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Substituent Effects on the Lifetimes and Reactivities of Arylnitrenium Ions Studied by Laser Flash Photolysis and Photothermal Beam Deflection

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Abstract: Photolysis of 5-substituted-*N*-*tert*-butyl-3-methylanthranilium ion produces transient *N*-*tert*-butyl-(2-acetyl-4-substituted) phenylnitrenium ions. This is confirmed by identification of the stable products, transient absorption experiments, and photothermal beam deflection experiments. Analysis of the stable photoproducts shows that the major decay pathway for these species is addition of nucleophiles to the aromatic ring. The kinetics of the these reactions were examined with the goal of determining how various ring substituents affect arylnitrenium ion stability. Rate constants measured for the 4-phenyl and 4-methoxy derivatives are compared with those from previous work. It is shown that a 4-phenyl group stabilizes the nitrenium ion to approximately the same extent as a 4-methoxy group. Both of these substituents stabilize the arylnitrenium ions considerably more than 4-halogens or a 4-methyl group. Time resolved photothermal beam deflection experiments were applied to the 4-cyano and 4-unsubstituted derivatives, which gave no transient absorption spectra. The latter two compounds are shown to have lifetimes of less than 100 ns.

Introduction

Arylnitrenium ions are cationic reactive intermediates that contain a divalent nitrogen atom having a phenyl or other aromatic ring directly attached to the nitrogen (Ar-N-R$^+$).[1,2] Investigation into the behavior of arylnitrenium ions has been motivated in part by the proposal that these species are intermediates in physiological DNA-damaging reactions which are responsible for carcinogenesis.[3−7] The *in vivo* mechanisms of carcinogenesis are complex, and a full picture of this process is still emerging. It has been proposed that aromatic amines are enzymatically oxidized to hydroxylamines, which in turn are enzymatically converted to hydroxylamine *O*-sulfate (or *O*-acetate) esters.[8] Heterolytic scission of the N−O bond[9,10] is thought to generate a transient arylnitrenium ion which covalently adds to guanine bases in DNA.[4,5,11−13]

The mutagenic potency of a given arylnitrenium ion depends upon a balance of reactivity and stability. The nitrenium ion in question must be reactive enough to add rapidly and irreversibly to the DNA molecule. On the other hand, it must be stable enough to survive attack by other nucleophiles present in the physiological environment such as water and glutathione. Novak et al.[14−16] have demonstrated that certain arylnitrenium ions which possess para-π-electron donating groups (such as 4-biphenylylnitrenium ion and 2-fluorenylnitrenium ion) meet this criterion. Apparently, the presence of an additional aromatic ring in the position para to the nitrenium center confers sufficient stability to the nitrenium ion that it can survive attack by water yet still add to guanine bases. In contrast, simple phenylnitrenium ions which lack such substituents in the para-position have very short lifetimes in aqueous solution. For example Fishbein and McClelland[17] estimate the lifetime of the unsubstituted phenylnitrenium ion at ca. 200 ps.

Work in this laboratory has employed anthranilium salts **1**[18] as precursors for studies of substituted alkylaryl nitrenium ions of general structure **2**.[19−22] On the basis of product studies and LFP experiments, we have proposed the general photochemical mechanism shown in Scheme 1. Direct irradiation of **1** gives

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Scheme 1

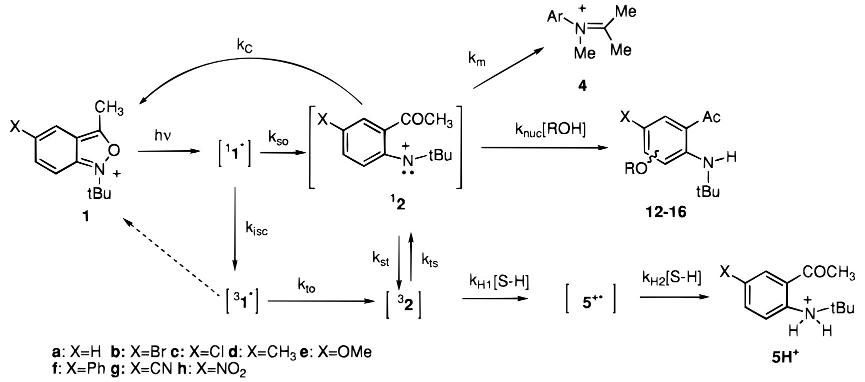
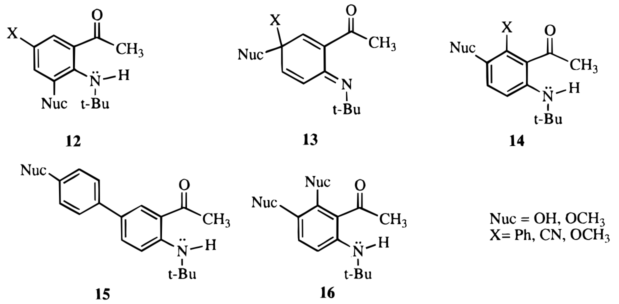


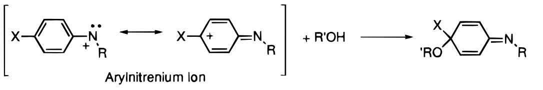
Chart 1. Nucleophilic Addition Products



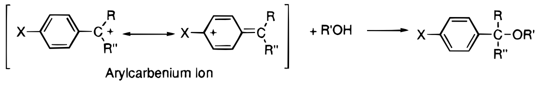
the singlet excited state (^{1}**1***) which can either ring-open to singlet nitrenium ion (path k_{so} to form ^{1}**2**) or intersystem cross to triplet excited state anthranilium (path k_{isc} to form ^{3}**1***). Once generated, ^{1}**2** can cyclize to regenerate ground-state anthranilium ion (k_c) or react intermolecularly (k_{nuc}) to give nucleophilic addition products (e.g., **12**−**16**, Chart 1), or intramolecularly (k_m) to give rearrangement products (**4**). If triplet excited state anthranilium (^{3}**1***) is generated (by either triplet sensitization or k_{isc}), then its ring opening generates the triplet nitrenium ion (^{3}**2**). The latter reacts via sequential H−atom abstractions (k_{H1} and k_{H2}) to give the parent amine (**5**).

The nature of the electronic spin state of nitrenium ions has been examined both theoretically and experimentally. The parent nitrenium ion, NH_2^+, is a ground state triplet. Quantum calculations[23] and high-resolution photoelectron spectroscopy[24] both give an energy gap ($E_S - E_T$) of ca. +30 kcal/mol. Arylnitrenium ions are generally ground state singlets. Density functional theory[25] as well as Hartree−Fock[26] calculations both predict that phenylnitrenium ion $PhNH^+$ is a ground state singlet with an energy gap of ca. −20 kcal/mol. Semiempirical calculations[27−31] predict that most substituted arylnitrenium ions also have singlet ground states. However, the magnitude of the energy gap is dependent upon the ring substitution pattern. Electron-withdrawing substituents shift the energy gap in favor of the triplet state, and electron donating groups favor the singlet state. With sufficiently electron-withdrawing groups it is possible to reverse the state energies and make the triplet the ground state. Recent experimental work on *N*-*tert*-butyl-(2-acetyl-4-nitrophenyl) nitrenium ion provides indirect evidence that this arylnitrenium ion might be a ground state triplet.[32]

The study described below was undertaken with the goal of learning how various ring substituents affect the lifetimes and reaction rates of singlet state arylnitrenium ions. In this regard, it is interesting to contrast the behavior of arylnitrenium ions with that of the arylcarbenium ions (eq 1), as there is considerable information about the latter class of intermediates.[33−36] On one hand, it might seem that substituent effects in the arylnitrenium ions would simply mirror those seen in the arylcarbenium ions. On the other hand, there are some significant differences in the mechanism by which the two intermediates are trapped. Nucleophiles such as alcohols and water add to the exocyclic atom of the arylcarbenium ions (eq 1a),[36] but they add to the para and ortho ring atoms of arylnitrenium ions (eq 1b).[20,37−40] For this reason, steric effects of para-substituents cannot be neglected in the nitrenium ions as they often are in the carbenium ions. Resonance and inductive electronic effects may be felt differently in the two different species. Novak[41] has suggested that the loss of aromatic character in the transition state for addition to arylnitrenium ions might cause them to respond differently to the electronic properties of various substituents than do the carbenium ions. Furthermore, a nitrenium ion center is much more electronegative than the corresponding carbenium center and therefore polarizes the *π*-electrons of the substituents more strongly.



(1a)



(1b)

Previous LFP experiments on arylnitrenium ions **2** showed that the 4-methyl derivative **2d** was significantly more reactive

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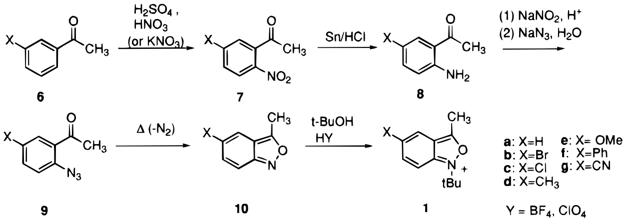
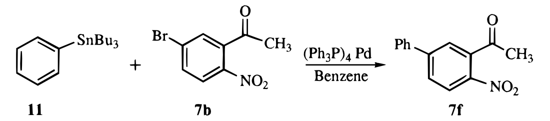
Scheme 2



Scheme 3



toward nucleophiles than the halogenated derivatives **2b** and **2c**. This contrasts with the effects of such groups on the stability of carbenium ions. With the latter, para-halogens act as net destabilizers and para-alkyl groups act as stabilizers.[42,43] In order to further elucidate electronic and steric effects on the reactions of arylnitrenium ions with nucleophiles, we have synthesized photoprecursors (**1**) to 4-methoxy, 4-phenyl, and 4-cyano substituted *N-tert*-butyl-(2-acetylphenyl) nitrenium ions (**2**). Product studies, laser flash photolysis, and photothermal beam deflection measurements were undertaken on these compounds, and the results are compared with the previously studied nitrenium ions. It is shown that the CN group destabilizes the arylnitrenium ions relative to the previously studied examples. Phenyl and methoxy substituents stabilize arylnitrenium ions to approximately the same extent as each other and considerably more than the halogens.

Results and Discussion

1. Synthesis of Substituted Anthranilium Ion Photoprecursors. Compounds **1e**−**g** were prepared from the appropriate 3-substituted acetophenone derivative **6** according to the general method depicted in Scheme 2. Nitration of **6** followed by reduction produced the arylamine **8**. Conversion of the latter to the arylazide **9**, followed by thermolysis, gave the anthranil free base **10**. The latter was alkylated by the generation of *tert*-butyl cation in the presence of a strong acid to give **1**.[18] The syntheses of anthranilium salts **1a**,[20] **1b**, **1c**,[22] and **1d**[21] have been reported elsewhere.

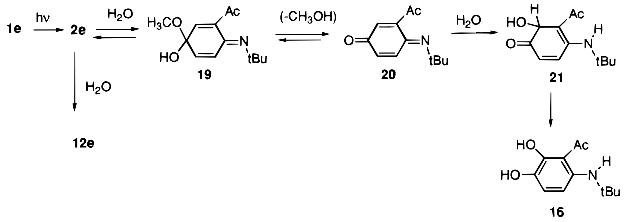
The phenyl derivative **1f** was prepared by a somewhat different route (Scheme 3). In this case 2-nitro-5-bromoacetophenone **7b** was first prepared. Stille coupling[44] was used to convert **7b** into the 5-phenyl derivative **7f** in 70% yield. The latter was taken through to the anthranil **10f** as indicated in Scheme 2. Likewise the cyano derivative **1g** was prepared by first converting **7b** into 2-nitro-5-cyanoacetophenone **7g** in 97% yield using a Pd-coupling procedure described by Kosugi.[45] The product from this reaction was converted into **1g** following Scheme 2. The 5-methoxy derivative (**1e**) was also synthesized following Scheme 2.

Table 1. Product Distributions (% Yield) from the Photolysis of Anthranilium Ions **1**

ion	trap (concn)	5	4	12	13	14	15	16	17
1e	H_2O (9.2 M)			23				77	
1e	MeOH (3.8 M)			91					
1e	(none)			65[a]					
1f	H_2O (4.1 M)	30		21	13	17	8		
1f	MeOH (2.1 M)	23		7	45	8			
1f	(none)	29	25						
1g	MeOH (3.5 M)			23					43
1g	(none)		60						

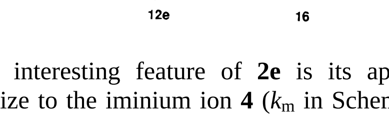
[a] Average of three runs.

Scheme 4



2. Product Studies. UV irradiation of solutions of the anthranilium ions **1** gives products derived from the arylnitrenium ions **2**. There are basically three types of products: (1) the parent amine **5**; (2) an iminium ion, **4**; and (3) a number of products all derived from addition of nucleophiles to the aromatic ring (**12**−**16**).

Irradiation of the methoxy derivative **1e** gives the product distribution listed in Table 1. There are two major products: the ortho adduct **12e** and the dihydroxy adduct **16** (eq 2). The latter is observed only at relatively high water concentrations. At low water concentrations or with CH_3OH as the trap, only **12e** is detected. We suggest that **16** is formed via the mechanism depicted in Scheme 4. Initial attack at the para position reversibly forms a hemiketal of the imine quinone (**19**). The productive pathway involves a proton-catalyzed elimination of methanol to give (following deprotonation) the imine quinone **20**. The latter is an especially electrophilic imine quinone due to the electron-withdrawing acetyl group. Michael addition of water to the 3-position yields **21** which is a tautomer of the stable product **16**. Because **16** is not seen at low [H_2O] or with CH_3OH as the trap, it is surmised that the first irreversible step leading to **16** must involve an additional H_2O molecule. One possibility is that the net elimination of MeOH from **19** is more sensitive to general acid catalysis than is the elimination of H_2O. Thus water, being more acidic than CH_3OH, would be a more effective catalyst for this reaction.



(2)

One interesting feature of **2e** is its apparent failure to isomerize to the iminium ion **4** (k_m in Scheme 1). Photolysis of **1e** was carried out in nominally anhydrous CH_3CN (i.e., distilled from CaH_2). Nonetheless in all cases a 40−80% yield of the ortho hydroxy adduct was detected. Thus, if k_m occurs at all, it is much slower than the k_{nuc} reaction with adventitious water. Similar behavior has been observed for the methyl derivative, **2d**.[21] In contrast, the other nitrenium ions in this series, **2a**, **2b**, **2c**, **2f**, and **2g** all give significant yields of **4** under the same conditions.

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[38] Gassman, P. G.; Campbell, G. A. *J. Chem. Soc., Chem. Commun.* **1970**, *1970*, 427.

[39] Fishbein, J. C.; McClelland, R. A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 653−662.

[40] Some nucleophiles do add to the nitrogen of nitrenium ions: most notably guanosine bases of DNA. For example, see ref 14.

[41] Novak, M.; Kahley, M. J.; Lin, J.; Kennedy, S. A.; Swanegan, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 11626−11627.

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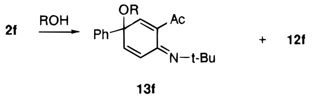
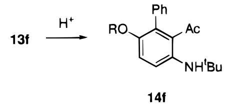
Photolysis of the 4-phenyl derivative **1f** affords several products, the majority of which originate from para ring addition. When **1f** was irradiated in the presence of MeOH, a small amount (7%) of ortho adduct **12f** (nuc = CH_3O) is observed, but the major product comes from para addition to give quinol imine **13f** (nuc = CH_3O) in 45% yield (eq 3). Proton-catalyzed isomerization of the latter occurs slowly under the reaction conditions, and **14f** is observed in 8% yield (eq 4). The other significant product is the parent amine **5f** which occurs from the parallel triplet pathway. Apparently with the phenyl derivative the excited state intersystem crossing pathway (k_{isc} in Scheme 1) becomes competitive with the singlet state ring opening (k_{so}). In the absence of nucleophiles, the iminium ion **4f** is formed.



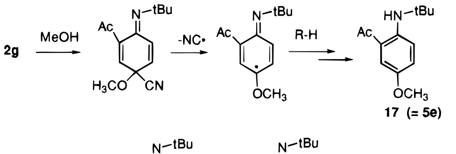
(3)



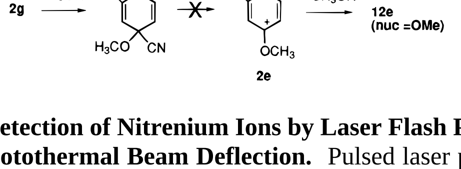
(4)

Water gives products analogous to those from CH_3OH, although there are some differences in the distribution. With H_2O, somewhat higher yields of the ortho adduct **12f** (nuc = OH) are seen. The major products still result from initial para addition: namely, the quinol imine **13f** (nuc = OH) in 13% yield and the addition/rearrangement product **14f** (nuc = OH) in 17% yield. Small amounts of a product that results from addition to the phenyl substituent (**15**, nuc = OH) are also observed.

Irradiation of **1g** in the absence of nucleophiles gives mainly iminium ion **4g**. In the presence of CH_3OH, **1g** behaves in a similar fashion to the halogenated derivatives. The ortho adduct **12g** (nuc = CH_3O) is observed as well as the methoxy substitution product **17**. This latter product is interesting; it clearly involves addition of CH_3OH and elimination of the elements of HCN. By analogy to earlier studies of the bromo-derivative, **1b**,[22] we attribute this product to an initial para-addition followed by homolysis of the cyano group to give an aminyl radical. The latter presumably abstracts a H-atom from the solvent to give **17** (eq 5a). We considered the possibility the the initial para adduct would decay by heterolysis (i.e., elimination of CN^-, eq 5b). This process would form the para methoxy substituted nitrenium ion **2e**. This would lead to the same products obtained from photolysis of the methoxy anthranilium ion **1e** in CH_3OH, namely **12e**. Because **12e** is not observed, the heterolysis mechanism is excluded.



(5a)



(5b)

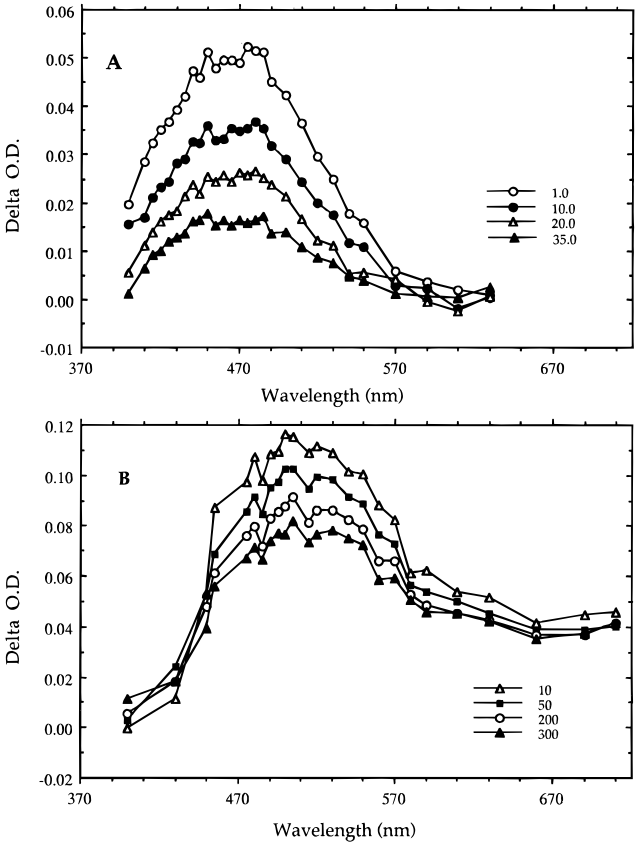


Figure 1. Transient absorption spectra obtained from pulsed laser photolysis (308 nm, 10 ns, 20−50 mJ/pulse) of anthranilium ions **1f** (panel A) and **1e** (panel B) in N_2-purged CH_3CN. These spectra are assigned to the corresponding arylnitrenium ions **2f** and **2e** (see text).

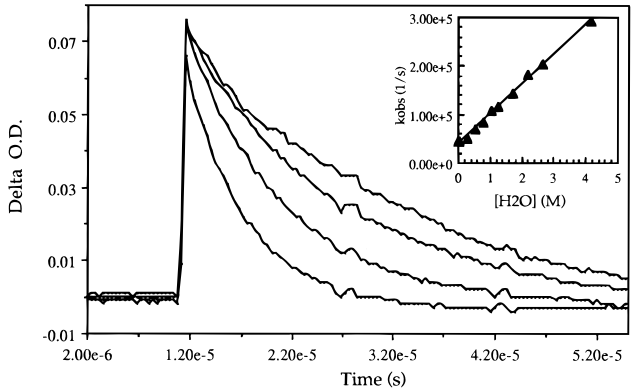


Figure 2. Decay waveforms from laser flash photolysis of **1f** in CH_3CN containing 0.00−4.17 M H_2O monitored at 470 nm, the absorption maximum of the arylnitrenium ion **2f** (see Figure 1 and text). Inset shows the dependence of the pseudo-first-order decay rate constant, k_{obs} on $[H_2O]$.

3. Detection of Nitrenium Ions by Laser Flash Photolysis and Photothermal Beam Deflection. Pulsed laser photolysis of anthranilium ions **1e** and **1f** gives the transient spectra shown in Figure 1. The λ_{max} for **1e** is 500 nm (Figure 1b), whereas for **1f** it is 470 nm (Figure 1a). The transient spectra are assigned to the singlet state of the corresponding arylnitrenium ions **2** on the basis of the following considerations. (1) The products described above are consistent with the formation of singlet arylnitrenium ion ^{1}**2**. The ring addition products are particularly characteristic of singlet arylnitrenium ions.[37,38,46,47] (2) The lifetimes of the transients are unaffected by O_2, a triplet quencher.[48] This argues against an excited triplet state of **1** being the signal carrier. (3) The lifetimes of the transient species are unaffected by the addition of H-atom donors such as nBu_3-

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[46] Gassman, P. G.; Campbell, G. A.; Frederick, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 3884−3891.

[47] Gassman, P. G.; Campbell, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3891−3896.

[48] Rosenthal, I. In *Singlet Oxygen*; Frimel, A. H., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I, pp 13−35.

SnH (in concentrations as high as 0.1 M). The triplet state of the nitrenium ions or aminyl radicals would be expected to react rapidly with such traps.[32] (4) McClelland[16,49] has reported LFP spectra of several similar phenyl-substituted arylnitrenium ions which were generated using different photoprecursors. These nitrenium ions also absorb in the region 450−500 nm. (5) The observed transients react rapidly with nucleophiles with rate constants of 10^5−10^{10} M^{-1} s^{-1} (Figure 2). This is the range typical for substituted arylnitrenium ions.[22,50] Furthermore the rate constants vary in the expected way as the nature of the nucleophile is varied. (These rate constants are discussed in more detail in section 4, below.)

As expected, the lifetimes of **2e** and **2f** are considerably longer than those of the previously studied examples. Nitrenium ions **2b−d** have lifetimes of 119−440 ns.[22] In contrast the phenyl and methoxy stabilized have lifetimes of 30 and 600 μs,[51] respectively. Earlier studies showed that in the absence of nucleophiles (e.g., water, alcohols) the lifetimes of the 2-acetylphenyl nitrenium ions are limited by a combination of the methyl migration (k_m, Scheme 1) and thermal reversion to the anthranilium ion (k_c). Inasmuch as **2e** yields no detectable iminium ions **4**, it can be assumed that this lifetime is limited primarily by ring closure—i.e., $1/k_c > 600$ μs for **2e**.

Neither **1a** nor **1g** give a detectable transient absorption under the conditions employed here. Earlier,[20,22] we speculated that **2a** might decay too rapidly to be detected with the nanosecond apparatus. This was based on the reasoning that the lack of a stabilizing substituent in the 4-position ought to leave this particular nitrenium ion more open to attack by nucleophiles. The lower π-delocalization of the positive charge in **2a** compared with **2b−d** also would be expected to make the cyclization process (k_c) more rapid. The same reasoning would also hold that the cyano-derivative **2g** is too short lived to detect with the nanosecond apparatus. However, it was of interest to verify these assumptions by obtaining experimental lifetimes, or at least upper limits for **2a** and **2g**.

To estimate the lifetimes of **2a** and **2g**, photothermal beam deflection calorimetry (PDC) was employed. This technique can measure the rates of fast photochemical reactions by monitoring the time-dependence of heat release that follows the excitation of a sample with a short pulse of light. Extensive treatments of the fundamentals[52−54] and practice[55−58] of this method are available elsewhere. Briefly, pulsed photolysis of a solution of **1a** or **1g** produces heat that is released as a consequence of both nonradiative relaxation of excited states as well as reactions of short-lived intermediates (i.e., **2**). The heating results in a thermal expansion of the solvent, which in turn lowers its index of refraction. The excitation beam illuminates only a small region of the sample cuvette creating a local zone of low refractive index surrounded by the higher index of refraction in the unilluminated regions of the sample. This is a virtual lens which can be used to deflect the propogation of a second laser beam. The deflection angle of the latter can be monitored as a function of time using a fast bi-cell detector. The rate at which the deflection angle varies is exactly the same as the rate of the exothermic processes producing the heat.

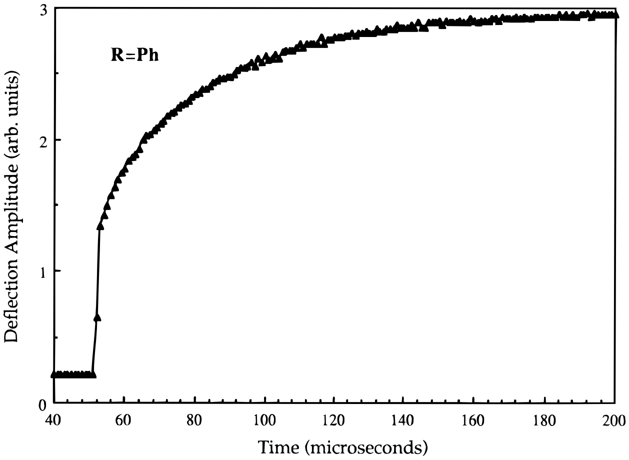

Figure 3. Time-resolved photothermal beam deflection signal generated from pulsed laser photolysis (308 nm, 10 ns, 0.2−1.0 mJ/pulse) of **1f** in Ar-purged CH_3CN. Laser pulse arrived at ca. 52 μs on the time axis shown.

In order to determine if the PDC technique would give reliable kinetic data for nitrenium ions, it was first applied to a species that could be independently examined by conventional LFP. Nitrenium ion **2f** is sufficiently long-lived that its lifetimes and reaction rates could be measured by both methods. Figure 3 shows an example of a PDC kinetic waveform obtained from photolysis of **2f** in CH_3CN. The rise of the deflection signal shows two parts, a fast jump followed by a slower exponential growth. The fast jump is assigned to processes that occur rapidly (i.e., <100 ns) following excitation. These include k_{so}, k_{isc}, and nonradiative relaxation to the lowest excited singlet state of **1**. We attribute the slower, exponential rise to the decay reactions of **2f**. In the absence of nucleophiles these include the ring-closure process (k_c) and the methyl shift (k_m). This rise fits well to first-order growth with a time constant of 32 μs. This is in reasonable agreement with the 30 μs lifetime for **2f** measured by LFP.

To further verify that the observed PDC growth was due to reactions of ^{1}**2**, the effect of nucleophiles on the rate constant was tested. Addition of CH_3OH causes an increase in the risetime that is proportional to the concentration of added CH_3OH. A pseudo-first-order analysis gives $k_{nuc} = 2.6\ (\pm 0.2) \times 10^5$ M^{-1} s^{-1}, a value in good agreement with that derived by conventional LFP (2.70×10^5 M^{-1} s^{-1}).

Having determined that PDC could give reliable kinetic data for the nitrenium ion systems, we next turned our attention to the anthranilium ions that did not give detectable transient absorptions. Anthranilium ions **1a** and **1g** were examined by PDC, the results of these experiments appear in Figure 4. For both derivatives, the thermal rise was indistinguishable from the instrument response function (ca. 100 ns). This demonstrates that the corresponding nitrenium ions **2a** and **2g** have lifetimes that are <100 ns and verifies our earlier conjecture.

4. Kinetic Studies on the Reactions of Arylnitrenium Ions with Nucleophiles. Nucleophilic trapping experiments provide further support for the assignment of the observed transient intermediates to the nitrenium ions **2**. The lifetimes of the

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(49) McClelland, R. A.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1995**, *117*, 4173−4174.

(50) Anderson, G. B.; Falvey, D. E. *J. Am. Chem. Soc.* **1993**, *115*, 9870−9871.

(51) In contrast to the previously studied examples **2b**, **2c**, and **2d**, the lifetimes of these longer-lived nitrenium ions are much more sensitive to traces of water in the solvent. The values cited would vary by ca. 10% from experiment to experiment.

(52) Braslavsky, S. E.; Heibel, G. E. *Chem. Rev.* **1992**, *92*, 1381−1410.

(53) Braslavsky, S. E.; Heinoff, K. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1, pp 327−355.

(54) Tam, A. C.; Sontag, H.; Hess, P. *Chem. Phys. Lett.* **1985**, *120*, 280−284.

(55) Yeh, S.-R.; Falvey, D. E. *J. Photochem. Photobiol. A: Chem.* **1995**, *87*, 13−21.

(56) Poston, P. E.; Harris, J. M. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 51−61.

(57) Poston, P. E.; Harris, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 644−650.

(58) Laman, D. M.; Falvey, D. E. *Rev. Sci. Instrum.* **1996**, (In Press).

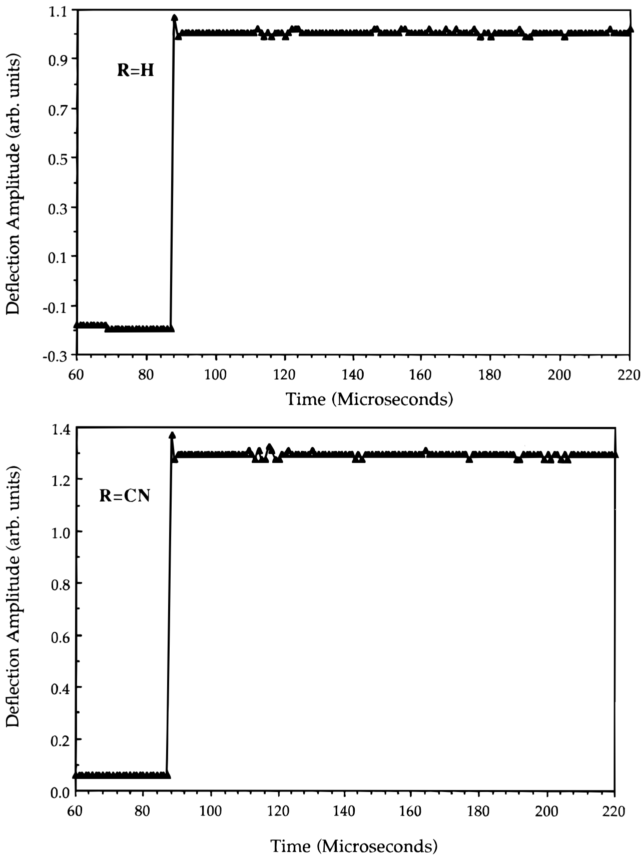


Figure 4. Time-resolved photothermal beam deflection signal generated from pulsed laser photolysis of **1a** (top panel) and **1g** (bottom panel) in Ar-purged CH_3CN. Excitation pulse arrived at ca. 88 μs on the time axis shown.

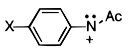
transient species are diminished when nucleophiles such as H_2O, alcohols, or halide ions are added. An example of this is illustrated in Figure 2 which shows the decay of nitrenium ion **2f** in the presence of varying concentrations of H_2O. In most cases the dependence of the observed first-order rate constant for decay (k_{obs}) on nucleophile concentration, [nuc], conformed to pseudo-first-order behavior (eq 6). We define k_o as the decay rate constant in the absence of nucleophile and k_{nuc} as the second-order rate constant for the reaction of **2** with a given nucleophile.

$$k_{obs} = k_o + k_{nuc}[\mathrm{nuc}] \tag{6}$$

The k_{nuc} (CH_3CN) derived from the slopes of the pseudo-first-order plots for a variety of nucleophiles with both nitrenium ions **2e** and **2f** are compiled in Table 2. Listed therein are also k_{nuc} values for the previously studied nitrenium ion **2d**.[22] For each nitrenium ion the trend of reactivity is conserved with respect to the nucleophile. For example in the series of hydroxylic nucleophiles, the trend MeOH > EtOH > i-PrOH $\sim$ H_2O $\gg$ t-BuOH holds true for all systems studied. For the alcohols, k_{nuc} is determined by steric hindrance due to branching at the α-carbon atom. Such a trend is typical for reactive cationic species such as vinyl cations,[59] alkene cation radicals,[60] and diarylcarbenium ions.[61] Water, lacking an inductively electron-donating alkyl group, falls at approximately the same value as i-PrOH.

In several cases, the behavior of some nonhydroxylic nucleophiles was examined. The halides Br^- and Cl^- have been shown to be much more reactive toward carbenium ions than are the alcohols.[61,62] This is true as well for the arylnitrenium ions. The phenyl derivative **2f** reacts at slightly less than the diffusion limit with these halides, and the methyl **2d** derivative reacts at the diffusion limit with Br^-. The electron-rich alkenes such as ethylvinyl ether[63] react rapidly with **2d**, **2e**, and **2f** having rate constants similar to or larger than to those of MeOH. Dihydropyran[63] showed similar quenching behavior with **2f**, in this case the k_{nuc} was 1.18×10^6 M^{-1} s^{-1}. Interestingly with these particular types of nucleophiles the phenyl derivative was seen to be much more reactive than the methoxy derivative. The unactivated alkene, cyclopentene, did not quench **2f** even at concentrations as high as 3 M. Likewise the electron-poor alkene, cyclopentenone did not quench **2f**.

Ring substituents affect the stabilities of the arylnitrenium ions in the following order: CN $\approx$ H < CH_3 < Br $\approx$ Cl << Ph $\approx$ MeO. This trend is qualitatively different from that seen for arylcarbenium ions.[36,42] In carbenium ions the MeO group ($\sigma^+ = -0.78$) is considerably more effective at stabilizing the positive charge than is the Ph group ($\sigma^+ = -0.18$). Furthermore, in the carbenium ions, the CH_3 ($\sigma^+ = -0.31$) group is more effective than Ph and much more effective than the halogens (+0.15 for Br and +0.11 for Cl). Similar substituent effects have been observed with different arylnitrenium ions studied by different methods. Novak's group[41] measured the relative trapping rates of the thermally generated *N*-acetyl-4-substituted phenylnitrenium ions **21**. In this case, the stabilization toward addition of water to **21** followed the order H < CH_3 < OEt $\approx$ Ph. In these particular arylnitrenium ions, the phenyl group is slightly more effective at stabilizing the arylnitrenium ion than alkoxy substituents.



X = Ph, OEt, CH_3, H

21

We considered that the differences between the arylcarbenium ions and the arylnitrenium ions might be due to steric effects. In this case, one would expect that those substituents which exerted the largest steric hindrance to be most sensitive to changes in the size of the nucleophile. Specifically, the change in k_{nuc} in going from MeOH to t-BuOH should be more dramatic for a nitrenium ion with a large substituent than one with a smaller substituent. For example the k_{nuc} values for cyclohexadienyl cations show little or no dependence on the size of the alcohol, varying by no more than a factor of 2 between MeOH and t-BuOH.[64] In contrast, these values vary by more than a factor of 10 for the more sterically congested triarylvinyl cations[65] and the diarylmethyl carbenium ions.[61,66]

Comparison of the k_{nuc} values for various alcohols shows that the steric hindrance from the various substituents studied here is roughly constant. Figure 5 shows a free energy correlation between the k_{nuc} values measured for the various arylnitrenium ions **2a**−**f** and the corresponding values for Ph_2CH^+.[61] In each case there is a good correlation. For the substituted systems **2b**−**f** the slopes all fall in the range of 0.80 ± 0.09. In contrast,

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[59] Ginkel, F. I. M. v.; Visser, R. J.; Varma, C. A. G. O.; Lodder, G. *J. Photochem.* **1985**, *30*, 453−473.

[60] Johnston, L. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564−6571.

[61] Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710−7716.

[62] Dorfman, L.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352−357.

[63] Product studies showed a complex mixture of products when nitrenium ion **2f** was generated in the presence of this nucleophile.

[64] Steenken, S.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 9648−9649.

[65] Kobayashi, S.; Kitamura, T.; Taniguchi, H.; Schnabel, W. *Chem. Lett.* **1983**, 1117−1120.

[66] Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918−6928.

Table 2. Rate Constants k_{nuc} (M^{-1} s^{-1}) for Reaction of Arynitrenium Ions with Nucleophiles in CH_3CN Solution Measured by LFP

	MeOH	EtOH	i-PrOH	t-BuOH	H_2O	EVE[a]	Br^-	Cl^-
2d	2.23×10^8 [b]	1.18×10^8 [b]	4.63×10^7 [b]	1.48×10^7 [b]	3.08×10^7 [b]	1.65×10^8	1.26×10^{10}	
2e	1.95×10^5	2.60×10^5	1.02×10^5	3.39×10^4	2.06×10^5	7.95×10^5 [c]	*d*	
2f	2.70×10^5	2.84×10^5	6.03×10^4	2.09×10^4	6.16×10^4	1.18×10^7	8.47×10^9	1.19×10^9

[a] Ethylvinyl ether. [b] From ref 22. [c] Above 0.01 M the pseudo-first-order plot curved upward. The cited value was determined at concentration below 0.01 M. [d] Nitrenium ion appears to be quenched, but the kinetics are complex.

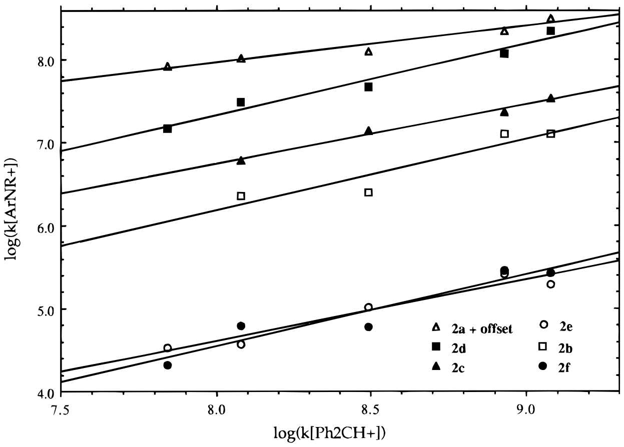

Figure 5. Correlation of the log(k_{nuc}) for reactions of various nitrenium ions **2a**−**f** with ROH in CH_3CN plotted as a function of the corresponding values for diphenylcarbenium ion (Ph_2CH^+). The values for **2a**−**d** were taken from ref 22, the values for Ph_2CH^+ were taken from ref 61.

parent system **2a** gives a significantly smaller slope of 0.44. The latter example shows that ring additions to nitrenium ions is indeed sensitive to steric hindrance. However, the nearly equal slopes for the substituents CH_3, Cl, Br, Ph, and MeO suggest that these particular substituents all exert roughly the same steric hindrance.

The above analysis indicates that the differences in substituent effects betwen arylcarbenium ions and arylnitrenium ions must have an electronic basis as well as a steric one. Novak, et al.[41] have argued that differences in transition state aromaticity account for at least part of this discrepency. In the transition state leading to the carbenium ion adduct, the delocalized π-electrons are relocalized into the phenyl ring, resulting in increased aromatic stabilization. In the transition state leading to the nitrenium ion adduct, the π-electrons are further delocalized onto the exocyclic bond, resulting in a loss of aromatic stabilization. It was demonstrated that the k_{nuc} (measured by competitive trapping) correlated well with the ab initio calculated enthalpies of hydration.[41]

It is also possible that the increased electronegativity of the nitrogen in the nitrenium ions compared with carbon in the carbenium ions leads to increasing demand for π-electron density. This is more readily satisfied by a polarizable substituent such as Ph than the far less polarizable CH_3O or CH_3 groups. Likewise, the halogens nonbonding electrons are more easily donated into the lower energy vacant nitrenium p orbital than they are in the higher energy carbenium ion p orbital.

Conclusions

LFP and photothermal beam deflection investigations of the 4-substituted *tert*-butyl phenylnitrenium ions **2** reveal some interesting effects of substituents on the stability of these species toward attack by water and alcohols. It is shown that a 4-phenyl substituent stabilizes the nitrenium center far more than a 4-methyl or 4-halo group and to almost the same extent as a 4-methoxy group. The 4-unsubstituted and 4-cyano systems are shown to be less stable than any of the other systems, including the 4-halo. It is clear that simple quantitative models derived for carbenium ions cannot be readily extrapolated to the nitrenium ions.

Experimental Section

General Photolysis Conditions. Photolysis reactions were performed in quartz or Pyrex vessels. In the cases where no nucleophilic trap was present, the vessels and necessary syringes were treated with a 5% v/v solution of Me_2SiCl_2 in CH_2Cl_2, rinsed, and oven-dried overnight before use. The solutions were purged of O_2 by passing N_2 or argon through the solutions for 10−15 min. The light source was a medium pressure 450 W Hg lamp.

Analysis of Steady-State Photoproducts. The product distributions/yields were determined by ^{1}H NMR spectroscopy of the photolysates. The corresponding anthranilium salt **1** was irradiated in a Pyrex vessel using a 450 W medium pressure Hg 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, hexamethyldisiloxane, or trimethylsilane as internal standards. Yields were determined by ^{1}H 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, ^{1}H NMR spectra of the conjugate acids of the authentic products were taken. A drop of concentrated $HClO_4$ was added to the NMR sample. Yields are corrected for conversion of the starting material.

LFP Experiments. LFP experiments were done using a Questek 2120 excimer laser using Xe/HCl as the reagent gas. The latter provides excitation 20−50 mJ light pulses of 10 ns duration at 308 nm. Kinetic traces were obtained by monitoring a CW probe beam from a 350 W Xe arc lamp which passed through the sample perpendicular to the path of the excitation beam. Sample solutions were placed in a 50 mL, continuous stirring, flow-cell (20−30 mg in 40−50 mL of specified solvent, 2−3 mM in anthranilium salt) or in quartz cuvettes (1 cm × 1 cm × 5 cm). Both vessels were sealed with rubber septa prior to bubbling N_2 through the solutions for 10−15 min. For nitrenium ion quenching experiments, the decay of transient generated upon irradiation of **1d** was monitored at 460 nm, whereas **1e** and **1f** derivatives were observed at 470 and 500 nm, respectively. Pseudo-first-order rate constants (k_{obs}) were obtained for the decay of the transient using 5−15 different nucleophile concentrations [nuc]. The nucleophilic quencher was added through the septum by means of a syringe. As in the previous study,[22] all of the nucleophile solutions contained 10% of H_2SO_4 to prevent a ground-state addition of the nucleophile to **1**.

Photothermal Beam Deflection Experiments. The PBD apparatus has been described elsewhere.[58] Experiments without nucleophiles present consisted of solutions of **1g** in CH_3CN (4.7 mg salt **1g** in 3 mL of solution). The solution was placed in quartz cuvette, sealed with a septum, and purged with argon for 10 min. Solutions with CH_3OH present were 8.2×10^{-2} and 4.1×10^{-2} M in MeOH (0.010 and 0.005 mL, respectively) and were prepared in the same fashion as the solution with no nucleophilic trap.

Synthesis of Anthranilium Salts. Detailed procedures for the preparation of synthetic intermediates **7f** (mp 78−80 °C), **8f** (mp 108−110 °C), **7e** (mp 120−122 °C), **8e** (a yellow oil), **7g** (mp 276 °C dec), and **8g** (mp 122−124 °C), along with spectroscopic data for each are provided in supporting information.

5-Phenyl-3-methylanthranil (10f). Amine (**8f**) (1.01 g, 4.8×10^{-3} mol) were dissolved in 25 mL of glacial acetic acid to which 1 mL of H_2SO_4 was added. Reaction mixture was cooled to 0 °C, and an aqueous solution of $NaNO_2$ (0.67 g, 9.7 × 10^{-3} mol in 2 mL of H_2O) was added in several aliquots. Reaction was allowed to stir for 1 h before aqueous NaN_3 (0.63 g, 1.0 × 10^{-2} mol in 2 mL of H_2O) was added. Gas evolution was observed. After addition was complete reaction was stirred for 20 min at 0 °C. Reaction mixture was extracted with Et_2O (3 × 50 mL). Organic layer was washed with H_2O until aqueous layer was neutral and then concentrated under vacuum. The residue was taken up in 30 mL of H_2O and heated at reflux for 4 h. Once cooled, the reaction mixture was extracted with Et_2O (3 × 25 mL), dried with $MgSO_4$, and concentrated under vacuum. **10f** was obtained in 57% yield: mp 61−65 °C; ^1H NMR ($CDCl_3$) 7.60−7.38 (m, 8H), 2.82 (s, 3 H);^{13}C NMR (CD_3CN) 168.2, 157.4, 140.9, 136.2, 132.9, 129.9, 128.6, 127.7, 118.5, 116.9, 115.8, 12.2; MS, *m/z* (rel intensity, %) 209 (100), 196 (19), 181 (42), 180 (80), 179 (11), 167 (16), 166 (18), 154 (20), 153 (13), 140 (15), 139 (20), 70 (13); HRMS, *m/z* 209.08268 (M^+ calcd for $C_{14}H_{11}NO$, *m/z* 209.08406); IR (CH_2Cl_2) 3700 (br, m), 3060 (br, s), 2999 (w), 2700, 2540, 2420, 1430, 1290, 1230 (s), 800.

5-Methoxy-3-methylanthranil (10e). Amine (**8e**) (2.04 g, 0.012 mol) was dissolved in 30 mL of glacial acetic acid to which 5 mL of H_2SO_4 was added. Reaction mixture was cooled to 0 °C. $NaNO_2$ (3.24 g, 0.049 mol) dissolved in 10 mL of H_2O was added in several aliquots, and the reaction was allowed to stir for 1 h. NaN_3 (5.09, 0.078 mol) was dissolved in 10 mL of H_2O and was added dropwise to cold acidic solution. Gas evolution was observed upon addition. After the addition was complete, the reaction mixture was stirred for an additional 20 min at 0 °C. Reaction mixture was extracted with Et_2O (3 × 50 mL). In order to remove all glacial acetic acid, the organic layer was washed with H_2O until the aqueous layer ran neutral. Organic solvent was then removed under vacuum and a reddish oil remained. **2-Azido-5-methoxy-acetophenone 9e** was carried on to the next step without further purification: ^1H NMR (200 MHz, CD_3CN) δ = 7.16−6.98 (m, 3H), 3.89 (s, 3H), 2.60 (s, 3H). The azide **9e** was taken up in 30 mL of H_2O and refluxed for 5 h. Aqueous media required that aliquots be removed from reaction mixture and extracted with Et_2O in order to monitor progress by TLC. Once cooled, the reaction mixture was extracted with Et_2O (3 × 25 mL), dried over $MgSO_4$, and concentrated under vacuum. A colorless oil remained which was identified as **10e** (40% yield): ^1H NMR (200 MHz, CD_3CN) δ = 7.14−7.06 (d, *J* = 7.13, 1H), 6.57−6.54 (d, *J* = 7.13, 1H), 6.57−6.54 (d, *J* = 7.13, 1H), (d, *J* = 9.07, 1H), 3.92 (s, 3H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$) 165.5, 152.5, 148.0, 123.6, 121.1, 117.3, 111.3, 105.4, 55.6, 12.0; MS, *m/z* (rel intensity, %) 163 (100), 162 (25), 161 (8), 148 (11), 120 (14); HRMS *m/z* 163.06218 (calcd for $C_9H_9NO_2$, *m/z* 163.06332); IR (CH_2Cl_2) 3960 (m), 3040 (s), 2930 (s), 2200, 2420, 2320, 1650 (s), 1550 (s), 1430, 1200, 1189, 1060, 895, 780.

5-Methoxy-3-methyl-*N-tert*-butylanthranilium Perchlorate (1e). Methoxy anthranil **10e** (0.58 g, 3.58 × 10^{-3} mol) was dissolved in CH_3NO_2 and treated with perchloric acid and *tert*-butyl alcohol as indicated above, yielding 0.69 g (60%): mp 136−138 °C dec; ^1H NMR (400 MHz, CD_3CN) δ =7.59−7.56 (dd, *J* =7.6, 1.7, 1 H), 7.44−7.43 (dd, *J* =7.6, 1 H), 7.42 (d, *J* =1.7 1H), 4.08 (s, 3 H), 2.99 (s, 3 H), 1.87 (s, 9 H); ^{13}C NMR (CD_3CN) 173.3, 144.1, 140.8, 128.6, 122.4, 118.4, 114.8, 72.4, 57.3, 29.1, 13.0; HRMS *m/z* 220.1343 (M + 1 − ClO_4 calcd for $C_{13}H_{18}NO_2$, *m/z* 220.1338); MS, *m/z* (rel intensity, %) M^+ 220 (0.3), 163 (100), 162 (50), 148 (31), 144 (19), 121 (18), 120 (62), 107 (10), 78 (20), 65 (13), 51 (14); IR (CH_2Cl_2) 3700 (m), 3050 (br), 2995, 2315, 2420, 1610 (w), 1420 (br), 1550 (s), 1250 (br), 1102, 900 (s).

5-Phenyl-3-methyl-*N-tert*-butylanthranilium perchlorate (1f) (1.11 g, 54%) was obtained from **10f** (1.17 g, 5.63 × 10^{-3} mol) using the method indicated above. Recrystallization with CH_3OH yielded tan crystals: mp 260−261 °C (dec); ^1H NMR (CD_3CN, 400 MHz) 8.36−8.26 (dd, *J* = 9.4, 1.63, 1 H), 8.26 (s, 1 H), 7.99−7.97 (d, *J* = 9.4, 1 H), 3.08 (s, 3 H), 1.88 (s, 9 H); ^{13}C NMR (CD_3CN, 110 MHz) 175.8, 146.9, 142.1, 141.9, 138.5, 130.3, 129.9, 128.2, 121.1, 112.8, 70.9, 28.7, 13.6; CIMS, *m/z* (rel intensity, %) 267 (M + 1, 8), 252 (11), 209 (92), 196 (15), 180 (100), 179 (15), 167 (16), 166 (21), 153 (28), 139 (27), 115 (13), 56 (57); HRMS, *m/z* 267.16207 (M + 1 − ClO_4 calcd for $C_{18}H_{20}NO$, *m/z* 267.16237); IR (CH_2Cl_2) 3960 (m), 3705, 3060 (s), 2990 (s), 2700, 2430, 2310, 1650 (s), 1458, 1417 (br), 1090.

5-Cyano-3-methylanthranil (10g). Amine **8g** (0.4 g, 2.3 mmol) was treated with $NaNO_2$ (0.4 g, 5.5 mmol) and NaN_3 (0.4 g, 5.6 mmol) at 0 °C. Workup was performed as previously indicated. Extraction of cooled solution yielded a yellow residue which after recrystallization with CH_3OH gave 0.17 g (47%) of **8g** as yellow crystals; mp 138−139 °C; ^1H NMR (CD_3CN, 200 MHz) δ = 8.21 (s, 1H), 7.61−7.56 (dd, *J* = 9.3, 1.0, 1H), 7.41−7.36 (dd, *J* = 9.3, 1.0, 1H), 2.82 (s, 3H); ^{13}C NMR (CD_3CN) 172.0, 156.7, 131.5, 119.5, 117.1, 115.8, 107.3, 12.6; MS, *m/e* (rel intensity, %) 158 (M^+, 100), 130 (14), 129 (78), 116 (18), 104 (18), 103 (41); HRMS, *m/e* 158.04815 (M^+ calcd for $C_9H_6N_2O$, *m/e* 158.04802); IR (CH_2Cl_2) 3960 (m), 3060 (s), 2990, (br, s), 2600, 2315, 1652 (s), 1550, 1420 (vs), 1255, 895.

5-Cyano-3-methyl-*N-tert*-butylanthranilium perchlorate (1g). From cyano substituted anthranil **10g** (0.13 g, 7.9 × 10^{-4} mol) was obtained **1g** (0.1 g, 37%), mp 168−170 °C (dec), as white crystals: ^1H NMR (CD_3CN, 200 MHz) 8.64 (dd, *J* = 0.9, 1.2, 1 H), 8.16−8.10 (dd, *J* = 1.2, 9.5, 1 H), 8.05−7.99 (dd, *J* = 9.5, 0.9, 1 H), 3.08 (s, 3 H), 1.87 (s, 9 H); ^{13}C NMR (CD_3CN, 55.1 MHz) 178.2, 146.9, 141.1, 132.9, 119.7, 117.4, 114.2, 111.5, 72.3, 28.7, 14.0; MS, *m/z* (rel intensity, %) 214 (M^+, 0.2), 159 (13), 158 (100), 129 (35), 103 (22), 63 (11), 59 (39), 56 (15); HRMS, *m/z* 214.10968 (M + 1 − ClO_4 calcd for $C_{13}H_{14}N_2O$, *m/z* 214.11061); IR (CH_2Cl_2) 3950 (m), 3045 (br, s), 2995 (s), 2318, 1432 (s), 1299, 910, 800.

Isolation of Photoproducts. The anthanilium ions **1** were dissolved to ca. 1 M in CH_3CN, along with the indicated trapping molecule. The solutions were purged with N_2 for 15 min and then irradiated for the indicated time with a 450 W medium pressure Hg lamp through a Pyrex vessel. The reaction mixture was partitioned between Et_2O and aqueous $NaHCO_3$, and the organic fraction was further extracted with H_2O and then dried over $MgSO_4$. The solvent was evaporated, and the residue was subjected to radial chromatography over silica gel using 20% EtOAc/hexane.

Preparative Photolysis of 1f in CH_3CN. Salt (**1f**) (34.0 mg) was dissolved in 20 mL of freshly distilled CH_3CN and irradiated for 90 min. The solvent was evaporated, and the residue was taken up in CD_3CN and analyzed by ^1H NMR. The mixture contained 29% **5f** and 25% **4f** of another product assigned to rearrangement product.

Iminium salt 5f based on the similarity of its ^1H NMR spectrum to previous examples:[20,22] (CD_3CN) 7.73−7.79 (m, 3 H), 7.59−7.46 (m, 5 H), 3.75−3.74 (m, 3 H), 2.70 (s, 3 H), 2.44 (br s, 6 H);

Preparative Photolysis of 1f in the Presence of CH_3OH. Irradiation of **1f** in CH_3CN, in the presence of CH_3OH (2.1 M), gave four products 23% **17f**, 7% **12f**, 45% **13f** (**nuc = CH_3O**), and 8% **14f** (**nuc = CH_3O**). Quinone imine **13f** could not be isolated, presumably it rearranges to **14f** upon workup. **2-Acetyl-4-phenyl-*N-tert*-butyl aniline** (**5f**): mp 93−95 °C; ^1H NMR (400 MHz, CD_3CN) δ = 9.26 (s, broad, 1H), 8.06 (d, *J* = 2.4, 1H), 7.64−7.60 (m, 3H), 7.59−7.58 (m, 2H), 7.43−7.39 (m, 1H), 7.30−7.26 (m, 1H), 2.61 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (CD_3CN) 201.9, 150.2, 141.0, 133.4, 132.3, 129.6, 127.0, 126, 118.9, 115.5, 51.2, 29.6, 28.4; MS, *m/z* (rel intensity, %) 267 (72), 253 (20), 252 (100), 234 (49), 220 (27), 211 (57), 210 (16), 196 (61), 167 (30), 91 (44), 56 (47); HRMS, *m/z* 216.16243 (M^+ calcd for $C_{18}H_{21}NO$, *m/z* 267.16232); IR (CH_2Cl_2) 3740 (b), 2995 (s), 2840, 2702, 2420, 2348, 1640 (s), 1420, 1280, 1315, 900. **2-Acetyl-6-methoxy-3-phenyl-*N-tert*-butylaniline** (**12f**, **nuc = CH_3O**): mp 72−74 °C; ^1H NMR (400 MHz, CD_3CN) δ =7.66.7.64 (m, 2H) 7.55 (d, *J* = 2.1, 1H), 7.46−7.42 (m, 2H), 7.34−7.32 (m, 1H), 7.29−7.28 (d, *J* = 2.1, 1H), 3.88 (s, 3H), 2.62 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (CD_3CN) 203.9, 154.1, 141.4, 140.1, 132.9, 130.2, 56.1, 55.3, 31.3, 30.0; MS, *m/z* (rel intensity, %) 297 (66), 283 (11), 282 (50), 264 (10), 241 (100), 226 (62), 198 (14); HRMS, *m/z* 297.17313 (M^+ calcd for $C_{18}H_{21}NO$, *m/z* 297.17288); IR (CH_2Cl_2) 3740 (s), 3700 (w), 3080, 2990 (s), 2318, 1610 (s), 1420, 1280, 990, 890, 788. **2-Acetyl-4-methoxy-3-phenyl-*N-tert*-butylaniline** (**14f nuc = CH_3O**): mp 93−95 °C; ^1H NMR (400 MHz, CD_3CN) δ =7.40−7.34 (m, 3H) 7.25−7.22 (m, 3H), 7.07−7.05 (d, *J* = 9.07, 1H), 7.03−7.00 (d, *J* = 9.07, 1H), 3.64 (s, 3H), 1.63 (s, 3H), 1.24 (s, 9H);^{13}C NMR (CD_3CN) 206.9, 149.74, 138.7, 138.0, 132.8, 131.4, 129.9, 128.7, 128.3, 120.3, 115.5, 56.8, 52.1, 32.1, 30.2; MS, *m/z* (rel intensity, %) 297 (100), 282 (82), 264 (11), 242 (15), 241 (62), 240 (18), 210 (25), 183 (31), 182 (10), 180 (15), 153 (12), 57 (20); HRMS, *m/z* 297.17294 (M^+ calcd for $C_{18}H_{21}NO$, *m/z* 297.17288); IR (CH_2Cl_2) 3905 (s), 3760 (w), 3058, 2980 (s), 2700, 1720 (s), 1415.

Preparative Photolysis of 1f in the Presence of H_2O. Salt **1f** (26.1 mg, 7.2×10^{-2} mmol) was dissolved in 15 mL of CH_3CN and 1 mL of a 10% $HClO_4$ in H_2O solution (3.1 M H_2O). Irradiation for 15 min gave several products. Ortho addition product (**12f nuc = OH**) was obtained in 21% yield. Reduction product **17f** was obtained in 30% yield. **14f** (**nuc = OH**) was obtained in 17% yield and **15** (**nuc = OH**) in 8%. **2-Acetyl-4-phenyl-6-hydroxy-*N-tert*-butylaniline** (**12f**, **nuc = OH**) was characterized as follows: ^1H NMR (400 MHz, CD_3CN) δ = 7.76−7.64 (m, 2H), 7.54−7.53 (d, *J* = 2.1, 1H), 7.47−7.34 (m, 3H), 7.30−7.29 (d, *J* = 2.1, 1H), 2.62 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (CD_3CN) 214.5, 132.0, 129.5, 128.0, 126.9, 121.0, 119.9, 119.4, 116.0, 105.0, 103.6, 68.9, 35.5, 29.0; MS, *m/z* (rel intensity, %) 283 (10, M^+), 228 (16), 264 (11), 227 (100), 212 (20), 206 (28), 154 (11), 130 (13), 115 (10), 105 (64), 77 (16), 57 (22); HRMS, *m/z* 283.15275 (M^+ calcd for $C_{18}H_{21}NO_2$, *m/z* 283.15723). **2-Acetyl-3-phenyl-4-hydroxy-*N-tert*-butylaniline** (**14f**, **nuc = OH**) was characterized as follows: ^1H NMR (400 MHz, CD_3CN) δ = 7.41−7.25 (m, 5H), 6.99−6.97 (d, *J* = 8.9, 1H), 6.88−6.85 (d, *J* = 8.9, 1H), 5.0 (broad s, 1H), 1.64 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (CD_3CN) 219.0, 147.0, 138.9, 131.6, 130.1, 129.3, 128.7, 127.7, 127.0, 126.9, 122.0, 119.4, 30.6, 27.2; MS, *m/z* (rel intensity, %) 283 (95, M^+), 269 (36), 268 (100), 250 (36), 227 (93), 226 (33), 213 (24), 194 (20), 183 (12), 159 (16), 130 (17), 57 (26); HRMS, *m/z* 283.15668 (M^+ calcd for $C_{18}H_{21}NO_2$, *m/z* 283.15723). **2-Acetyl-4-(4-hydroxy-phenyl)-*N-tert*-butylaniline** (**15f**, **nuc = OH**): ^1H NMR (400 MHz, CD_3CN) δ = 7.97−7.96 (d, *J* = 2.3, 1H), 7.56−7.52 (m, 1H), 7.44−7.42 (d, *J* = 8.5, 2H), 7.07−7.05 (m, 2H), 6.85−6.83 (d, *J* = 8.5, 2H), 2.59 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (CD_3CN); MS, *m/z* (rel intensity, %) 283 (95, M^+), 269 (20), 268 (100), 250 (30), 228 (12), 227 (75), 226 (18), 184 (17); HRMS, *m/z* 283.15621 (M^+ calcd for $C_{18}H_{21}NO_2$, *m/z* 283.15723);

Preparative Photolysis of 1e in the Presence of CH_3OH. Solution of **1e** (86.1 mg, 2.7×10^{-4} mol) in 20 mL of CH_3CN, in the presence of CH_3OH (2.3 M) was irradiated for 30 min. Only one product (**12e**) was isolated in 66% yield. **2-Acetyl-4,6-dimethoxy-*N-tert*-butylaniline** (**12e nuc = CH_3O**) was a yellow oil: ^1H NMR (400 MHz, CD_3CN) δ = 6.66−6.65 (d, *J* = 2.8, 1H), 6.63−6.62 (d, *J* = 2.8, 1H), 3.76 (s, 3H), 2.57 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (CD_3CN) 204.8, 156.8, 156.2, 136.6, 130.4, 104.9, 103.3, 56.2, 55.7, 30.4, 30.2; MS, *m/z* (rel intensity, %) 251 (27, M^+), 195 (32), 180 (63), 152 (7), 69 (100); HRMS, *m/z* 251.1516 (M^+ calcd for $C_{12}H_{21}NO_3$, *m/z* 251.1522); IR (CH_2Cl_2) 3922 (w), 3690 (s, br), 2440 (s, br), 2300 (w), 1735 (s), 1510 (s), 1230, 985.

Preparative Photolysis of 1e in the Presence of H_2O. Compound **1e** (39.8 mg, 1.3×10^{-1} mmol) was dissolved in 20 mL of CH_3CN and 2.2 mL of a 10% $HClO_4$ in H_2O (4.9 M in H_2O). The solution was irradiated for 35 min. Two products were obtained: (1) the ortho adduct, 2-acetyl-6-hydroxy-4-methoxy-*N-tert*-butylaniline (**12e, nuc = OH**), and (2) a dihydroxy adduct, 2-acetyl-3,4-dihydroxy-*N-tert*-butylaniline (**16, nuc = OH**). **2-Acetyl-6-hydroxy-4-methoxy-*N-tert*-butylaniline** (**12e**, **nuc = OH**) was obtained in 23% yield: ^1H NMR (400 MHz, CD_3CN) δ = 6.57−6.55 (d, *J* =2.7, 1H), 6.51−6.49 (d, *J* = 2.7, 1H), 3.75 (s, 3H), 2.54 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (CD_3CN) 201.0, 147.2, 138.5, 132.2, 128.9, 125.3, 125.0, 30.3, 21.5, 21.3, 14.2; MS, *m/z* (rel intensity, %) 237 (38, M^+), 222 (40), 182 (12), 181 (88), 166 (100), 152 (16), 138 (13), 57 (14); HRMS, *m/z* 237.13631 (M^+ calcd for $C_{13}H_{19}NO_3$, *m/z* 237.13649); IR ($CHCl_3$) 3685 (w), 3619 (br), 2938 (s, br), 2895 (br), 2400 (w), 1600 (s), 1410 (s), 1182, 1033. **2-Acetyl-3,4-dihydroxy-*N-tert*-butylaniline** (**16**, **nuc = OH**) was obtained in 87% yield as an orange oil: ^1H NMR (400 MHz, CD_3CN) δ = 6.67−6.64 (d, *J* =10.2, 1H), 6.63−6.61 (d, *J* = 10.2, 1H), 2.49 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (CD_3CN) 182.5, 134.3, 124.8, 1237., 121.6, 120.2, 106.8, 57.6, 28.0, 27.1; MS, *m/z* (rel intensity, %) 223 (4, M^+), 181 (100), 166 (70), 149 (30), 138 (20), 111 (14), 97 (19), 57 (76), 56 (76); HRMS, *m/z* 223.11918 (M^+ calcd for $C_{12}H_{17}NO_3$, *m/z* 223.12085).

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Supporting Information Available: Synthetic procedures and spectroscopic data for synthetic intermediates **7e**, **8e**, **7f**, **8f**, **7g**, and **8g** (4 pages). See any current masthead page for ordering and Internet instructions.

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