On the Solution Chemistry of Parent Nitrenium Ion NH_2^+: The Role of the Singlet and Triplet States in Its Reactions with Water, Methanol, and Hydrocarbons

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Chemical reactions of the parent nitrenium ion NH_2^+ were examined. The latter was generated in various solutions through photolysis of 1-amino-2,4,6-triphenylpyridinium perchlorate. It was found that the hydrocarbons, toluene and triphenylmethane, trap NH_2^+ through two independent pathways. There is a free radical pathway which leads to bibenzyl (in the case of toluene) or the trityl radical (in the case of triphenylmethane). There is also a hydride transfer pathway which leads to benzyltoluene (in the case of toluene) or triphenylmethanol (in the case of triphenylmethane). Results from dilution, triplet sensitization, and EPR experiments lead to the assignment of the hydride transfer pathway to the singlet state of NH_2^+ and the radical pathway to the triplet state of NH_2^+. Trapping experiments with H_2O and CH_3OH were also carried out, and it was shown that the singlet state of NH_2^+ undergoes a net insertion into the O−H bonds of these substrates.

Nitrenium ions[1−3] are reactive intermediates with the general structure $R{-}N{-}R'^+$. As a rule these species are extremely electrophilic and their lifetimes in solution are in the picosecond to microsecond range. Nitrenium ions are isoelectronic with carbenes and thus have two low-energy electronic states: a singlet and a triplet. In the case of the parent system, NH_2^+, the triplet is theoretically predicted[4−6] and experimentally found[7] to be the ground state with an energy gap (ΔE_{st}) of ca. +30 kcal/mol (a positive sign for ΔE_{st} means the triplet is lower in energy). This energy gap is strongly dependent on the ligands attached to the nitrogen atom. For example, theoretical calculations predict that substitution of a single phenyl ring on the nitrogen is sufficient to reverse the state ordering, making $\Delta E_{st} = -20$ kcal/mol.[8−10]

Much of the recent interest in nitrenium ions relates to the postulated role of aromatic substituted nitrenium ions in cellular DNA-damaging reactions leading to carcinogenesis.[11−13] For this reason, most of the experimental information on nitrenium ion chemistry has focused on the specific situation where arylnitrenium ions are generated in aqueous solution. In that case, the primary decay pathway is attack of water on the aromatic ring of the nitrenium ion rather than on the nitrogen.[14−16] In fact most nucleophiles add to the aromatic ring of the arylnitrenium ions as depicted in Scheme 1. A notable exception to this pattern is the reaction of 4-biphenylylnitrenium ion and 2-flourenylnitrenium ion with the DNA base guanine. This nucleophile reacts at the arylnitrenium ion's nitrogen rather than at the aromatic ring.[11,17−19] The precise reason for this divergent behavior is unclear at the present time.

In contrast to the aryl series, little is known about the chemical behavior of alkyl and parent nitrenium ions. With the alkyls, one problem that has vexed both theoreticians[8,20] and experimentalists[21,22] has been rapid 1,2-shifts of alkyl groups and hydrides from the neighboring carbon to nitrogen. This has made it difficult to distinguish products due to free nitrenium ions from those arising from concerted pathways. Of course for NH_2^+, neither a 1,2 shift nor nucleophilic attack on the aromatic ring are possible. Recently Takeuchi et al.[23,24]

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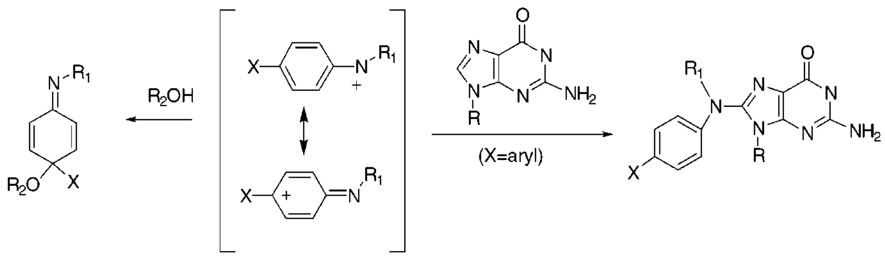
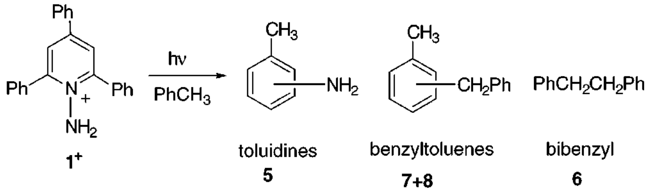
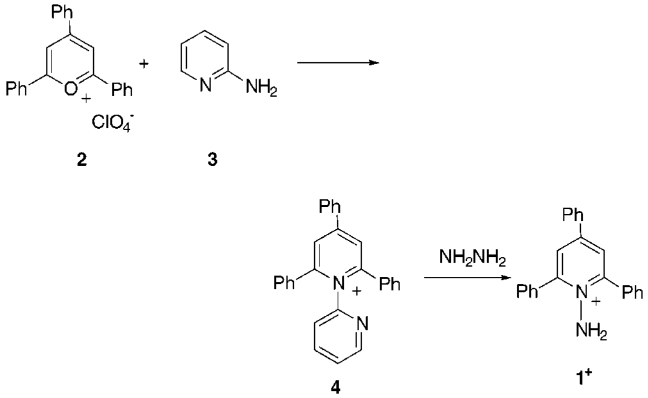
Scheme 1



Scheme 2



Scheme 3. Synthesis of Precursor



have reported a general procedure for the generation of NH_2^+ in solution, namely, photolysis of 1-amino-2,4,6-triphenylpyridinium perchlorate in the presence of strong acids. That study was primarily concerned with the trapping of the singlet state of NH_2^+ by aromatic compounds. For example, it was shown that NH_2^+ could be trapped by addition to the ring of toluene in modest to good yields (Scheme 2).

The following work was undertaken with the aim of further delineating the differences in chemical behavior between the singlet state and triplet state of NH_2^+. Given that insertion into O−H bonds is a characteristic reaction of the isoelectronic carbene, CH_2,[25−27] we were particularly interested in determining if an analogous process occurred with the nitrenium ion. Trapping experiments with H_2O and CH_3OH show that this is indeed the case. Moreover, through triplet sensitization experiments and competitive trapping it is demonstrated that this pathway is characteristic of the singlet state. In the course of these investigations, we also examined the trapping of NH_2^+ by toluene. While we obtained essentially the same products reported in the earlier studies,[23,24] a closer examination of the toluene dimers revealed that their formation mechanisms differed. The product 1,2-diphenylethane forms from the coupling of two benzyl radicals. The latter are produced when the triplet state of NH_2^+ abstracts an H atom from toluene. However, the other dimers, *o*- and *p*-benzyltoluene, arise from attack of a benzyl cation on a neutral toluene. The benzyl cation is found to be a product of the singlet nitrenium ion.

Results and Discussion

The photoprecursor to NH_2^+, 1-amino-2,4,6-triphenylpyridinium perchlorate **1**, was synthesized using previously reported procedures. 2,4,6-Triphenylpyrylium perchlorate **2** was combined with 2-aminopyridine **3** in ethanol to give 1-(2′-pyridyl)-2,4,6-triphenylpyridinium perchlorate **4**. The latter was treated with hydrazine in refluxing ethanol to give **1** (Scheme 3).

Photolysis of **1** in toluene containing 10% (v/v) of trifluoroacetic acid (TFA)[28] gives a mixture of ammonia, toluidines **5**, and three dimers of toluene, namely, 1,2-diphenylethane (bibenzyl) **6**, 2-benzyltoluene **7**, and 4-benzyltoluene **8** (Scheme 4). The yields of the organic products were determined by GC analysis, and the yield of ammonia was determined through a spectrophotometric assay using its reaction with phenol and hypochlorite.[29,30] The yields are listed in Table 1. Our results are in good qualitative agreement with the previous reports.[23,24] Any discrepancies in the yields are likely due to minor differences in the reaction conditions employed by the two studies. For example, the present study employed only 10% TFA whereas the previous workers used much higher concentrations (30−50%).

Scheme 4

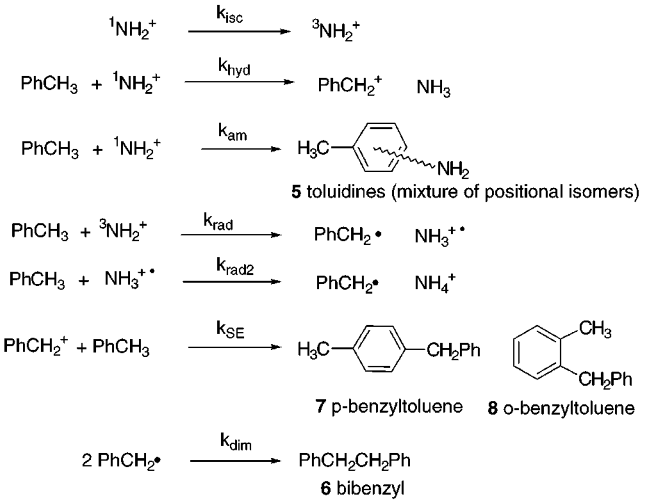


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Table 1. Photoproduct Distributions from 1

conditions	**5**[a]	**6**	**7** + **8**[b]	NH_3	NH_2OR	**9**
$PhCH_3$/TFA	11	23	24	31		
xanthone/ $PhCH_3$/TFA	<2	44	14	26		
$PhCH_3$/TFA/CH_3OH	<2	20	<5	28	37	
CH_3CN/H_2O (1:1)				30	52	
PhH/$PhCH_3$/TFA[c] (100/10/1)	<2	26	<5	30		11
C_6F_6/$PhCH_3$/TFA	<2	85	5			
CCl_4/$PhCH_3$/TFA		80	6			

[a] Toluidine isomers were not resolved. [b] The ratio of **8** to **7** was 1.1:1.0.

Table 2. Ratio of Singlet Products to Triplet Products at Various Concentrations of $PhCH_3$ in C_6F_6

[$PhCH_3$]	**(7 + 8)/6**	[$PhCH_3$]	**(7 + 8)/6**
2.00	0.06	6.60	0.60
3.47	0.16	7.16	0.74
5.71	0.37	7.82	0.96

The effects of trap dilution were studied in order to determine the spin state responsible for the dimers. Consider the mechanism proposed in Scheme 4. Because the triplet is the ground state, it follows that all of the singlet NH_2^+ that is formed in the photolysis will eventually relax to the triplet state (pathway k_{isc}) provided that the singlet is not trapped ($k_{hyd} + k_{am}$) more rapidly than the intersystem crossing event. Thus, addition of a nonreactive diluent is expected to result in greater yield of the triplet products and a lower yield of the singlet. The effects of diluting the toluene/TFA mixture are illustrated in Table 2. With C_6F_6, the yield of bibenzyl increases and the yield of the two benzyltoluene isomers is diminished. This effect increases as more diluent is added. To confirm the generality of this effect, an alternative diluent, CCl_4, was also employed. Again the yield of bibenzyl increased and the yield of benzyltoluenes decreased.

This result implies that there are at least two distinct pathways to the dimeric products. Had both the benzyltoluene isomers and bibenzyl arose through coupling of two benzyl radicals, addition of a nonreactive solvent would not be expected to have such a dramatic effect on the regiochemistry. On the other hand, this result is perfectly consistent with an alternative mechanism where the bibenzyl arises from reactions of the triplet and the benzyltoluenes are the result of singlet reactions. More specifically it is argued that singlet NH_2^+ abstracts a hydride from toluene, yielding ammonia and a benzyl cation (k_{hyd}). The latter adds to an unreacted toluene to give the benzyltoluene isomers (k_{SE}). Bibenzyl, on the other hand, is a product of the triplet state NH_2^+. We assume the latter reacts with toluene through two sequential H atom abstractions (see the results with triphenylmethane, below), giving ammonia and benzyl radicals (k_{rad} and k_{rad2}). The benzyl radicals then couple in a head-to-head fashion to give bibenzyl (k_{dim}).

The variation in product distribution with the concentration of toluene is due to the competition between hydride transfer k_{hyd} and intersystem crossing k_{isc}. This relationship is embodied in eq 1 which predicts the ratio

$$\frac{\mathbf{6}}{\mathbf{5}+\mathbf{7}+\mathbf{8}} = \frac{k_{isc2}}{k_s} + \frac{k_{isc}}{k_{hyd}[PhCH_3]} \qquad (1)$$

of the triplet product, **6**, to singlet products, **5**, **7**, and **8** (the term k_{isc2}/k_s arises from the occurrence of a parallel triplet pathway illustrated in Scheme 6 and discussed below). Using the data in Table 2 (the yield of **5** is small and is neglected), the ratio of triplet to singlet products is plotted against 1/[$PhCH_3$]. This yields a line with a slope that provides the ratio of the rate constants $k_{isc}/k_{hyd} = 31$ mol/L.

In a recent study of 2-pyrimidylnitrenium ion, Takeuchi and Watanabe[31] detected benzyltoluenes when the nitrenium was generated in the presence of toluene. They assumed that the benzyltoluenes formed from coupling of the *benzyl radical* which in turn was thought to be generated from the *triplet* state of the nitrenium ion. In their study of the parent system, benzyltoluenes and bibenzyl were all regarded as radical products and thus diagnostic for triplet behavior. The previous assignment of these products is clearly at odds with the mechanism for NH_2^+ proposed in Scheme 2. For this reason further comment on the formation of the benzyltoluenes is provided.

There is little, if any, evidence in the literature suggesting that benzyl radicals ever dimerize in a head-to-tail fashion to give benzyltoluenes. For example, when benzyl radicals are generated from the thermolysis of *tert*-butylperoxy phenylacetate, bibenzyl and *tert*-butylbenzyl ether are formed, but not benzyltoluenes.[32] Likewise, when benzyl radicals are generated through the photolysis of dibenzyl ketone, bibenzyl and CO are the exclusive products; again no benzyltoluenes were reported by any of the groups who investigated this reaction.[33,34] Photolysis of benzyl chloride in *tert*-butyl alcohol creates a mixture of benzyl radicals and benzyl cations. Again the only radical dimerization product detected was bibenzyl, and none of the benzyltoluene isomers.[35] Finally, when benzyl radicals are generated through the photolysis of phenylacetic acid, bibenzyl, but not benzyltoluenes, is formed.[36]

In contrast, the *o*- and *p*-benzyltoluenes are known to form from the attack of benzyl cation on toluene.[37] The ratio of the positional isomers depends on the method of cation generation. When the cation is complexed with the Lewis acid that was used to generate it, a relatively high proportion of the para isomer is seen. When relatively free cations are generated, ortho isomers predominate.[38] The large proportion of ortho formed in the present case implies that the benzyl cations in this case are relatively free from complexation with counterions.

The above considerations, as well as additional experiments described below, lead us to conclude that the formation of benzyltoluenes is evidence for reactions of *singlet* state nitrenium ions, rather than triplets. Bibenzyl, on the other hand, can be regarded as an indicator of radical chemistry and, by implication, reactions of a *triplet* state nitrenium ion. We do not dispute the general findings of these earlier papers, only the assignment of these particular products. In fact, where there is overlap, our experimental results confirm those of the previous

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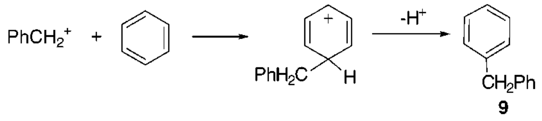
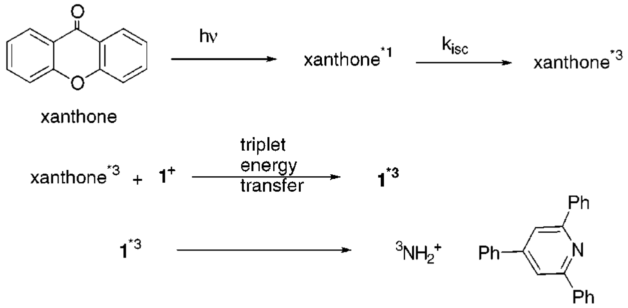
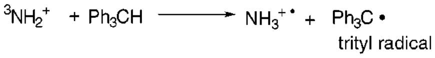
Scheme 5. Electrophilic Attack of Benzyl Cation on Benzene



Scheme 6. Triplet Sensitization



Scheme 7. Formation of the Trityl Radical



$$^3NH_2^+ + Ph_3CH \longrightarrow NH_3^{+\bullet} + \underset{\text{trityl radical}}{Ph_3C\bullet}$$

workers. Nonetheless, it is clear that the attribution of benzyltoluenes to reactions of the triplet state is based on inaccurate assumptions concerning the chemistry of benzyl radicals.

To further verify the formation of benzyl cations, we endeavored to trap them by an alternative reaction. Photolysis of **1** was therefore carried out in a 10:1 mixture of benzene and toluene. Under these conditions we detect bibenzyl, ammonia, trace amounts of the benzyltoluenes, and the toluidines. In addition we detect a new product, diphenylmethane. This is precisely the product that would be expected from reaction of the benzyl cation with benzene through an aromatic substitution process that is analogous to the formation of the benzyltoluenes (Scheme 5).[38]

Triplet-sensitized irradiation experiments were carried out as a further test of the spin selectivity model. In these experiments, the pyridinium substrate is decomposed by first irradiating a sensitizer molecule which is designed to rapidly intersystem cross to its triplet state. Excitation of **1** occurs through a triplet energy transfer mechanism whereby the triplet excited state (T_1) of $\mathbf{1}^+$ is populated in a way that bypasses the singlet manifold. It is expected that the triplet state of $\mathbf{1}^+$ will dissociate to give a triplet NH_2^+ as well as a ground-state pyridine (Scheme 6). Because the singlet state of NH_2^+ is 30 kcal/mol higher in energy than the triplet, it can be regarded as thermally inaccessible from the triplet state.

Ideally the triplet sensitization experiment is designed such that the sensitizer absorbs at wavelengths where the substrate is transparent. Unfortunately we were unable to identify a sensitizer that would both meet this requirement and at the same time possess a triplet energy high enough to effect efficient decomposition of the substrate. Xanthone provides a reasonable compromise. Its triplet energy is 72 kcal/mol, and it can be excited with wavelengths >320 nm. As can be seen in Table 1, xanthone sensitization increases the yield of the triplet product bibenzyl and decreases the yield of the singlet products toluidines and 2- and 4-benzyltoluene. Such singlet products that are formed in the triplet sensitization experiments are attributed to reactions initiated through direct absorption by **1**.

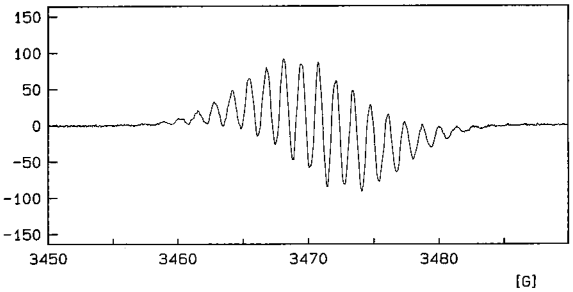


Figure 1. EPR spectrum (X-band) obtained following photolysis of 1-amino-2,4,6-triphenylpyridinium perchlorate in the presence of triphenylmethane in an N_2-purged CH_2Cl_2 solution.

In Scheme 4 it is implied that the triplet state of NH_2^+ reacts with toluene and other H atom donors through sequential H atom transfers. This is a plausible mechanism given earlier results with triplet carbenes and in one case a triplet arylnitrenium ion. To obtain experimental verification of such radical pathways, we carried out generation of NH_2^+ in the presence of a probe substrate, triphenylmethane. Abstraction of an H atom from this substrate generates a persistent radical which can be detected by EPR spectroscopy (Scheme 7).

The data shown in Figure 1 confirm the radical mechanism. Photolysis of **1** in CH_2Cl_2 containing 0.1 M Ph_3CH was carried out over a period of time. The EPR spectrum shown in Figure 1 was seen to grow in as a function of irradiation time. A good match to a digitally simulated spectrum constructed from published proton hyperfine coupling constants confirmed that this species is in fact the trityl radical.[39]

In addition to the EPR experiments, a GC analysis of the photolysis mixture was carried out. Two products were observed: the triphenylpyridine and triphenylmethanol. We attribute the latter to a hydride transfer pathway analogous to the behavior seen in toluene. The trityl cation (Ph_3C^+), being significantly more stable than the benzyl cation, does not add to substrate but instead is trapped by traces of water. Thus NH_2^+ reacts with triphenylmethane in a way that is qualitatively similar to its reactions with toluene. The singlet state abstracts a hydride to give the corresponding carbocation. The triplet abstracts a hydrogen atom to give the corresponding radical.

Singlet carbenes are well known to insert into the O−H bonds of alcohols and water. There has been some discussion of the precise mechanism. The simplest mechanism would be a concerted insertion. However, the extant evidence favors either a proton transfer followed rapidly by a combination of the carbocation and the alkoxide anion[26,40] or else complexation of the carbene with the alcohol to form an oxonium−ylide intermediate, followed by a net proton shift. The former pathway is followed by nucleophilic carbenes such as diphenylcarbene, and the latter pathway is followed by electrophilic carbenes such as carbethoxycarbene.[41,42]

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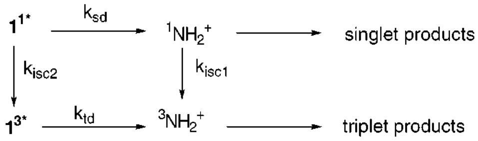
Scheme 8. OH Insertion

$$ROH + {}^1NH_2^+ \longrightarrow RONH_3^+ \qquad R= H, CH_3$$

Scheme 9. Alternate Triplet Pathway



It was of some interest to determine if the nitrenium ions would show analogous behavior. To this end **1** was photolyzed in a 1:1 CH_3CN/H_2O cosolvent mixture. Two products were detected: NH_3 and NH_2OH. The latter was determined through a spectrophotometric assay involving the reduction of an iron(III) phenanthroline complex (see Experimental Section).[43]

By analogy with carbene chemistry, it seems reasonable to assign the O−H bond insertion reaction leading to NH_2OH as a reaction of the singlet state. Experimental verification of this assignment was obtained through studies in toluene/CH_3OH mixtures (H_2O proved insufficiently miscible with toluene). Addition of methanol to toluene (50% v/v) results in the formation of CH_3ONH_2 along with bibenzyl and ammonia. The yields of the other singlet products, benzyltoluenes and toluidines, are suppressed below the detection limit (<4% yield). This is consistent with both the benzyltoluenes and the NH_2-OCH_3 arising from the same intermediate. We considered the possibility that any benzyl cations formed might be trapped by methanol to give methyl benzyl ether. Only traces (<2% yield) of this product were observed in the GC analysis. This suggests that, under these conditions, the singlet NH_2^+ is intercepted by methanol more rapidly than it is by toluene (Scheme 8).

These initial observations do not directly address the precise mechanism of O−H bond insertion. However, we note that the proton transfer/ion collapse pathway would involve an NH_3^{2+} intermediate. Electrostatic considerations alone would suggest that this a high-energy pathway. Therefore, we favor initial complexation of the nitrenium ion with the alcohol followed by deprotonation of the oxonium cation intermediate.

Interestingly, the yields of the triplet products, bibenzyl and NH_3, are not significantly diminished when the additional singlet trap is added. This suggests that there is an alternative pathway to the triplet NH_2^+ that does not pass through the singlet state of NH_2^+. We suggest that this alternate pathway involves intersystem crossing in the excited state of **1**. This would generate the triplet excited state of **1** which is expected to dissociate, giving the triplet state of NH_2^+. The yields of triplet products which arise through this pathway ought to be insensitive to the presence of traps for the singlet nitrenium ion (Scheme 9).

Conclusions

The solution chemistry of the parent nitrenium ion NH_2^+ can be understood on the basis of spin-selective reactivity. The higher energy singlet state abstracts hydride from toluene and triphenylmethane giving ammonia and the corresponding carbocations. Singlet NH_2^+ is also capable of reacting with water and methanol through a net O−H insertion reaction. The triplet state of NH_2 decays primarily through sequential H atom abstractions giving NH_4^+ as the stable product.

Experimental Section

1-Amino-2,4,6-triphenylpyridinium perchlorate 1 was prepared according to the procedures described by Katritzky et al.[44,45] 1-(2-Pyridyl)-2,4,6-triphenylpyridinium perchlorate (4.9 g, 0.01 mol), hydrazine hydrate (5 g, 0.15 mol), and 50 mL of ethanol were refluxed for 4 h. A precipitate separated on cooling and was recrystallized from ethanol to give the perchlorate **1** (3.6 g, 85%), mp 161−163 °C. IR spectrum matched that reported previously.[45] ^1H NMR (CD_3CN) 8.00 7.25 (17 H, m), 5.50 (2H, s). 1-(2-Pyridyl)-2,4,6-triphenylpyridinium perchlorate was prepared by combining 2-aminopyridine with 2,4,6-triphenylpyrylium perchlorate.

Photolysis of 1. This photoprecursor (100 mg) was dissolved in 10 mL of CH_3CN and irradiated for 120 min. The mixture was analyzed by GC chromatography for product distributions. GC conditions under which analyses were done are as follows: Column was 18 M capillary column loaded with 5% OV-1. Oven temperature: 300 °C. Retention times: toluidines, 4.2 min (under our conditions all of the toluidine isomers coelute); bibenzyl, 15.3 min; 2-benzyltoluene, 15.6 min; 4-benzyltoluene, 15.8 min The procedure followed to determine dissolved ammonia relies on the blue complex formed by the reaction of phenoxide ion with ammonia.[30] The photolysis mixture was neutralized using 5 mL of a 1 M sodium hydroxide solution, and the aqueous layer was extracted. To 1.5 mL of the aqueous layer were added added 0.65 mL of bleach and 5 mg of phenol. After 10 min, the absorption maximum was measured at 625 nm. Using the known absorption coefficient of the complex (8320 M^{-1} cm^{-1}), the concentration was calculated. Hydroxylamines were estimated by their reaction with iron(III) 1,10-phenanthroline to form a red complex.[43] The photolysis mixture was neutralized with 1 mL of a 1 M sodium acetate solution. To this solution were added 0.5 mL of 0.01 M $Fe_2(SO_4)_3$ and 0.5 mL of a 0.01 M 1,10-phenanthroline solution. The resulting solution was filtered, and the absorption maximum was measured at 508 nm.

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