either the analogs of **14** or are secondary photoproducts from these species. Even allowing for this possibility, ortho-addition is the predominant mode of attack in our system. In contrast with Novak's nitrenium ion, our structures have an acetyl groups in the position ortho to the nitrenium center, and *tert*-butyl groups on the nitrenium nitrogen (rather than an acetyl group). Further investigations into substituent effects on the regiochemistry of addition would be informative.

Alcohols, which are stronger nucleophiles than water, add in a much less regioselective fashion to the halogen-substituted nitrenium ions. The products that are formed with methanol, for example, are the ortho adducts **11b** and **c** as well as products **9** and **12**. The latter two products are derived from initial para addition to the singlet arylnitrenium ion ^{1}**2**. A mechanism which accounts for these products is shown in Scheme 5. Initial para addition gives **10b** or **10c**. These are doubly allylic α-haloethers and are expected to be quite reactive. Homolytic elimination of the halogen atom provides the conjugated arlyaminyl radical **15**.[56] The latter abstracts a H-atom from the solvent (or methanol) giving the methoxy adduct **9**. Heterolytic dissociation of the halide ion would give the *p*-alkoxy nitrenium ion **16**. Para addition of a second methoxyl group to this nitrenium ion gives ketal **17**. The latter rearranges following the acid-catalyzed mechanism described in Scheme 3, giving the dimethoxy adduct **12**.

Consistent with this picture are the differing ratios of **9** to **12** when the bromo derivative is compared with the chloro derivative. The bromo-derivative gives a higher yield of **9**, the product from homolytic dissociation. The chloro derivative provides higher yields of **12**, the product from heterolytic dissociation. Chlorine, being more electronegative and forming a stonger bond to carbon than bromine, would be expected to favor heterolysis over homolysis. Bromine, being less electronegative and forming a weaker bond to carbon, would be expected to favor homolysis over heterolysis.

When low concentrations of nucleophiles are employed, two other products are observed: The iminium ion **8** is formed and the parent amine **7**. The former forms as the result of a net 1,2-sigmatropic shift of a methyl group from the *tert*-butyl substituent to the nitrenium nitrogen. This is assigned to a reaction of the singlet nitrenium ion based on our earlier mechanistic study. This is formed in significant yields from anthranilium ions **1a**, **1b**, and **1c**. The iminium ion was never detected in the photolysis of **1d**. Only the products from H-atom transfer (**7d**, discussed below) and addition of residual water (**13**)[49] were ever observed with this system.

The parent amine **7** derives from H-atom transfer to the triplet nitrenium ion (^{3}**2**). Referring to Scheme 1, ^{3}**2** is formed when the excited singlet anthranilium ions ^{1}**1*** intersystem crosses to the triplet manifold to give ^{3}**1***. Ring opening of the triplet anthranilium ion ^{3}**1*** gives the triplet nitrenium ion ^{3}**2 ***. Two features of this kinetic scheme are especially important to understanding the results. First, excited state intersystem crossing (^{1}**1*** → ^{3}**1***) occurs in competition with singlet ring-opening (^{1}**1*** → ^{1}**2**) . The relative importance of the two pathways depends on the ratio of rate constants $k_{\mathrm{so}}/k_{\mathrm{ISC}}$. Second, ^{1}**2** ion can revert to the starting material. This process is expected to predominate at low concentrations of nucleophile. The relative efficiencies of the singlet and triplet pathways, therefore, depend on the concentration of nucleophile. As the nucleophile concentration is decreased, the overall quantum yield for photolysis decreases, and a greater fraction of the anthranilium ion is consumed via triplet reactions (i.e., formation of **7**).

With **1a**, **1c**, and **1d**, the yield of **7** becomes negligible when sufficient quantities of nucleophile are added to the photolysis mixture. This suggests that for these anthranilium ions, $k_{\mathrm{so}} > k_{\mathrm{ISC}}$. With the bromo derivative, however, **7** is formed in ca. 25% yield, even at the highest concentrations of nucleophiles employed implying that $k_{\mathrm{so}} \approx 2k_{\mathrm{ISC}}$. Bromine is a heavy atom and its incorporation into the anthranilium ions might be expected to catalyze electron spin inversion. This would be seen in an accceleration of the rate of the ^{1}**1*** → ^{3}**1*** reaction relative to the singlet ring-opening process. That effect, in turn, would cause an increase in the yield of **7**.

3. Laser Flash Photolysis Experiments and Reactions with Nucleophiles. In order to determine how reactive and selective arylnitrenium ions **2** are toward nucleophiles, LFP experiments were carried out with the corresponding anthranilium ion precursors **1**. In addition, competitive trapping experiments/product analysis were done in several cases. The latter experiments were used to confirm the results of the LFP experiments and to study the reactivity of **2a** which could not be observed by LFP.

Pulsed laser photolysis (308 nm, 10 ns, 40–80 mJ) of solutions containing the precursors **1b**–**d** gives the transient

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(56) This intermediate does not appear in the LFP experiments discussed below. Presumably the homolytic dissociation, while fast relative to product isolation time scales, is slow relative to the microsecond–millisecond time scales accessible to LFP.

Table 3. Decay Rate Constants (s^{-1}) for Nitrenium **2a**, **2b**, and **2c** in Various Solvents

	solvents		
nitrenium ion	CH_3CN	TFE	CH_2Cl_2
2b (395 nm)	$(8.4 \pm 0.5) \times 10^6$	$(1.9 \pm 0.02) \times 10^7$	$(1.4 \pm 0.2) \times 10^7$
2c (385 nm)	$(8.1 \pm 0.7) \times 10^6$	$(1.5 \pm 0.2) \times 10^7$	$(1.1 \pm 0.2) \times 10^7$
2d (460 nm)	$(2.3 \pm 0.3) \times 10^6$	$(4.6 \pm 0.3) \times 10^6$	$(3.0 \pm 0.7) \times 10^6$

UV−vis spectra shown in Figure 2. The time-dependence of these transients all showed good fits to first-order decay. Decay rate constants ($k_o = 1/\tau$) and absorption maxima (λ_{max}) for these transients, measured in CH_3CN, CH_2Cl_2, and CF_3CH_2OH, are given in Table 3. The lifetimes (τ) ranged from 85 to 425 ns. The transient spectra obtained from the halogen derivatives, **1b** and **1c**, both show very strong absorption maxima at 380 and 395 nm accompanied by a weaker shoulder which extends out to the visible region (ca. 600 nm). The stronger, low wavelength transition in these spectra appears to fall off sharply below 360 nm. It is important to realize that the transient spectra are difference spectra, where the absorptions of the starting material are subtracted from the total. As seen in Table 1, the anthranilium ions all absorb out to 380 nm. Consequently, the observed maxima for **2b** and **2c** may or may not be the true peaks. Any absorptions below 380 nm are diminished or canceled by the bleaching of the starting material.

The transient spectrum obtained from the methyl derivative **1d**, on the other hand, showed only the weaker shoulder. Despite this difference, the transient species detected from LFP of **1d** is also assigned to the corresponding nitrenium ion **2d**. This is based on its similar lifetime and reaction rates with chemical traps (described below). The methyl substituent appears to shift the nitrenium ion absorption maximum to lower wavelengths where it is obscured by the absorption of the starting material.

The transient spectra are assigned to the singlet state of the corresponding arylnitrenium ions **2b**−**d** based on the following considerations. (1) The product studies described above and elsewhere are all consistent with the formation of arylnitrenium ion **2** upon photolysis of the anthranilium ions **1**. (2) The lifetimes of the transients are unaffected by O_2, a triplet quencher. This argues against an excited triplet state of **1** as being the signal carrier. (3) The lifetimes of the transient species are unaffected by the addition of H-atom donors such as $n\mathrm{Bu_3SnH}$ (in concentrations as high as 0.1 M). The triplet state of the nitrenium ions[35,49] or aminyl radicals[57,58] would be expected to react rapidly with such traps.

Further confirmation of the assignment comes from nucleophilic trapping experiments. The observed transient species react with added alcohols and water. The traps were added to the photolysis solution, and the decay of the nitrenium ions was monitored by LFP. In most of the experiments, the nucleophile solutions contained 10% (v/v) of $HClO_4$ to suppress formation of the 3-adduct (eq 1). The observed first-order rate constant for decay of the nitrenium ions **2** (k_{obs}) was proportional to the concentration of nucleophile consistent with psuedo-first-order behavior as described in eq 3. In this expression k_o is the rate constant for decay in the absence of nucleophile, k_{nuc} is the second-order rate constant for reaction with the nucleophile, and [nuc] is the molar concentration of the nucleophile in the photolysis solution, uncorrected for the added acid. An example of the decay waveform (**1d** in CH_3CN) is shown in Figure 3, and an example of the pseudo-first-order plot (**1d** with CH_3OH) is shown Figure 4. The k_{nuc} derived from the slopes of the pseudo-first-order plots for each nucleophile and each nitrenium ion in CH_3CN are compiled in Table 4. The values for these rate contants range from 10^6−10^8 M^{-1} s^{-1}.

$$k_{obs} = k_o + k_{nuc}[\mathrm{nuc}] \qquad (3)$$

A competitive trapping experiment was carried out on **1d** in order to further verify our assignment of the transient. A solution of $\mathbf{1d}BF_4^-$ was irradiated in the presence of both MeOH (1.98 M) and EtOH (2.04 M). The ratio of the photoproducts Y_{MeOH}/Y_{EtOH} was determined from relative peak areas in the ^1H NMR spectrum of the photolysis mixture. The ratio of rate constants for nucleophilic addition, k_{MeOH}/k_{EtOH}, can be estimated from Y_{MeOH}/Y_{EtOH} after correcting for the relative concentration of nucleophiles as described in eq 4. The ratio k_{MeOH}/k_{EtOH} determined from LFP (Table 4) is 1.43. The corresponding value determined from competitive trapping is 1.67. This is reasonable agreement considering the uncertainties associated with NMR peak integration.

$$\frac{k_{MeOH}}{k_{EtOH}} = \frac{Y_{MeOH}[\mathrm{EtOH}]}{Y_{EtOH}[\mathrm{MeOH}]} \qquad (4)$$

Relative rate data were obtained for **2a**. We were unable to detect any transient signals from LFP of the unsubstituted compound, **1a**. Therefore absolute rate data could not be obtained for nitrenium ion **2a**. However, it was possible to obtain relative rate constants for nucleophilic addition by carrying out a series of competitive trapping experiments. In these experiments, **1a** was irradiated in a series of CH_3CN solutions that contained both MeOH and one of the other alchohols (or water). The relative k_{nuc} for **2a** were determined from the relative yields of the photoproducts (**9**). These values are listed in Table 5. As was the case for nitrenium ions **2b**−**d**, nucleophilic reactivity follows the order MeOH > EtOH > *i*-PrOH ~ H_2O > *t* -BuOH.

Recent work by Pienta and Kessler[59−61] has shown that nucleophilic addition to retinyl and other cations can be modulated by hydrogen bonding solvents. For example the k_{nuc} for addition of fluoride ion to retinyl cation decreases by more than four orders of magnitude when dry acetonitrile is compared with acetonitrile containing 11 M water. This was attributed to coordination of the H-bond donating solvent with the nucleophile.

The effect of solvent on the nucleophilic addition to the present nitrenium ions was explored. The k_{nuc} for **2d** were measured with the series of alcohols and water in CH_3CN, CH_2Cl_2, and 2,2,2-trifluoroethanol (TFE). TFE is a polar, H-bond donating solvent and, by analogy with the earlier work, is expected to give lower k_{nuc} values. CH_2Cl_2 is not hydrogen bond donor and is less polar than CH_3CN and is expected to give higher values for k_{nuc}. The values for CH_2Cl_2 and TFE are listed in Table 6 (the corresponding values for CH_3CN are listed in Table 4). In each solvent, the same order of nucleophilicity obtains viz., MeOH > EtOH > *i*-PrOH ~ H_2O > *t*-BuOH. As expected, for any given nucleophile, k_{nuc} follows the order CH_2Cl_2 > CH_3CN > TFE. With CH_2Cl_2 there is a marginal increase in the k_{nuc} relative to CH_3CN. With TFE the effect was considerably more pronounced—a decrease of more than an order of magnitude was observed.

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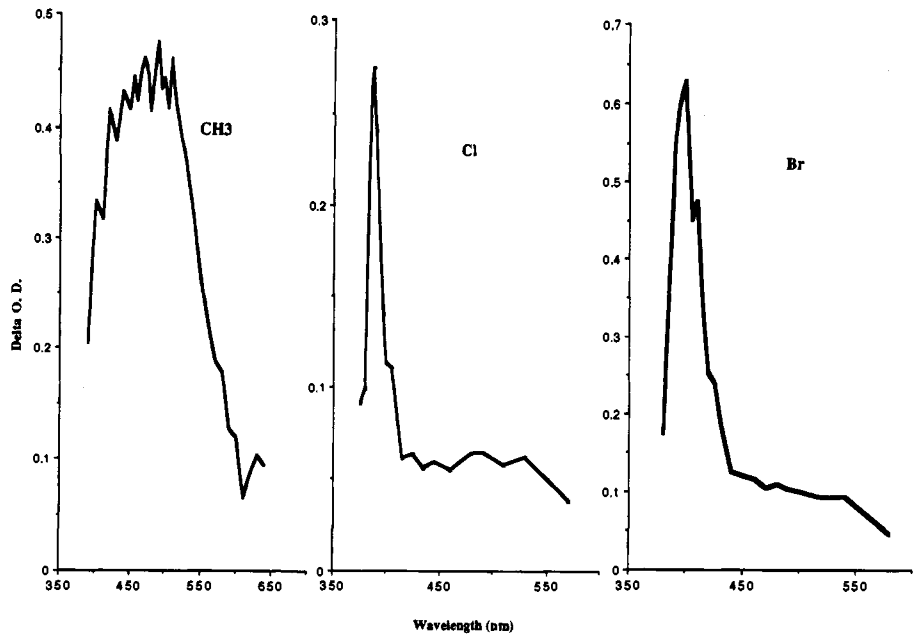

Figure 2. Transient spectra of nitrenium ions **2b**–**d** obtained from the LFP of the corresponding anthranilium ions **1b**–**d** in CH_3CN. Experimental conditions were chosen to optimize the signal-to-noise ratio for each spectrum. Therefore the intensities of each spectrum are not directly comparable.

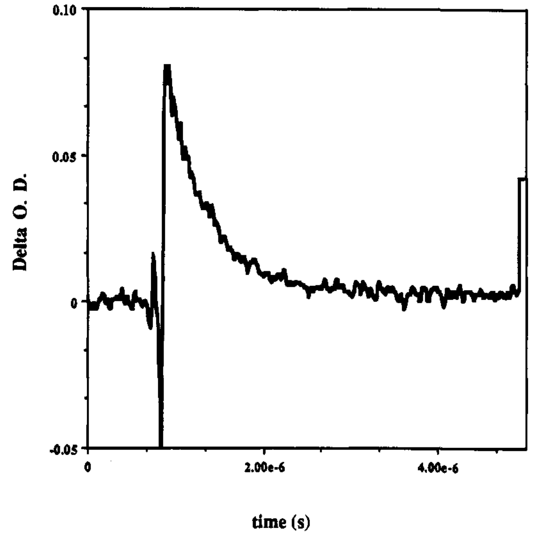

Figure 3. Decay waveform of nitrenium ion **2d** generated from photolysis of **1d** in CH_3CN.

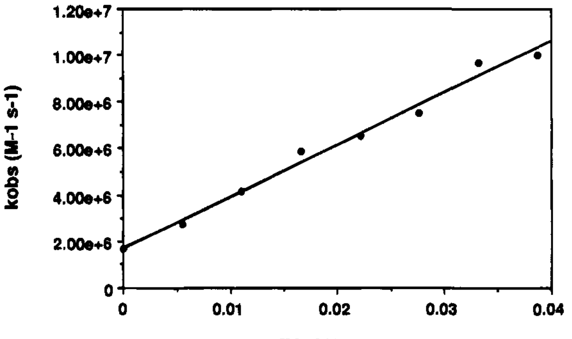

Figure 4. Change in observed decay rate constant (k_{obs}) for **2d** with increasing [CH_3OH]. Solvent is CH_3CN.

Table 4. k_{nuc} (M^{-1} s^{-1}) Determined from Pseudo-First-Order Plots for Nitrenium Ions in CH_3CN

	nitrenium ion		
nucleophile	**2d**	**2c**	**2b**
methanol	2.23×10^{8}	3.43×10^{7}	1.25×10^{7}
ethanol	1.18×10^{8}	2.27×10^{7}	1.25×10^{7}
isopropyl alcohol	4.63×10^{7}	1.37×10^{7}	2.48×10^{6}
tert-butyl alcohol	1.48×10^{7}	no quenching	no quenching
H_2O (H_3O^+)	3.08×10^{7}	3.15×10^{6}	1.34×10^{6}

Table 5. Relative Reactivity of **2a** with a Series of Alcohols: k_{nuc}/k_{MeOH}

	MeOH	EtOH	*i*-PrOH	*t*-BuOH	H_2O
k_{ROH}/k_{MeOH}	1.0	0.72	0.40	0.26	0.33

Table 6. k_{nuc} (M^{-1} s^{-1}) Determined from Pseudo-First-Order Plots for Nitrenium Ion **2d** in TFE and CH_2Cl_2

	solvent	
nucleophile	TFE	CH_2Cl_2
methanol	1.94×10^{7}	1.26×10^{9}
ethanol	1.50×10^{7}	3.15×10^{8}
isopropyl alcohol	2.34×10^{6}	6.49×10^{7}
tert-butyl alcohol	no quenching	2.22×10^{7}
H_2O (H_3O^+)	1.80×10^{6}	5.35×10^{7}

4. Quantum Yield Studies. Measurements of the quantum yield of anthranilium ion decomposition were carried out in order to determine some typical values for the ring closure rate constant (k_c, in Scheme 1) as well as the rate constant for methyl shift (k_M) of the singlet nitrenium ion. Decomposition quantum yields (Φ) were measured for the anthranilium ions **1b** and **1c** in the absence and in the presence of nucleophiles.

In all cases, Φ increases with the concentration of added nucleophiles. For example with **1c** the quantum yield is 0.021 in dry CH_3CN and it increases to 0.78 in 5 M CH_3OH. Increasing [CH_3OH] beyond 5 M results in no further increase in Φ. This saturation effect holds in all cases examined. This saturation behavior is the result of the ring closure process (reaction k_c). In the absence of added traps, the large majority of the nitrenium ions cyclize back to ground state anthranilium ion. At sufficient trap concentrations, all of the singlet nitrenium ions are trapped. Figure 5 illustrates this behavior in the case of **1c** with CH_3OH. The Φ's with no added nucleophile (Φ_o) and at saturating nucleophile concentrations (Φ_∞) for **1a**, **1b**, and **1c** are listed in Table 7.

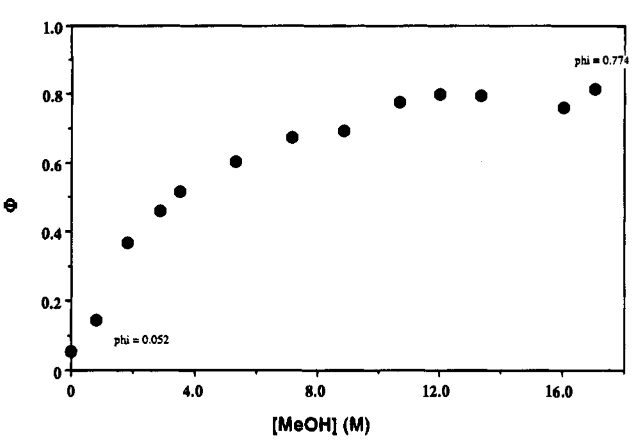

Figure 5. Dependence of quantum yield of decomposition of **1c** on [CH_3OH] in CH_3CN.

Table 7. Quantum Yields of Decomposition for **1b** and **1c** in CH_3CN with No Nucleophile (Φ_o) and at Saturating Concentrations of Nucleophile (Φ_∞) and Rate Constants for Ring Closure (k_c) and Migration (k_M)

	Φ_0	Φ_∞	k_M (s^{-1})	k_c (s^{-1})
1b	0.066	0.836	7.8×10^5	7.6×10^6
1c	0.059	0.774	7.8×10^5	1.0×10^7

$$k_o = k_M + k_c \tag{5}$$

$$k_M = k_o\left(\frac{\Phi_0(1 - Y_7^0)}{\Phi_\infty(1 - Y_7^\infty)}\right) \tag{6}$$

The unimolecular rate constants, k_c and k_M, for **2b** and **2c** were calculated from eqs 5 and 6. The decay rate constant observed by LFP for the nitrenium ions **2** in the absence of added trap, k_o, is the sum of the rate constants for iminium ions formation (k_M) and ring closure (k_c). The ring closure process leads to no net chemistry. Therefore the measured quantum yields can be used to independently calculate k_M after correcting for the chemical yields of the triplet process leading to **7** (eq 6). Y_7^0 and Y_7^∞ are the yields of the parent amine **7** at zero and saturating nucleophile concentrations, respectively. For the methyl derivative **2d** no rearrangement was detected; only inefficient reactions with residual water were observed. Therefore it is possible to estimate k_c from the decay rate constant (i.e., $k_c \sim k_o$ where [nuc] = 0). The values for k_c are all ca. 10^7 s^{-1}. The k_M are more dependent on the substituents and range from $<10^4-10^6$ s^{-1}.

Discussion

The key photochemical step in our experiments creates a cationic intermediate (the arylnitrenium ion) from a cationic precursor (the anthranilium ion). As a consequence, these reactive intermediates can be studied in relatively nonpolar solvents such as CH_2Cl_2. In most previous LFP studies of reactive cations, the intermediates were generated from neutral precursors. In nonpolar solvents, charge recombination dominates the kinetics. The analogous process in this system is unimolecular ring closure (k_c) of the singlet nitrenium ion which reforms the ground-state starting material. It is this process that dominates the decay rate of the nitrenium ions in the absence of nucleophiles.

The iminium ion **8** arises from a net 1,2-shift of the methyl group to the nitrenium nitrogen. There is ample precedent for such Wagner–Meerwein shifts in the case of alkyl nitrenium ions,[25,62–65] but only a few examples where this occurs in alkylarylnitrenium ions.[35,37] It has been previously shown that this reaction occurs from the singlet state of the nitrenium ion. The behavior of the methyl derivative illustrates the pronounced effects of substituents on the rate constant for the methyl shift reaction (k_M). This rearrangement is not seen for **1d**. Instead the only photoproducts come from nucleophilic addition. This illustrates the strong dependence of k_M on the ring substitution. Electron withdrawing substituents such as the halogens appear to increase positive charge density on the nitrenium center and accelerate the rearrangement. Electron donating substituents remove positive charge density from the nitrogen and slow the rearrangement. Elsewhere we will show that a 4-nitro substituted derivative undergoes the methyl shift to the exclusion of nucleophilic addition.[66]

The parent amine **7** forms as a consequence of sequential H-atom abstractions by the triplet nitrenium ion.[67] The triplet nitrenium ion itself forms from intersystem crossing in the excited state of the anthranilium ions and subsequent ring opening in the triplet manifold (Scheme 1). Calculations[42,45,46,48,68] and most experimental evidence agree that simple arylnitrenium ions are ground state singlets. In the present systems most of the stable photoproducts originate from the singlet state, rather than the triplet. The LFP show that the observed transients lifetime is unaffected by the addition of H-atom donors. This excludes its assignment to the triplet. Furthermore, the H-atom abstraction reaction of the singlet via pre-equilibration to the higher energy singlet must be negligible. Therefore the triplet state of the nitrenium ions (^{3}**2**, Scheme 1) is effectively invisible in the LFP experiments.

In accord with a number of earlier studies,[7,52,69–72] we find that the main site for nucleophilic addition is the aromatic ring carbons of the arylnitrenium ions. The preferred site of attack appears to be the para position. This is seen in cases where the nucleophiles are especially reactive, or the para position is unhindered. The only case where the nucleophiles are seen to attack the ortho position occurs when the reacting partners are unreactive (water adding to **2b** and **2c**). The rate constants for these reactions fall between 10^5 and 10^8 M^{-1} s^{-1}. These values appear to be typical for additions of alcohols and water to cationic species. For example, Bartl, Steenken, and Mayr report that diphenylcarbenium ion reacts with the same nucleophiles with rate constants of 10^6-10^9 M^{-1} s^{-1}.[14] Likewise Johnston and Schepp[15] measured a rate constant of 1.8×10^5 M^{-1} s^{-1} for addition of methanol to the styryl cation. The 1-anisyl-2,2-dimethylvinyl cation reacts with methanol with a rate constant of 1.3×10^7 M^{-1} s^{-1}.[20] This correspondence of rate constants provides further evidence in favor of our assignment of the observed transient species to the singlet arylnitrenium ions.

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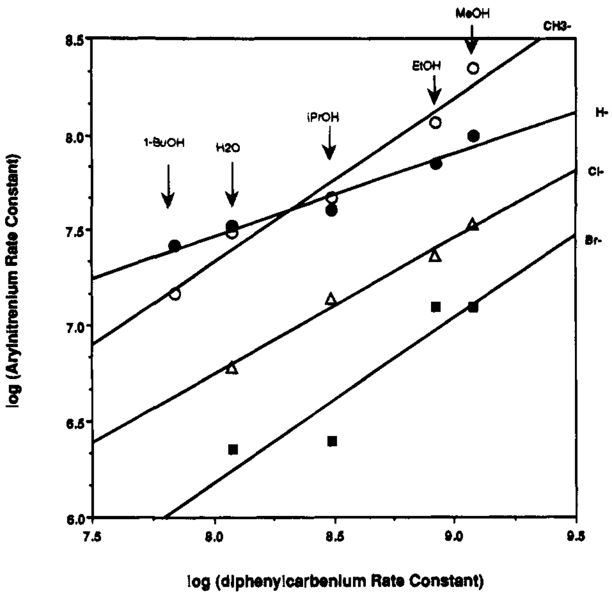

Figure 6. Plot of log (k_{nuc}) for nitrenium ions **2** plotted against corresponding values of log(k_{nuc}) for Ph_2CH^+: solid squares, **2d**; open squares, **2b**; open triangles, **2d**; solid circles, **2c**; open circles, **2a.** Note that the values for **2a** are determined from relative yields; their absolute magnitudes are not known. Therefore while the slope for this system is accurate, the intercept of this line is arbitrarily chosen for comparison purposes.

The nitrenium ions all react with nucleophiles following the order MeOH > EtOH > *i*-PrOH ~ H_2O > *t*-BuOH. This is the same ordering observed for diarylcarbenium ions,[14] vinyl cations,[20] and styrene radical cation.[73] The rationale for this trend is that the alkyl groups in the alcohols serve as electron donors, increasing basicity. This makes unhindered alcohols more nucleophilic than water. However, increasing branching at the α-carbon increases steric hindrance without significantly increasing basicity. For this reason the branched alcohols are less nucleophilic.

It is interesting to note that there is a quantitative correlation between the reaction rate constants for the addition of alcohols to the nitrenium ions **2** and the corresponding rate constants for addition to diphenylmethyl carbocation (Ph_2CH^+). A plot of log(k_{nuc}) for **2a**, **2b**, **2c**, and **2d** versus the same values for Ph_2CH^+ measured by Bartl et al.[13] all give a reasonable fit to a straight line (Figure 6). The slopes are 0.85 ± 0.10 for each of the 4-substituted phenylnitrenium ions. In part the ability of the arylnitrenium to distinguish between nucleophiles is influenced by steric factors. The parent system **2a** shows significantly less selectivity in its reactions having a slope of 0.5.

Conclusions

Laser flash photolysis of anthranilium ions **1** gives transient spectra (Figure 2) assigned to arylnitrenium ions **2**. This assignment is supported by the quenching behavior of the transients and by analysis of the stable photoproducts. LFP experiments make it possible to characterize absolute rate constants for the reactions of ^{1}**2**. It is shown that each of the arylnitrenium ions react with alcohols following the order MeOH > EtOH > *i*-ProH ~ H_2O > *t*-BuOH. These reactions are slower in hydrogen bonding solvents and are faster in nonpolar solvents. Quantum yield measurements show that ring closure and rearrangement (k_c and k_M in Scheme 1) are the major decay pathways for ^{1}**2** when nucleophiles are not present.

Experimental Section

General Methods. CH_2Cl_2 was distilled from P_2O_5. CH_3CN was distilled from CaH_2. ^1H NMR spectra were run at 200 MHz and ^{13}C NMR spectra at 55.1 MHz unless otherwise noted. Mass spectra were performed using electron impact ionization (70 eV).

Analysis of Steady-State Photoproducts. The product distributions listed in Table 2 were determined by ^1H NMR spectroscopy of the photolysates. The corresponding anthranilium salt **1** was irradiated in a Pyrex vessel using a 400 W Xe arc lamp. The sample solutions were 7−20 mM in starting material and purged with N_2 prior to photolysis. Following the irradiation, the solvent was evaporated under vacuum, and the residue was dissolved in a known volume of CD_3CN containing either triphenylmethane or hexamethyldisiloxane as internal standards. Yields were determined by ^1H NMR integration of the product peaks and comparison of these values to the peak integration of the internal standard. The observed peaks correspond to the conjugate acids of the product amines. For comparison, ^1H NMR spectra of the conjugate acids of the products (**7**−**12**) were obtained. Yields are corrected for conversion of the starting material. The isolation and spectroscopic characterization of products **7a**, **8a**, **9a** (nuc = HO, CH_3O),[35] **10d** (nuc = HO, CH_3O), and **11d**[49] have been previously reported.

Quantum Yield Determinations. Solutions of anthranilium salts (**1a**−**d**) (22−33 mg in specified solvents, typically 3 mL) were purged with N_2 in quartz cuvettes and irradiated at 313 or 365 nm (slit width of 9 nm) while being 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.[74] The extent of reaction was measured by steady-state UV absorption spectroscopy. Quantum yields were determined from the intial slopes (10−20% conversion) from plots of mole of starting material vs mole of photons absorbed.

Laser Flash Photolysis Studies. Laser flash photolysis (LFP) experiments were performed using a Questek 2120 laser system with XeCl as the source gas (308 nm and 10 ns time resolution). The UV−vis light source was an Oriel 400 W lamp. The transmitted light was detected with a Hamamatsu photomultiplier tube. The waveforms were recorded by a LeCroy 9420 350 MHz digital oscilloscope and transferred to an IBM PS/2 where the data was manipulated using programs developed in this lab. Sample solutions were charged in a 50 mL volume continuous stirring flow cell (20−30 mg in 40−50 mL of specified solvent, 2−3 mM in anthranilium). The flow cell was sealed with a septum and solutions were purged of O_2 by bubbling N_2 through the solutions. Laser pulse energy was 40−80 mJ/pulse. For quenching experiments, the decay of transient generated upon irradiation of **1d** was monitored at 460 nm, whereas **1c** and **1b** were monitored at 390 or 400 nm. Pseudo-first-order rate constants (k_{obs}) were obtained for the decay of the transient using 5−15 different nucleophile concentrations [nuc].

General Procedure for Synthesis of Anthranilium Salts 1. Following Haley's procedure, to a 0.13 M solution of the corresponding anthranil (2,1-benzisoxazoles) **3** in CH_3NO_2 was added 48% tetrafluoroboric acid solution (to a final concentration of 0.45 M) along with *tert*-butyl alcohol (to 0.15 M). The solution was stirred for 48 h. Ether was added, the resulting solid was collected by filtration and recrystallized from methanol to give $\mathbf{1^+BF_4^-}$. The corresponding perchorate salts were prepared by an analogous procedure using 70% aqueous perchloric acid. The spectral data below are given for the tetrafluoroborate salts. The perchlorate salts gave virtually identical NMR, UV, and IR spectra. Syntheses of **1a**, **3b**,[75] and **3c** [76] have been reported previously.

5-Bromo-3-methyl-N-*tert*-butyl-2,1-benzisoxazolium Tetrafluoroborate ($\mathbf{1b^+BF_4^-}$). From **3b** (283 mg, 1.33 mmol) was obtained

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1b$^+$BF$_4^-$ (280 mg, 59%), mp 160 °C dec, as pink crystals: ^{1}H NMR 400 MHz (CD$_3$CN) 8.32 (dd, *J* = 1.7, .7, 1 H), 8.06 (dd, *J* = 9.6, 1.7, 1 H), 7.83 (dd, *J* = 9.6, .7, 1 H), 3.00 (s, 3 H), 1.85 (s, 9 H); ^{13}C NMR 110.2 MHz (CD$_3$CN) 175.0, 146.2, 144.6, 126.5, 121.6, 120.1, 114.2, 71.6, 28.7, 13.6; MS, *m/z* (rel intensity, %) 270 (12), 268 (11), 254 (4), 252 (2), 214 (10), 213 (99), 212 (15), 211 (100), 185 (29), 184 (94), 183 (30), 182 (96), 158 (18), 156 (18), 104 (15); HRMS, *m/z* 268.0356 (M$^+$ − BF$_4$ calcd for C$_{12}$H$_{15}$NOBr, *m/z* 268.0337); IR (CD$_3$CN) 3001 (w), 2990 (w),1631 (vs), 1537 (m), 1472 (m), 1420 (w), 1378 (w), 1278 (w), 1190 (w), 1102 (vs), 1067 (vs); UV (CH$_2$Cl$_2$) 221 (4.3), 276 (3.5), 351 (3.6). From **3b** (650 mg, 3.07 mmol) was obtained **1b$^+$ClO$_4^-$** (920 mg, 81%), mp 171−173 °C dec, as brown crystals.

5-Chloro-3-methyl-N-*tert*-butyl-2,1-benzisoxazolium Tetrafluoroborate (1c$^+$BF$_4^-$). From **3c** (450 mg, 2.69 mmol) was obtained **1c** (623 mg, 74%), mp 162−164 °C dec, as white crystals: ^{1}H NMR (CD$_3$CN) 8.13 (dd, *J* = 1.8, 1.0, 1 H), 7.96 (dd, *J* = 9.6, 1.8, 1 H), 7.90 (dd, *J* = 9.6, 1.0, 1 H), 3.01 (s, 3 H), 1.85 (s, 9 H); ^{13}C NMR (CD$_3$CN) 175.2, 146.2, 142.4, 132.8, 122.9, 121.0, 114.3, 71.7, 28.7, 13.6; MS, *m/z* (rel intensity, %) 225 (7), 224 (2), 223 (16), 210 (5), 208 (4), 169 (22), 168 (7), 167 (49), 140 (15), 139 (18), 138 (43), 84 (100); HRMS, *m/z* 224.0837 (M$^+$ − ClO$_4$ calcd for C$_{12}$H$_{15}$NOCl, *m/z* 224.0842); IR (CD$_3$CN) 3008 (w), 2997 (m), 2936 (w), 1644 (w), 1538 (s), 1476 (s), 1427 (m), 1378 (m), 1284 (w), 1234 (w), 1192 (s), 1104 (vs), 1072 (vs). From **3c** (650 mg, 3.89 mmol) was obtained **1c$^+$ClO$_4^-$** (925 mg, 76%), mp 170−172 °C dec, as white crystals.

3,5-Dimethyl-*N*-*tert*-butyl-2,1-benzisoxolium Tetrafluoroborate (1d$^+$ BF$_4^-$). 5-Methyl-2-nitrobenzoic acid was converted to 5-methyl-2-nitroacetophenone (**4d**).[77] The methyl substituted anthranil **3d** was obtained in 60% upon reduction of **4d** using Sn/HCl. Alkylation of **3d** according to the general procedure gave **1d** (53%): mp 150−152 °C dec; ^{1}H NMR (CD$_3$CN) 7.90 (dd, *J* = 1.3, 8.8, 1 H), 7.87 (d, *J* = 8.88, 1 H), 7.82−7.79 (m, 2 H), 2.98 (s, 3 H), 2.47 (s, 3 H), 1.84 (s, 9 H); ^{13}C NMR 110.2 MHz (CD$_3$CN) 174.8, 146.7, 144.8, 138.4, 121.7, 120.7, 111.9, 70.6, 28.6, 21.2, 13.3; CIMS, *m/z* (rel intensity, %) 205 (M + 1, 4), 148 (19), 147 (68), 118 (100), 91 (58), 77 (41), 61(63), 51(36); HRMS *m/z* 205.1472 (M + 1 − BF$_4$ calcd for C$_{13}$H$_{19}$NO, *m/z* 205.1466); IR (CD$_3$CN) 3310 (br, w), 3530 (br, w), 2990 (w), 1660(s), 1570(m), 1480 (s), 1390(w), 1200 (s).

Iminium Salt 8b. Salt **1b$^+$BF$_4^-$** (70 mg, 0.22 mmol) was irradiated in 10 mL of freshly distilled CH$_2$Cl$_2$ for 0.5 h with a 320 nm filtered Xe lamp. The solvent was evaporated, and the residue was dissolved in CD$_3$CN and observed by ^{1}H NMR. A trace amount of **7b**, 2% of **11b** (nuc = OH), along with 93% of **8b** was detected. A crude analysis of **8b** is as follows: ^{1}H NMR (CD$_3$CN) 8.34 (d, *J* = 1.8, 1 H), 7.99 (dd, *J* = 8.5, 1.7, 1 H), 7.37 (d, *J* = 8.5, 1 H), 3.68 (m, 3 H), 2.61 (s, 3 H), 2.41 (br s, 6 H); ^{13}C NMR (CD$_3$CN) 198.0, 195.8, 140.1, 139.0, 136.6, 132.2, 128.4, 125.7, 47.0, 28.9, 26.4, 26.2.

Iminium Salt 8c. Salt **1c$^+$BF$_4^-$** (54 mg, 0.15 mmol) was dissolved in 10 mL CH$_3$CN and irradiated for 20 min with >320 nm light from a 400 W Xe-arc lamp. The solvent was evaporated, and the residue was taken up in CD$_3$CN and analyzed by ^{1}H NMR. The mixture contained 10% of **7c** and 72% of another product assigned to **8c**: (CD$_3$CN) 8.20 (d, *J* = 2.3, 1 H), 7.84 (dd, *J* = 8.5, 2.3, 1 H), 7.50 (d, *J* = 8.5, 1 H), 3.70 (m, 3 H), 2.62 (s, 3 H), 2.42 (br s, 6 H); ^{13}C NMR (CD$_3$CN) 198.0, 195.9, 139.6, 137.7, 135.8, 133.6, 132.1, 128.3, 47.0, 28.9, 27.2, 26.2.

Preparative Photolysis of 5-Chloro-3-methyl-N-*tert*-butylanthranilium Tetrafluoroborate in the Presence of CH$_3$OH. **1c** (0.0242 g, 7.79 × 10^{-5} mol) was dissolved in 10 mL of CH$_3$CN. One milliliter of CH$_3$OH as well as 0.1 mL of a 10% HClO$_4$ in CH$_3$OH solution was added to the reaction flask. The solution was purged with N$_2$ for 5 min. The solution was irradiated, with a 450 W medium pressure Hg lamp, through the Pyrex reaction vessel for 10 min. Workup consisted of removing the solvent, via high vacuum, and redissolving the reaction mixture with diethyl ether (20 mL) followed by extraction with saturated NaHCO$_3$ (10 mL). After separation of layers the aqueous layer was taken to pH 7 (10% HCl/H$_2$O) and extracted with another 20 mL portion of ether. Organic layers were combined, washed with H$_2$O (2 × 10 mL), dried with MgSO$_4$, and concentrated in vacuo. Purification with radial chromatography yielded three major products (**9c** , **11c** , **12c** (Nuc = MeOH)) and two present in trace quantities (**11c** (Nuc = OH), **7**. (Eluent was 5% EtOAc/hexane ramped to 40%.) **2-Acetyl-3,4-dimethoxy-*N*-*tert*-butylaniline** (**12**, nuc = CH$_3$O) was a bright yellow oil (24% yield): ^{1}H NMR (CD$_3$CN) δ = 7.02−6.98 (d, 1H, *J* = 9.17), 6.71−6.66 (d, 1H, *J* = 9.17), 3.81 (s, 3H), 3.75 (s, 3H), 2.47 (s, 3H), 1.26 (s, 9 H); ^{13}C (CD$_3$CN) 204.3, 150.9, 144.5, 142.6, 121.8, 119.9, 113.3, 61.7, 57.6, 51.9, 33.2, 30.2; MS (EI) *m/e* 251 (M$^+$, 63), 237 (17), 236 (68), 195 (37), 180 (100), 152 (40), 149 (34), 122 (19), 95 (20), 71 (25); MS *m/z* calcd (M$^+$) 251.15215, obsd 251.15326; IR 3505 cm^{-1}, 2516, 1610 (m), 1420. **2-Acetyl-4-chloro-6-methoxy-*N*-*tert*-butylaniline** (**11c**, nuc = CH$_3$O) is a yellow solid (27% yield): mp: 81−82 °C; ^{1}H NMR (CD$_3$CN) δ = 7.25−7.24 (d, 1H, *J* = 2.35), 7.00−7.01 (d, 1H, *J* = 2.35), 6.7 (br s, 1H), 3.80 (s, 3H), 2.54 (s, 3H), 1.17 (s, 9H); ^{13}C (CD$_3$CN) 202.8, 154.8, 139.2, 131.3, 124.8, 122.7, 115.7, 56.2, 55.4, 30.9, 29.8; MS (EI) *m/e* 255 (M$^+$, 77), 242 (23), 240 (66), 222 (26), 201 (31), 199 (100), 184 (87); MS *m/z* calcd (M$^+$) 255.10260, obsd 255.10234; IR 3004 (b), cm^{-1}, 1820, 1751, 1640 (m), 1600, 1431, 1210.

Preparative Photolysis of 5-Bromo-3-methyl-N-*tert*-butylanthranilium Tetrafluoroborate (1b) in the Presence of CH$_3$OH. Irradiation was performed on **1b** in the presence of MeOH. Reaction conditions were identical to those of **1c**. Purification gave three products: **11b** (nuc = CH$_3$O) (24%), **7b** (29%), **9** (47%). **2-Acetyl-4-bromo-6-methoxy-*N*-*tert*-butylaniline** (**11b**) in 24% yield: ^{1}H NMR (CD$_3$CN) δ = 7.44−7.43 (d, 1H, *J* = 2.22), 7.17−7.16 (d,1H, *J* = 2.22), 3.81 (s, 3H), 2.55 (s, 3H), 1.23 (s, 9H).

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Supplementary Material Available: Additional equations (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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