

# Photochemically Generated Arylnitrenium Ions: Laser Flash Photolysis and Product Studies of the Photochemistry of *N*-*tert*-Butyl-3-methyl-6-chloroanthranilium Ions

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Nitrenium ions are electrophilic reactive intermediates which contain a divalent nitrogen atom.<sup>1,2</sup> Much of the recent interest in these species is due to the possible role of aryl-substituted nitrenium ions in chemical carcinogenesis.<sup>3–7</sup> Other studies have explored applications of nitrenium ion chemistry to organic synthesis.<sup>8–12</sup> Theoretical investigations have examined the electronic structure of nitrenium ions.<sup>13–15</sup> Like carbenes and nitrenes, nitrenium ions can exist in either a singlet state or a triplet state (Figure 1). While the parent system,  $\text{NH}_2^+$ , is a ground-state triplet,<sup>13,15,16</sup> aryl substitution is predicted to make the singlet the ground state.<sup>17–20</sup>

Several earlier papers describe efforts in this laboratory to generate aryl nitrenium ions using photochemical methods.<sup>17,21–25</sup> Our approach is based on a previously discovered<sup>26</sup> photochemical electrocyclic ring opening of *N*-alkylanthranilium ions **1** (Scheme 1). The alkyl-

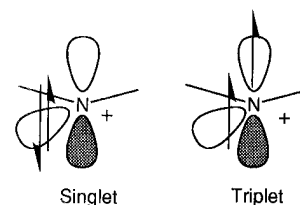
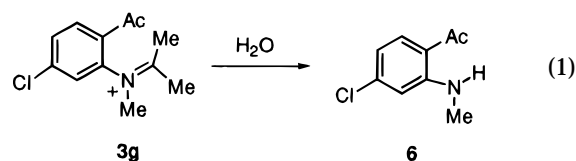


Figure 1. Singlet and triplet nitrenium ions.

arylnitrenium ions (**2**) thus generated decay by a variety of pathways. The stable photoproducts observed depend on the spin state of the nitrenium ion and the concentration of nucleophiles. Singlet-state nitrenium ions decay through (1) nonproductive electrocyclicization to the anthranilium ion, (2) 1,2-alkyl shifts to give the iminium ion **3**, and (3) nucleophilic attack on the phenyl ring to give adducts such as **4**. Triplet-state aryl nitrenium ions react to give the parent amine **5**. It has recently been shown<sup>21</sup> that this process occurs through sequential H-atom abstractions giving first the amine cation radical  $5^{\bullet+}$  and then the amine conjugate acid  $5\text{H}^+$ .

As part of a general effort to explore the effects of substituents on aryl nitrenium ion lifetime and behavior, we have prepared **1g** and examined its photochemistry. This anthranilium ion has an inductively electron-withdrawing chloro group substituted meta to the incipient nitrenium center. This is expected to increase its reactivity toward nucleophiles. Product studies and laser flash photolysis measurements agree with this expectation. Arylnitrenium ion **2g** is highly reactive, having a lifetime of less than 10 ns. Triplet sensitization and chemical trapping experiments support a spin-selective reactivity model that we have proposed earlier.<sup>25</sup>

The photochemical behavior of **1g** follows the general mechanism shown in Scheme 2. Product distributions obtained using various photolysis conditions are given in Table 1. Direct photolysis of **1g** in  $\text{N}_2$ -purged anhydrous  $\text{CH}_3\text{CN}$  produces mainly iminium ion **3g** (54%) and an acetamide derivative **7g** (38%), along with trace amounts of the parent amine **5g** and OH adduct **4g** ( $\text{R} = \text{H}$ ). Iminium ion **3g** was detected by  $^1\text{H}$  NMR in the unpurified photolysis mixture. Exposure of **3g** to silica gel converted it to the *N*-methylaniline derivative **6** (eq 1). The latter was purified and was fully characterized.



The acetamide derivative **7g** arises from addition of  $\text{CH}_3\text{CN}$  to the position para to the nitrenium ion center. The resulting nitrilium ion is hydrolyzed by traces of

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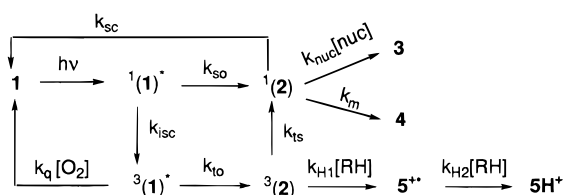
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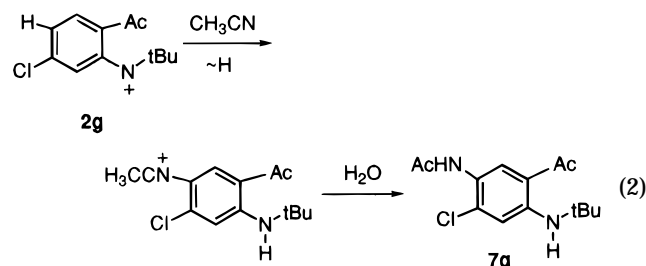
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Scheme 1



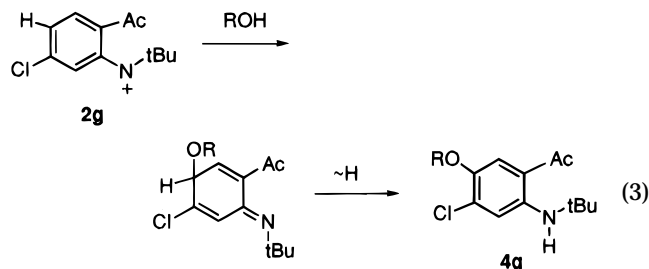
water in the reaction mixture (eq 2). The formation of



**7g** illustrates the high electrophilicity of **2g**.  $\text{CH}_3\text{CN}$  is a relatively weak nucleophile. Of the alkylarylnitrenium ions studied previously, only **1a** was sufficiently reactive to form this product.<sup>25</sup> The para-substituted derivatives **1b–f** did not give this product.<sup>22,23</sup>

Although it is formed only in trace amounts, the appearance of the parent amine **5g** in the direct photolysis experiments is significant. It indicates that the triplet nitrenium ion<sup>3</sup> (**2g**) is formed in the reaction. Previous work<sup>24,25</sup> demonstrated that anthranilium ions are not converted to nitrenium ions instantaneously upon photolysis. Rather, the excited singlet state <sup>1</sup>(**1g**) partitions between ring opening ( $k_{so}$ ) and intersystem crossing ( $k_{isc}$ ). Intersystem crossing leads to the parallel triplet reaction pathway. The ratio of triplet products to singlet products depends (in part) on the ratio of these two rate constants ( $k_{isc}/k_{so}$ ). In the present example, the triplet pathway accounts for ca. 5% of the products.

The singlet nitrenium ion can be trapped with water or methanol (eq 3). Direct irradiation in the presence of these traps (3.14 and 1.20 M, respectively) gives the adducts **4g** in ca. 90% yield. These arise from attack of nucleophiles at the ring position para to the nitrenium center, followed by a net 1,5-migration of a proton (eq 3). Preparative scale photolyses under the same condi-



tions yield the adducts in 88% (R = H) and 86% (R = Me) isolated yields. Approximately the same yield (1–5%) of the triplet product **5g** is observed when the traps are present.

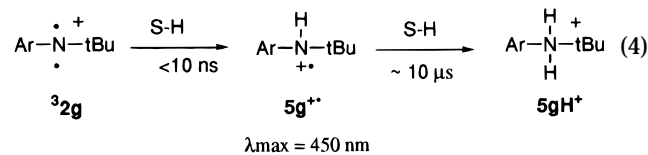
The spin-selective reactivity mechanism that we proposed earlier<sup>24,25</sup> is further confirmed in the case of **2g** (Scheme 2). Triplet-sensitized irradiation gives the characteristic triplet product **5g** (>80% yield) at the expense of the singlet nitrenium products **3g** and **4g**. Addition of the singlet scavenger,  $\text{H}_2\text{O}$ , has little or no

effect on the yield of triplet products. Triplet aryl nitrenium ions are typically higher in energy than the corresponding singlets.<sup>17–20</sup> However, it has been shown that the triplets are sufficiently reactive that they can be kinetically trapped before relaxation to the singlet. This is the case with **2g**: only small amounts of the singlet products **4g** and **3g** are detected under triplet-sensitized irradiation.

The triplet-sensitized irradiations provide small amounts of the singlet products. Their appearance reveals that the triplet nitrenium ion <sup>3</sup>(**2g**) can convert to the singlet <sup>1</sup>(**2g**). On this basis alone, it can be concluded that either the singlet is the ground state or else that the spin states are close enough in energy that the triplet can equilibrate to the singlet. We favor the former interpretation. Most theoretical calculations<sup>17–20</sup> and experimental observations suggest that typical aryl nitrenium ions are ground-state singlets.

Laser flash photolysis (308 nm, 30–80 mJ/pulse, 10 ns) gives two weak and overlapping transient absorption bands: one at 400 and another at 450 nm (Figure 2). There is also a bleaching (negative absorption change) at 360 nm. All of these features appear within the 10 ns window of the excitation pulse. The starting material (**1g**) has an absorption maximum at 340 nm. Its depletion causes the bleaching.

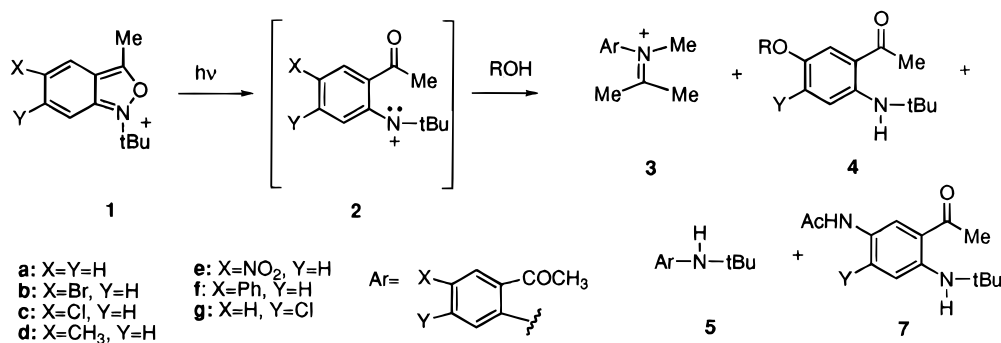
We assign the 450 nm band to the radical cation of the parent amine, **5g**<sup>+</sup>. The latter is formed via H-atom abstraction by the triplet state nitrenium ion <sup>3</sup>(**2g**) (eq 4). Four observations support this assignment. (1)



Saturation of the solutions with  $\text{O}_2$  (a triplet quencher) reduces the amplitude of this signal (Figure 1B), but not its lifetime.  $\text{O}_2$  is expected to deactivate the excited triplet state <sup>3</sup>(**1g**) and thus reduce the yield of its product, **5g**<sup>+</sup> (Scheme 2).<sup>21</sup> (2) Its 10  $\mu\text{s}$  lifetime is considerably longer than similar nitrenium ions such as **2c** or **2b** (both ca. 100 ns under similar conditions).<sup>22,24</sup> The chloro substituent in **2g** is meta relative to the nitrenium center and is expected to be more, not less, reactive than its para-isomer **2c**. (3) The transient lifetime is relatively insensitive to nucleophiles. Addition of  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{OH}$  decreases its lifetime. However, the fits to pseudo-first-order kinetics were not good. An upper limit of the rate constants for these reactions would be  $<10^4 \text{ M}^{-1} \text{ s}^{-1}$ . In contrast, **2c** reacted rapidly with these nucleophiles; the rate constants are on the order of  $10^6$ – $10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This low rate for the 450 nm transient is inconsistent with high reactivity expected for the *m*-chloro nitrenium ion. (4) Finally, we note that a 450 nm absorption maximum is typical for arylamine cation radicals. For example, *N,N*-dimethylaniline cation radical absorbs at 460 nm.<sup>27</sup> Although the stable product, **5g**, is produced in small yield relative to the singlet products, it is not unexpected that we would be able to detect its precursor, **5g**<sup>+</sup>. Extinction coefficients for arylamine cation radicals are quite high; for *N,N*-dimethylaniline it is  $6.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 460 nm.<sup>27</sup>

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## Scheme 2



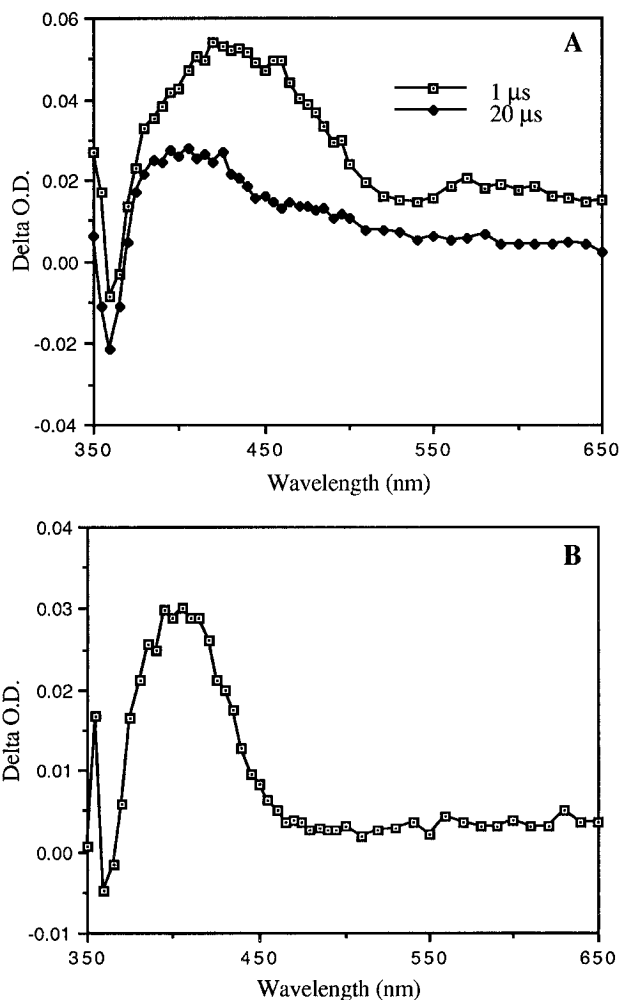
**Table 1. Product Distributions as Percentage of Converted Starting Material Obtained from Irradiation<sup>a</sup> of Anthranilium Ion **1g** in CH<sub>3</sub>CN under Various Conditions**

trap	<b>3g</b>	<b>7g</b>	<b>4g</b>	<b>5g</b>
no trap	54	38	<5 <sup>b</sup>	3
no trap/triplet sens <sup>d</sup>	5	3	<5 <sup>b</sup>	85
0.27 M H <sub>2</sub> O	22	3	72 <sup>b</sup>	<5
3.14 M H <sub>2</sub> O	<3	<3	90 <sup>b</sup>	3
3.14 M H <sub>2</sub> O/triplet sens <sup>d</sup>	<3	<3	3 <sup>b</sup>	92
1.20 M MeOH	<3	<3	91 <sup>c</sup>	<3

<sup>a</sup> Unless otherwise noted light source was a 400 W Xe arc lamp through a Pyrex vessel. <sup>b</sup> R = H. <sup>c</sup> R = Me. <sup>d</sup> Triplet sensitizer is thioxanthene-9-one added to 135–170 μM. In this case a 385 nm cutoff filter was employed.

The 400 nm band persists for at least several ms. Its lifetime and amplitude are not noticeably affected by the presence of O<sub>2</sub> or addition of the nucleophiles, H<sub>2</sub>O and CH<sub>3</sub>OH. The strong overlap of this signal with both the bleaching signal at 360 nm and the **5g**<sup>+</sup> band at 450 nm combined with its weak intensity makes it difficult to assign this absorption to a specific species. However, several possible assignments are readily excluded. The insensitivity of the signal to O<sub>2</sub> argues against it being a stable product of the triplet manifold (e.g., **5H**<sup>+</sup>). In that case its intensity would be expected to diminish in the presence of O<sub>2</sub>, as was observed for **5g**<sup>+</sup>. Its long lifetime excludes assignment of this signal to the triplet nitrenium ion <sup>3</sup>(**2g**). Decay of the latter would coincide with the growth of **5g**<sup>+</sup> and this process is observed to occur in <10 ns. Its kinetic behavior is inconsistent with what would be expected for a singlet aryl nitrenium ion. The (4-haloaryl)nitrenium ions **2b** and **2c** have lifetimes of ca. 100 ns.<sup>22,24</sup> By contrast, the 400 nm signal persists for several ms. Second, the lifetime of this species is unaffected by addition of the singlet scavengers, CH<sub>3</sub>OH and H<sub>2</sub>O (up to ca. 1 M). This excludes its assignment to the singlet state of the nitrenium ion <sup>1</sup>(**2g**). Previously studied nitrenium ions react very rapidly with nucleophiles (10<sup>6</sup>–10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>).<sup>22,24,28,29</sup> Finally, we note that a similar long-lived absorption at this wavelength appears in steady-state UV spectra of the photolysate (Figure 3).

We assign the long-lived 400 nm band to long-lived products of <sup>1</sup>(**2g**). These consist of the iminium ion **3g** along with the solvent adduct **7g** and/or the corresponding nitrilium adduct depicted in eq 2. It should be emphasized that the apparent λ<sub>max</sub> in this experiment does not necessarily correspond to the true λ<sub>max</sub> of these compounds. The bleaching at 360 nm subtracts from the



**Figure 2.** Transient absorption spectra obtained from laser flash photolysis of anthranilium ion **1g** in CH<sub>3</sub>CN solutions were purged with N<sub>2</sub> (panel A) and O<sub>2</sub> (panel B).

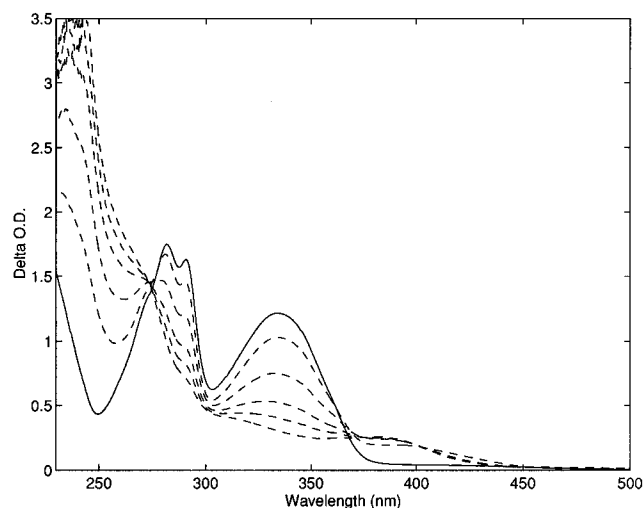
spectrum. Thus, the 400 nm signal represents end absorptions or shoulders that are common to all these products.<sup>30</sup> In the presence of O<sub>2</sub> the overlapping signal for **5g**<sup>+</sup> is suppressed and the 400 nm band can be seen to appear within the 10 ns laser pulse. Thus, it is concluded that the singlet nitrenium ion lives for <10 ns under these conditions.

The rise time for the cation radical **5g**<sup>+</sup> is also <10 ns, and therefore this value can be taken as a conservative upper limit for the lifetime of the triplet nitrenium

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(30) Photolysis of **1g** in the presence of 4 M H<sub>2</sub>O gives a steady-state UV/vis spectrum that has a weak shoulder at 400 nm similarly to Figure 2, but differs at lower wavelengths.



**Figure 3.** Steady-state UV-vis absorption spectra of **1g** in  $\text{CH}_3\text{CN}$  before (solid line) and at various times after (dashed lines) photolysis.

ion  $^3(2\mathbf{g})$ . It is interesting to compare this to the behavior of the nitro derivative **2e**.<sup>21</sup> The triplet state of the latter has a lifetime with a lower limit of 2  $\mu\text{s}$ . This difference can be partly attributed to the different ground state electron configurations of the two nitrenium ions. Nitrenium ion **2e** is a ground state triplet, and its lifetime is limited mainly by the rate constant for H-atom abstraction (i.e.,  $\tau = 1/k_{\text{H}}$ ). In contrast, **2g** behaves as a ground state singlet. Therefore, the lifetime of  $^3(2\mathbf{g})$  is limited by both H-atom abstraction and intersystem crossing (i.e.,  $\tau = 1/(k_{\text{H}} + k_{\text{isc}})$ ).

**Conclusions.** Photolysis of anthranilium ion **1g** produces arylnitrenium ion **2g**. The latter species is highly electrophilic and can be trapped by  $\text{CH}_3\text{CN}$ , a relatively weak nucleophile. A comparison of direct and triplet-sensitized irradiations shows that the chemistry of nitrenium ion **2g** is spin-state dependent. The singlet state reacts with nucleophiles to give phenyl ring adducts (**4g** and **7g**) or else it undergoes a net 1,2-shift of a methyl group (**3g**). The triplet state abstracts a H atom from the solvent to give (ultimately) the parent amine **5g**. Laser flash photolysis experiments show that both the singlet state and triplet state nitrenium ions are highly reactive and possess lifetimes of under 10 ns.

## Experimental Section

**General.** Yields in Table 1 were determined by  $^1\text{H}$  NMR of the photolysate where the integrated product resonances were compared with an internal standard (hexamethyldisiloxane) that was added after the photolysis ( $J$  values are given in Hz). Irradiations were carried out with a 400 W Xe lamp. Solutions for these experiments were 6–25 mM in anthranilium salt. Triplet-sensitized irradiations were carried out with thioxanthone-9-one (135–170  $\mu\text{M}$ ) as the triplet sensitizer. A 385 nm cutoff filter was used to ensure that the light was absorbed by the sensitizer, rather than the substrate.

Laser flash photolysis experiments were carried out with an excimer laser using Xe/HCl reagent gas in a He buffer. This supplies 308 nm pulses of 10 ns duration. The gas mixture and pressure was adjusted in order to create pulses of 30–70 mJ. However, during a given experiment the pulse energy varied by ca. 5%. The transient behavior was monitored using a probe beam from a CW 300 W Xe arc lamp passed through the sample cuvette perpendicular to the excitation beam. Sample concentrations were adjusted to an optical density of 1–2  $\text{cm}^{-1}$  at 308

nm. Approximately 40 mL of sample solution was placed in an all-glass flow cell and stirred continuously throughout the experiment.

Unless otherwise noted, all compounds characterized below were judged to be >95% pure by  $^1\text{H}$  NMR.

**6-Chloro-3-methyl-*N*-tert-butyl-2,1-benzisoxazolium perchlorate (1g ClO<sub>4</sub>).** 6-Chloro-3-methylanthranil (2.20 g, 13.17 mmol) was prepared by the procedure of Boulton,<sup>31</sup> following Haley's general procedure.<sup>26</sup> The crude crystals, mp 160–163 °C dec, were recrystallized from MeOH to give **1g ClO<sub>4</sub>** (3.00 g, 70%), mp 165–168 °C dec, as slight yellow needles: IR ( $\text{CD}_3\text{CN}$ ) 3062 (w), 2997 (w), 1637 (vs), 1523 (m), 1474 (m), 1436 (m), 1378 (m), 1273 (m), 1235 (w), 1191 (m), 1114 (vs), 1093 (vs)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 8.06 (dd,  $J = 9.2, .7, 1\text{ H}$ ), 7.96 (dd,  $J = 1.5, .7, 1\text{ H}$ ), 7.49 (dd,  $J = 9.2, 1.5, 1\text{ H}$ ), 3.03 (s, 3 H), 1.84 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ) 176.6, 149.0, 147.9, 129.8, 126.7, 119.5, 112.0, 71.8, 29.0, 14.0; EI-MS  $m/z$  (rel intensity) 225 (8), 223 (12), 210 (10), 181 (21), 169 (45), 168 (14), 167 (100), 153 (27), 140 (20), 138 (56); HRMS  $m/z$  223.0756 ( $\text{M}^+ - \text{HClO}_4$  calcd for  $\text{C}_{12}\text{H}_{14}\text{NOCl}$ ,  $m/z$  223.0764).

**2-Acetyl-5-chloro-4-hydroxy-*N*-tert-butylaniline (4g, R = H).** Salt **1g ClO<sub>4</sub>** (75 mg, 0.23 mmol) in 10.0 mL of  $\text{CH}_3\text{CN}$  with 0.6 mL of 1% aqueous  $\text{HClO}_4$  added was irradiated in a Pyrex test tube (320 nm filter) for 45 min with a Xe lamp. The mixture was neutralized, extracted with ether, and concentrated under vacuum. Radial chromatography gives 2-acetyl-4-chloro-4-hydroxy-*N*-tert-butylaniline (**4g**, R = H) (48 mg, 86%) as a yellow oil:  $R_f = 0.18$ ; 5:1 hexanes/EtOAc; IR ( $\text{CD}_3\text{CN}$ ) 3455 (br s), 3107 (w), 2985 (s), 2938 (m), 2872 (w), 1604 (vs), 1585 (m), 1477 (s), 1411 (s), 1392 (m), 1364 (s), 1312 (w), 1214 (s), 1129 (vs), 1120 (vs)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 8.71 (br, s, 1 H), 7.40 (s, 1 H), 6.93 (s, 1 H), 2.47 (s, 3 H), 1.36 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ) 201.0, 145.8, 141.5, 129.3, 121.0, 118.7, 115.8, 51.3, 29.9, 28.7; EI-MS  $m/z$  (rel intensity) 243 ( $\text{M} + 2, 8$ ), 241 ( $\text{M}^+, 21$ ), 228 (11), 226 (36), 210 (13), 208 (18), 185 (32), 172 (12), 170 (40), 57 (100); HRMS  $m/z$  241.0864 ( $\text{M}^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}_2\text{Cl}$ ,  $m/z$  241.0869).

**2-Acetyl-5-chloro-4-methoxy-*N*-tert-butylaniline (4g, R = CH<sub>3</sub>).** Salt **1g ClO<sub>4</sub>** (65 mg, 0.20 mmol) in 10.0 mL of  $\text{CH}_3\text{CN}$  with 0.6 mL of 1%  $\text{HClO}_4$  in MeOH added was irradiated in a Pyrex test tube (320 nm filter) for 25 min with a Xe lamp. The mixture was neutralized, extracted with ether, and concentrated under vacuum. Radial chromatography gives 2-acetyl-5-chloro-4-methoxy-*N*-tert-butylaniline (**4g**, R =  $\text{CH}_3$ ) (45 mg, 88%) as a yellow oil:  $R_f = 0.30$ ; 5:1 hexanes/EtOAc; IR ( $\text{CD}_3\text{CN}$ ) 3434 (m), 2977 (m), 2938 (w), 1641 (vs), 1577 (s), 1511 (s), 1433 (m), 1409 (m), 1369 (m), 1331 (w), 1248 (s), 1212 (vs), 1186 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 8.92 (br s, 1 H), 7.35 (s, 1 H), 6.99 (d, 1 H), 3.80 (s, 3 H), 2.52 (s, 3 H), 1.36 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 200.9, 146.5, 144.7, 131.0, 118.0, 117.9, 116.4, 57.7, 51.4, 29.9, 28.8, 28.7; EI-MS  $m/z$  (rel intensity) 257 ( $\text{M} + 2, 11$ ), 255 ( $\text{M}^+, 36$ ), 242 (22), 240 (74), 224 (9), 222 (28), 201 (7), 199 (22), 186 (28), 184 (100); HRMS  $m/z$  299.1006 ( $\text{M}^+$  calcd for  $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{Cl}$ ,  $m/z$  299.1026).

**Photolysis To Produce Iminium Salt 3g ClO<sub>4</sub>.** Salt **1g ClO<sub>4</sub>** (115 mg, 0.36 mmol) was irradiated in 10 mL of freshly distilled  $\text{CH}_3\text{CN}$  for 30 min with a 320 nm filtered Xe lamp. The solvent was evaporated, and the residue was dissolved in  $\text{CD}_3\text{CN}$  and observed by  $^1\text{H}$  NMR. Trace amounts of **5g** and **4g** (R = H) along with 38% of **7g**, and 54% of **3g** were detected. The following resonances are assigned to **3g**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 8.21 (dd,  $J = 7.7, 1.5, 1\text{ H}$ ), 7.84 (td,  $J = 7.7, 1.5, 1\text{ H}$ ), 7.77 (td,  $J = 7.7, 1.3, 1\text{ H}$ ), 7.44 (dd,  $J = 7.7, 1.3, 1\text{ H}$ ), 3.70 (m, 3 H), 2.62 (s, 3 H), 2.39 (br s, 6 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ) 199.0, 194.7, 141.2, 133.8, 132.4, 130.4, 126.5, 46.9, 28.7, 26.2, 26.1.

**Preparative Irradiation of 1g ClO<sub>4</sub> in Anhydrous CH<sub>3</sub>CN.** The title salt (115 mg, 0.36 mmol) was irradiated in 10 mL of  $\text{CH}_3\text{CN}$  for 1 h with a Xe lamp through a 320 nm filter. The mixture was neutralized, extracted with ether, concentrated under vacuum, and subjected to radial chromatography to give 2-acetyl-5-chloro-*N*-methylaniline (**6**) (32 mg, 49%) as yellow needles:  $R_f = 0.39$ ; 5:1 hexanes/EtOAc; IR ( $\text{CDCl}_3$ ) 3333 (br w), 2979 (s), 2940 (m), 2881 (w), 1636 (s), 1602 (vs), 1566 (s), 1512 (s), 1474 (m), 1419 (m), 1365 (m), 1243 (s), 1214 (m);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 8.80 (br s, 1 H), 7.75 (d,  $J = 8.6, 1\text{ H}$ ), 6.72 (d,  $J = 2.0, 1\text{ H}$ ), 6.55 (dd,  $J = 8.6, 2.0, 1\text{ H}$ ), 2.84 (d,  $J = 5.0, 3\text{ H}$ ), 2.49 (s,

(31) Rahman, A.-U.; Boulton, A. J. *Tetrahedron Suppl.* **1966**, 7, 49–56.

3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 201.1, 153.6, 141.4, 135.5, 117.2, 114.7, 111.5, 29.7, 28.2; EI-MS  $m/z$  (rel intensity) 185 ( $M + 2$ , 14), 183 ( $M^+$ , 57), 170 (27), 168 (76), 166 (25), 151 (19), 133 (25), 113 (22), 57 (100); HRMS  $m/z$  183.0449 ( $M^+$  calcd for  $\text{C}_9\text{H}_{10}\text{NOCl}$ ,  $m/z$  183.0451). This mixture also provided 33 mg (33%) of a crude solid which was recrystallized from EtOH to give **2-acetyl-4-acetamido-5-chloro-*N*-tert-butylaniline (7g)**, mp 150 °C, as a yellow needles:  $R_f = 0.12$ ; 5:1 hexanes/EtOAc; IR ( $\text{CD}_3\text{CN}$ ) 3370 (m), 3293 (br m), 2985 (m), 2948 (w), 1687 (s), 1646 (vs), 1577 (s), 1540 (vs), 1510 (s), 1433 (w), 1409 (m), 1371 (m), 1253 (m), 1214 (s), 1198 (s);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 7.98 (d,  $J = 2.6$ , 1 H), 7.41 (dd,  $J = 9.2$ , 2.6, 1 H), 6.94 (d,  $J = 9.2$ , 1 H), 2.48 (s, 3 H), 2.01 (s, 3 H), 1.23 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ) 201.2, 170.1, 149.0, 135.6, 132.2, 122.2, 117.8, 115.6, 51.5, 29.6, 28.6, 23.0; EI-MS  $m/z$  (rel intensity) 284 ( $M + 2$ , 8), 282 ( $M^+$ , 25), 269 (12), 267 (39), 249 (10), 226 (9), 213 (20), 191 (10), 186 (32), 184 (100), 169 (22); HRMS,  $m/z$  282.1109 ( $M^+$  calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_2\text{Cl}$ ,  $m/z$  282.1135). This mixture also provided trace amounts of **4g** ( $Z$

= OH) and 2 mg (2%) of **2-acetyl-5-chloro-*N*-tert-butylaniline (5g)** (76.2 mg, 40%) as a yellow oil:  $R_f = 0.38$ ; 5:1 hexanes/EtOAc; IR ( $\text{CD}_3\text{CN}$ ) 3274 (br m), 2980 (m), 293 (w), 2888 (w), 1634 (vs), 1599 (vs), 1580 (vs), 1510 (s), 1438 (m), 1418 (m), 1397 (w), 1369 (m), 1247 (s), 1213 (s), 1146 (m);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) 9.33 (br s, 1 H), 7.75 (d,  $J = 8.6$ , 1 H), 6.91 (d,  $J = 2.1$ , 1 H), 6.52 (dd,  $J = 8.6$ , 2.1, 1 H), 2.49 (s, 3 H), 1.39 (s, 9 H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ) 201.3, 151.7, 140.7, 136.1, 117.6, 114.4, 114.0, 51.5, 30.0, 28.5; EI-MS,  $m/z$  (rel intensity) 227 ( $M + 2$ , 14), 225 ( $M^+$ , 37), 212 (29), 210 (95), 194 (32), 192 (75), 169 (18), 168 (18), 156 (31), 154 (100); HRMS  $m/z$  225.0934 ( $M^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{NOCl}$ ,  $m/z$  225.0920). Amine **5g** was also produced in 82% yield by reduction of **1g** with Sn in 1:2 HCl/AcOH solution.

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