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Reactions of a Triplet Arylnitrenium Ion: Laser Flash Photolysis and Product Studies of *N-tert*-Butyl(2-acetyl-4-nitrophenyl)nitrenium Ion

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Abstract: Photolysis of **1e** (*N-tert*-butyl-5-nitro-3-methylanthranilium ion) (ClO_4^- or BF_4^- salt) generates the isomeric *tert*-butyl(4-nitro-2-acetylphenyl)nitrenium ion (**2e**). The latter further reacts to form iminium ion **4e** and parent amine **5e** as stable products. On the basis of triplet sensitization and quenching studies, it is shown that **4e** is a product of the singlet state of **2e** and **5e** is a product of the triplet state of **2e**. Laser flash photolysis experiments on **1e** give a short-lived (ca. 300 ns) transient spectrum having maxima at 390 and 540 nm which is assigned to the excited triplet state of **1e**. It was not possible to directly detect nitrenium ion **2e** under these conditions. However, its lifetime and reactivity could be studied through the use of a probe substrate. Triphenylmethane does not affect the decay of triplet **1e**. However, its addition causes a new transient species to grow in over much longer time scales than the decay of triplet **1e**. The new, longer lived species is identified as the triphenylmethyl radical ($Ph_3C^\bullet$). Its formation is attributed to hydrogen atom abstraction by the triplet state of **2e**. Analysis of the growth kinetics for $Ph_3C^\bullet$ shows that **2e** lives for ca. 2 μs in CH_2Cl_2. On the basis of this observation as well as several other mechanistic and kinetic considerations, it is argued that arylnitrenium ion **2e** has a triplet ground state.

Nitrenium ions[1−4] are reactive intermediates that contain a divalent, positively charged nitrogen atom. The proposal that arylnitrenium ions are intermediates in the carcinogenic, DNA-damaging reactions of activated aromatic amines[5−8] has motivated much of the recent research in this area. Indeed, the past several years have seen significant advances in characterizing arylnitrenium ion lifetimes in aqueous solution,[9−12] their reactivity and selectivity toward nucleophiles,[12−15] effects of ion pairing,[16−18] and the mechanisms of their reactions with DNA and related nucleophiles.[19−26]

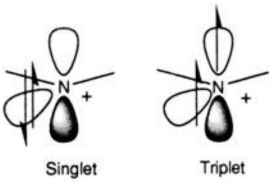

Figure 1. Singlet and triplet nitrenium ions.

Less understood are the behavior and properties of triplet state arylnitrenium ions. Nitrenium ions are isoelectronic with carbenes and nitrenes and therefore have low-energy triplet and singlet states (Figure 1). Both theory[27,28] and sophisticated gas phase experiments[29] agree that the simplest nitrenium ion, NH_2^+, is a ground state triplet with a singlet−triplet energy gap of ca. +30 kcal/mol. For the phenyl- and most simple arylnitrenium ions semiempirical,[30−33] ab initio,[30,34,35] and density functional

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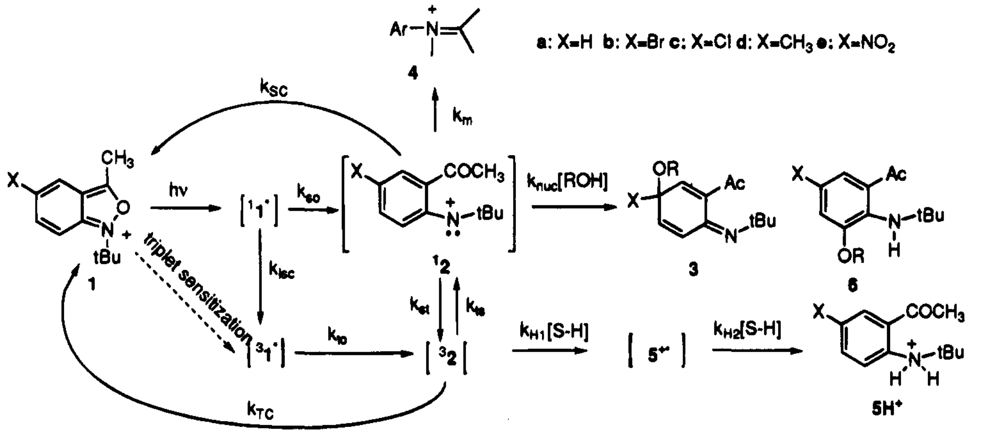
Scheme 1

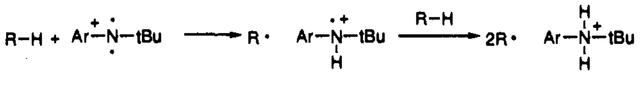


theory (DFT)[35] predict singlet ground states. The predicted value for phenylnitrenium ion is −17.7 kcal/mol from the DFT calculations, and the ab initio calculations give qualitatively similar values. Aryl substitution preferentially stabilizes the singlet state because the filled π-orbitals on the aromatic ring interact with and raise the energy of the out-of-plane p orbital relative to the in-plane σ orbital. It follows then that π-donor substituents on the aromatic ring should further stabilize the singlet relative to the triplet. Likewise π-acceptors are predicted to stabilize the triplet relative to the singlet.[30]

The paucity of experimental information on triplet arylnitrenium ions can be attributed to their short lifetimes and the fact that they are usually inaccessible by ground state (thermal) generation. Photochemical methods make it possible to selectively generate triplet nitrenium ions and characterize their chemistry. Following earlier reports,[36,37] we found that photolysis of anthranilium salts **1** produces arylnitrenium ions **2** (Scheme 1).[38,39] It was shown that the singlet state nitrenium ions ^{1}**2** react via a 1,2 shift from the alkyl group to the nitrogen, giving iminium ion **4**. Nucleophiles such as water and alcohols attack ^{1}**2**, giving ring adducts **3** and **6**. The triplet nitrenium ion ^{3}**2** reacts with H-atom donors to yield the parent amine **5**.

Two features of Scheme 1 are especially relevant to the present work. First, the photoproduct distributions often reflect the spin state first generated, rather than the lowest energy spin state. As with the arylcarbenes,[40−42] both the singlet and triplet arylnitrenium ions are highly reactive and can be kinetically trapped before equilibrium between the spin states is achieved. Second, the precursor anthranilium ion **1** is not photolyzed instantaneously to **2**. Rather, its excited singlet state ^{1}**1*** partitions between ring opening (k_{so}) and intersystem crossing to the triplet state ^{3}**1*** (k_{isc}). The partition ratio k_{isc}/k_{so} depends on the particular anthranilium ion. This ratio is negligible for methyl derivative **1d**, but significant (ca. 0.25) for bromo derivative **1b**.[13,14]

Scheme 2



There are several unresolved issues regarding triplet arylnitrenium ions. The first is the mechanism of the formation of parent amine **5**. This is the result of a net two-electron reduction of the arylnitrenium ion **2**. On the basis of analogous behavior in the arylcarbenes,[40−42] we proposed that **5** was formed from two sequential H atom abstractions by ^{3}**2** (Scheme 2). However, the earlier experiments provided no direct evidence for the radical intermediates that would be formed in such a mechanism. Second, the possibility that the excited triplet anthranilium ion ^{3}**1** reacted directly, rather than through ^{3}**2**, to give **5** was never excluded. While perhaps intuitively unlikely, this direct pathway was nonetheless consistent with available data.

Herein are reported our investigations of the photochemistry of *N*-*tert*-butyl-3-methyl-5-nitroanthranilium ion (**1e**). In addition to the issues noted above, work on this particular compound was also motivated by the prediction that strongly electron withdrawing groups on the aromatic ring would stabilize the triplet state relative to the singlet. Product analysis and laser flash photolysis (LFP) studies confirm our proposed mechanism for the origin of **5** (Scheme 2). Specifically, radical coupling products from the H atom transfer reaction are isolated, and the intermediate radicals are detected by LFP. The excited triplet state of the precursor, ^{3}**1e***, is also detected by LFP and is shown to be unreactive toward H atom donors. Finally, it is shown that the triplet state nitrenium ion ^{3}**2e** lives for ca. 2 μs in CH_2Cl_2. This observation and several other mechanistic considerations suggest that **2e** has a triplet ground state.

Results and Discussion

1. Synthesis and Ground State Reactivity. The anthranilium salt **1e** is prepared from the free base 5-nitro-3-methylanthranil (**7e**) by treatment of the latter with *tert*-butyl alcohol in the presence of strong acid. The counterion of **1** is determined by the acid used to effect the alkylation. Thus, $HClO_4$ gives the perchlorate salt, and HBF_4 gives the tetrafluoroborate salt. Preparation of **7e** was accomplished by nitration of 3-methylanthranil (Scheme 3).

In the dark, certain nucleophiles (e.g., CH_3OH, H_2O) add rapidly and reversibly to the C-3 position of anthranilium ions

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Scheme 3

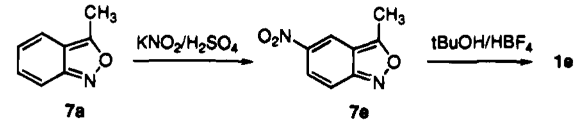


Table 1. Product Yields from Photolysis of Anthranilium Ion **1e**

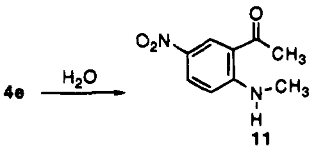
conditions	4e	5e	conditions	4e	5e
CH_3CN	35	63	CH_2Cl_2	42	56
CH_3CN/CH_3OH (5 M)[a]	38	61	CH_2Cl_2/CH_3OH (5 M)[a]	39	51
CH_3CN/H_2O (5 M)[a]	31	55	CH_3OH[a]	38	61
CH_3CN/H_2O (27 M)[a]	34	48	THF[a]	30	43

[a] 10% H_2SO_4 added to the nucleophile.

1. To avoid this potential artifact, nucleophilic trapping experiments were carried out with a small amount of acid added to the nucleophile. This issue is discussed in an earlier paper.[13]

2. Direct Irradiation Photochemistry. Photolysis of **1e** (ClO_4^- or BF_4^- salt) (Xe arc lamp, $\lambda > 320$ nm) in various solvents gives only two products: the parent amine **5e** and the iminium ion **4e** (eq 1). The latter undergoes facile hydrolysis. Although it can be detected in ^{1}H NMR spectra of the photolysis mixtures, it was not isolated. Instead, its hydrolysis product, amine **11** (eq 2), was isolated and fully characterized. The yields of the two stable photoproducts **4e** and **5e** depend on the reaction conditions as shown in Table 1.

$$\mathbf{1e} \xrightarrow{h\nu} \mathbf{4e} + \mathbf{5e} \qquad (1)$$



(2)

The quantum yield for decomposition of **1e** was measured in both N_2-saturated and O_2-saturated CH_3CN. The value was 0.14 under the N_2 conditions and was decreased to 0.04 under 1 atm of O_2. These values are typical for the other anthranilium ions (**1a**–**d**) in the series.[13,38]

One characteristic reaction of arylnitrenium ions is addition of nucleophiles to the aromatic ring, providing adducts with structures **3** and/or **6**.[43-45] Such products are not observed with the nitro derivative. For example, photolysis of **1e** in 27 M H_2O/CH_3CN (containing 10% H_2SO_4 in order to suppress the addition reaction at C-3) provides only the iminium ion **4e** and the parent amine **5e**. No products corresponding to **6e** or **3e** were detected in ^{1}H NMR of the crude photolysate. Similar studies in CH_3OH and at lower concentrations of H_2O also failed to provide the expected adducts.

It is always possible that small amounts of the expected adducts **3e** and/or **6e** are formed but not detected. Therefore, a comparison with previously studied systems is useful. Photochemistry of the unsubstituted analog **1a** is highly sensitive to the presence of H_2O; at 0.27 M H_2O/CH_3CN, **3a** (R = H) is the exclusive product.[38] The *p*-bromo (**2b**) and -chloro (**2c**) arylnitrenium ions are also significantly more reactive toward nucleophiles. In these cases 65–90% yields of the ortho adducts **6** were observed at 3.14 M H_2O.[14] More interestingly, the *p*-methyl-substituted arylnitrenium ion **1d** was observed to give quantitative yields of the para adduct **3d** when photolyzed in 4 M H_2O/CH_3CN.[39] Results with the substituted species **1b**, **1c**, and **1d** indicate that the lack of reactivity toward nucleophiles observed for **1e** is not simply the result of steric hindrance to substitution. It appears that the effect of nitro substitution is to accelerate the unimolecular reactions ring closure (k_{sc}) and rearrangement (k_m) such that trapping by nucleophiles does not compete effectively with these reactions.

Table 2. Effect of Triplet Sensitization and Quenching on Product Yields

conditions	4e	5e	conditions	4e	5e
CH_3CN/N_2	35	63	CH_2Cl_2/N_2	42	56
CH_3CN/O_2	50	40	CH_2Cl_2/O_2	79	13
CH_3CN/TS[a]	<2	88	CH_2Cl_2/TS[a]	<2	95

[a] Irradiation >390 nm with 9-fluorenone added as a triplet sensitizer.

3. Triplet-Sensitized Photolysis and Triplet Quenching. To independently ascertain the reactivity of the triplet nitrenium ion, triplet-sensitized photolysis was carried out. This was based on the reasoning that triplet energy transfer to anthranilium ion **1e** would provide its triplet state ^{3}**1e*** which would ring-open, giving the triplet nitrenium ion ^{3}**2e**, bypassing the singlet manifold.[46] These experiments were carried out using 9-fluorenone as the triplet sensitizer and irradiating the samples at wavelengths (>390 nm) where it, but not **1e**, absorbs.[47] Under all conditions examined, the parent amine **5e** was the exclusive photoproduct detected in the NMR of the photolysate (eq 3). None of the singlet product **4e** was ever detected in these experiments. Even with CH_2Cl_2, a solvent that is a relatively poor H atom donor, all of the nitrenium ions are trapped as the triplet product **5e**. Results of experiments done in THF, CH_2Cl_2, and CH_3CN are shown in Table 2.

$$\mathbf{1e} \xrightarrow{h\nu\ /\ \text{9-fluorenone}} \mathbf{5e} \qquad (3)$$

We considered the possibility that iminium ion **4e** might be unstable to the triplet-sensitized irradiation conditions. To test for this, a mixture of **5e** and **4e** was first generated by direct photolysis of **1e** in CH_2Cl_2. The solvent was removed, and ^{1}H NMR on the residue showed **4e** and **5e** were formed in a ratio of ca. 5:1. The triplet sensitizer was added, the mixture was taken up in CH_3CN, and the solution was subjected to the same irradiation conditions for the same times as employed in the triplet sensitization experiments. The ^{1}H NMR spectrum of this photolysate showed that the **4e**:**5e** ratio was unchanged. Thus, we conclude that **4e**, had it been produced in the triplet sensitization, would have been stable to the irradiation conditions.

The differing product distributions obtained from direct and triplet-sensitized irradiations show that equilibration between the spin states is never realized under our conditions. That no singlet product is ever detected from triplet-sensitized irradiation implies that either the reactions of the triplet ^{3}**2e** are very rapid relative to intersystem crossing (i.e., process k_{TS} in Scheme 1) or the singlet is higher in energy than the triplet.

Triplet quenching experiments were undertaken in order to determine which products originated from the triplet manifold (i.e., $^1\mathbf{1}^* \rightarrow {}^3\mathbf{1}^* \rightarrow {}^3\mathbf{2}^+$). The purpose of a triplet quencher is to remove energy from a triplet excited molecule (e.g., $^3\mathbf{1}^*$) before it is able to react.[48] Molecular oxygen can act as a

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Table 3. Yield Ratios and Asymptotic Transient Absorption at 370 nm (A_f) from Photolysis of **1e** in the Presence of Ph_3CH

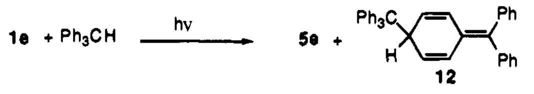
[Ph_3CH] (M)	**5e**:**4e**	A_f	[Ph_3CH] (M)	**5e**:**4e**	A_f
0.00	1.30	<0.02	0.18	8.90	0.169
0.03	3.70	<0.02	0.20	9.20	0.172
0.06	6.50	<0.02	0.24	9.50	0.197
0.08	7.20	0.090	0.25	9.80	0.205
0.10	8.40	0.116	0.27	9.60	0.204
0.12	8.70	0.129	0.30	10.30	0.207
0.15	9.00	0.162			

quencher of excited triplet states whose energies are in excess of ca. 30 kcal/mol.[49] The triplet state energy of **1e** is not known exactly. However, on the basis of its absorption onset (400 nm), and the fluorenone sensitization experiment described above, we estimate its triplet energy at 40–55 kcal/mol. Therefore, the expectation was that O_2 would quench ^{3}**1*** and reduce the yield of triplet products relative to those which originate from the singlet manifold (i.e., ^{1}**1*** → ^{1}**2**$^+$). On the other hand, the singlet–triplet energy gaps in nitrenium ions are calculated to be <20 kcal/mol. For this reason O_2 is not expected to quench the triplet nitrenium ions ^{3}**2**.

The yield of **5e** is reduced from 63% to 40% in CH_3CN and from 56% to 13% in CH_2Cl_2. Not all of the triplet chemistry is avoided under these conditions. Because of its short lifetime in the absence of O_2 (see part 5, below), many of the ^{3}**1*** ions are able to react (process k_{TO}, Scheme 1) before they can collide with an O_2 molecule. Only at infinite quencher concentrations would all of the ^{3}**1*** ions interact with O_2 prior to ring-opening. The changes in yields are limited by the solubility of the quencher in the solvents used (ca. 10^{-3} M).[47]

4. Trapping with H Atom Donors. To further clarify the nature of the process that leads to the parent amine **5e**, a series of chemical trapping experiments were carried out. Triphenylmethane (Ph_3CH, a H atom donor[50]) was used as the trapping agent. Two possibilities were considered. First, the singlet nitrenium ion could abstract a hydride. This would give the triphenylmethyl cation which, after reaction with residual water, would result in triphenylmethanol. Second, H atom transfer to the triplet nitrenium ion would result in the triphenylmethyl radical ($Ph_3C^•$). The latter would dimerize to give the Ullman hydrocarbon **12**.

Our results are consistent with the triplet, H atom transfer mechanism shown in Scheme 2. Photolysis of **1** in CH_3CN solutions containing 0.12 M Ph_3CH gives both **4e** and **5e** in a ratio of 1:9. Dimer **12** was also detected in the ^{1}H NMR of the photolysis mixture (eq 4). Its identity was confirmed by comparison of its ^{1}H NMR to that of independently synthesized material. Dimer **12** comes from para-coupling of two triphenylmethyl radicals. No evidence for the hydride transfer product triphenylmethanol is seen in the ^{1}H NMR of the reaction mixtures.



(4)

Addition of Ph_3CH increases the yield of parent amine **5e** formed upon direct irradiation. The **4e**:**5e** product ratio was examined as a function of added Ph_3CH (Table 3). At low concentrations of the trap, the proportion of **5** increases. Above ca. 0.1 M the ratio saturates, remaining constant at 9:1 (Figure 2, Table 3).

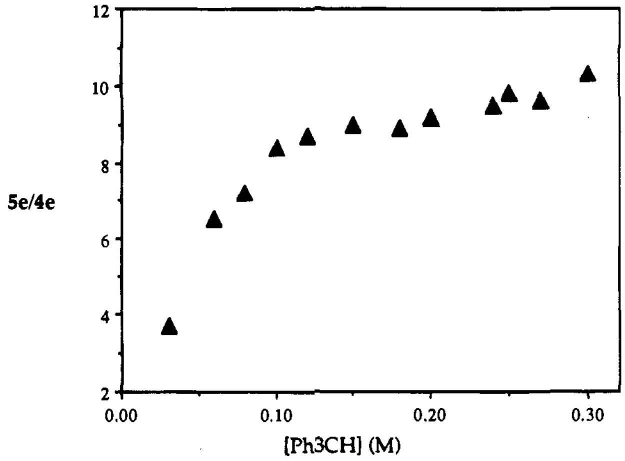


Figure 2. Yield ratio of parent amine **5e** to iminium ion **4e** as a function of added Ph_3CH from photolysis of **1e** in N_2-purged CH_2Cl_2.

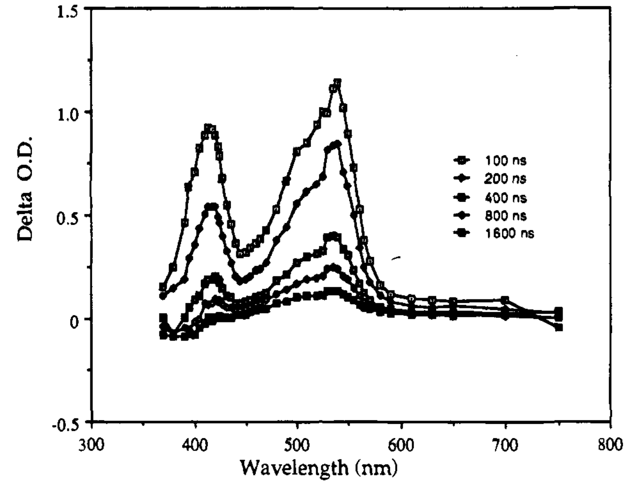


Figure 3. Transient absorption spectrum obtained from laser flash photolysis of **1e** in CH_3CN. Spectra were taken 100–1600 ns after the laser pulse. This spectrum is assigned to the excited triplet state of **1e**.

5. Laser Flash Photolysis. Pulsed laser (308 nm, 10 ns, 20–50 mJ) irradiation of solutions of **1e** in CH_3CN gives a transient spectrum having absorption maxima at 390 and 540 nm (Figure 3) of approximately equal intensity. Nearly identical spectra are obtained in CH_2Cl_2, CH_3OH, and THF. In N_2-purged solutions, this species has a lifetime of 312 ns. The transient absorption is assigned to the excited triplet state of the anthranilium ion ^{3}**1e** on the basis of observations enumerated below.

(1) The transient spectrum obtained differs qualitatively from what would be expected for an alkylarylnitrenium ion. Absorption spectra of analogs have been previously characterized. For example, the halogen-substituted derivatives **2b** and **2c** each show a single maximum at 380 or 395 nm with a much smaller tail in the visible region.[14] *p*-Phenyl-substituted phenylnitrenium ions have a single peak near 460 nm.[10,51]

(2) The transient is quenched by O_2. Purging the CH_3CN solution with O_2 reduces its lifetime from 300 to 100 ns (Figure 4). O_2 is a very efficient quencher of excited triplet states. Assuming a saturated (1 atm) O_2 concentration of 9.1×10^{-3} M,[47] the quenching rate constant can be estimated to be 7×10^8 M^{-1} s^{-1}. This value is typical for triplet energy transfer from cationic dyes.[52] The lifetimes of the previously character-

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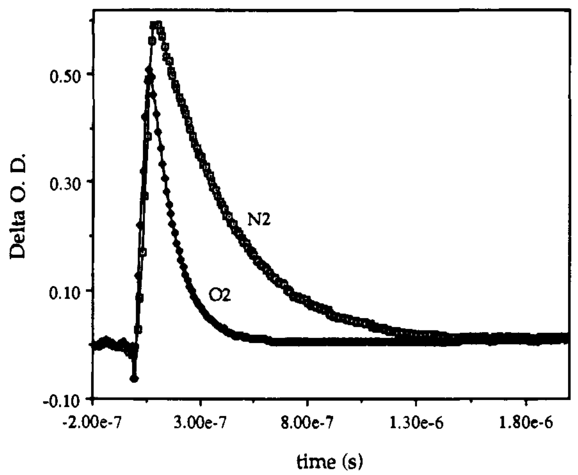

Figure 4. Transient absorption waveforms at 400 nm obtained from laser flash photolysis of **1e** in N_2-purged and O_2-purged CH_3CN.

ized nitrenium ions **2b**, **2c**, and **2d**[13,14] as well as those reported by others[10,53] were not noticeably affected by O_2.

(3) The lifetime of the transient is not affected by addition of nucleophiles. For example, when up to 3 M CH_3OH was added, there was no significant change in the lifetime of the transient. In contrast earlier LFP experiments showed that the halogenated nitrenium ions **2b** and **2c** react rapidly with alcohols and H_2O (10^6–10^8 M^{-1} s^{-1}).[13,14]

(4) The transient is not quenched by H atom donors. Addition of up to 0.3 M Ph_3CH or THF does not significantly increase the decay rate. This result is significant in view of the change in product distributions observed when these reagents are added to the photolysis mixture. Clearly the transient species does not react to form the parent amine **5e** as would be predicted for the triplet nitrenium ion ^{3}**2e** on the basis of the model in Scheme 1.

In the absence of trapping agents, no longer lived absorptions were detected following the decay of ^{3}**1e***. Scheme 1 predicts that the triplet nitrenium ion ^{3}**2e** is formed following this decay. That ^{3}**2e** is not detected implies that either its lifetime is too short or it absorbs at wavelengths inaccessible to our apparatus. The results in the following section argue that the lifetime of **2e** is in fact several microseconds. Therefore, we favor the latter explanation.

6. Detection of Radical Intermediates. LFP of **1e** in the presence of Ph_3CH gives additional transient species. Figure 5 shows transient spectra obtained 10–200 μs after LFP of **1e** in CH_2Cl_2 containing 0.35 M Ph_3CH. There is a strong absorption in the region below 450 nm and a weak, ill-defined absorption tail above this wavelength. The low-wavelength band increases steadily after the laser pulse, while the high-wavelength tail grows in over several microseconds, and then decays. There is an isosbestic point at 450 nm. At very short times after the laser pulse the 540/390 nm spectrum, assigned above to ^{3}**1e***, was detected. Following the decay of this signal, the new absorption grows in. This behavior is illustrated in Figure 6, which shows the time dependence monitored at 370 nm. At this wavelength both ^{3}**1*** and the new species absorb. The growth rate of the new species depends on [Ph_3CH] and is significantly slower than decay of ^{3}**1e*** (i.e., there is a lag time between the two processes). Thus, the new species cannot be formed directly from ^{3}**1e***. On the basis of these observations, we exclude ^{3}**2e** as the species responsible for the new transient.

We attribute the long-lived species at wavelengths <450 nm to the triphenylmethyl radical ($Ph_3C^\bullet$) which is the product of the reaction of ^{3}**2e** with the trap. This radical is known to have an absorption maximum at 330 nm.[54] The observed absorption intensity increases with decreasing wavelength down to ca. 370 nm. Absorption of the starting material obscures any transient signals below this wavelength. This assignment is consistent with the detection of the dimeric product **12** in the preparative photolysis experiments.

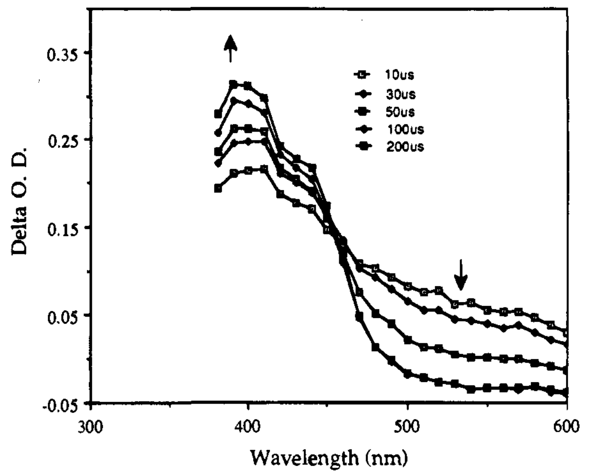

Figure 5. Transient absorption spectra obtained from laser flash photolysis of **1e** in CH_2Cl_2 containing 0.35 M triphenylmethane. Spectra were taken 10–200 μs after the laser pulse.

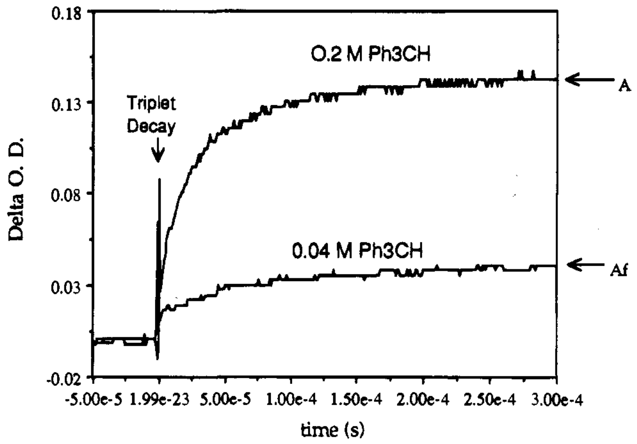

Figure 6. Transient absorption waveforms at 370 nm obtained from laser flash photolysis of **1e** in CH_2Cl_2 containing 0.040 and 0.20 M triphenylmethane. The feature near 0 μs is the growth and decay of the excited triplet state of **1e** (Figure 3).

Further support for this assignment comes from a kinetic analysis. The asymptotic intensity of the long-lived absorption (A_f) at 370 nm increases with added Ph_3CH. This value saturates at trap concentrations >0.2 M. This behavior as well as the dependence of the product ratios **5e**:**4e** is compared in Table 3. Note that a similar growth and saturation behavior is observed. This indicates that the same process that creates the long-lived intermediate (i.e., $Ph_3C^\bullet$) in the LFP experiment also gives rise to parent amine **5e**.

The growth of $Ph_3C^\bullet$ is biphasic in nature. There is a fast pseudo-first-order growth (k_{obs1}) followed by a slower pseudo-first-order growth (k_{obs2}). Both rate constants increase linearly with [Ph_3CH] (Figure 8) following eqs 5 and 6. From the slopes

$$A^{370} = A^{\infty}\{1 - A_1 \exp(-k_{obs1}t) - A_2 \exp(-k_{obs2}t)\} \quad (5)$$

$$k_{obs1} = k_o + k_{H1}[Ph_3CH] \text{ and } k_{obs2} = k'_o + k_{H2}[Ph_3CH] \quad (6)$$

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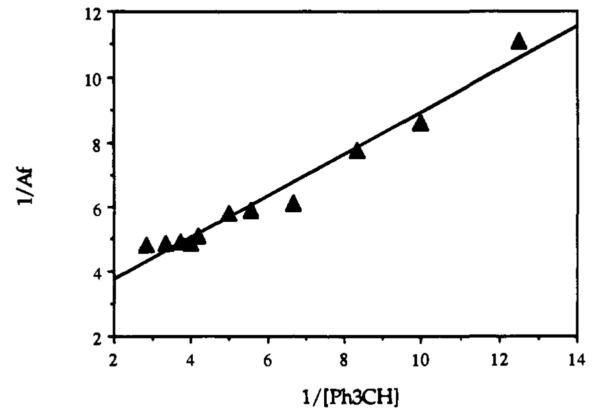

Figure 7. Double reciprocal plot of asymptotic transient absorption at 370 nm (A_f; see Figure 6) plotted against the reciprocal of the triphenylmethane concentration. Data were taken from laser flash photolysis of **1e** in N_2-purged CH_2Cl_2.

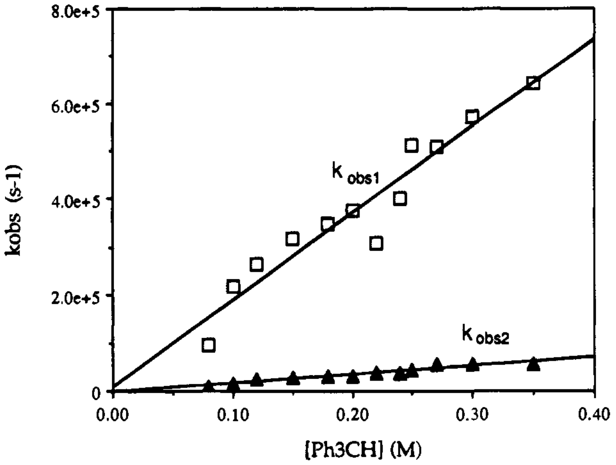

Figure 8. Pseudo-first-order analysis of the growth of the triphenylmethyl radical measured by laser flash photolysis of **1e** in the presence of various concentrations of triphenylmethane. The absorbance growth at 370 nm was fit to consecutive first-order growth k_{obs1} and k_{obs2}.

of these lines are calculated bimolecular rate constants of $k_{H1} = 1.8 \times 10^6$ M^{-1} s^{-1} for the fast reaction and $k_{H2} = 1.8 \times 10^5$ M^{-1} s^{-1} for the slow reaction. The relative contributions of the two reactions to the total signal are equal and independent of [Ph_3CH] ($A_1/A_2 = 1.0 \pm 0.2$ at all concentrations).

The mechanism of the biphasic growth is sequential H atom transfer from Ph_3CH to ^{3}**2e** and to **5e**$^{\bullet+}$ as shown in eq 7. Such

$$^{3}\mathbf{2e} \xrightarrow{k_{H1}[Ph_3CH]} \mathbf{5e}^{\bullet+} + Ph_3C^{\bullet} \xrightarrow{k_{H2}[Ph_3CH]} \mathbf{5e}H^{+} + 2Ph_3C^{\bullet} \longrightarrow \mathbf{5e}H^{+} + \mathbf{12} \qquad (7)$$

a mechanism predicts roughly equal contributions to the signal from both of the reactions. The long wavelength absorption is assigned to the parent amine cation radical **5e**$^{\bullet+}$. Aromatic amine cation radicals are known to have absorption maxima in the region 400–500 nm. *N,N*-Dimethylaniline cation radical, for example, has an absorption maximum at 460 nm.[55]

We considered the possibility that the initial growth of $Ph_3C^{\bullet}$ might be caused by reactions of solvent radicals with the trap. However, the effect of the Ph_3CH on the **5e**:**4e** product ratio argues against such a mechanism. If **5e** were formed primarily through reactions of ^{3}**2** with the solvent, then Ph_3CH would have no effect on its yield. The data in Table 3 show that the relative yield of **5e** increases almost 10-fold when saturating concentrations of the trap are added. Therefore, the solvent pathway could contribute no more than 10% to the observed signal. The clean biphasic first-order kinetics observed also indicates that this contribution is negligible.

The data also exclude reaction of ^{1}**2** with Ph_3CH. In this case the product ratio **5e**:**4e** would be expected to increase in a linear fashion with [Ph_3CH], rather than saturate as observed in Figure 2. Nor can it be the case that rapidly equilibrating singlet and triplet nitrenium ions are reacting with Ph_3CH. The different product distributions obtained from direct irradiation and triplet sensitization indicate that equilibrium is not achieved—even in the absence of the trap.

The lifetime of the triplet nitrenium ion ^{3}**2** can be determined from k_{H1} and the data in Figure 7 using a modified Stern–Volmer expression given in eq 8. A_f represents the asymptotic

$$\frac{1}{A_f} = \frac{1}{C} + \frac{1}{Ck_{H1}\tau[Ph_3CH]} \qquad (8)$$

value for the transient absorption (see Figure 6). τ is the lifetime of the triplet in the absence of the trap, and C is a constant that accounts for the laser pulse energy and the instrumental geometry. A plot of $1/A_f$ vs 1/[Ph_3CH] gives a slope equal to $1/Ck_{H1}\tau$ and an intercept equal to $1/C$ (Figure 7). The intercept-to-slope ratio provides a Stern–Volmer constant $k_{H1}\tau = 3.8$ M^{-1} (CH_2Cl_2). The use of $k_{H1} = 1.8 \times 10^6$ M^{-1} s^{-1} from the pseudo-first-order analysis, above, gives $\tau = 2.1$ μs.

The accuracy of this lifetime is limited by the complexity of the transient behavior. It is possible that overlapping absorption of **5e**$^{\bullet+}$ and the minor solvent radical reactions alluded to above act to distort the kinetic fits in some systematic way. However, a qualitative inspection of the data in Figure 6 shows that the growth of $Ph_3C^{\bullet}$ begins well after decay of ^{3}**1***. Therefore, its precursor **2** must have a lifetime well in excess of 300 ns. This is true even at high concentrations (0.2 M) of the trap where the lifetime of **2** is near its lowest (due to its rapid consumption by k_{H1}). For these reasons we are confident that the lifetime is well in excess of 500 ns.

7. Triplet State of Arylnitrenium Ion 2e. The experimental results and mechanistic analysis outlined above reveal some unique features of arylnitrenium ion **2e**. First, it appears that there is a kinetically significant pathway that leads from ^{3}**2e** to starting material **1e**, *bypassing the singlet state* (i.e., k_{TC} in Scheme 1). This follows from several observations: (1) Parent amine **5e** comes exclusively from reactions of the triplet nitrenium ion. (2) Triplet sensitization of **1e** leads only to the formation of parent amine **5e** even in the absence of added H atom donors (i.e., Ph_3CH). Therefore, the triplet cannot convert to or reach equilibrium with the singlet. (3) Direct irradiation gives **5e** in a yield that depends on the concentration of the trap Ph_3CH. This comes from the pathway $^1\mathbf{1} \rightarrow {^3\mathbf{1}} \rightarrow {^3\mathbf{2}} \rightarrow \mathbf{5}$. Therefore, the H atom transfer reaction that provides product **5e** must compete with some other process. Nitrenium intersystem crossing ($^3\mathbf{2} \rightarrow {^1\mathbf{2}}$) is excluded as it would be inconsistent with observation 2.

Consistent with these observations is the following scenario. Absorption of a photon by **1** gives its excited singlet state ^{1}**1***. The latter partitions between ring-opening in the singlet manifold (k_{so} in Scheme 1) and intersystem crossing (k_{isc} in Scheme 1). Process k_{isc} leads to ^{3}**2** which partitions between H atom transfer (k_{H1}) to give **5e** and return to the ground state (k_{TC}). When high concentrations of Ph_3CH are present, virtually all of the ^{3}**2** ions are trapped by H atom transfer. The residual 10% of **4e** formed at saturating concentrations of Ph_3CH is attributed to the fraction of ^{1}**1e** that ring-opens in the singlet manifold

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(k_{so}) and rearranges (k_m). In the absence of Ph_3CH, the majority of the ^{32} ions are recycled back to starting material.

That **1e** would undergo rapid intersystem crossing (k_{isc}) after excitation is not surprising. This is true of most nitroarenes. Nitrobenzene[56] and 2-nitronaphthalene[57] have intersystem crossing quantum yields of 0.85 and 0.87, respectively.

Closure of the triplet nitrenium ion to the singlet, ground state anthranilium ion requires a change in the spin state. This could occur in one of several ways. Triplet nitrenium ion could adiabatically cyclize to ^{3}**1***, and the latter would relax to the ground state through the usual nonradiative triplet decay mechanisms. Alternatively the spin flip could be coupled with the ring closure reaction. In this case, the spin flip would occur as the geometry of the triplet approached the transition state for ring closure. This reaction coordinate would presumably correspond to the bond rotations that bring the nitrenium nitrogen and the carbonyl oxygen into proximity. Wagner has proposed an analogous mechanism for the ring closure of triplet 1,5-biradicals.[58,59] Intersystem crossing coupled with reactions has been proposed by Griller et al. for the addition of nucleophiles to triplet carbenes.[60] Our experiments are incapable of distinguishing between the concerted and adiabatic ring closure mechanisms.

A second interesting feature of **2e** is the nature of its lowest energy electronic state. A key result is the kinetic analysis of $Ph_3C^\bullet$ formation as illustrated in Figures 5 and 7. On the basis of this, we conclude the triplet nitrenium ion ^{3}**2e** has a lifetime of ca. 2 μs in the absence of trapping agent. The processes that limit this lifetime appear to be k_{TC} and k_{HI}. None of our evidence indicates that the triplet interconverts to the singlet. However, if even with the conservative assumption that this process (k_{TS}) is the *only* one in the absence of the trap, an upper limit for triplet-to-singlet intersystem crossing is $k_{TS} \ll 5 \times 10^5\ s^{-1}$.

There are two interpretations consistent with this low rate constant: (1) the triplet state is the ground state, or (2) the singlet is the ground state, and the barrier to spin relaxation (k_{TS}) is unexpectedly high in this particular nitrenium ion.

Rates of intersystem crossing[61] are controlled by the energy difference between the two spin states, the relative orientation of the nonbonding orbitals involved in the process, and the matching of vibrational energy levels in the two spin states. Spin−orbit coupling, and thus the rate of spin inversion, is maximized when the energy gap is small, the orbitals involved are orthogonal, and the vibrational energy levels are well matched.[62] It is for these reasons that the rate constants for spin inversion in the aromatic carbenes are fast (typically $>10^{10}\ s^{-1}$).[63,64]

The same considerations apply to the arylnitrenium ions, including **2e**. We would therefore predict relatively rapid intersystem crossing for these species. With the previously studied derivatives **2a−d**, the corresponding k_{TS} process was observed to occur rapidly (i.e., triplet sensitization of **1a−d** still gives significant yields of singlet products).[13,38,39] The nitro group is predicted to *reduce* the singlet−triplet energy gap and should thus increase k_{TS} beyond that observed for the previous systems.

We regard the assignment of a triplet ground state to **2e** as the more likely interpretation of the data. This interpretation has the advantage of being consistent with theoretical predictions. Semiempirical calculations predict that arylnitrenium ions having sufficiently strong electron-withdrawing groups should be ground state triplets.[30−32] AM1 calculations on **2e** predict a singlet−triplet gap of −13.1 kcal/mol compared with −18.1 kcal/mol for **2d**.[65] Such calculations involve a number of approximations. Therefore, the trends in the numbers, rather than the absolute magnitudes, should be considered.

Conclusions

Consistent with earlier predictions, it is demonstrated that formation of the parent amine **5** proceeds via free radical intermediates. This is supported by isolation of the dimeric product **12** when the Ph_3CH is used as a trapping agent. The LFP experiments exclude the possibility that **5** is formed from an initial H atom transfer to the excited triplet state of the anthranilium precursor. Finally, the long lifetime of triplet **2e** determined from the Ph_3CH trapping experiments leads to the conclusion that this arylnitrenium ion has a triplet ground state. An alternative, but less likely, explanation is that the singlet is the ground state and the rate constant for spin relaxation (k_{TS}) is unusually low ($<10^5\ s^{-1}$).

Experimental Section

General Procedures. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. CH_3CN and CH_2Cl_2 were distilled from CaH_2 through a vacuum-sealed column (30 cm) packed with glass helices. ^1H NMR spectra were run at 200 MHz and ^{13}C NMR spectra at 55.1 MHz. Mass spectra were performed using electron impact ionization (70 eV). Photochemical reactions were carried out with a 400 W Xe arc lamp using a 320 nm cutoff filter for the direct irradiation experiments. For triplet-sensitized photolysis 9-fluorenone (20−25 mM) was added as the triplet sensitizer. The solutions were analyzed by UV to ensure that the sensitizer was absorbing ca. 90−95% of the light at 400 nm and then irradiated with the Xe lamp through a 390 nm cutoff filter for 2−3 h.

^{1}H NMR Product Yields. Yields in Tables 1 and 2 were determined by ^1H NMR integration vs an added internal standard and reported as fractions of converted starting material. Photolysis reactions were performed on solutions 5−10 mM in anthranilium salt **1e**,BF_4^-. After photolysis, the solvent was removed under reduced pressure and products were observed by ^1H NMR in CD_3CN with a known amount of triphenylmethane as the internal standard. Product **5e** was determined as its conjugate acid. Photolyses were typically carried out to 50−80% conversion of starting material. Quantum yields were determined as previously described.[38]

Laser Flash Photolysis. Laser flash photolysis experiments were done using a Questek 2120 laser system with XeCl as the source gas. The laser gives out light in 10 ns pulses at 308 nm and has an energy of ca. 50 mJ. The probe beam UV−vis light source was an Oriel 400 W Xe arc 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 were manipulated. Samples were made in millimolar concentrations. A glass flow cell was used for all experiments.

3-Methyl-5-nitro-*N*-*tert*-butylanthranilium Tetrafluroborate (1e,BF_4^-). 3-Methyl-5-nitroanthranil (**7e**) was prepared according to Rahman and Bolton's procedure.[66] Tetrafluoroboric acid (48%) was added to a solution of **7e** to a final concentration of 0.45 M along with

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[61] Intersystem crossing refers to any nonradiative transition that involves an electronic spin change. In this discussion, we are mainly concerned with intersystem crossing pathways labeled k_{TS} and k_{ST} in Scheme 1 and the corresponding processes in carbenes and nitrenes.

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tert-butyl alcohol (to 0.15 M) and stirred for 48 h. The product was precipitated by addition of diethyl ether and then filtered. The crude solid was recrystallized by methanol, yielding yellow needles with mp 148 °C: IR (neat) 3049 (br), 1630 (s), 1523 (s), 1469 (s), 1346 (m), 1280 (m), 1133 (s), 1028 (vs) cm^{-1}; ^{1}H NMR (CD_3CN) δ 9.09 (d, 1 H), 8.65 (dd, 1 H), 8.04 (d, 1 H), 3.14 (s, 3 H), 1.89 (s, 9 H); ^{13}C NMR (CD_3CN) δ 180.2, 147.7, 134.7, 123.2, 119.7, 118.9, 114.2, 72.6, 28.7, 14.2; MS *m/z* (rel intens) 235 (M − BF_4,7), 234 (25), 221 (5), 180 (24), 179 (69), 178 (100), 148 (24); high-resolution MS *m/z* 234.1014 (M^+ − HBF_4, calcd for $C_{12}H_{14}N_2O_3$, 234.1004).

Preparative Irradiation of 1e,BF_4^-. **1e** (100 mg) was irradiated in 10 mL of CH_3CN for 120 min. The mixture was concentrated by evaporation of the solvent, and subjected to preparative TLC. The mixture yielded 2-acetyl-4-nitro-*N*-*tert*-butylaniline (**5e**) (45%) as a yellow solid with mp 98 °C: $R_f = 0.48$, hexanes/ethyl acetate; IR (neat) 3294 (br), 1663 (s), 1560 (m), 1391 (m), 1110 (s) cm^{-1}; ^{1}H NMR (CD_3CN) δ 9.99 (br s, 1 H), 8.70 (d, $J = 2.7$, 1 H), 8.05 (dd, $J = 9.6, 2.7$, 1 H), 7.05 (d, $J = 9.6$, 1 H), 2.61 (s, 3 H), 1.45 (s, 9H); ^{13}C NMR (CD_3CN) δ 201.9, 154.9, 135.5, 131.5, 114.8, 52.7, 29.4, 28.4; MS *m/z* (rel intens) 236 (53), 221 (100), 203 (52), 180 (58), 164 (80), 157 (41); high-resolution MS *m/z* 236.1159 (M^+, calcd for $C_{12}H_{16}N_2O_3$, 236.1160). The mixture also contained 2-acetyl-4-nitro-*N*-methylaniline (**9**), a pale yellow solid, mp 81 °C: $R_f = 0.32$, 5:1 hexane/EtOAc; IR (neat) 3295 (br), 1637 (s), 1554 (m), 1320 (m), 1114 (s) cm^{-1}; ^{1}H NMR (CD_3CN) δ 8.70 (d, $J = 2.6$, 1 H), 8.22 (dd, $J = 9.5, 2.6$, 1 H), 6.8 (d, $J = 9.5$, 1 H), 2.97 (d, $J = 5.2$, 3 H), 2.60 (s, 3 H); ^{13}C NMR (CD_3CN) δ 201.6, 156.5, 130.8, 130.6, 116.9, 112.5, 30.1, 28.1; MS *m/z* (rel intens) 194 (1.9), 179 (100), 166 (25), 164 (99), 107 (20); high-resolution MS *m/z* 194.0675 (M^+, calcd for $C_9H_{10}O_3N_2$, 194.0691).

3-Hydroxy-3-methyl-5-nitro-2,1-benzoxazole (8e). Treatment of **1e** (20−100 mg) in CH_3CN (10 mL) with a saturated aqueous solution of $NaHCO_3$ (4 mL) followed by extraction with diethyl ether, washing the organic layer with water, and concentrating *in vacuo* produces isoxazoline. It was 90% pure by ^{1}H NMR and was not subjected to further purification. The product is a yellow solid, mp 80−84 °C; ^{1}H NMR (CD_3CN) δ 8.1 (dd, 2H), 7.1 (d, $J = 8.9$, 1 H), 4.57 (s, 1H), 1.70 (s, 3H), 1.34 (s, 9H); MS *m/z* (rel intens) 252 (2.2), 235 (10), 196 (17.1), 179 (95.1), 57 (100).

Triphenylmethyl Dimer 12. Photolysis of **1e** was carried out in the presence of 0.2 M triphenylmethane in dichloromethane. The dimer was characterized by ^{1}H NMR. Peaks were identified according to spectroscopic data reported by Lankamp.[67]

Acknowledgment. This work was supported by the National Science Foundation.

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