Photophysics and Photochemistry of Intramolecular Stilbene−Amine Exciplexes

Frederick D. Lewis,*,† Dario M. Bassani,† Eric L. Burch,† Bliss E. Cohen,† Jeffrey A. Engleman,† G. Dasharatha Reddy,† Siegfried Schneider,*,‡ Wighard Jaeger,‡ Peter Gedeck,‡ and Michael Gahr‡

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, and Institüt fur Physikalische und Theoretische Chemie, Universität Erlangen-Nürnberg, D-8520 Erlangen, Germany

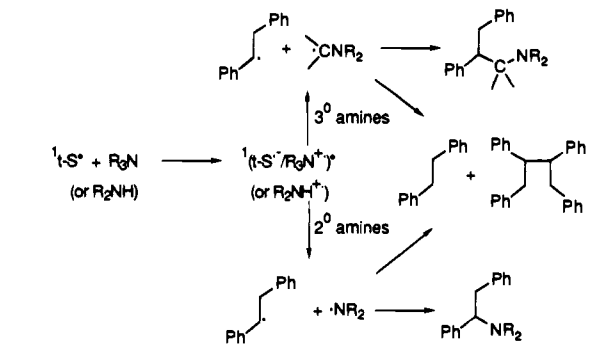
Received August 9, 1994[⊗]

Abstract: The photophysical and photochemical behavior of a series of *trans*- (aminoalkyl)stilbenes in which a primary, secondary, or tertiary amine is appended to the stilbene ortho position with a methyl, ethyl, or propyl linker has been investigated. The tertiary (aminoalkyl)stilbenes form fluorescent exciplexes and undergo trans−cis isomerization, but fail to undergo intramolecular reactions analogous to intermolecular addition reactions observed for stilbene with tertiary amines. The photophysical behavior of the tertiary (aminoalkyl)stilbenes is dependent upon the choice of linker, solvent, and temperature. The secondary (aminoalkyl)stilbenes do not form fluorescent exciplexes but undergo intramolecular N−H addition to the stilbene double bond. Unlike the intermolecular reactions of substituted stilbenes with secondary amines, which yield mixtures of regioisomeric adducts and reduction products, the intramolecular reactions are highly selective, providing an efficient method for the synthesis of tetrahydrobenzazepines. Direct irradiation of the primary (aminoalkyl)stilbenes results only in trans−cis isomerization. However, irradiation in the presence of the electron acceptor *p*-dicyanobenzene results in regioselective intramolecular N−H addition to the stilbene double bond. These results are discussed in terms of the mechanisms of direct and electron-transfer-sensitized irradiation.

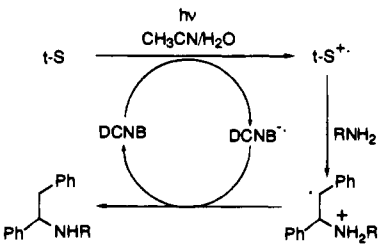
Introduction

The interactions between singlet *trans*-stilbene (*t*-S) and ground state amines have been extensively investigated.[1−6] Quenching of *t*-S* by triethylamine and other tertiary aliphatic amines in nonpolar solvents yields fluorescent, chemically unreactive exciplexes. Increasing solvent polarity results in a decrease in the exciplex fluorescence intensity and lifetime and the appearance of stilbene−amine adducts along with stilbene reduction products. The mechanism proposed for adduct formation is outlined in Scheme 1. Electron-transfer quenching in polar solvents yields a radical ion pair which undergoes α-C−H proton transfer from the amine cation radical to the stilbene anion radical to form a radical pair, which is the precursor of the observed products. Quenching of *t*-S* by diethylamine and other secondary aliphatic amines is not accompanied by exciplex fluorescence, but results in adduct formation in both nonpolar and polar solvents. Electron transfer followed by N−H proton transfer has been proposed as the mechanism for radical pair formation (Scheme 1). The fluorescence of *t*-S* is not quenched by primary aliphatic amines, presumably due to their high oxidation potentials.

Scheme 1



Scheme 2



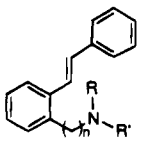
While direct irradiation of stilbene with primary amines fails to yield stilbene−amine adducts, Yasuda and co-workers[7] have observed that the addition of ammonia or primary amines to stilbene can be effected by means of dicyanobenzene (DCNB) sensitized irradiation in polar solvents. The proposed mechanism for sensitized addition is outlined in Scheme 2. Electron-transfer quenching of DCNB* by *t*-S (or vice versa) yields the *t*-S cation radical (*t*-S$^{\bullet+}$). Nucleophilic addition of ammonia

† Northwestern University.
‡ Universität Erlangen-Nürnberg.
⊗ Abstract published in *Advance ACS Abstracts*, December 15, 1994.

(1) (a) Lewis, F. D. *Adv. Photochem.* **1986**, *13*, 165. (b) Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401.
(2) Kawanisi, M.; Matsunaga, K. *J. Chem. Soc., Chem. Commun.* **1972**, 313.
(3) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991.
(4) Lewis, F. D.; Simpson, J. T. *J. Phys. Chem.* **1979**, *83*, 2015.
(5) Hub, W.; Schneider, S.; Dörr, F.; Oxman, J. D.; Lewis, F. D. *J. Am. Chem. Soc.* **1984**, *106*, 708.
(6) Mai, J.-C.; Lin, Y.-C.; Ho, T.-I. *J. Photochem. Photobiol., A* **1990**, *54*, 299.
(7) (a) Yasuda, M.; Kubo, J.; Shima, K. *Heterocycles* **1990**, *31*, 1007. (b) Yamashita, T.; Shiomori, K.; Yasuda, M.; Yasuda, M.; Shima, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 366. (c) Yasuda, M.; Isami, T.; Kubo, J.; Mizutani, M.; Yamashita, T.; Shima, K. *J. Org. Chem.* **1992**, *57*, 1351.

0002-7863/95/1517-0660$09.00/0

Chart 1



R	R'	n=1	n=2	n=3
H	H	1°S1	1°S2	1°S3
Me	H	2°S1	2°S2	2°S3
Me	Me	3°S1	3°S2	3°S3

or the primary amine to *t*-S$^{\bullet+}$ followed by proton- and electron-transfer steps yields the adduct and regenerates the electron-transfer sensitizer. This reaction is a variation of the electron-transfer-sensitized addition of nucleophiles to terminal arylolefins originally investigated by Arnold and co-workers.[8] Whereas the cation radicals of terminal arylolefins react with a variety of nucleophiles,[9] the delocalized stilbene cation radical reacts only with strong nucleophiles such as amines.

Our recent investigations of inter- and intramolecular styrene–amine exciplexes have demonstrated that their behavior is highly dependent upon the length of the polymethylene chain connecting the two chromophores and its point of attachment to the styrene chromophore.[10] These observations prompted a collaborative investigation of the photochemical behavior of the *o*-(aminoalkyl)stilbenes whose structures are indicated in Chart 1. We find that the tertiary (aminoalkyl)stilbenes form fluorescent exciplexes which display interesting chain-length-, solvent-, and temperature-dependent photophysical behavior, but are chemically nonreactive. The secondary (aminoalkyl)-stilbenes undergo intramolecular photoamination upon either direct or electron-transfer-sensitized irradiation, while the primary (aminoalkyl)stilbenes undergo intramolecular photoamination only upon electron-transfer-sensitized irradiation.[11] These reactions provide an efficient and highly regioselective method for the construction of tetrahydrobenzazepines and tetrahydroisoquinolines. Mechanistic and synthetic aspects of these reactions are discussed.

Results and Discussion

***o*-Methylstilbene.** The model selected for the stilbene chromophore of the (aminoalkyl)stilbenes is *o*-methylstilbene (MS). The photophysical behavior of MS has not previously been investigated. Its absorption and emission maxima (294 and 354 nm, respectively) are similar to those of *t*-S (299 and 350 nm). The fluorescence spectrum of MS in methylcyclohexane solution displays a structure similar to that of *t*-S, and its decay is single exponential over an extended temperature range (110–300 K). Thus, we conclude that MS exists predominantly as a single rotamer, unlike its meta isomer which exists as a mixture of s-trans and s-cis rotamers.[12] The MS rotamer in which the styryl substituent is s-trans with respect to the methyl group should be favored energetically.[13] The fluorescence quantum yield and lifetime of MS in hexane solution at room temperature (Φ_{fs} = 0.045 and τ_s = 0.10 ns) are similar to the values for *t*-S (0.050 and 0.11 ns).[14] Plots of Φ_{fs} and τ_s vs temperature for MS in methylcyclohexane are shown in Figure 1. The value of τ_s continues to increase below the glass transition temperature (147 K), whereas the change in optical properties upon glass formation makes it impossible to compare values of Φ_f in solution vs the glass. The increase in Φ_{fs} and τ_s with decreasing temperature in methylcyclohexane solution is similar to that for *t*-S reported by Sharafi and Muszkat[15] and by Sumitani et al.,[16] respectively. An Arrhenius plot of $\tau_s^{-1} - k_f$ vs T^{-1} (200–300 K) provides an activation energy slightly lower than that for isomerization of *t*-S (2.84 kcal/mol vs 3.53 kcal/mol) and a preexponential slightly smaller than that for *t*-S (1.08×10^{12} vs 3.98×10^{12}) in hexane solution.[14] The smaller E_a for MS vs *t*-S may reflect nonbonded repulsion between the methyl and styryl substituents.

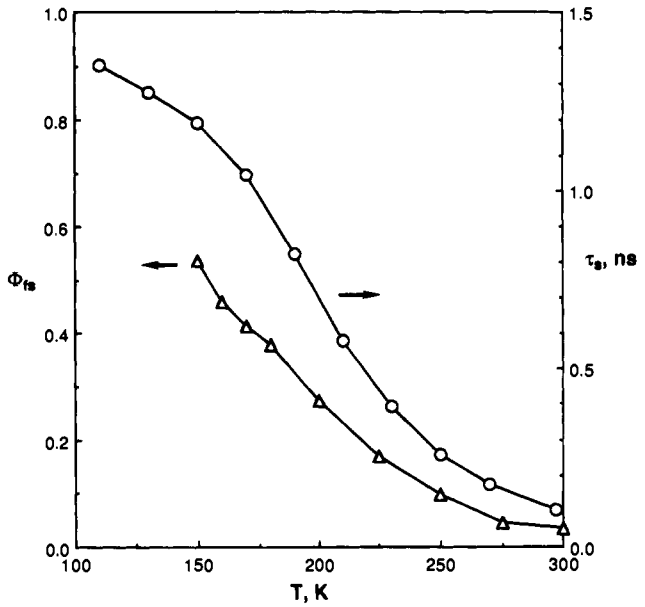


Figure 1. Temperature dependence of the fluorescence lifetime (○) and fluorescence quantum yield (△) for *o*-methylstilbene in methylcyclohexane solution.

Addition of triethylamine (TEA) results in quenching of MS fluorescence and the appearance of broad structureless exciplex emission with a maximum at slightly higher energy than that for the *t*-S–TEA exciplex (435 nm vs 440 nm).[5] The MS–TEA exciplex, like the *t*-S–TEA exciplex, is formed reversibly and is quenched by ground state amine, resulting in complex exciplex kinetics which we have not investigated in detail.[17] The free energy for electron transfer from TEA to *t*-S* calculated using Weller's equation is reported to be −0.16 eV.[1a] The electron-donating substituent in MS should render electron-transfer quenching slightly less favorable, as reported by Mai et al.[6] for the *p*-methylstilbene–TEA exciplex. Exciplex fluorescence maxima and decay times at fixed TEA concentrations are reported in Table 1. Exciplex fluorescence cannot be detected in tetrahydrofuran or acetonitrile solvents. The fluorescence of MS is also quenched by diethylamine. While quenching of singlet stilbenes and styrenes by secondary amines is presumed to result in exciplex formation, exciplex fluores-

(8) (a) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 535. (b) Lewis, F. D. In *Photoinduced Electron Transfer*; Chanon, M., Fox, M. A., Eds.; Elsevier: Amsterdam, 1988.

(9) Johnston, L. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564.

(10) (a) Lewis, F. D.; Reddy, G. D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1989**, *111*, 6465. (b) Lewis, F. D.; Reddy, G. D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1991**, *113*, 3498. (c) Lewis, F. D.; Reddy, G. D.; Bassani, D.; Schneider, S.; Gahr, M. *J. Photochem. Photobiol., A.* **1992**, *65*, 205. (d) Lewis, F. D.; Reddy, G. D.; Bassani, D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1994**, *116*, 597.

(11) (a) Lewis, F. D.; Reddy, G. D. *Tetrahedron Lett.* **1992**, *33*, 4249. (b) Lewis, F. D.; Bassani, D. M.; Reddy, G. D. *Pure Appl. Chem.* **1992**, *64*, 1271.

(12) Spangler, L. H.; Bosman, W. B.; Van Zee, R. D.; Zwier, T. S. *J. Chem. Phys.* **1988**, *88*, 6768.

(13) Mazzucato, U.; Momicchioli, F. *Chem. Rev.* **1991**, *91*, 1679.

(14) (a) (1) Saltiel, J.; Sun, Y.-P. In *Photochromism. Molecules and Systems*; Dürr, H., Bouais-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64. (b) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415. (c) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr.; Garrett, C. Z. *J. Phys. Chem.* **1993**, *97*, 2516.

(15) Sharafi, S.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119.

(16) Sumitani, M.; Nakashima, N.; Yoshihara, K.; Nagakura, S. *Chem. Phys. Lett.* **1977**, *51*, 183.

(17) For the full kinetic analysis of a related styrene–amine exciplex, see: Lewis, F. D.; Bassani, D. *J. Photochem. Photobiol., A* **1992**, *66*, 43.

Table 1. Fluorescence and Photoisomerization Data for the Tertiary (Aminoalkyl)stilbenes

exciplex	solvent	λ_{ex},[a] nm	τ_{ex},[b] ns	Φ_{fex}[c]	$10^{-7}k_f$,[d] s^{-1}	Φ_i[e]	$10^{-8}k_{st}$,[f] s^{-1}
MS−TEA	hexane	435	2.6[g]				
	diethyl ether	468	5.5[g]				
	MTHF[h]	*i*					
3°S1	hexane	390	2.2	0.027	1.2	0.35	3.2
	diethyl ether	454	1.1	0.005	0.5	0.30	5.6
	MTHF[h]	*i*	0.31				
3°S2	hexane	395	1.4	0.021	1.5		
	diethyl ether	445	19.0	0.12	0.63		
	MTHF[h]	485	7.0	0.028	0.40	0.23	0.6
	acetonitrile	520	5.8	0.010	0.17	0.10	0.4
3°S3	hexane	430	10.9	0.18	1.6		
	diethyl ether	475	12.6	0.075	0.60		
	MTHF[h]	502	6.1	0.026	0.42	0.11	0.4
	acetonitrile	535	0.5	0.001	0.2	0.09	3.6

[a] Exciplex fluorescence maximum. [b] Exciplex fluorescence decay time. [c] Exciplex fluorescence quantum yield. [d] Exciplex fluorescence rate constant ($k_f = \Phi_{fex}\tau_{ex}^{-1}$). [e] Quantum yield for photoisomerization. [f] Rate constant for intersystem crossing ($k_{st} = 2\Phi_i\tau_{ex}^{-1}$). [g] Data for 0.6 M TEA in hexane solution and 0.4 M TEA in diethyl ether solution. [h] Methyltetrahydrofuran. [i] No exciplex emission observed.

cence is not observed.[3,10] Primary amines do not quench the fluorescence of MS, as is the case for *t*-S.[2,3]

Tertiary (Aminoalkyl)stilbenes. The absorption spectra of the tertiary (aminoalkyl)stilbenes 3°S1, 3°S2, and 3°S3 are similar to that of MS. They display very weak structured fluorescence in nonhydroxylic solvents ($\Phi_{fs} \leq 0.005$) in the spectral region where MS has moderately intense fluorescence. Broad structureless fluorescence attributed to intramolecular exciplexes was observed for all of the tertiary (aminoalkyl)-stilbenes in nonpolar solvents. Exciplex fluorescence cannot be detected for 3°S1 in tetrahydrofuran or acetonitrile solution and is very weak for 3°S3 in acetonitrile solution. No exciplex fluorescence is observed in alcohol solvents. The intensity of locally excited fluorescence is slightly larger in methanol vs hexane or THF and increases with decreasing alcohol polarity (methanol < 2-propanol < 2-methyl-2-propanol). Hydrogen bonding of the amine by alcohol solvents is presumably responsible for inefficient intramolecular quenching. The absence of exciplex fluorescence in alcohol solvents might reflect either a small exciplex binding energy or rapid exciplex nonradiative decay.

Exciplex fluorescence maxima, decay times, and quantum yields for several solvents are summarized in Table 1. Lippert−Mataga plots of exciplex energy vs the solvent polarity parameter Δf (eqs 1 and 2) for the MS−TEA and (aminoalkyl)-

$$\nu_{ex} = \nu_{ex}^{\circ} - (2\mu^2/hc\varrho^3)\Delta f \quad (1)$$

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2) \quad (2)$$

stilbene exciplexes are shown in Figure 2. The exciplex maxima for MS−TEA and 3°S3 are at lower energies than those for 3°S1 or 3°S2, the difference being most pronounced in nonpolar solvents. A similar chain-length dependence of the fluorescence maxima has been observed for other intramolecular (aminoalkyl)arene exciplexes and is attributed to more effective orbital overlap in exciplexes possessing trimethylene linkers than those with shorter linkers.[10d,18] The convergence of exciplex energies for 3°S2 and 3°S3 in polar solvents may reflect a looser exciplex geometry in more polar solvents. The exciplex fluorescence maxima are independent of temperature in methylcyclohexane solution but are shifted to lower energy with decreasing temperature in 2-methyltetrahydrofuran solution ($\lambda_{ex} = 510$ nm

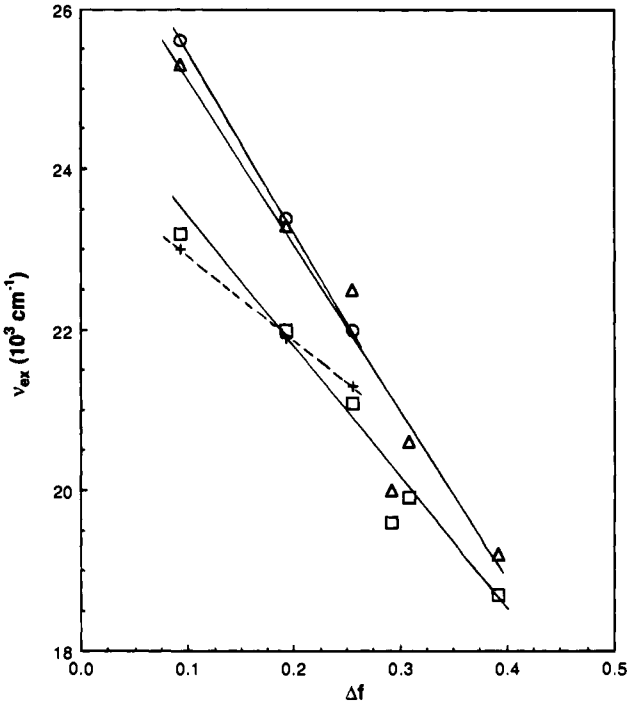


Figure 2. Solvent polarity dependence of the exciplex fluorescence maxima for MS−TEA (+), 3°S1 (○), 3°S2 (△), and 3°S3 (□).

for 3°S2 at 255 K and $\lambda_{ex} = 525$ nm for 3°S3 at 250 K). This shift is similar to that observed for other (aminoalkyl)arene exciplexes[18a,19] in moderately polar solvents and can be attributed, in part, to an increase in the dielectric constant of methyltetrahydrofuran with decreasing temperature from 7.0 at 293 K to 8.0 at 250 K.[20]

The temperature dependence of the (aminoalkyl)stilbene locally excited fluorescence quantum yields in methylcyclohexane and methyltetrahydrofuran is shown in Figure 3 along with the data for MS in methylcyclohexane solution. The fluorescence quantum yields of the (aminoalkyl)stilbenes are lower than that of MS over the entire temperature range investigated, as a consequence of intramolecular fluorescence quenching. Quenching is more efficient in methylcyclohexane vs methyltetrahydrofuran at temperatures below 200 K. The decay times for locally excited fluorescence (τ_s) from the (aminoalkyl)stilbenes cannot be fit to a single exponential. The dominant component for all of the (aminoalkyl)stilbenes has a decay time shorter than the time resolution of the instrumentation employed for these measurements (0.05 ns) at room temperature. The decay time of the dominant component increases with decreasing temperature. The values for 3°S2 and 3°S3 at 150 K (0.21 and 0.12 ns, respectively) are shorter than that for MC at the same temperature (1.44 ns). Assuming that the shorter decay times are a consequence of intramolecular electron transfer quenching, rate constants for this process calculated from the decay times for 3°S2 and 3°S3 ($k_{et} = \tau_s^{-1} - \tau_{MS}^{-1}$) are 4×10^9 and 8×10^9 s^{-1}, respectively, at 150 K. These rate constants presumably increase with increasing temperature.

The temperature dependence of the exciplex fluorescence quantum yield (Φ_{fex}) in methylcyclohexane and methyltetrahydrofuran solution is shown in Figure 4. Exciplex fluorescence is observed immediately above the glass transition temperature in methylcyclohexane solution, reaches maximum intensity at

(18) (a) Van der Auweraer, M. *Acad. Anal.* **1986**, *48*, 27. (b) Van der Auweraer, M.; Grabowski, Z. R.; Rettig, W. *J. Phys. Chem.* **1991**, *95*, 2083.
(19) Lewis, F. D.; Cohen, B. E. *J. Phys. Chem.* **1994**, *98*, 10591.
(20) Furutsuka, T.; Imuar, T.; Kojima, T.; Kawabe, K. *Technol. Rep. Osaka Univ.* **1974**, *24*, 367; *Chem. Abstr.* **1974**, *81*, 160915c.

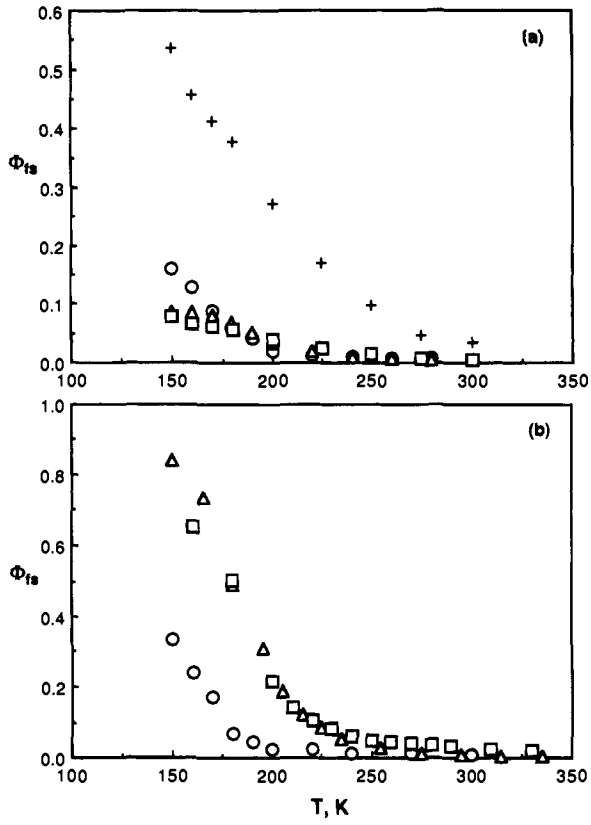


Figure 3. Temperature dependence of the quantum yield for stilbene fluorescence from MS (+), 3°S1 (○), 3°S2 (△), and 3°S3 (□) in methylcyclohexane (a) and methyltetrahydrofuran (b) solution.

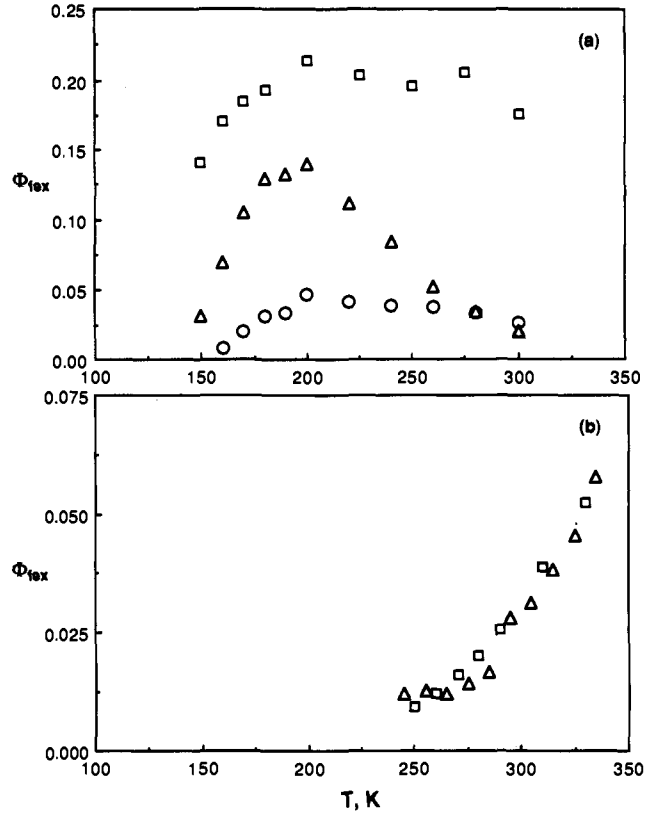


Figure 4. Temperature dependence of the quantum yield for exciplex fluorescence from 3°S1 (○), 3°S2 (△), and 3°S3 (□) in methylcyclohexane (a) and from 3°S2 and 3°S3 in methyltetrahydrofuran (b) solution.

ca. 200 K, and decreases at higher temperatures. In contrast, exciplex fluorescence in methyltetrahydrofuran solution is only observed above 250 K for 3°S2 and 3°S3 and increases in intensity with increasing temperature. Exciplex fluorescence is not observed at any temperature for 3°S1 in methyltetrahydrofuran solution.

Stevens–Ban[21] plots of the $\ln(\Phi_{fex}/\Phi_{fs})$ vs T^{-1} (not shown) are linear over the range of temperatures investigated for 3°S2 and 3°S3 in methyltetrahydrofuran solution and for 3°S3 in methylcyclohexane solution, indicative of irreversible exciplex formation. Plots for 3°S1 and 3°S2 in methylcyclohexane solution display downward curvature at high temperatures, indicative of reversible exciplex formation. The slopes of the linear portions of these plots provide similar values for the activation energy of exciplex formation for all of the (aminoalkyl)stilbenes in methylcyclohexane solution ($E_{act} \approx 2.2 \pm 0.5$ kcal/mol). These low activation energies are consistent with the large values of k_{et} calculated from the decay times for locally excited fluorescence at 150 K. Activation energies for 3°S2 and 3°S3 in methyltetrahydrofuran solution ($E_{act} \approx 6.1 \pm 0.5$ kcal/mol) are also independent of chain length, but are significantly larger than those in methylcyclohexane solution. An increase in the activation energy for intramolecular exciplex formation with increasing solvent polarity has previously been observed by Van der Auweraer[18a] for other (aminoalkyl)arenes and is presumably a consequence of the larger solvent reorganization energy for exciplex formation in the more polar solvent.[22] The absence of a chain-length dependence suggests that E_{act} is determined by a process other than conformational change, plausibly rehybridization of nitrogen.

Exciplex fluorescence displays single exponential decay. The room temperature decay times (τ_{ex}) in several solvents are summarized in Table 1, and the temperature dependence of the decay rates (τ_{ex}^{-1}) in methylcyclohexane and diethyl ether or methyltetrahydrofuran solution are shown in Figure 5. Rate constants for exciplex fluorescence calculated from the measured quantum yield and lifetime ($k_{fex} = \Phi_{fex}\tau_{ex}^{-1}$) are reported in Table 1. The values of k_{fex} display little variation with chain length but decrease with increasing solvent polarity. Similar solvent dependence has been observed for other intramolecular exciplexes and was attributed to a solvent-induced change in exciplex conformation.[10d,23] The weak exciplex fluorescence of 3°S1 and 3°S3 in polar solvents apparently is a consequence of rapid nonradiative decay rather than very slow fluorescence.

Exciplex decay rates increase with increasing temperature in methylcyclohexane solution (Figure 5a). The decreases in Φ_{fex} (Figure 4a) and increase in τ_{ex}^{-1} (Figure 5a) with increasing temperature for 3°S1 and 3°S3 are modest and may result from either partially reversible exciplex formation or a decrease in solvent refractive index with increasing temperature.[24] The temperature dependence for 3°S2 is much more pronounced, reflecting reversible exciplex formation at higher temperatures. The greater extent of exciplex dissociation for 3°S2 vs 3°S3, like its higher energy fluorescence maximum in nonpolar solvents (Figure 2), can be attributed to less effective orbital overlap, as observed for other (2-aminoethyl)- vs (3-aminopropyl)arene exciplexes.[18b,19] Exciplex formation apparently is irreversible over the temperature range investigated for 3°S1 in diethyl ether solution and for 3°S2 and 3°S3 in methyltetrahydrofuran solution. Solvent stabilization of the polar exci-

(21) Stevens, B.; Ban, M. I. *Trans. Faraday Soc.* **1964**, *60*, 1515.
(22) Harrison. R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429.
(23) Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1992**, *191*, 371.
(24) Olmsted, J. *Chem. Phys. Lett.* **1976**, *38*, 287.

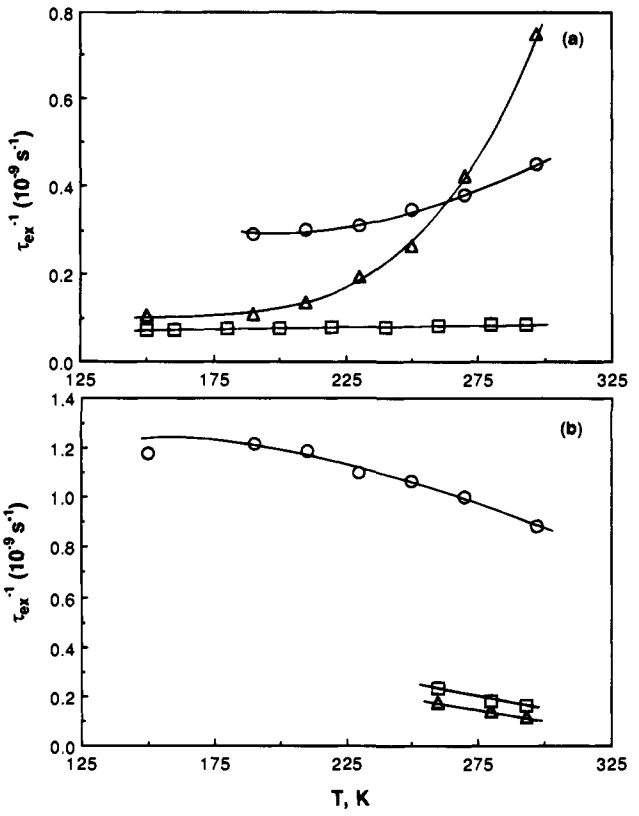


Figure 5. Temperature dependence of the decay rate for exciplex fluorescence from 3°S1 (○), 3°S2 (△), and 3°S3 (□) in methylcyclohexane (a) and from 3°S1 in diethyl ether and 3°S2 and 3°S3 in methyltetrahydrofuran (b) solution.

plexes renders their formation irreversible. The observed increase in τ_{ex} with increasing temperature for 3°S2 and 3°S3 in methyltetrahydrofuran solution (Figure 5b) may reflect the aforementioned decrease in solvent dielectric constant with increasing temperature.

The tertiary (aminoalkyl)stilbenes undergo moderately efficient trans → cis photoisomerization under conditions where exciplex formation is essentially quantitative and irreversible. Quantum yields for isomerization in several solvents are reported in Table 1. The isomerization of stilbene–amine exciplexes has been attributed to intersystem crossing of the singlet exciplex to the locally excited stilbene triplet, whose energy (E_T = 47 kcal/mol[25]) lies well below that of the exciplex.[4] Assuming that the quantum yield for triplet state isomerization is 0.5,[14a] rate constants for exciplex intersystem crossing can be calculated from the measured isomerization quantum yield and singlet lifetime ($k_{st} = 2\Phi_i\tau_{ex}^{-1}$). The values of k_{st} reported in Table 1 are similar to those reported for intramolecular styrene–amine exciplexes,[10d] intermolecular *t*-S–amine exciplexes,[4] and singlet *t*-S.[14a] The value of k_{st} for 3°S1 is larger than those of its longer chain homologs, as is the case for other (aminomethyl)arenes.[26] Enhanced spin–orbit coupling may result from interaction of the chromophores through a single methylene.

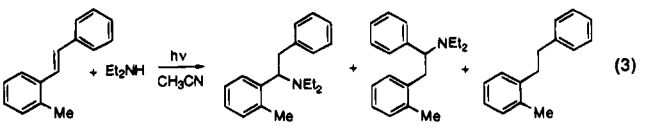
In addition to undergoing trans → cis photoisomerization, the tertiary (aminoalkyl)stilbenes are slowly converted upon prolonged irradiation to complex product mixtures, which have not been analyzed. Products which retain the stilbene chromophore could be responsible for the multicomponent decay of the 350 nm fluorescence. The failure to observe stilbene–amine adduct formation from either *t*-S–TEA or the (aminoalkyl)stilbenes in nonpolar solvents may reflect the low basicity of the delocalized stilbene anion radical. The analogous styrene–amine exciplexes undergo both inter- and intramolecular addition reactions in nonpolar solvents.[10d] Adduct formation is observed for the *t*-S–TEA[3] and *p*-methylstilbene–TEA exciplexes in acetonitrile solution,[6] but not for the (aminoalkyl)stilbenes. We observe similar behavior upon irradiation of MS with TEA in acetonitrile solution; however, the products have not been fully characterized. Thus, the *o*-methyl group does not inhibit intermolecular stilbene–amine addition. It is possible that the tertiary (aminoalkyl)stilbene exciplexes adopt loose geometries in polar solvents which do not provide a least-motion pathway for proton transfer.[10d,23]

Table 2. Secondary (Aminoalkyl)stilbene Quantum Yields for Locally Excited Fluorescence, Isomerization, and Product Formation

exciplex	solvent	Φ_{fs}	Φ_i	Φ_p
2°S1	hexane	0.045		
	acetonitrile	<0.002	0.48	<0.002
2°S2	hexane	0.028		
	acetonitrile	0.005	0.17	0.013
2°S3	hexane	0.038		
	acetonitrile	0.015	0.30	<0.002

Secondary (Aminoalkyl)stilbenes. The absorption and fluorescence spectra of 2°S1, 2°S2, and 2°S3 are essentially identical to those of MS. Quantum yields for locally excited stilbene fluorescence are reported in Table 2. The values of Φ_{fs} in hexane solution are chain-length-dependent, increasing in the order 2°S2 < 2°S3 < 2°S1 ≈ MS and are smaller in acetonitrile vs hexane solution. Less efficient intramolecular quenching of stilbene by secondary vs tertiary amines (Figure 3) is consistent with the higher oxidation potentials of the secondary amines. Exciplex fluorescence is not observed for the secondary (aminoalkyl)stilbenes, as is the case for intermolecular quenching of *t*-S by secondary amines.[3] The fluorescence lifetimes for 2°S2 and 2°S3 are shorter than that for MS; however, the observed values are near the time resolution of the instrumentation used for these measurements (ca. 0.05 ns) and are not reported. On the basis of the values of Φ_{fs} (Table 2), intramolecular quenching is more rapid for the secondary (2-aminoethyl)- vs (3-aminopropyl)stilbene, opposite the order observed for the tertiary (aminoalkyl)stilbenes. This may reflect a difference in the structures of the exciplexes formed by secondary vs tertiary amines.

Irradiation of *t*-S with diethylamine in either nonpolar or polar solvents results in the formation of a stilbene–amine adduct and reduced stilbene (Scheme 1).[3] Irradiation of MS with diethylamine in acetonitrile solution results in the formation of two regioisomeric adducts in a 1:1 ratio and a comparable amount of reduced MS (eq 3). The formation of both regioisomers indicates that the N–H proton-transfer process is nonregioselective, as previously observed by Alfano[27] for addition of *p*-methoxystilbene with diethylamine and by Mai et al.[6] for the addition of several substituted stilbenes with TEA. The formation of comparable yields of adducts and reduced



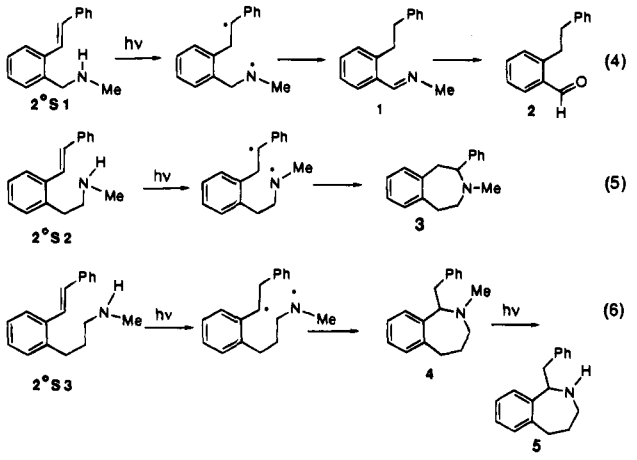
(25) Ni, T.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

(26) Okada, T.; Karaki, I.; Matsuzawa, E.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1981**, *85*, 3957.

(27) Alfano, J. Unpublished results.

stilbene indicates that the radical pair formed upon N–H transfer undergoes both combination and disproportionation.[28]

The secondary (aminoalkyl)stilbenes undergo product formation in competition with trans → cis isomerization.[11] Product formation, like intramolecular fluorescence quenching (Table 2), is more efficient in acetonitrile vs hexane solution. Michler's ketone sensitization results in isomerization but not formation of these products. Thus, product formation occurs via the singlet state and not following intersystem crossing. Irradiation of 2°S1 results in the slow formation of several products. The major product was tentatively identified as the imine **1** based upon its GC/MS and conversion to the aldehyde **2** (26% isolated yield) upon chromatography (eq 4). The low yield of **2** may reflect the anticipated instability of **1** under the reaction conditions. Irradiation of 2°S2 results in the formation of *N*-methyl-2-phenyltetrahydro-3-benzazepine, **3**, as the only significant product detected by GC or ^{1}H NMR analysis of the irradiated solution (eq 5). Benzazepine **3** is relatively stable under the reaction conditions and is obtained in 65% isolated yield at high conversions (>95%) of starting material. Irradiation of 2°S3 results in the formation of *N*-methyl-1-benzyltetrahydro-2-benzazepine, **4**, as the only significant primary photoproduct (eq 6). Benzazepine **4** undergoes secondary photochemical N-demethylation, yielding a mixture of **4** (38%) and **5** (25%) at high (>95%) conversions of starting material.



Unlike the intermolecular reaction of MS with diethylamine, the intramolecular reactions of the secondary (aminoalkyl)-stilbenes are highly selective processes. The formation of **3** and **4** but not their regioisomers requires that proton transfer occurs selectively to the proximal end of the stilbene double bond in 2°S2 and to the distal end in 2°S3. The analogous reactions of the secondary β-(aminoalkyl)styrenes are nonregioselective, proton transfer occurirng to both the proximal and distal ends of the styrene double bond.[10b] Inspection of molecular models indicates that the aminomethyl or aminoethyl group in 2°S1 or 2°S2, respectively, can adopt a folded conformation which provides a least-motion pathway for N–H transfer to the proximal but not to the distal end of the stilbene double bond. The aminopropyl group in 2°S3 can adopt folded conformations appropriate for N–H transfer to either end of the double bond, and thus the regioselective formation of **4** is particularly remarkable. The behavior of the biradicals formed upon intramolecular N–H transfer is also more selective than that of the radical pair formed in the intermolecular reaction (eq 3). The biradical from 2°S1 selectively disproportionates

(28) (a) Lewis, F. D.; Zebrowski, B. E.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 187. (b) Lewis, F. D.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 194.

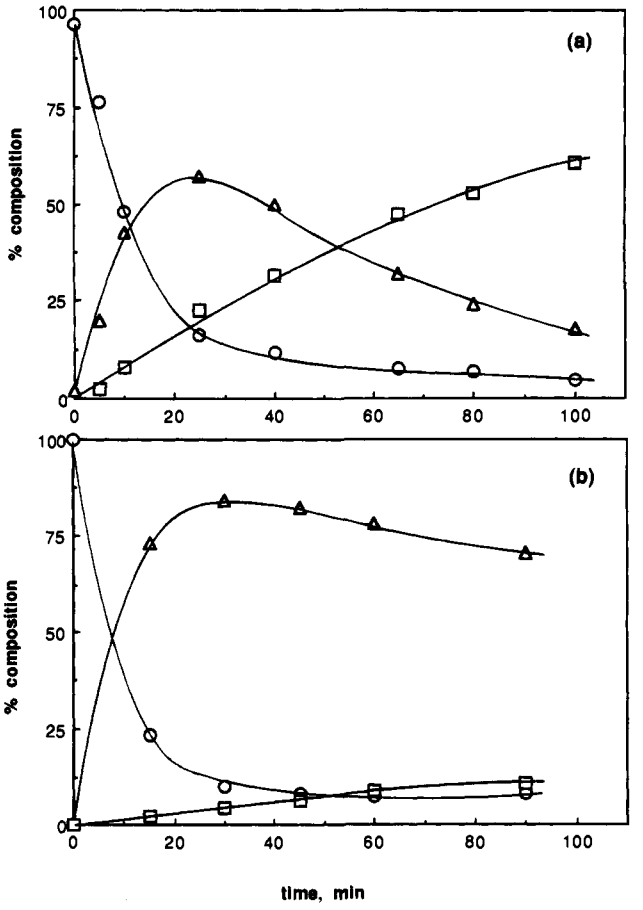


Figure 6. Conversion of starting material (○) to the cis isomer (△) and adduct (□) for 2°S2 (a) and 2°S3 (b) in acetonitrile solution.

while the biradicals from 2°S2 and 2°S3 selectively combine. We have previously observed that the alkyl–aminyl biradicals formed from (aminoalkyl)styrenes selectively cyclize except in cases where the cyclization process yields a product with ring strain or large nonbonded interactions.[10b] This is evidently the case for the 1,6-biradical intermediate from 2°S1 which disproportionates to yield **1** (eq 4) rather than cyclize to yield a tetrahydroisoquinoline. While the tetrahydroisoquinoline is not highly strained, the presence of two adjacent sp^2 carbons might prevent overlap between the two radical p orbitals of the biradical intermediate.

Plots of the composition vs irradiation time for acetonitrile solutions of 2°S2 and 2°S3 are shown in Figure 6, and quantum yields for product formation (Φ_p) are reported in Table 2. Adduct formation competes more effectively with isomerization in the case of 2°S2 vs 2°S3, resulting in a larger quantum yield for adduct formation and a lower maximum conversion to the cis isomer (Figure 6). The larger value of Φ_p for 2°S2 vs 2°S3 plausibly reflects more efficient intramolecular quenching by 2°S2 in acetonitrile solution (Table 2). The rate of formation of **3** decreases only slightly during the first 40 min of irradiation, even though the stilbene chromophore is largely converted from trans to cis (Figure 6a). This suggests that intramolecular addition of the secondary amine occurs with comparable efficiency for both *cis*- and *trans*-stilbenes. Several possible explanations for comparable addition efficiency can be envisioned. These include reaction via folded ground state conformers, exceptionally rapid intramolecular quenching of the short-lived *cis*-stilbene singlet ($\tau_s \approx 1$ ps[29a]), more efficient proton transfer for the intramolecular *cis*- vs *trans*-stilbene exciplex, and reaction of the amine with the short-lived perpendicular singlet state ($\tau_s < 1$ ps[29b]). Investigation of the

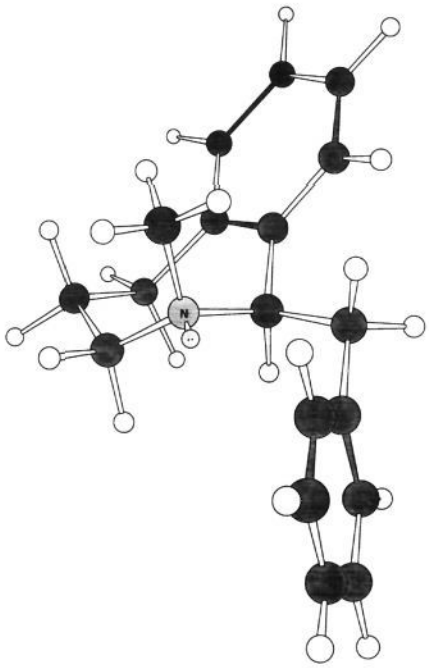


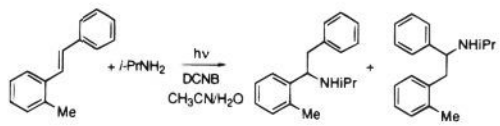
Figure 7. Minimized MM2 structure for the lowest energy conformation of *N*-methyl-1-benzyltetrahydro-2-benzazepine, 4.

isomerization and addition reactions of the pure cis isomer of 2°S2 might provide additional information about its excited state behavior.

The secondary photochemical conversion of **4** to **5** is a process without precedent in our studies of inter- and intramolecular photoamination reactions.[1,10] Homolytic C−N cleavage of arylmethyl groups has been observed for several tertiary (aminomethyl)arenes including *N,N*-dimethylbenzylamine.[30] This process would convert **4** to the biradical intermediate from which it was formed (eq 6) and thus not be detected. The photochemical cleavage of a *N*-methyl bond in **4** may be related to its unusual conformation. Molecular mechanics calculations and ^{1}H NMR analysis indicate that the azepine ring in **4** adopts a chair conformation in which the benzyl substituent is equatorial and the methyl group is axial (Figure 7). The diequatorial conformation is calculated to be ca. 4 kcal/mol less stable. The structure of **4** is similar to that previously established crystallographically for a structurally related *N*-methylphenanthroazepine.[31] Nonbonded repulsion between the axial *N*-methyl and fused benzene ring may provide the driving force for the occurrence of photochemical N-demethylation in **4**. Several *N*-methylalkaloids have also been reported to undergo demethylation upon photooxidation with the strong electron acceptor *N,N'*-dimethyl-2,7-diazapyrenium tetrafluoroborate.[32] The mechanism of these reactions involves oxidation to an immonium ion which is hydrolyzed to the secondary amine and formaldehyde and is presumably not related to the mechanism for conversion of **4** to **5**.

Primary (Aminoalkyl)stilbenes. The absorption and fluorescence spectra and fluorescence quantum yields of 1°S1, 1°S2, and 1°S3 in hexane or acetonitrile solution are essentially identical to those of MS, indicative of the absence of intramolecular electron-transfer quenching. Quantum yields for photoisomerization of the primary (aminoalkyl)stilbenes in acetonitrile solution are also similar to that of MS. As is the case for irradiation of *t*-S in the presence of primary amines,[3] no adducts are formed upon direct irradiation of the primary (aminoalkyl)stilbenes.

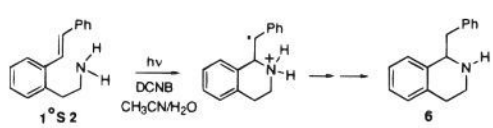
Yasuda et al.[7c] reported that irradiation of an equimolar mixture of *t*-S and *p*-dicyanobenzene in a 9:1 acetonitrile−water solution bubbled with ammonia results in the formation of 1,2-diphenylethylamine in 46% yield. The analogous reaction of *p*-methylstilbene is modestly regioselective, yielding a 1.7:1 mixture of 1-phenyl-2-tolylethylamine and its regioisomer.[7c] Similarly, we find that irradiation of MS with isopropylamine under similar conditions yields a 1.5:1 mixture of regioisomers as the only significant products detected by GC/MS analysis (eq 7). While the intramolecular electron-transfer-sensitized



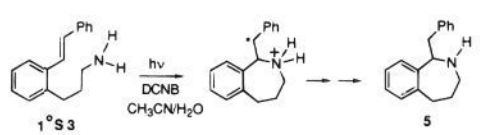
(7)

addition reactions of methylstilbenes display only modest regioselectivity, photoamination of *p*-methoxystilbene is highly regioselective, presumably reflecting the charge distribution in the cation radical intermediate.[7c]

Irradiation of 1°S1 (0.01 M) and *m*-dicyanobenzene (0.015 M) in deoxygenated 9:1 acetonitrile−water solution with 300 nm light results in photoisomerization and slow conversion to a complex mixture of products. Irradiation of 1°S2 under similar conditions results in photoisomerization and the formation of 1-benzyltetrahydroisoquinoline, **6**, in 76% isolated yield (eq 8). Irradiation of 1°S3 under similar conditions results in photoisomerization and the formation of 1-benzyltetrahydro-2-benzazepine, **5**, in 70% isolated yield (eq 9). Benzazepine **5** proved to be identical to the secondary photoproduct obtained upon direct irradiation of 2°S3 (eq 6).



(8)



(9)

Under the conditions of DCNB-sensitized irradiation, more of the incident light is absorbed by the (aminoalkyl)stilbene (ca. 75%) than by DCNB (ca. 25%). However, quenching of the short-lived (aminoalkyl)stilbene by DNCB is much less efficient than quenching of DCNB (τ = 8.8 ns in acetonitrile soltuion) by the (aminoalkyl)stilbene. By analogy to the mechanism proposed for intermolecular electron-transfer-sensitized addition (Scheme 2),[7] the formation of **6** and **5** is presumed to occur via intramolecular nucleophilic attack of nitrogen upon the stilbene cation radical to yield the distonic cation radical intermediates shown in eqs 8 and 9. In both cases, nucleophilic attack occurs regioselectively at the proximal end of the C=C double bond. The ring-forming nucleophilic addition step in these reactions can be described in terms of Baldwin's rules[33] as 6-exo-trig and 7-exo-trig processes. Their occurrence to the exclusion of

(29) (a) Todd, D. C.; Fleming, G. R.; Jean, J. M. *J. Chem. Phys.* **1992**, *97*, 8915. (b) Saltiel, J.; Waller, A. S.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 2453.

(30) (a) Ratcliff, M. A., Jr.; Kochi, J. K. *J. Org. Chem.* **1971**, *36*, 3112. (b) Er-Rhaimini, A.; Mohsinaly, N.; Mornet, R. *Tetrahedron Lett.* **1990**, *31*, 5757. (c) Yoon, B. A.; Cohen, B. E.; Lewis, F. D. Unpublished results.

(31) Berney, D.; Petcher, T. J.; Schmutz, J.; Weber, H. P.; White, T. G. *Experientia* **1975**, *31*, 39571327.

(32) Santamaria, J.; Ouchabane, R.; Rigaudy, J. *Tetrahedron Lett.* **1989**, *30*, 2927.

(33) Baldwin, J. E.; *J. Chem. Soc., Chem. Commun.* **1976**, 734.

the alternative 7-endo-trig and 8-endo-trig processes might be a consequence of either kinetic or thermodynamic control of the nucleophilic addition of the amine to the stilbene cation radical. Since the *trans*-stilbene cation radical is known to have a planar geometry,[34] the preference for exo vs endo ring closure may be biased by the connecting benzene ring. The planarity of the stilbene cation radical could also account for the failure of 1°S1 to undergo sensitized addition to yield an isoindole. Pandey et al.[35] have, in fact, observed that electron-transfer-sensitized intramolecular photoamination of (2-aminoethyl)-arenes yields substituted indoles. While isoindoles are not strained, the trajectory for intramolecular addition in the cation radical of 1°S1 may be unfavorable.

DCNB-sensitized intermolecular photoamination of stilbene and 1,1-diphenylethylene with ammonia and primary amines occurs in moderate to high yield.[7] The analogous reactions with secondary amines were not successful, presumably due to the low oxidation potentials of the secondary amines, which must be present in excess in order to intercept the arylolefin cation radical. We have briefly investigated the DCNB-sensitized reactions of the secondary (aminoalkyl)stilbenes 2°S2 and 2°S3 in 9:1 acetonitrile–water solution. Direct irradiation of 2°S2 and 2°S3 is much less efficient in this solvent than in acetonitrile, presumably due to specific solvation of the amine by water. The primary photoproducts of the DCNB-sensitized reactions are *N*-methyl-1-benzyltetrahydroisoquinoline and benzazepine **4**, respectively. The formation of the isoquinoline rather than benzazepine **3** from 2°S2 indicates that the DCNB-sensitized reaction is much more efficient than the reaction of unquenched singlet 2°S2 under these conditions. In the case of 2°S3, both the direct and DCNB-sensitized reactions yield the same product. Since the primary products of the DCNB-sensitized reactions are tertiary amines, they undergo secondary photooxidation reactions. In the case of 2°S3, the optimum conversion to **4** (ca. 50%) is larger than that obtained upon direct irradiation.

Concluding Remarks. Connection of stilbene and amine chromophores with a short polymethylene chain has a profound effect on the formation and behavior of stilbene–amine exciplexes and stilbene cation radicals. The tertiary (aminoalkyl)-stilbenes form fluorescent exciplexes, permitting detailed investigation of the initial interaction between singlet stilbene and ground state amine. Exciplex stability in nonpolar solvents decreases in the order 3°S3 ≈ MS–TEA intermolecular exciplex > 3°S2 ≈ 3°S1, presumably reflecting differences in stilbene–amine orbital overlap. The intramolecular exciplexes are fluorescent but nonreactive in polar solvents while MS–TEA is nonfluorescent but chemically reactive. These differences are also most likely related to differences in inter- vs intramolecular exciplex geometry.

The secondary (aminoalkyl)stilbenes undergo photochemical N–H transfer to yield biradical intermediates. Both the regioselectivity of N–H transfer and the behavior of the resulting biradical intermediate are dependent upon the length of the polymethylene chain. Hydrogen transfer in 2°S1 and 2°S2 occurs at the proximal end of the stilbene double bond while hydrogen transfer in 2°S3 occurs at the distal end. The resulting biradicals from 2°S2 and 2°S3 selectively combine to yield the tetrahydrobenzazepines **3** and **4**, while the biradical from 2°S1 disproportionates to yield the imine **1**. The analogous intermolecular reaction of MS with diethylamine is nonregioselective and yields both combination and disproportionation products.

The primary (aminoalkyl)stilbenes fail to undergo intramolecular electron transfer upon direct irradiation due to the high ionization potential of the primary amines. However, electron-transfer-sensitized irradiation of 1°S2 and 1°S3 results in formation of the tetrahydroisoquinoline **6** and the tetrahydrobenzazepine **5**, respectively. The regioselectivity of these reactions is determined by intramolecular nucleophilic addition of the neutral amine to the oxidized stilbene, which occurs at the proximal end of the stilbene double bond for both 1°S2 and 1°S3. The failure of 1°S1 to undergo sensitized intramolecular addition may reflect an unfavorable trajectory for nucleophilic addition.

The synthesis of phenyl- and benzyl-substituted tetrahydrobenzazepines[36] and tetrahydroisoquinolines[37] is of continuing interest due to their activity as medicinal agents. The overall preparative yields for the photochemical synthesis of **3**–**6** are significantly higher than those for previously-reported nonphotochemical syntheses.[36,37] The occurrence of intramolecular stilbene–amine addition under the conditions of both direct and electron-transfer-sensitized irradiations significantly extends the versatility of the photoamination reaction.[10] Since the regioselectivity of addition is determined by the hydrogen-transfer step in the direct irradiation and by C–N bond formation in the electron-transfer-sensitized reaction, different regioisomers may be obtained, as in the case of direct irradiation of 2°S2 vs sensitized irradiation of 1°S2. Electron-donating and -withdrawing aromatic substituents are also expected to have different effects upon the direct and sensitized reactions, since stilbene anion radicals are intermediates in the direct irradiation and stilbene cation radicals in the sensitized irradiation.

Experimental Section

General Methods. NMR spectra were recorded in $CDCl_3$ solution using a Gemini 300 or Varian XLA 400 spectrometer with TMS as an internal standard. High resolution mass spectra were determined with a Hewlett-Packard 5985 GC/VG70-250SE MS system using an ionizing voltage of 70 V. Ultraviolet absorption spectra were obtained using a Hewlett-Packard 8452 diode-array spectrophotometer. Steady state fluorescence spectra were obtained using a Perkin-Elmer MPF-44A or a PTI-LS1 spectrofluorometer. Fluorescence quantum yields were determined relative to that of *trans*-stilbene in hexane solution (Φ_f = 0.05[15]). Fluorescence decay times were measured with two different single photon counting apparatus with different excitation sources, one with a gated arc lamp (PTI-LS1, time resolution ca. 0.2 ns) and the other with a mode-locked dye laser (time resolution ca. 50 ps). The method of analysis of the fluorescence decay curves has previously been described.[10b,17]

Preparative scale irradiations of 0.01 M (aminoalkyl)stilbene were carried out under nitrogen in Pyrex test tubes using a Rayonet reactor fitted with RPR 3000 lamps. Direct irradiations were performed in acetonitrile solution while sensitized irradiations were performed in 9:1 acetonitrile–water solutions containing 0.01 M 1,4-dicyanobenzene. Solutions were irradiated to >95% conversion of starting material while monitoring the progress of the reaction by GC. Products were isolated by preparative thick layer chromatography followed by bulb-to-bulb distillation. Quantum yield measurements were carried out using an optical bench (200 W xenon–mercury high pressure lamp and 0.25 m high intensity monochromator at 310 nm) with conversions limited to

(34) (a) Suzuki, H.; Koyano, K.; Shida, T.; Kira, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3609. (b) Suzuki, H.; Ogawa, K.; Shida, T.; Kira, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 66.

(35) Pandey, G.; Sridhar, M.; Bhalerao, U. T. *Tetrahedron Lett.* **1990**, *31*, 5373.

(36) (a) Reby, C.; Gardent, J. *Bull. Soc. Chim. Fr.* **1972**, 1574. (b) Berney, D.; Schuh, K. *Helv. Chim. Acta* **1976**, *59*, 2059. (c) Busacca, C. A.; Johnson, R. E. *Tetrahedron Lett.* **1992**, *33*, 165. (d) Gentles, R. G.; Middlemiss, D.; Proctor, G. R.; Sneddon, A. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1423.

(37) (a) Gray, N. M.; Cheng, B. K.; Mick, S. J.; Lair, C. M.; Contreras, P. C. *J. Med. Chem.* **1989**, *32*, 1242. (b) Charifson, P. S.; Bowen, J. P.; Wyrick, S. D.; Hoffman, A. J.; Cory, M.; McPhail, A. T.; Mailman, R. B. *J. Med. Chem.* **1989**, *32*, 2050.

10%. Light intensities were determined using *trans*-stilbene actinometry.[38] Irradiated solutions were analyzed by gas chromatography (Hewlett-Packard 5890 equipped with a flame ionization detector) with a 10 × 0.53 mm fused silica column coated with poly(methyldisiloxane). Solvents were all spectrograde and were distilled from drying agents prior to use.

***trans*-2-(Aminomethyl)stilbene (1°S1).** 2-Cyanostilbene[39] was synthesized as a mixture of cis and trans isomers via the Wittig reaction of 2-cyanobenzaldehyde (Aldrich) with triphenylbenzylphosphonium chloride. Flash chromatography (eluent 50% $CHCl_3$, 50% hexane) followed by photoisomerization in benzene solution with a catalytic amount of iodine afforded the *trans* isomer. Reduction of *trans*-2-cyanostilbene with $LiAlH_4$ in tetrahydrofuran solution followed by acid–base extraction provided the primary amine 1°S1[40] as a colorless oil in 64% yield. ^1H NMR ($CDCl_3$): δ 7.66–7.30 (m, 9H aromatic, 1H vinylic); 7.05 (d, 1H vinylic, J = 16.2 Hz); 4.02 (s, 2H); 1.72 (br s, 2H). HRMS: 209.1204 (calcd) and 209.1188 (obsd).

***trans*-2-[(*N*-Methylamino)methyl]stilbene (2°S1) and *trans*-2-[(*N*,*N*-Dimethylamino)methyl]stilbene (3°S1).** The ethyl ester of 2-carboxybenzaldehyde (Aldrich) was reacted with triphenylbenzylphosphonium chloride to afford ethyl 2-stilbenecarboxylate[41] as a mixture of isomers. The ester was converted to the *N*-methyl amide[42] by the method of Stella et al.[43] and the amide reduced with $LiAlH_4$ and isolated as described above to provide 2°S1[40] in 81% yield from the ester. ^1H NMR (trans isomer) ($CDCl_3$): δ 7.7–7.1 (m, 9H aromatic, 1H vinylic); 7.02 (d, 1H vinylic, J = 16.2 Hz); 3.88 (s, 2H); 2.50 (s, 3H). MS (*m/e*): 223 (M^+), 146, 118, 91. Reductive alkylation of the *N*-methylamine using the method of Borch and Hassid[44] followed by preparative thick layer chromatography (eluent 11% MeOH, 89% CH_2Cl_2) afforded 3°S1[45] as a colorless oil (40% yield). ^1H NMR ($CDCl_3$): δ 7.7–7.1 (m, 10 H aromatic); 7.02 (d, 1H vinylic, J = 16.2 Hz); 3.53 (s, 2H); 2.30 (s, 6H). HRMS: 237.1517 (calcd) and 237.1500 (obsd).

***trans*-2-(2-Aminoethyl)stilbene (1°S2).** *trans*-2-(Bromomethyl)-stilbene, prepared by the method of Sindler-Kulyk and Laarhoven,[46] was reacted with sodium cyanide to give *trans*-2-(cyanomethyl)stilbene, which was purified by flash chromatography (eluent 50% $CHCl_3$, 50% hexane) and obtained in 91% yield. ^1H NMR ($CDCl_3$): δ 6.9–7.8 (m, 11H aromatic and vinylic); 4.65 (s, 2H). Reduction of the nitrile with $LiAlH_4$ followed by acid–base extractions afforded 1°S2 as a colorless oil in 83% yield. ^1H NMR ($CDCl_3$): δ 7.2–7.67 (m, 10 H); 7.02 (d, 1H, J = 16.2 Hz); 2.96 (m, 4H); 1.25 (br s, NH).

***trans*-2-[2-(*N*-Methylamino)ethyl]stilbene (2°S2) and *trans*-2-[2-(*N*,*N*-Dimethylamino)ethyl]stilbene (3°S2).** *trans*-2-(Cyanomethyl)-stilbene (2.0 g; see above), 2 g of NaOH, 50 mL of ethylene glycol were combined and refluxed for 72 h. After cooling, dilute HCl was added, and *trans*-2-(carboxymethyl)stilbene precipitated and was isolated in 85% yield. ^1H NMR ($CDCl_3$): δ 6.99–7.67 (m, 11H); 3.80 (s, 2H). The acid was converted to the secondary amide and reduced to yield 2°S2 as described above. After acid–base extractions, the amine was purified by preparative thick layer chromatography (eluent 95% $CHCl_3$, 5% MeOH), providing a colorless oil. ^1H NMR ($CDCl_3$): δ 7.69–7.23 (m, 10 H); 7.02 (d, 1H, J = 16.2 Hz); 2.97 (m, 2H); 2.85 (m, 2H); 2.46 (s, 3H). In an analogous manner, the acid was converted to the tertiary amide and reduced to yield 3°S2[47] in quantitative yield. ^1H NMR ($CDCl_3$): δ 7.65–7.22 (m, 10 H); 7.02 (d, 1H, J = 16,2 Hz)); 2.96 (m, 2H); 2.52 (m, 2H); 2.33 (s, 6H). HRMS: 251.1674 (calcd) 251.1675 (obsd).

***trans*-2-(3-Aminopropyl)stilbene (1°S3).** *trans*-2-(Bromomethyl)-stilbene[46] was reacted with sodium diethylmalonate in EtOH to give the diester, which was purified by flash chromatography (eluent 50% $CHCl_3$, 50% hexane), in 56% yield. Decarboxylation of the diester using the method of Krapcho and Lovey[48] afforded the monoester which was hydrolyzed to yield *trans*-2-stilbenepropanoic acid in 80% yield. ^1H NMR ($CDCl_3$): δ 7.22–7.64 (m, 10 H); 7.03 (d, 1H, J = 16.2 Hz); 3.12 (t, 2H); 2.67 (t, 2H). The acid was converted to the primary amide via the acid chloride and reduced with $LiAlH_4$ to yield 1°S3, which was isolated via acid–base extraction and obtained as a colorless oil. ^1H NMR ($CDCl_3$): δ 7.95–7.12 (m, 10 H); 7.03 (d, 1H, J = 16 Hz)); 2.88 (s, 2H); 2.78 (t, 2H, J = 7.2 Hz); 2.63 (t, 2H, J = 7.6 Hz); 1.77 (q, 4H, $J \approx$ 7.4 Hz). MS (*m/e*): 237 (M^+), 146, 129, 91.

***trans*-2-[3-(*N*-Methylamino)propyl]stilbene (2°S3) and *trans*-2-[3-(*N*,*N*-Dimethylamino)propyl]stilbene (3°S3).** *trans*-2-Stilbenepropionic acid was converted to the secondary amide via the acid chloride. Reduction followed by acid–base extraction and preparative thick layer chromatography (eluent 50% $CHCl_3$, 50% MeOH) afforded 3°S2 in 40% overall yield. ^1H NMR ($CDCl_3$): δ 7.66–7.19 (m, 10 H); 7.00 (d, 1H, J = 16.1 Hz); 2.82 (t, 2H, J = 7.6 Hz); 2.64 (t, 2H, J = 7.3 Hz); 2.43 (s, 3H); 1.80 (quin, 2H, $J \approx$ 7.4 Hz); 1.25 (br s, 1H). Similarly, synthesis and reduction of the tertiary amide followed by acid–base extraction and preparative thick layer chromatography (eluent 50% $CHCl_3$, 50% MeOH) afforded 3°S3 in 41% overall yield. ^1H NMR ($CDCl_3$): δ 7.62–7.2 (m, 10 H); 7.00 (d, 1H, J = 16.4 Hz); 2.79 (t, 2H, J = 7.6 Hz); 2.32 (t, 2H, J = 7.2 Hz); 2.21 (s, 6H); 1.78 (quin, 2H, $J \approx$ 7.4 Hz). HRMS: 265.1830 (calcd) 265.1830 (obsd).

2-(2-Phenylethyl)benzaldehyde (2). GC/MS analysis of an irradiated acetonitrile solution of 2°S1 revealed the formation of a major product tentatively identified as the imine **1**, on the basis of its mass spectral fragmentation. MS (*m/e*): 223 (M^+, 75), 208 (100). Preparative thick layer chromatography of the irradiated solution afforded **2**[49] in 26% isolated yield. ^1H NMR ($CDCl_3$): δ 7.95–7.12 (m, 10 H); 7.03 (d, 1H, J = 16 Hz)); 2.88 (s, 2H); 2.78 (t, 2H, J = 7.2 Hz); 2.63 (t, 2H, J = 7.6 Hz); 1.77 (q, 4H, $J \approx$ 7.4 Hz). MS (*m/e*): 210 (M^+, 28), 192 (15), 91 (100).

***N*-Methyl-2-phenyltetrahydro-3-benzazepine (3).** Irradiation of 2°S2 in acetonitrile solution followed by preparative thick layer chromatography afforded **3**[36a] as a colorless oil in 65% isolated yield. ^1H NMR ($CDCl_3$): δ 7.0–7.4 (m, 9H); 3.45 (dd, 1H); 3.30 (m, 2H); 3.10 (d, 1H); 2.86 (d, 1H); 2.68 (d, 1H); 2.40 (t, 1H); 2.06 (s, 3H). HRMS: 237.1514 (obsd) and 235.1517 (calcd). MS (*m/e*): 237 (M^+, 100), 222 (28), 181 (40), 132 (60), 118 (50), 91 (42).

***N*-Methyl-1-benzyltetrahydro-2-benzazepine (4).** Irradiation of 2°S3 in acetonitrile solution followed by preparative thick layer chromatography afforded **4**[36b] as a colorless oil in 38% isolated yield. ^1H NMR ($CDCl_3$): δ 7.0–7.4 (m, 9H); 3.66 (dd, 1H); 3.20 (m, 1H); 2.98 (br t, 2H); 2.78 (m, 2H); 2.46 (m, 1H); 2.13 (s, 3H); 1.85 (m, 1H); 1.64 (m, 1H). ^{13}C NMR: 142.3 (s), 140.7 (s), 138.1 (s), 128.6 (d), 128.05 (d), 127.08 (d), 126.8 (d), 125.7 (d), 125.5 (d), 124.8 (d), 70.09 (d), 51.28 (t), 42.93 (q), 38.83 (t), 32.45 (t), 30.94 (t). HRMS: 251.1676 (obsd) and 251.1674 (calcd). MS (*m/e*): 251 (M^+, 67), 236 (5), 146 (100), 132 (55), 118 (57), 91 (36).

1-Benzyltetrahydro-2-benzazepine (5). DCNB-sensitized irradiation of 1°S3 in acetonitrile–water solution followed by preparative thick layer chromatography afforded **5**[36b] as a colorless oil in 70% isolated yield. ^1H NMR ($CDCl_3$): δ 6.9–7.5 (m, 9H); 3.84 (dd, 1H); 3.18 (m, 2H); 3.05 (dt, 1H); 2.94 (dd, 1H); 2.72 (dt, 1H); 2.22 (td, 1H); 1.92 (m, 1H); 1.55 (m, 1H). ^{13}C NMR: 145.38 (s), 141.38 (s), 138.92 (s), 130.06 (d), 129.14 (d), 128.52 (d), 127.19 (d), 126.92 (d), 126.27 (d), 66.67 (d), 45.75 (t), 42.97 (t), 33.97 (t), 30.62 (t). MS (*m/e*): 237 (M+, 35), 132 (100), 118 (40), 91 (24).

1-Benzyltetrahydroisoquinoline (6). DCNB-sensitized irradiation of 1°S2 in acetonitrile–water solution followed by preparative thick layer chromatography afforded **6**[37a] as a colorless oil in 76% isolated yield. ^1H NMR ($CDCl_3$): δ 7.1–7.4 (m, 9H); 4.22 (AB q, 1H); 3.25 (m, 2H); 2.78–3.0 (m, 4H), 1.95 (br s, 1H). MS (*m/e*): 223 (M^+, 9), 132 (M − 91, 100), 91 (12).

Irradiation of 2-Methylstilbene with Diethylamine. GC/MS analysis of an irradiated acetonitrile solution of MS (0.01 M) and

(38) Lewis, F. D.; Johnson, D. E. *J. Photochem.* **1977**, 421.
(39) op den Brouw, P. M.; Laarhoven, W. H. *J. Org. Chem.* **1982**, *47*, 1546.
(40) Remy, D. C.; Van Saun, Jr., W. A.; Engelhardt, E. L. *J. Med. Chem.* **1975**, *18*, 142.
(41) Natelson, S.; Gottefried, S. P. *J. Am. Chem Soc.* **1941**, *63*, 487.
(42) Napolitano, E.; Fiaschi, R.; Marsili, A. *Tetrahedron Lett.* **1983**, *24*, 1319.
(43) Stella, L.; Raynier, B.; Surzur, J.-M. *Tetrahedron Lett.* **1977**, *31*, 2721.
(44) Borch, R. F.; Hassid, Aviv I. *J. Org. Chem.* **1972**, *37*, 1673.
(45) Murahashi, Shun-Ichi; Yamamura, M.; Yanagisawa, Ken-ichi; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408.
(46) Sindler-Kulyk, M.; Laarhoven, W. H. *J. Am. Chem. Soc.* **1978**, *100*, 3819.
(47) Bersch, H.-W.; Hoff, D.; Schon, D. *Arch. Pharm. (Weinheim, Ger.)* **1978**, *311*, 1029.
(48) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, *12*, 957.
(49) Harris, T. D.; Roth, G. P. *J. Org. Chem.* **1979**, *44*, 2004.

diethylamine (1.0 M) indicated the presence of 2-(2-phenylethyl)toluene and two stilbene–amine adducts. MS (*m/e*): 267 (M^+, 1), 176 (100) and 267 (M^+, 1), 162 (100). Preparative thick layer chromatography afforded pure samples of 2-(2-phenylethyl)toluene (^{1}H NMR ($CDCl_3$): δ 7.0–7.3 (m, 9 H), 2.88 (m, 4 H), 2.30 (s, 3 H)) and the stilbene–amine adduct of longer retention time (^{1}H NMR ($CDCl_3$): δ 6.82–7.25 (m, 9 H), 3.86 (d of d, 1 H), 3.26 (d of d, 1 H), 2.92 (d of d, 1 H), 2.73 (m, 2 H), 2.45 (m, 2 H), 2.18 (s, 3 H), 1.01 (t, 3 H, J = 7.0 Hz). Comparison of this NMR with that of the crude reaction mixture allows assignment of a singlet at δ 1.90 to the *o*-methyl of the second adduct.

Sensitized Irradiation of 2-Methylstilbene with Isopropylamine. GC/MS analysis of an irradiated 9:1 acetonitrile–water solution of MS (0.01 M), DCNB (0.01 M), and diethylamine (1.0 M) indicated the presence of two stilbene–amine adducts in a ratio of 1.5:1. MS (*m/e*): 253 (M^+, 1), 164 (100) and 253 (M^+, 1), 150 (100). The ^{1}H NMR spectrum of the mixture of adducts displays singlets assigned to the *o*-methyls at δ 2.21 (major adduct) and δ 2.16 (minor adduct).

Acknowledgment. Financial support for this research has been provided by the National Science Foundation and the Deutsche Forschungsgemeinschaft, and travel expenses have been supported by a NATO Research Grant.

JA942637M