Photogenerated Nitrenium Ions: A Search for Triplet-State Reactivity in the Chemistry of the Diphenylnitrenium Ion

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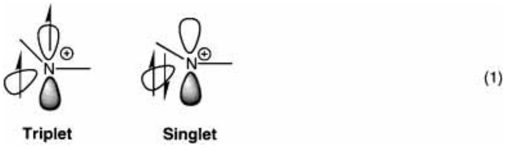
The N,N-diphenylnitrenium ion (Ph_2N^+) was generated from the photolysis of a stable precursor, the 1-(N,N-diphenylamino)-2,4,6-trimethylpyridinium ion. The behavior of this nitrenium ion was studied by laser flash photolysis (LFP) and the analysis of its stable products. In accord with an earlier communication, Ph_2N^+ is found to have absorption maxima at 425 and 660 nm, to live for ca. 1.5 μs in CH_3CN, and to react with Cl^- at or near the diffusion limit. However, no evidence for concurrent formation of the diphenylamine cation radical ($Ph_2NH^{+\bullet}$) is found. Its formation in the earlier experiments is attributed to small amounts of accumulated photoproducts. The LFP experiments also show that Ph_2N^+ is quenched by various H atom donors, including 1,4-cyclohexadiene and tri(*n*-butyl)tin hydride. However, the radical cation that would be expected from a homolytic H atom transfer, $Ph_2NH^{+\bullet}$, is not detected in these experiments. Moreover, the rate constants for trapping do not vary in the expected way with the bond dissociation energies of the traps. The rate constants do, however, show a reasonable correlation with the hydride affinities of the traps. It is argued that the quenching mechanism is a hydride transfer to the singlet state of Ph_2N^+ and that the triplet state of this nitrenium ion is not involved in these reactions.

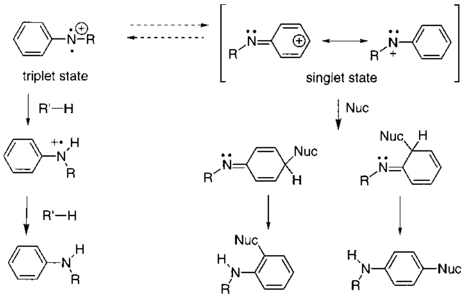
1. Introduction

Nitrenium ions are electrophilic reactive intermediates that contain a divalent, positively charged nitrogen atom.[1−3] These species can exist in two low-energy electronic configurations: a singlet state where the two nonbonding electrons are paired and a triplet state where they are unpaired (eq 1).[4−6] We have had longstanding interests in determining how the ligands on nitrogen affect the relative energies of the singlet and triplet states and how these electronic states might differ in chemical reactivity. Intuitive considerations would suggest that the triplet state should behave as a diradical, abstracting H atoms and participating in one-electron-transfer reactions. The singlet, having a low-energy unoccupied orbital, should behave more like a carbocation, participating in processes that involve shifts of electron pairs. While systematic studies on the spin-specific reactivity of nitrenium ions are far less extensive than they are for the carbenes,[7−9] the extant data on the nitrenium ions show that there is validity to this intuitive expectation. Generally, aromatic nitrenium ions have singlet ground states.[5,10−17] However, when these intermediates are generated photochemically, it is possible to first create the higher-energy triplet state, which can be kinetically trapped before it relaxes to the lower-energy singlet state. Previous experiments have shown that the triplet reacts through H atom abstraction, ultimately producing the parent amine of the nitrenium ion, whereas the singlet preferentially reacts with nucleophiles, resulting in products where the aromatic ring is substituted (Scheme 1).[18−21]

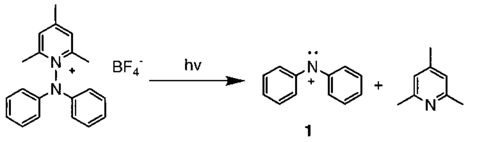


(1)

SCHEME 1



An earlier communication[22] from this laboratory described laser flash photolysis (LFP) studies of diphenylnitrenium ion **1**, which was generated through the photolysis of 1-(N,N-diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate **2** (eq 2). This nitrenium ion showed kinetic behavior consistent with it having a singlet ground state. For example, Cl^- traps it at the diffusion limit (1×10^{10} M^{-1} s^{-1}). Indeed, DFT calculations on **1** predict it to have a singlet ground state, which is substantially more stable than the triplet state ($\Delta E_{st} = -11.6$ kcal/mol).[23] More significantly, it was possible to characterize **1** using time-resolved infrared laser flash photolysis. The IR bands thus detected were found to be much more consistent with bands of the charge-delocalized singlet state than bands of the triplet.[24] On the other hand, the preliminary LFP experiments (using conventional UV−vis detection) seemed to indicate that the diphenylamine cation radical **3** was also being generated simultaneously with, or subsequently after, **1**.[22] The



2 **1** (2)

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TABLE 1: Product Distributions from Photolysis of 2 in CH_3CN in the Presence of Various Concentrations of Trapping Agents

CHD[a]	Cl^-	Ph_2NH	**7** + **8**[b]	carbazole	mass balance
0	0	76	0	24	28
0.63	0	97	0	3	57
0	0.05	13	87	0	92
0.21	0.05	17	83	0	95
4.2	0.05	26	74	0	92
0	0.01	17.7	82	0.03	82
0	0.1	7.9	92.1	<0.1	91

[a] 1,4-cyclohexadiene. [b] *ortho*- and *p*-*N*-phenylchloroaniline.

former is precisely the intermediate that would be expected from the triplet state of **1**.[21]

We considered two pathways by which the photolysis of **2** might provide the triplet state of **1**. The first would be that the photodissociation process would provide a nonequilibrium mixture of the two spin states. Specifically, the excited singlet state of the precursor could partition between intersystem crossing and N−N bond scission. Bond scission from the excited triplet state would be expected to generate the triplet state of the nitrenium ion. The latter would abstract an H atom from a solvent molecule to provide **3**. The second requires the singlet state to be in rapid equilibrium with the higher-energy triplet state. Given the short lifetime of **1** (ca. 1.5 μs), this latter pathway requires $\Delta E_{st} < -1.5$ kcal/mol, a value significantly smaller than the theoretical (B3YLP) prediction.[23]

The experiments discussed below were undertaken with the goal of critically evaluating the possible role of the triplet state of **1** in its chemical reactions and LFP behavior. It is shown that the radical cation **3** detected in the preliminary LFP experiments does not come from the photolysis of **2** but instead arises from the photolysis of strongly absorbing photoproducts which can accumulate during the experiment. The trapping of **1** by a series of potential H atom donors is also examined by LFP. The radical intermediates expected in this process are not detected, nor do the trapping rate constants correlate with the bond dissociation energies of the donors. It is therefore concluded that the quenching mechanism is hydride transfer, rather than H atom transfer. Thus, it is not necessary to invoke rapid-spin equilibration and reaction via the triplet state to explain the experimental results. In fact, all current experimental data are consistent with **1** possessing a singlet ground state and the theoretically calculated singlet−triplet energy gap.

2. Results and Discussion

The yields of the stable photoproducts under various conditions are presented in Table 1. In the absence of efficient trapping agents, the photolysis of **1** produces highly colored and complex reaction mixtures, and the mass balances are low.[25] We are able to identify two monomeric products from these mixtures, carbazole **5** and diphenylamine **6**. Both carbazole and diphenylamine are known to polymerize under oxidizing conditions,[26] and both the pyridinium salt **2** and the transient nitrenium ion **1** can function as oxidants. The details of the secondary decay pathways have not been fully elucidated. However, it is reasonable to assume that the colored products are oligomers and polymers of these species and their corresponding cation radicals.

Regardless of the mechanism, the formation of reactive photoproducts can complicate a LFP experiment. When such products produce their own strongly absorbing transients, the LFP spectrum can become complicated by signals from the accumulated photoproducts. To avoid this problem, it is customary to use a flow cell which rapidly introduces fresh samples into the irradiated zone and replaces the photolyzed material. In the preliminary study, we used an all-glass, recirculating 100 mL flow cell based on a design by Winkler et al.[27] While this has proven to be adequate for most samples, the above concerns lead us to reexamine the LFP behavior of **2** using an improved flow cell based on a design suggested by Grabowski.[28] This improved flow cell does not recirculate the sample but instead discards the photolyzed material. Although it is less convenient and consumes more reagent, the improved apparatus is far less likely to give signals due to accumulated photoproducts.

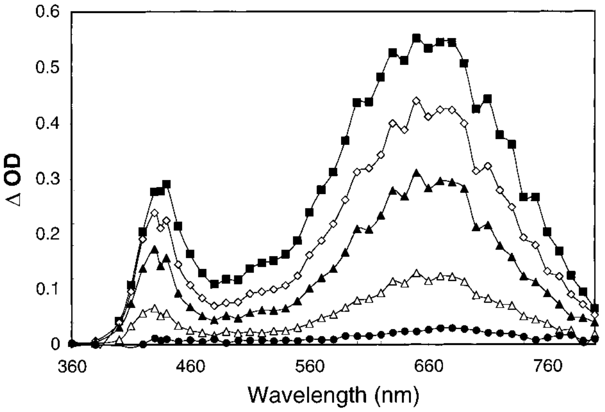


Figure 1. Transient absorption spectra from the LFP (355 nm, 1−5 mJ, 6 ns) of **2** in CH_3CN taken 100 ns (■), 800 ns (◇), 1.6 μs (▲), 3.2 μs (△), and 6.4 μs (●) following the excitation pulse.

The transient spectra obtained upon LFP (355 nm, 6 ns, 1−5 mJ/pulse) of **2** in CH_3CN are shown in Figure 1. There is a sharp band at 440 nm and a broader peak at 690 nm. The transient spectra obtained from the same compound in CH_2Cl_2 or CH_3CN with 266 nm excitation are almost indistinguishable. Both peaks decay with lifetimes of 1.5 μs in CH_3CN and 1.6 μs in CH_2Cl_2. This transient spectrum agrees well with the transient spectrum attributed to the diphenylnitrenium ion **1** in the earlier work.[22] This assignment was later confirmed by time-resolved IR.[24] The observed transient species also exhibits the same qualitative reactivity patterns and even the same rate constants (to within the stated experimental uncertainties) as those reported in the earlier paper. Thus, our assignment of these peaks to **1** is unchanged from the earlier report.

The current experiments, however, show no long-lived diphenylamine radical cation **3** (or neutral diphenylamine radical **4**) following the decay of the nitrenium ion. The negligible baseline signals in the region of 600−800 nm leads to the conclusion that the cation radical (**3** or its conjugate base) is not formed in significant yields from the photolysis of **2**. Our previous statements to this effect are therefore revised. Figure 2 shows results from repetitive LFP measurements carried out on a small, unflowed sample of **2**, where the absorbance changes at 650 nm were monitored. At this wavelength, both **1** and **3** absorb light. Following the first shot, there is only a short-lived absorbance, corresponding to **1**. However as the experiment is repeated, an additional long-lived species corresponding to **3** appears. The intensity of the long-lived signal increases with the number of pulses from the excitation laser and is thus clearly a result of accumulated byproducts.[29]

The behavior of **1** was also investigated by competitive trapping reactions using Cl^- and 1,4-cyclohexadiene (CHD). Stable products from the photolysis of **2** in the presence of varying concentrations of the trapping reagents are listed in Table 1. In the presence of Cl^- (0.01 M), ortho and para chloro adducts **7** and **8**, respectively, are the predominant products, formed in a ratio of 2:1 and accounting for 82% of the

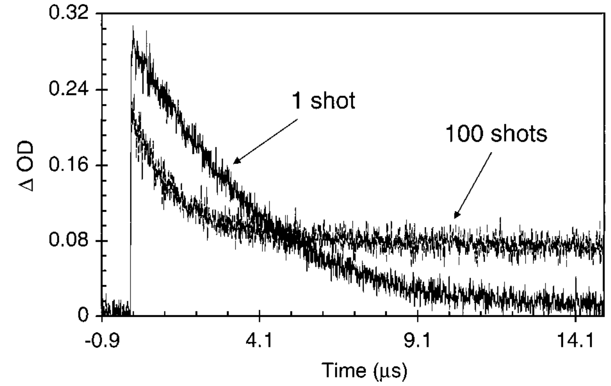
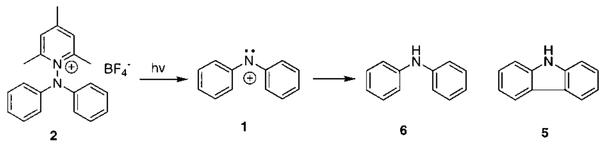
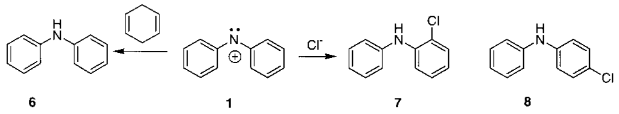


Figure 2. Kinetic traces taken from the LFP of **2** in CH_2Cl_2 using a 3 mL unflowed cuvette after 1 shot and 100 shots monitored at 690 nm.

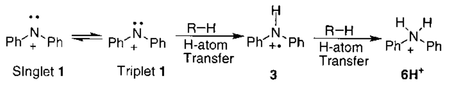
SCHEME 2



SCHEME 3



SCHEME 4



products.[30] Diphenylamine **6** and carbazole **5** are also formed. Increasing the [Cl^-] increases the proportion of the chloride adducts formed and suppresses the yields of both **5** and **6**. Table 1 illustrates the effect of adding CHD. At high concentrations, **6** is the predominant product, accounting for 97% of the observed photolysate. The low mass balances in this experiment are attributed to the low photostablity of this product. Higher mass balances are observed when both Cl^- and CHD are present. It is significant that increasing the [CHD] suppresses the yields of the Cl^- adducts **7** and **8** and increases the yield of the parent amine **6.**

While it is clear that **3** (and, by implication, the triplet state of **1**) are not formed concurrently with the singlet state of **1**, significant yields of parent amine **6** in the photolysis of **2** led us to investigate the mechanism of its formation. Parent amines are generally considered to be products of the triplet nitrenium ions.[19,31,21,32] One possible mechanism for the formation of **6** would have the singlet state of **1** first convert to the higher-energy triplet through rapid spin equilibrium and then react to give the parent amine (Scheme 4). In that case, **6** would be formed from two sequential H atom abstractions by the triplet state. Such a pathway would predict that the radical cation **3** (or its conjugate base) would form and be detected following the decay of **1**. Additionally, the observed quenching rate constant (k_H) should increase as the BDE (bond dissociation energy) of the trap decreases.

A similar rapid spin equilibration model was used to account for the chemistry of diphenylcarbene.[33,7,34,35] In the latter case, the triplet is the ground state. Singlet products arising from the reactions of diphenylcarbene are considered to be the result of the triplet state first converting to the higher-energy singlet via rapid equilibrium and then reacting. Others have pointed out that singlet products could also result from direct but slower reactions of the triplet state.[36]

SCHEME 5

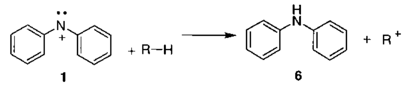


TABLE 2: Rate Constants (M^{-1} s^{-1} in CH_3CN) for the Reaction with 1 and Bond Dissociation Energies (kcal mol^{-1}) and Hydride Affinities for Various Traps

trap	BDE, kcal/mol	ΔH_{IA}, kcal/mol[a] (Mayr *N*)	$k_H(\mathbf{1})$, $M^{-1}\,s^{-1}$
1-methyl-1,4-cyclohexadiene		194	$1.0 \pm 0.1 \times 10^8$
tri(*n*-butyl)tin hydride	73.7 ± 2.0^b	(9.3)	$1.6 \pm 0.3 \times 10^7$
cycloheptatriene	73.0 ± 2.0^c	201	$1.4 \pm 0.1 \times 10^7$
1,4-cyclohexadiene	73.0 ± 2.0^b	212	$6.5 \pm 0.2 \times 10^6$
1,3-cyclopentadiene	71.1 ± 1.5^c	258	$<1.7 \pm 0.1 \times 10^{6\,e}$
tris(trimethylsilyl)lsilane	79.0 ± 1.0^d	(4.5)	$<10^6$
toluene	88.0 ± 1.0^b	238	$<10^6$

[a] Hydride affinities refer to the process $R{-}H \rightarrow R^+ + H^-$.[41] [b] Ref 39. [c] Ref 38. [d] Ref 40. [e] The observed trapping rate constant is an upper limit for k_H. This trap also reacts via addition to the nitrenium ion (Scheme 6).

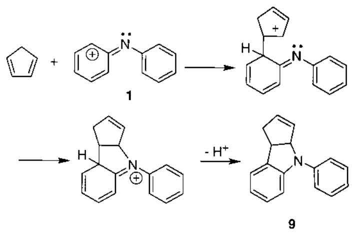
An alternative mechanism that we considered would have the singlet state react directly with the donor via a hydride transfer (Scheme 5). Such a mechanism would be consistent with the theoretical prediction of a large (11.6 kcal/mol) energy gap.[23] The hydride transfer pathway would give **6** directly with no radical intermediates. The observed rate constants in this case would not necessarily follow the homolytic bond strengths of the traps.

The trapping of **1** by various H atom/hydride donors was examined by LFP. The choice of reagents was constrained by three considerations. First, the relatively short lifetime of nitrenium ion **1** means that quenching can be detected only with highly reactive reagents at high concentrations. Second, because nitrenium ions are also electrophilic, hydride/H atom donors that are also nucleophiles are not employed. This excludes phenolic and thiol-based traps. This also excludes electron-rich aromatic compounds, as other work has shown that these are subject to rapid electrophilic aromatic substitution by nitrenium ions.[37] Finally, the traps must not have absorption bands that overlap with those of the substrate. A series of traps meeting these constraints is listed in Table 2 along with the respective BDE[38−40] and gas-phase hydride affinity (ΔH_{IA})[41] for each trap. It is clear that there is no correlation between the BDE and the k_H. For example, cyclopentadiene is far less reactive than cyclohexadiene, cycloheptatriene, or (n-Bu)$_3$SnH, even though its BDE is nominally lower than the BDEs of these other traps.

The hydride transfer mechanism readily accounts for this pattern of reactivity. Hydride transfer from cyclopentadiene would generate an antiaromatic cyclopentadienyl cation. This is seen in the high ΔH_{IA} for this cation (258 kcal/mol). The observed trapping rate constant for cyclopentadiene is several times lower than that for the other traps. In fact, product studies indicate that cyclopentadiene traps **1** by several pathways with hydride transfer contributing little, if anything, to the observed rate constant. Thus, the observed rate constant for cyclopentadiene represents a conservative upper limit on its rate of hydride transfer.

The photolysis of **2** in the presence of cyclopentadiene gives **6** along with several other products whose mass spectra indicate that they are isomeric adducts resulting from a combination of

SCHEME 6



1 and cyclopentadiene The major isomer was isolated and shown by MS, ^{1}H NMR, and COSY to have the structure of **9**. This is the result of a net cycloaddition whereby the cyclopentadiene is joined to the nitrogen and the ortho-ring carbon of **1**. Scheme 6 shows our proposed mechanism for the process. Low yields and difficulties in purifying the remaining isomer have thus far precluded its complete characterization. However, the strong similarity of its MS fragmentation pattern implies that it too is a cycloadduct. In any case, the formation of these adducts makes it clear that the observed k_H for cyclopentadiene greatly overestimates its proclivity for H atom or hydride transfer.

In contrast, hydride transfer from cycloheptatriene would give a stable aromatic tropylium cation. Again, this is seen in a much lower value for ΔH_{IA}, 201 kcal/mol. Cycloheptatriene traps **1** nearly 10 times faster than cyclopentadiene. More significantly, the diphenylamine was the only compound detected in this process. 1,4-Cyclohexadiene has a ΔH_{IA} (212 kcal/mol) slightly larger than that for cyclopheptatriene, and as expected, it shows a rate constant that is slightly lower than that of the latter. More significant is the 10-fold increase of k_H for 1,4-CHD compared to the k_H of its methylderivative, 1-methyl-1,4-cyclohexadiene. Although the BDE for the latter is not available, it is expected to vary little from CHD. On the other hand, ΔH_{IA} of the methyl derivative (194 kcal/mol) is significantly lower than that of CHD. This again supports the hydride transfer mechanism.

Hydride affinities for tributyltin hydride and tris(trimethylsilyl)silane are apparently not available. However, Mayr and Patz[42] have characterized an empirical nucleophilicity parameter *N*, where a higher value of *N* indicates a faster reaction with a given electrophile. Specifically, they characterized the rates of hydride transfer from these traps to various diarylcarbenium ions. According to that scale, tri-(*n*-butyl)tin hydride (9.3) is predicted to be >4 orders of magnitude more reactive toward a given carbocation than tris(trimethylsilyl)silane (4.5). Our data do not permit the quantitative aspects of this prediction to be tested—we are not able to observe quenching by the silane. However, the latter observation and the high k_H observed for tin hydride are also consistent with the hydride transfer mechanism.

The H atom transfer pathway depicted in Scheme 4 predicts the formation of a radical/radical cation pair. Inasmuch as this pair was the result of a triplet state reaction, the product would likely be a triplet pair, and as such, the components would escape the initial solvent cage competitively with in-cage reactions leading to singlet products. Thus, if the triplet mechanism were operative, we would expect to observe radical cation **3** in the LFP experiment following quenching by the various traps. However, when these experiments are carried out under flowed conditions, the characteristic transient peak for **3** at 690 nm[43] is not detected. For example, an LFP experiment was carried out where 46.5 mM (n-Bu$_3$)SnH is added as a quencher. As is apparent in Figure 3, there is, at best, only a very weak signal present at long times in the region where **3** would be observed. Similar experiments were carried out using the other traps listed in Table 2, and in no cases were significant amounts of long-lived absorption due to **3** detected.

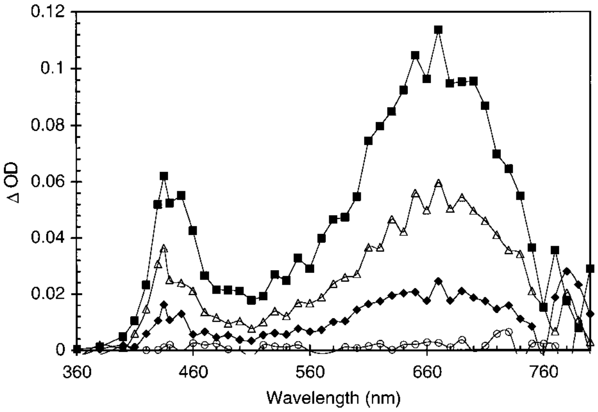


Figure 3. Transient absorption spectra from the LFP of **2** in CH$_2$Cl$_2$ with 46.5 mM (n-Bu)$_3$SnH taken 140 ns (■), 560 ns (△), 1120 ns (◆), and 8960 ns (○) following the excitation pulse.

It should be noted, however, that with 1,4-cyclohexadiene, 1,3,5-cycloheptatriene, and 3-methyl-1,4-cyclohexadiene, some weak residual long-lived absorbance was observed following the nitrenium ion decay. An upper limit of the quantum yield for cation radical formation, Φ_R, can be estimated from the ratio of absorbances of the nitrenium ion and the cation radical (A_N/A_R), the ratio of molar absorptivities of these species (ϵ_R/ϵ_N), and the quantum yield of nitrenium ion formation (Φ_N) (eq 3). Previous measurements on **3** provide $\epsilon_R = 2 \times 10^5$ M^{-1} cm^{-1}.[43] By comparing the initial LFP absorbance of the benzophenone triplet ($\epsilon_{525} = 6200$ M^{-1} cm^{-1}) to that of the nitrenium ion (controlling for excitation power and sample absorbance), we determine the product $\Phi_N\epsilon_N = 5000$ M^{-1} cm^{-1}. The ratio A_N/A_R was determined by LFP experiments at a high concentration of the trap where the A_N was taken from the absorbance immediately following the laser pulse and A_R was taken from the absorbance after three half-lives of the nitrenium ion. For each of these traps, $\Phi_R < 0.04$, and in some cases, it is possible to state an even lower limit for radical formation

$$\Phi_R = \frac{A_R\epsilon_N}{A_N\epsilon_R}\Phi_N \qquad (3)$$

The LFP results show that negligible amounts of cage-escaped radicals are formed in the trapping process. Of course it is always possible to postulate that either the triplet states or the radical pairs are formed and rapidly consumed by subsequent reactions before any significant cage escape takes place. In that sense, it may not be possible to rigorously exclude the involvement of some undetectable triplet state in these (or any other) reaction. However, it can be stated with certainty that all the experimental information on **1** can be explained by assuming that it has a singlet ground state and that all of its presently known chemical reactions occur from that state.

3. Experimental Section

Laser flash photolysis experiments were performed using a Continuum Surelite II-10 Nd(:YAG) as the excitation source. The UV−vis light source, the probe beam, was produced with a CW 300 W Xe arc lamp. Transient waveforms were captured and stored using a Lecroy 9420 digital oscilloscope. Kinetic studies were performed with solutions of **2** (15 mg) in 40 mL of solvent, the solvent being CH$_2$Cl$_2$ for n-Bu$_3$SnH and toluene or MeCN for all other quenchers. Pseudo-first-order decay rate constants (using the peak at 440 nm) were obtained using at least five different concentrations, ranging from 0 to 100 mM. Dicyclopentadiene was cracked through distillation immediately prior to the experiment. The second-order rate constants (k_H) shown in Table 2 were derived from the dependence of the pseudo-first-order rate constant on the concentration of quencher, which in all cases gave a good linear fit.

Transient absorption spectra were acquired from solutions of **1** (ca. 30 mg in 80 mL of MeCN or CH_2Cl_2), which were placed in a sealed round-bottom flask and purged with N_2. During the LFP experiment, this solution was continuously transferred using N_2 pressure into a 10 × 10 mm quartz cuvette (where the LFP measurement was made) and from there into a waste container. Both the solvent reservoir and the cuvette were sealed with rubber serum caps, and the system was kept under a positive pressure of N_2.

Photoproduct Analysis. Photolysis for the product studies of N,N-diphenylaminyl-2,4,6-trimethylpyridinium tetrafluoroborate **2** in CH_3CN were performed in a Rayonet photoreactor equipped with 350 nm lamps. A 20 mL solution of 0.0950 mmol of the sample and 25 mmol of the quencher was purged under standard conditions for 10 min with N_2 and photolyzed with continuous stirring for 30 min. The photoproducts were detected using a Rainin Instruments HPLC equipped with a C_{18} reverse-phase column. All injections were 50 μL, and the solvent was a 40:60 MeCN:H_2O solution ramped for 13 min to 100% MeCN over 4 min and held at 100% MeCN for 15 min with a flow rate of 1 mL/min. The absorbance was measured at 254 nm. HPLC chromatogram peaks were identified by the co-injection of the crude sample with authentic samples purchased from Aldrich. Concentrations of the products were calculated using concentration curves generated from authentic samples. The product identities were also verified by GC/MS using a Shimadzu GC-17A gas chromatograph with a QP-5000 MS mass spectrum detector.

Photolysis of 2 with Cyclopentadiene. A 20 mL solution of 0.0950 mmol of N,N-diphenylaminyl-2,4,6-trimethylpyridinium tetrafluoroborate and 25 mmol of freshly distilled cyclopentadiene was purged for 10 min with N_2 and photolyzed in the Rayonet reactor for 30 min with continuous stirring. The combination of three photolyzed solutions, followed by the removal of the solvent, yielded a brown oil. The oil was taken up in a 5:1 hexane:EtOAc solution, directly added to a preparative flash chromatography column, and eluted with 200 mL of a 5:1 hexane:EtOAc solution. This products was further purified by preparative HPLC using a C_{18} column and a MeCN/H_2O mobile phase, yielding 7 mg (3.3%) of cycloadduct **9**. ^{1}H NMR (CD_3CN): δ 7.38−7.30 (m, 5H), 7.19−7.17 (m, 1H), 7.10−7.04 (m, 1H), 6.96−6.92 (m, 1H), 6.79−6.75 (m, 1H), 5.99 (m, 1H,), 5.91 (m, 1H,), 5.20 (dm, 8.4 Hz, 1H,), 4.09 (t, 8.4 Hz, 1H), 2.96 (m, 1H), 2.60 (dp, 16.8 Hz, 2 Hz, 1H). ^{1}H COSY spectrum is included as supporting material.

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Supporting Information Available: ^{1}H COSY spectrum for compound **9**.

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