radiation on a computer-controlled diffractometer (Siemens AED). Crystal data: $a = 6.5497$ (5), $b = 12.654$ (1), $c = 13.887$ (2) Å; $\beta = 101.902$ (8); $V = 1126.2$ Å^3; space group $P2_1/c$; $Z = 4$; $M_r = 224.22$; $d_c = 1.32$ g cm^{-3}. With a crystal of the dimensions 0.27 × 0.30 × 0.57 mm^3 mounted on the diffractometer 2711 independent reflections were recorded for $\sin\theta/\lambda \leq 0.664$ Å^{-1} with graphite-monochromated Mo Kα radiation. A total of 1086 reflections were treated as unobserved ($F_o^4/[\sigma(F_o^2)]^2 < 7$). Lorentz and polarization corrections were applied, and absorption effects were neglected.

The crystal structure was solved by direct methods with the program MULTAN.[9] The positions of the hydrogen atoms were calculated according to geometrical requirements or were found by a difference Fourier synthesis. After several least-squares refinement cycles in the full-matrix procedure with isotropic temperature parameters for the hydrogen atoms and anisotropic temperature parameters for the carbon and oxygen atoms we obtained a final R values of 0.05 (excluding unobserved reflections) and 0.06 (unobserved reflections included); $R = \sum|kF_o - |F_c||/\sum kF_o$. In the last refinement cycle 297 unobserved reflections were included ($|F_c| > kF_o$). Three of the strongest reflections affected by extinction were assigned zero weight. The final positional coordinates of the atoms are listed in Table I. Further information is given in the supplementary material. The scattering factors were obtained from the literature.[10] The computations were carried out in the computer center (IBM 370/168) at the University of Heidelberg.

Acknowledgment. We acknowledge financial support by the Deutsche Forschungsgemeinschaft, Bad Godesberg, by the the Fonds der Chemischen Industrie, Frankfurt, and by the National Science foundation.

Registry No. I, 1573-17-7; II, 82903-05-7; III, 82903-06-8; IV, 82903-07-9; V, 78998-60-4; VI, 78998-59-1; VII, 78998-61-5; VIII, 82903-08-0; IX, 78998-62-6; X, 82903-09-1; XI, 82917-45-1; XII, 78998-58-0; XIII, 81710-08-9; XIV, 82903-10-4; XVa, 82903-11-5; XVb, 82903-12-6; XVIa, 82903-13-7; XVIb, 82903-14-8; ethyl diazoacetate, 623-73-4; dirhodium(II) tetraacetate, 15956-28-2; *tert*-butyl diazoacetate, 35059-50-8; oxalyl bromide, 15219-34-8.

Supplementary Material Available: Thermal parameters for compound XII and a table of some short intramolecular contacts (2 pages). Ordering information is given on any current masthead page.

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(9) J. P. Declerq, G. Germain, P. Main, M. M. Woolfson, *Acta Crystallogr., Sect. A*, **A29**, 231 (1973).

(10) J. A. Ibers and W. C. Hamilton, Eds., "International Tables of X-ray Crystallography", Kynoch Press, Birmingham, 1974, Vol. IV.

Photocleavage of Diarylnitrosamines in Neutral Media

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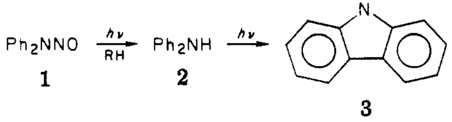
N-Nitrosodiphenylamine, *N*-nitroso(2-nitrophenyl)phenylamine, *N*-nitroso(3-methylphenyl)phenylamine, and *N*-nitrosocarbazole were irradiated in degassed neutral solution to give the corresponding diarylamine as the initial photoproduct. The effects of changing solvents, concentrations, and substituents and of adding catalysts were examined. Quantum yield studies, sensitization work, and ESR studies were used to study the mechanism of this photolysis.

The early reports[5] of low photoreactivity for nitrosamines in the absence of acid catalysts led to extensive studies on the acid-catalyzed photoreactions.[6] Although a few compounds[7-9] were reported to be photolabile in the absence of acid, there was no study of the efficiency of the uncatalyzed photoreactions. We began investigating the efficiency of the uncatalyzed photoreactions of diarylnitrosamines in order to clarify their mechanisms and to perhaps better understand the relationships between the excited states in these molecules. We note that *N*-nitrosodiphenylamine (**1**) has been found to be only weakly carcinogenic[10a,b] after extensive studies.[10c]

Exploratory Photochemical Results

Our initial studies[11] showed that **1** was converted to diphenylamine (**2**) on Pyrex-filtered irradiation in deoxygenated neutral solution (see Table I) as had been previously reported.[7] The production of **2** showed a clear solvent dependence in that more of the amine **2** was produced in solvents of better hydrogen-donating ability. Catalytic amounts of both thiol and proton acid also increased the amine production. Extended irradiation gave the expected secondary photoproduct carbazole (**3**).[12] If



1 **2** **3**

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[3] Research Corp. Undergraduate Fellow.

[4] Loyola University Dissertation Fellow, 1979–1980.

[5] (a) Burgess, E. M.; Lavinish, J. M. *Tetrahedron Lett.* **1964**, 1221. (b) Chow, Y. L. *Can. J. Chem.* **1967**, *45*, 53. (c) Bamford, C. H. *J. Chem. Soc.* **1939**, 12.

[6] Chow, Y. L. *Acc. Chem. Res.* **1973**, *10*, 354 and references therein.

[7] Tanikaga, R. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 210.

[8] Axenrod, T.; Milne, G. W. A. *Tetrahedron* **1968**, *24*, 5775.

[9] Jakubowski, E.; Wan, J. K. S. *Mol. Photochem.* **1973**, *5*, 439.

[10] (a) Cardy, R. H.; Lijinsky, W.; Hildebrandt, P. R. *Ecotoxicol. Environ. Saf.* **1979**, *3*, 29. (b) Schuman, R. F.; Lebherz, W. B.; Pienta, R. *Carcinogenesis* (*London*) **1981**, *2*, 679. (c) "Survey of Compounds Which Have Been Tested for Carcinogenic Activity 1961–1967"; DHEW Publ. No. (NIH) 73-35, Acc No. 450, p 493.

[11] (a) Crumrine, D. S.; Nabor, P.; Padleckas, H. "Abstracts of Papers", 169th National Meeting of the American Chemical Society, Philadelphia, PA, 1975; American Chemical Society: Washington, DC, 1975; ORGN 104. (b) Crumrine, D. S.; Dombrowski, P.; Haberkamp, T. J.; Kekstas, R. J.; Nabor, P.; Nomura, G. S.; Padleckas, H.; Suther, D. J. "Abstracts of Papers", 174th National Meeting of the American Chemical Society, Chicago, IL, 1977; American Chemical Society: Washington, DC, 1977; ORGN 21.

[12] (a) Forester, E. W.; Grellmann, K. H.; Linschitz, H. *J. Am. Chem. Soc.* **1973**, *95*, 3108. (b) Shizjka, H.; Takayama, Y.; Tanaka, I.; Morita, T. *Ibid.* **1970**, *92*, 7270.

0022-3263/82/1947-4246$01.25/0

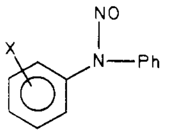
Table I. Pyrex-Filtered Hanovia Photolyses (10^{-3} M, 1.5-2 h)

ArAr'NNO	solvent/additive	mmol of NNO	% recovd NNO	% amine	% other
DPH[a]	benzene	0.505	82	20	
DPH	acetone	0.500	63	35	6 (Cb)[b]
DPH	ether	0.506	18	52	33 (Cb)
DPH	methanol	0.496	73	22	
DPH	methanol/10^{-2} M Isop[c]	0.510	89	11	
DPH	methanol/10^{-2} M RSH[d]	0.510	0	22	69 (Cb)
2-NO_2	benzene	0.405	56	43	
2-NO_2	acetone	0.426	69	36	
2-NO_2	ether	0.423	15	82	
2-NO_2	methanol	0.413	78	24	
2-NO_2	methanol/10^{-2} M RSH[d]	0.436	65	33	
3-Me	methanol	0.490	64	28	
3-Me	methanol	0.474	71	20	
Cb[b]	benzene	0.521	71	18	1.2 (DiCb)[e]
Cb	acetone	0.521	23	51	8.3 (DiCb)
Cb	ether	0.519	15	55	16 (DiCb)

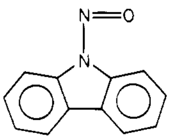
[a] DPH = diphenylamine. [b] Cb = carbazole. [c] Isop = isoprene. [d] RSH = *t*-dodecanethiol. [e] DiCb = *N*,*N'*-dicarbazole.

the solution was not well degassed, other products began to appear as had been previously reported,[7] but this was not studied further.

The substituted compounds *N*-nitroso(2-nitrophenyl)-phenylamine (**4**) and *N*-nitroso(3-methylphenyl)phenylamine (**5**) and *N*-nitrosocarbazole (**6**) were also studied.



4, X = 2-NO_2
5, X = 3-Me



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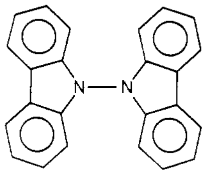

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In each case, the initial photoproduct was the corresponding amine. Although some *N*,*N'*-dicarbazole (**7**)[13] was found when *N*-nitrosocarbazole was irradiated, none of the corresponding tetraarylhydrazine (**8**)[14] was found when either **1** or **5** was irradiated. These results are shown in Table I.

Mechanistic Results

Quantum yield studies were run to low conversions using standard techniques and HPLC analysis (see Experimental Section). The values for the quantum yield of amine production are reliable to ±10% and are an average value from several reliable runs. The greatest experimental problem was the removal of residual acid from the photolysis cell after actinometry. Actinometry and sample irradiations could not be done in the same cell, since the residual acid varied depending on the method of washing, and thus the quantum yield values varied. Reliable work necessitated distilling the solvents through base-washed glassware, washing the cell with concentrated ammonia and then water before each run, and careful nitrogen degassing. The values for the quantum yield of nitrosamine disappearance were not reliable since they involved the measurement of a very small change in a very large peak area and thus showed significant scatter for duplicate injections. The quantum yield values are summarized in Table II, and more detail is shown in the Experimental Section.

Table II. Quantum Yields of Diarylamine Production at 313 nm

ArAr'-NNO	10^4[NNO], M	solvent/addition	ϕ of NH form
DPH[a]	12.1	MeOH	0.020
DPH	1.17	MeOH	0.049
DPH	0.226	MeOH	0.091
DPH	1.17	MeOH/366 nm	0.039
DPH	11.7	MeOH/H^+[b]	0.093
DPH	1.57	MeOH/RSH[c]	0.10
DPH	5.38	MeOH/Sens/270 nm	0.016
DPH	14.9	ether	0.0095
DPH	4.2	ether	0.097
2-NO_2	3.33	ether	0.0056
2-NO_2	0.99	MeOH	0.0055
2-NO_2	3.22	MeOH/H^+[b]	0.018
2-NO_2	0.99	MeOH/RSH[c]	0.0048
2-NO_2	3.17	acetone/H^+[b]	0.015
2-NO_2	3.08	benzene	0.0047
3-Me	1.15	MeOH	0.028
3-Me	1.11	ether	0.075
Cb[a]	1.1	benzene	0.014
Cb	1.15	MeOH	0.014
Cb	1.02	MeOH/366 nm	0.040

[a] DPH = diphenylamine; Cb = carbazole. [b] Cell rinsed with acid then with water and dried before using. [c] 1 × 10^{-3} M in *t*-dodecanethiol.

There is a very clear concentration effect here in both methanol and ether, and it probably has to do with self-quenching. The addition of thiol or proton catalysts increased the cleavage efficiency but only to about 10%. Sensitization by 4-methoxyacetophenone (**9**) gave very inefficient amine production. If the observed quantum yield value of 0.016 is corrected for 11% direct light absorption by **1** and a value of 0.04 for the direct quantum yield is used, the maximum sensitized quantum yield is 0.012. No quantum yield is reported for benzene solvent because the tailing of solvent benzene on the HPLC column was too large.

The irradiation of the methyl derivative **5** showed a slightly decreased efficiency of amine production. The irradiation of nitrosocarbazole **6** showed both diminished cleavage efficiency and a wavelength effect which will receive more study in the future with a laser. The irradiation of the 2-nitro compound **4** was much more interesting. The cleavage efficiency was greatly diminished in neutral solution and showed some increase on the addition of acid but was even more diminished on the addition of thiol. This is obviously quite different from the parent system.

Clearly, the triplet state does not cleave efficiently. Sensitization of the parent case showed little cleavage and nitro substitution, which is known to increase intersystem crossing,[15] decreased the cleavage efficiency by an order

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(13) Perkin, W. H.; Tucker, S. H. *J. Chem. Soc.* **1921**, 218.

(14) (a) Musso, H. *Chem. Ber.* **1959**, *92*, 2881. (b) Wieland, H.; Gambarjan, S. *Ibid.* **1906**, *39*, 1499.

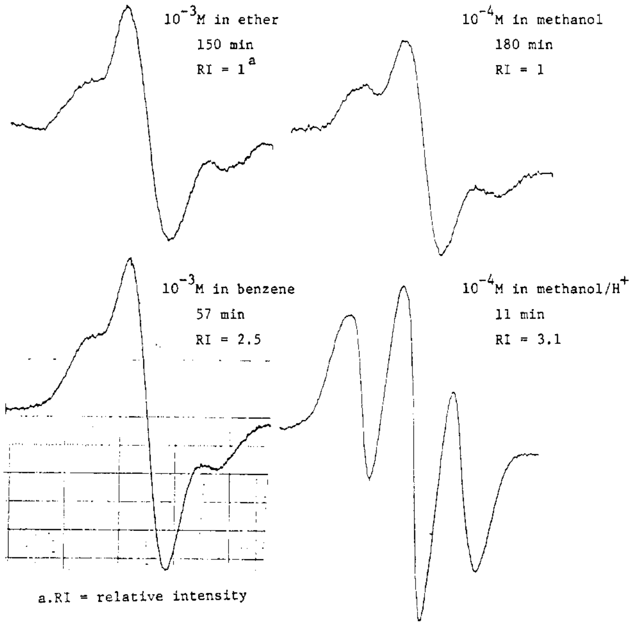


Figure 1. ESR spectra of radicals from *N*-nitrosodiphenylamine at 77 K.

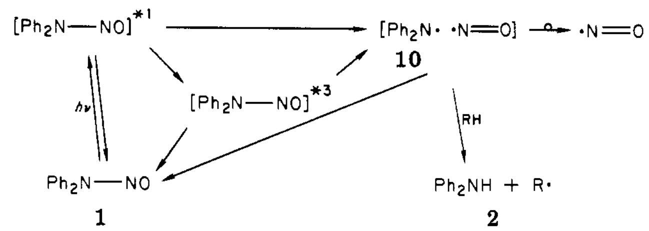
of magnitude. Moreover, the addition of thiol did not increase the cleavage efficiency but actually decreased it in the 2-nitro case. The thiol was perhaps acting as a quencher[16] of the *N*-nitroso(2-nitrophenyl)phenylamine triplet state even at these concentrations.

Although no fluorescence was observed at higher concentrations (10^{-3} M or greater) in agreement with another report,[17] a small amount did appear at lower concentrations and increased with irradiation time. The spectrum of this emission matched that from the product amine. Thus we ascribe the observed weak luminescence to fluorescence from the amine photoproduct. Fluorescence was seen from all the amines except (2-nitrophenyl)phenylamine. Here the increased intersystem crossing rate[15] caused decay of the singlet before appreciable fluorescence could occur.

Nitrosodiphenylamine (**1**) quenched naphthalene fluorescence, but no rate could be determined because the n,π^* tail of **1** overlapped the naphthalene absorption. At concentrations of 5×10^{-4} M in ethanol glass with 270-nm excitation, about 58% of the phosphorescence from **9** was quenched by **1**. This is corrected for direct light absorption by **1**. The use of 5×10^{-4} M **1** and 9.5×10^{-4} M **9** permitted about 89% of the light to be directly absorbed by the sensitizer **9** in the previously mentioned sensitization experiment.

Some ESR experiments were run to examine the expected[6] radical intermediates. No signal was seen without irradiation, and no signal was seen in benzene or ether until the sample was cooled to 77 K. With methanol as the solvent, the probe could not be tuned until it had been cooled to 77 K. In the absence of acid, it took longer to get a reasonable signal, and less signal was produced in the better hydrogen-donating solvents such as methanol and ether. After the addition of hydrochloric acid to the sample in methanol solution, a better defined but strikingly similar signal was produced some 15 times faster. It did not, however, show coupling with a hydrogen on the nitrogen as one would have expected for an aminium radical cation[6] (see Figure 1).

Scheme I. Mechanism of *N*-Nitrosodiphenylamine Photolysis



We interpret these signals as a nitrogen triplet derived from the diphenylamino radical (**10**).[18] Some previous attempts to generate this radical at 77 K by irradiation of tetraphenylhydrazine produced a triplet pair of caged radicals as demonstrated by a half-field signal at 1650 G. Recent[19] work indicates that annealing the matrix containing the radical pair at 119 K produced the same spectrum that we assign to **10**. They also photolyzed **1** to produce the same spectrum at 77 K. Most of the recent work on diphenylamino radicals has been done in fluid solution where all the hyperfine couplings can be measured and is not comparable to these spectra.

It has been recently suggested[20] that nitroxyl radicals are intermediates in the photolysis of dialkylnitrosamines. These nitroxyl radicals are thought to be formed by photochemical oxidation since the amount of formation is dependent on the amount of degassing that was done. Our samples were well degassed, so we are hesitant to assign these signals to a diphenylnitroxyl radical.[21a] This would, however, offer an alternate explanation to the lack of a proton coupling in the presence of acid.[21b] More work is currently being done to clarify this.

Discussion

Thus we find that the diarylnitrosamines do cleave in neutral media with reasonable (5%) efficiency, but acid increases that efficiency to about 10%. The simplest mechanism for the photolysis involves formation of the lowest energy singlet followed by cleavage to a diphenylamino radical (**10**) and nitric oxide held in a tight cage. Loss of the nitric oxide followed by abstraction of a hydrogen from solvent completes the cycle. The sensitization work showed little triplet cleavage for the diphenyl case, and the use of added acid or thiol suggested that 10% is the maximum cleavage efficiency. Thus the cleavage must be occurring from the singlet excited state in competition with intersystem crossing. About 90% of the excitation is lost either by direct decay of the singlet or by intersystem crossing to the unreactive triplet which then decays by a variety of rotational and vibrational modes to the ground state. Experimental quantum yield values of less than 10% represent radical recombination which occurs in competition with loss of nitric oxide from the cage. The addition of either thiol or acid decreased the radical recombination rate, and gave, in both cases, about 10% quantum efficiencies of amine production. This mechanism is shown below in Scheme I.

The methyl derivative **5** photolyzed to the corresponding amine somewhat less efficiently probably because the

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(15) Morrison, H. A. "The Chemistry of the Nitro and Nitroso Groups"; Patai, S., Ed.; Wiley-Interscience: New York, 1969; p 165.

(16) Guttenplan, J. B.; Cohen, S. G. *J. Org. Chem.* **1973**, *38*, 2001.

(17) Bunce, N. J. *Chem. Phys. Lett.* **1978**, *59*, 66.

(18) (a) Neugebauer, F. A.; Bamberger, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 71. (b) Shida, T.; Kira, A. *J. Phys. Chem.* **1967**, *13*, 241. (c) Wiersma, D. A.; Kommandeur, K. *Mol. Phys.* **1967**, *13*, 241.

(19) Murai, H. Tokyo Institute of Technology, private communication.

(20) Yang, G. C.; Joshi, A. *Org. Magn. Res.* **1981**, *17*, 138.

(21) (a) Strom, E. T.; Bluhm, A. L.; Weinstein, J. *J. Org. Chem.* **1967**, *32*, 3853. (b) Malatesta, V.; Ingold, K. V. *J. Am. Chem. Soc.* **1973**, *95*, 6404.

Table III. Quantum Yield Determinations of Diarylamine Production at 313 nm

PhArNNO	solvent/additive	mg of NNO	10^4[NNO], M	mg (μmol) of amine	% conv	μmol of light absd	ϕ of NH form
DPH	MeOH	6.01	12.1	0.176 (1.04)	3.3	52.0	0.020
DPH	MeOH	0.58	1.17	0.048 (0.284)	9.7	5.84	0.049
DPH	MeOH	0.113	0.226	0.0092 (0.054)	9.6	0.60	0.091
DPH	MeOH/366 nm	0.58	1.17	0.038 (0.225)	7.7	5.8	0.039
DPH	MeOH/H^+ [a]	5.8	11.7	0.149 (0.88)	3.0	9.45	0.093
DPH	MeOH/RSH [b]	0.78	1.57	0.049 (0.29)	7.3	2.8	0.103
DPH	MeOH/sens [c] 270 nm	2.67	5.38	0.037 (0.219)	1.6	13.3	0.016
DPH	ether	7.39	14.9	0.00586 (0.00346)	0.49	3.65	0.0095
DPH	ether	2.5	4.2	0.0416 (0.21)	1.7	2.16	0.097
2-NO_2	ether	2.43	3.33	0.088 (0.41)	4.1	72.6	0.0056
2-NO_2	MeOH	0.60	0.99	0.0088 (0.041)	1.7	7.5	0.0055
2-NO_2	MeOH/H^+ [a]	2.35	3.22	0.149 (0.696)	7.2	39.2	0.018
2-NO_2	MeOH/RSH [b]	0.60	0.99	0.018 (0.082)	3.3	17.1	0.0048
2-NO_2	acetone/H^+ [a]	2.31	3.17	0.065 (0.303)	3.2	20.0	0.015
2-NO_2	benzene	2.24	3.08	0.32 (0.149)	16	32.0	0.0047
3-Me	MeOH	0.611	1.15	0.026 (0.142)	4.9	51.1	0.028
3-Me	ether	0.592	1.11	0.032 (0.175)	6.3	23.3	0.075

[a] Cell rinsed with acid and water then dried. [b] 1×10^{-3} M in *t*-dodecanethiol. [c] 9.48×10^{-4} M in 4-methoxyacetophenone.

methyl destabilized the radical intermediate. The cleavage of *N*-nitrosocarbazole (**6**) is less efficient than that of the parent and thus could not be an intermediate in carbazole formation from **1**. The wavelength effect is real although we have no simple explanation for it yet. Work is continuing on this.

The 2-nitro nitrosamine **4** is clearly different. Since there was no fluorescence from (2-nitrophenyl)phenylamine and since the efficiency of diarylamine formation is so much lower, it is probable that most of the excitation is decaying to a relatively unreactive triplet. Added acid did increase the efficiency up to about 1%, but this value is much less than for the unsubstituted case. Since there was a slight decrease in the quantum yield on addition of thiol, there may be some triplet cleavage that was partially quenched by the added thiol. However, the work on both the parent **1** and the 2-nitro compound **4** suggested that triplet cleavage is less important than singlet cleavage.

The lack of either reaction or luminescence from the n,π^* singlet of the nitroso group is very interesting, and we are studying the intersystem crossing efficiencies of a variety of nitroso compounds.

Experimental Section[22]

Compounds. *N*-Nitrosodiphenylamine, diphenylamine, (2-nitrophenyl)phenylamine, and carbazole were available from Eastman Kodak. The (3-methylphenyl)phenylamine was obtained from Aldrich. The other nitrosamines were synthesized by nitrosation in glacial acetic acid[23] to give the following: *N*-nitrosocarbazole, mp 80–81 °C (lit.[23] mp 82 °C); *N*-nitroso(2-nitrophenyl)phenylamine, mp 99–100 °C (lit.[24] mp 99–100 °C), and *N*-nitroso(3-methylphenyl)phenylamine [mp 64–65 °C; IR (Nujol) 1450 cm^{-1} (N—N=O str); ^{1}H NMR ($CDCl_3$, δ 6.7–7.5 (9 H, Ar H), 2.36 (3 H, CH_3). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70. Found: C, 73.57; H, 5.89]. Tetraphenylhydrazine [mp 144–145 °C (lit.[14b] mp 144–145 °C] and *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)hydrazine (mp 112–114 °C) were synthesized by oxidation of the corresponding diarylamine with potassium permanganate in acetone.[14b]

Hanovia Photolyses. All *N*-nitrosodiaryl compounds were chromatographed on Florisil and recrystallized the day before photolyses were done. A ca. 100-mg sample was dissolved in 500 mL of distilled solvent in a Hanovia well, degassed with a stream of nitrogen for 45 min, and irradiated with a Pyrex-filtered 400-W Hanovia lamp for 1.5–2 h with a slow stream of deoxygenated nitrogen. An aliquot was removed for HPLC analysis, and the remainder was concentrated in vacuo (temperature <30 °C) and chromatographed on a slurry packed Florisil column (ca. 1 × 40 cm) with collection of 50-mL fractions. Elution with hexane generally afforded the diarylamine while 2–5% ether in hexane gave the starting diarylnitrosamine.

Quantum Yields. Quantum yield studies were run to low conversions (<10%) by using ferrioxalate actinometry,[25] a Bausch and Lomb HPO-200 lamp, and reversed-phase (C-18, 37–50-μm beads, MeOH/water) HPLC analysis with the internal standard added after the irradiation was completed. Duplicate injections were made for each run without sample concentration, and the average value was reported. Light absorption was corrected for transmitted light with an actinometry cell placed behind the sample cell. The sample cell was carefully washed with concentrated ammonia and then with water and finally dried before a run. The sample cell was never used for actinometry. Solvents were distilled through base-washed glassware. The reported values for the quantum yield of amine production are the average of at least two runs and are reproducible to ±10%. The results are summarized in Table II and are detailed in Table III.

Fluorescence and Phosphorescence Spectra. All luminescence spectra were run on an Aminco-Bowman spectrofluorimeter using quartz cells or quartz tubes. The phosphorescence studies were done at 77 K in a quartz Dewar flask with a rotating shutter.

ESR Spectra. The ESR spectra were run on a Varian V-line X-band spectrometer operating at 9.505 MHz and 3.395 G and using a quartz liquid nitrogen Dewar flask inserted in a rectangular cavity. The degassed sample was contained in a 4-mm quartz tube and was irradiated at 313 nm with the Bausch and Lomb 200-W lamp and monochromator. Samples were repetitively scanned, and the last spectra of several series are shown in Figure 1.

Acknowledgment. We thank the Research Corp., the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation Undergraduate Research Program, and the Loyola University Research Committee for support of this research. We thank Micro-Tech Laboratories, Skokie, IL, for the elemental analyses.

Registry No. **1**, 86-30-6; **4**, 21565-15-1; **5**, 82880-43-1; **6**, 2788-23-0; *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)hydrazine, 82880-44-2.

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(22) All melting points are corrected. The IR spectra were run on a Beckman Acculab 1. NMR spectra were recorded on a Varian EM-360 with Me_4Si as an internal standard. All HPLC work was done on a Waters ALC-202 with a 5000-psig pump with a 254-nm UV detector calibrated with internal standards.

(23) Wieland, H.; Susser, A. *Justus Liebigs Ann. Chem.* **1912**, *392*, 169.

(24) Fischer, P. *Chem. Ber.* **1891**, *24*, 3785.

(25) (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, 235, 518. (b) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 783.