Photophysical and Photochemical Behavior of Intramolecular Styrene-Amine Exciplexes

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Abstract: The photophysical and photochemical behavior of a series of secondary and tertiary ω-(β-styryl)aminoalkanes with one to five methylenes separating the styryl and amino groups has been investigated and compared to the intermolecular reactions of 1-phenylpropene with secondary and tertiary amines. The tertiary styrylamines form fluorescent intramolecular exciplexes, but fail to undergo intramolecular addition reactions. Both the rate constant for exciplex formation and the stability of the exciplex are dependent upon the length of the polymethylene chain connecting the chromophores. The failure of the tertiary amine exciplexes to undergo intramolecular addition is attributed to an unfavorable exciplex geometry for α-C-H transfer to the styrene double bond. While the secondary styrylamines do not form fluorescent exciplexes, the dependence of the styrene singlet lifetime upon the polymethylene chain length is similar to that for the tertiary styrylamines. Intramolecular N-H addition to the styrene double bond results in the formation of two regioisomeric (α-phenyl and α-benzyl) cyclic amines of different ring size. The regioisomer of larger ring size is favored except in the case in which four methylenes separate the chromophores. The effects of polymethylene chain length, solvent polarity, temperature, and the bulk of the *N*-alkyl group upon product yields and ratios are discussed in terms of a mechanism involving singlet exciplex and biradical intermediates.

Introduction

The intermolecular photochemical reactions of aryl olefins with secondary and tertiary aliphatic amines results in the formation of N-H and α-C-H adducts, respectively, along with products of the reduction and reductive dimerization of the aryl olefin.[1-3] The mechanism proposed for stilbene-amine addition (Scheme I) involves electron-transfer quenching of singlet stilbene (t-S) by ground-state amine to form a singlet exciplex which undergoes N-H transfer (secondary amines) or α-C-H transfer (tertiary amines) to form a radical pair which can either combine, disproportionate, or diffuse apart.[3] In the case of the stilbene-tertiary amine exciplexes, exciplex fluorescence is observed in nonpolar solvents and adduct formation in polar solvents. The absence of exciplex fluorescence from singlet stilbene and other arenes with secondary amines may be due to rapid N-H transfer which occurs in both nonpolar and polar solvents.[4,5]

The low preparative yields of stilbene-amine adducts are due at least in part to the competition of radical pair combination with disproportionation and diffusion. Higher yields of adducts would be expected from intramolecular addition reactions in which the intermediate biradical cannot diffuse apart. We have recently reported that high yields of styrene-secondary amine adducts are obtained upon irradiation of several ω-styryl(*N*-methylamino)-alkanes with one to five methylenes separating the styrene and secondary amino groups.[6] The corresponding ω-styryl(*N*,*N*-dimethylamino)alkanes fail to undergo intramolecular addition but do form fluorescent intramolecular exciplexes. We report here our detailed investigation of the photophysical and photochemical behavior of both the secondary and tertiary ω-styrylaminoalkanes. The comparison of these results to those of the corresponding intermolecular reactions serves to elucidate the effects of alkane chain length, N-alkylation, solvent, and temperature upon the initial electron-transfer process, N-H and C-H transfer, and the behavior of the resulting biradical intermediates.

Results

Preparation and Spectroscopic Properties. The ω-styryl-aminoalkanes were prepared by standard procedures as described in the Experimental Section. In cases where mixtures of trans and cis isomers were obtained, the pure trans isomer was obtained by photoinitiated isomerization with molecular iodine. Cis isomers were obtained by means of triplet-sensitized irradiation (Michler's ketone, 365-nm light) followed by silica gel chromatography. The purity of cis and trans isomers (>98%) was confirmed by gas chromatography. Deuterated amines were obtained by means of repeated exchange with D_2O and the isotopic purity determined mass spectroscopically.

The absorption[7] and fluorescence[8-12] spectra of styrene (**1**) and

Scheme I

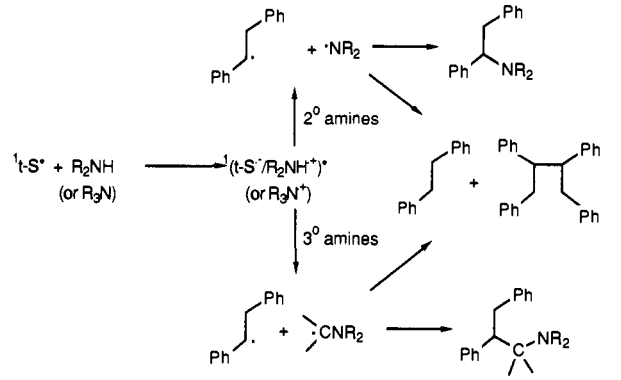

Chart I

PhCH=CH(CH$_2$)$_3$NH$_2$ (**3**)
PhCH=CHCH$_2$NHCH$_3$ (**4**)
PhCH=CH(CH$_2$)$_2$NHCH$_3$ (**5**)
PhCH=CH(CH$_2$)$_3$NHCH$_3$ (**6**)
PhCH=CH(CH$_2$)$_4$NHCH$_3$ (**7**)
PhCH=CH(CH$_2$)$_5$NHCH$_3$ (**8**)
PhCH=CH(CH$_2$)$_3$NHCH(CH$_3$)$_2$ (**9**)
PhCH=CH(CH$_2$)$_3$NHC(CH$_3$)$_3$ (**10**)
PhCH=CHCH$_2$N(CH$_3$)$_2$ (**11**)
PhCH=CH(CH$_2$)$_2$N(CH$_3$)$_2$ (**12**)
PhCH=CH(CH$_2$)$_3$N(CH$_3$)$_2$ (**13**)
PhCH=CH(CH$_2$)$_4$N(CH$_3$)$_2$ (**14**)
PhCH=CH(CH$_2$)$_5$N(CH$_3$)$_2$ (**15**)

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Table I. Fluorescence and Photoisomerization Data for Styrene and Styrylamines

		τ_s,[a] ns	Φ_f[b]	$10^7 k_t$, s^{-1}	Φ_i[c]
1	styrene	14.6[e]	0.24[e]	1.6	
t-**2**	*trans*-1-phenylpropene	11.6	0.30	2.6	0.030
c-**2**	*cis*-1-phenylpropene	2.2	0.030	1.4	0.030
3	*trans*-5-phenyl-4-penten-1-amine	3.7	0.19	5.0	
4	*trans*-*N*-methyl-3-phenyl-2-propen-1-amine	*d*			0.016
5	*trans*-*N*-methyl-4-phenyl-3-buten-1-amine	0.73	0.046	6.3	<0.001
t-**6**	*trans*-*N*-methyl-5-phenyl-4-penten-1-amine	0.51	0.021	4.1	0.0029
c-**6**	*cis*-*N*-methyl-5-phenyl-4-penten-1-amine	0.36	0.015	4.2	<0.001
7	*trans*-*N*-methyl-6-phenyl-5-hexen-1-amine	1.6	0.070	4.3	0.012
8	*trans*-*N*-methyl-7-phenyl-6-hepten-1-amine	2.8	0.13	4.6	
9	*trans*-*N*-isopropyl-5-phenyl-4-penten-1-amine	<0.5	0.025	<5.0	
10	*trans*-*N*-*tert*-butyl-5-phenyl-4-penten-1-amine	0.45	0.025	5.5	
11	*trans*-*N*,*N*-dimethyl-3-phenyl-2-propen-1-amine	*d*			
12	*trans*-*N*,*N*-dimethyl-4-phenyl-3-buten-1-amine	0.15			0.048
t-**13**	*trans*-*N*,*N*-dimethyl-5-phenyl-4-penten-1-amine	0.35			0.035
c-**13**	*cis*-*N*,*N*-dimethyl-5-phenyl-4-penten-1-amine	<0.5			
14	*trans*-*N*,*N*-dimethyl-6-phenyl-5-hexen-1-amine	1.5	0.07	2.0	
15	*trans*-*N*,*N*-dimethyl-7-phenyl-6-hepten-1-amine	3.4	0.10	2.9	

[a] Fluorescence lifetime of ca. 5×10^{-5} M styrene or styrylamine in nitrogen-purged cyclohexane solution at 300 K. [b] Fluorescence yields determined relative to the value for styrene under the conditions of footnote *a*. [c] Quantum yields for cis,trans isomerization of 0.005–0.01 M **2** or styrylamine irradiated at 288 nm in nitrogen-purged acetonitrile solution. [d] No fluorescence observed. [e] Data from ref 9.

trans- and *cis*-1-phenylpropene (*t*-**2** and *c*-**2**) have been extensively studied. The solution absorption maxima of all of the *trans*- and *cis*-ω-styrylaminoalkanes are similar to those of *t*-**2** and *c*-**2**, respectively; however, the band intensities display considerable variation due in part to the absorption of aliphatic amines at wavelengths below 290 nm. For the trans isomers, a weak band (^1L_b) with vibrational structure (λ_{max} = 294 nm, ϵ = 700–1500) is resolved from the strong band (^1L_b) at shorter wavelength (λ_{max} = 244–252 nm, ϵ = 4000–25000). For the cis isomers, the long-wavelength band appears as an unresolved shoulder on the strong band (λ_{max} = 244 nm). The weakly structured solution fluorescence spectra of **1** and *t*-**2** display 0,0 bands at 294 and 295 nm and maxima at 304 and 308 nm, respectively. The unstructured fluorescence of *c*-**2** displays an onset at ca. 287 nm and a maximum at 304 nm.

Fluorescence lifetimes and quantum yields for **1**, *t*-**2**, and *c*-**2** and several ω-styrylaminoalkanes (**3**–**15**, Chart I) in cyclohexane solution are reported in Table I. Fluorescence decays were analyzed by means of a standard single photon timing apparatus with either a mode-locked dye laser or a gated spark lamp as the exciting source. The time resolution of the later apparatus is ca. 0.5 ns, necessitating the use of the former apparatus for the measurement of more rapid decay profiles. Analysis of the fluorescence decay curves is discussed in Appendix I. The measured lifetimes for **1** and *t*-**2** are sufficiently long to display dependence upon the solvent purity and the extent of deoxygenation, providing a possible explanation for some literature values[8-10] substantially shorter than those in Table I. Fluorescence quantum yields were determined relative to that of **1** for which the literature value of Φ_f = 0.24[9] was assumed. Values of the radiative decay rate constant ($k_f = \Phi_f/\tau$) for all of the styrenes (**1**–**15**) are in the range $1.4–6.3 \times 10^7$ s^{-1}.

The singlet lifetimes of all of the ω-styrylaminoalkanes are shorter than those of **1** or **2**, presumable due to the occurance of intramolecular quenching of the styrene singlet by ground-state amine. Intermolecular quenching of **1** or *t*-**2** by triethylamine in cyclohexane solution is reported to result in the formation of a fluorescent exciplex.[11] Our results for the quenching of **1**, *t*-**2**, and *c*-**2** by primary, secondary, and tertiary aliphatic amines are reported in Table II. Quenching of **1** and *c*-**2** by secondary or tertiary amines is observed to occur with rate constants near the rate of diffusion (3×10^{10} M^{-1} s^{-1} in hexane solution) while quenching of *t*-**2** is somewhat slower. Quenching of singlet **1** by the primary amine is significantly slower than quenching by the tertiary amine. Quenching of **1**, *t*-**2**, and *c*-**2** by triethylamine, but not by the primary or secondary amine, results in the appearance of exciplex emission. The exciplex lifetimes are dependent upon amine concentration, presumably due to quenching of the exciplex by ground-state amine.[13] Values of the exciplex lifetimes extrapolated to low triethylamine concentration are reported in Table II.

Table II. Intermolecular Styrene Fluorescence Quenching and Exciplex Fluorescence Data

styrene	amine	$k_q\tau$,[a] M^{-1}	$10^9 k_q$,[b] M^{-1} s^{-1}	τ_{ex},[c] ns	λ_{max},[d] nm
1	$BuNH_2$	(2.2)	(0.26)		
	Et_3N	76.9 (79.8)	9.2 (9.5)	9.3	399
t-**2**	Et_2NH	48.7	4.1		
	Et_3N	41.7	3.5	11.5	390
c-**2**	Et_2NH	28.5	13.0		
	Et_3N	53.5 (22.0)	24.0 (10.0)	7.2	390

[a] Slope of Stern–Volmer plot for quenching of the fluorescence intensity or lifetime (data in brackets) of 5×10^{-5} M styrene by 0.01–0.10 M amine in nitrogen-purged cyclohexane solution. [b] Calculated using the lifetime data in Table I. [c] Lifetime of the exciplex fluorescence monitored at 410 nm. [d] Maximum intensity of exciplex fluorescence in cyclohexane solution.

Table III. Styrylamine Intramolecular Exciplex Fluorescence

styrylamine	solvent	λ_{max}, nm	τ_{ex},[a] ns
12	hexane	357	2.2
	dibutyl ether	388	
	diethyl ether	395	
	tetrahydrofuran	443	
	acetonitrile	470	
t-**13**	hexane	378	1.5
	dibutyl ether	395	
	diethyl ether	406	
	tetrahydrofuran	435	
c-**13**	hexane	380	2.0

[a] Decaying component of 410-nm emission for solutions as described in Table I, footnote *a*.

Styrene-like (monomer) fluorescence is observed for all of the ω-styrylaminoalkanes except the 3-phenyl-2-propen-1-amines **4** and **11**. Room temperature exciplex emission is observed only for the tertiary amines **12**, *t*-**13**, and *c*-**13** for which exciplex lifetimes are reported in Table III. Exciplex fluorescence (410 nm) displays a rising component with a time constant similar to that of the monomer decay (308 nm) as well as the decaying component whose time constant is reported in Table III. Also

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Table IV. Product Yields for ω-Styryl(*N*-methylamino)alkanes

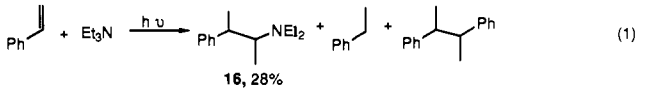
styrylamine	Φ_{add}[a]	yield,[b] %	b/a[c]
4		15	>10
5	0.024	63	14
t-**6**	0.011	57	2.4
c-**6**	0.019	62	2.0
7	0.050	82	0.15
8		30	>10

[a] Quantum yield for total adduct formation using monochromatic 288-nm irradiation of 0.005–0.01 M styrylamine in nitrogen-purged acetonitrile solution. [b] Yield of the major adduct (**b** or **a**) determined by GC analysis at conversions <20%. [c] Product ratio determined by GC analysis.

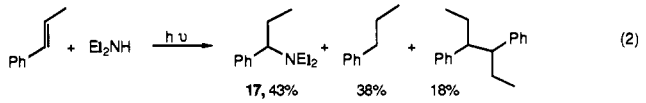
reported in Table III is the solvent dependence of the exciplex fluorescence maxima. For these styrylamines, monomer emission is not spectrally resolved from the much stronger exciplex emission, making the measurement of Φ_f for the monomer impossible. The exciplex fluorescence maxima shift to longer wavelength and the intensity of fluorescence decreases with increasing solvent polarity (Table III). In the case of **12**, exciplex fluorescence can be detected even in acetonitrile solution.

Photochemical Reactions. Quantum yields for cis,trans isomerization (Φ_i) determined with monochromatic 288-nm irradiation for the 1-phenylpropenes and several ω-styrylaminoalkanes in acetonitrile solution are reported in Table I. Quantum yields are low in all cases, reflecting the inherent inefficiency of cis,trans isomerization of β-alkyl styrenes in solution.[14] The value of Φ_i for the trans styrylamines decreases with decreasing singlet lifetime. The value of Φ_i for *c*-**2** is the same as that for *t*-**2**, in spite of its shorter lifetime, while Φ_i is much smaller for *c*-**6** vs *t*-**6**. Triplet-sensitized (Michler's ketone) isomerization of the ω-styrylaminoalkanes results in relatively efficient isomerization and no intramolecular addition.

Irradiation of **1** with triethylamine is reported to yield a single 1:1 adduct (**16**), 1-phenylethane, and 2,3-diphenylbutane (eq 1).[2] While the total quantum yield for product formation is higher in acetonitrile vs hexane solution (0.34 vs 0.07), the yield of **16** is lower (9% vs 28% of total product). Similarly, we find that irradiation of *t*-**2** (0.05 M) with diethylamine (0.1 M) yields a single 1:1 adduct (**17**), 1-phenylpropane, and 3,4-diphenylhexane in both cyclohexane and acetonitrile solution (eq 2). The yield of styrene dimers is lower in the presence than in the absence of amines.

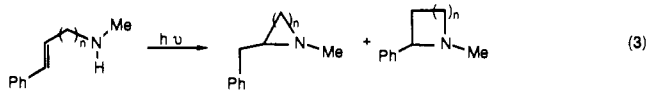


16, 28% (1)



17, 43% 38% 18% (2)

The tertiary ω-styrylaminoalkanes **11–15** fail to undergo intramolecular addition upon irradiation in either polar or nonpolar solvents. Inefficient cis,trans isomerization is the only photoprocess observed for these compounds. Quantum yields for isomerization of several secondary and tertiary styrylamines are reported in Table I. The secondary ω-styryl(*N*-methylamino)alkanes **4–8** undergo intramolecular addition to yield mixtures of regioisomeric adducts in which C–N bond formation has occurred at either the β-carbon (**4a–8a**) or the α-carbon (**4b–8b**) (eq 3). Preparative yields,



(3)

4 n = 1 **4a** **4b**
5 n = 2 **5a** **5b**
6 n = 3 **6a** **6b**
7 n = 4 **7a** **7b**
8 n = 5 **8a** **8b**

(14) A reported value of $\Phi_i = 0.22$ for *t*-**2**[8] appears to be in error.

Table V. Solvent Dependence of the Cycloadduct Ratios for ω-Styryl(*N*-methylamino)alkanes

solvent	**5b/5a**[a]	Φ_{rel}[b]	**6b/6a**[a]	Φ_{rel}[b]	**7b/7a**[a]	Φ_{rel}[b]
cyclohexane	2.9	1.4	0.93	1.6	0.80	1.3
benzene	2.5	1.1	0.76	1.7	0.64	1.3
dichloromethane	7.8	1.3	0.79	1.4	0.36	0.8
acetonitrile	13.3	(1.0)	2.4	(1.0)	0.16	(1.0)
methanol			1.4	0.61		

[a] Product ratio determined by GC analysis. [b] Total adduct yield relative to that for acetonitrile solution.

Table VI. Temperature Dependence of Cycloadduct and Adduct/Isomerization Ratios

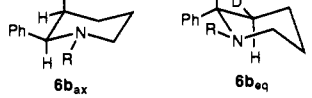
temp, °C	**6b/6a**	(**6a** + **6b**)/*c*-**6**[a]
30	2.4	1.5
10	2.6	0.84
−10	4.6	0.85
−30	6.4	0.65
−40	6.2	0.49

[a] Ratio of total adduct to isomerization at <20% conversion.

adduct ratios, and quantum yields for intramolecular addition (Φ_{add}) are reported in Table IV. Preparative yields are good for **5–7**, but modest for **4** and **8**. Addition efficiencies are also lower for the two latter compounds. Two regioisomeric adducts were isolated and characterized for **5–7**, but only a single adduct was characterized for **4** and **8**, as in the analogous intermolecular addition reaction (eq 2). The lower limits for **4b/4a** and **8b/8a** are based on comparisons of GC peak sizes for **4b** and **8b** to those of the largest peak of similar retention time. The quantum yields for total adduct formation decrease in the order **7** > **5** > *c*-**6** > *t*-**6** ≫ **4** or **8**.

The solvent dependence of the intramolecular adduct ratios and relative quantum yields for total adduct formation for styrylamines **5–7** are reported in Table V. The regioselectivity is observed to increase with increasing solvent polarity, both for **5** and **6**, which yield more of the type-**b** adduct, and for **7**, which yields more of the type-**a** adduct. The relative quantum yields decrease moderately with increasing solvent polarity. Both the ratio **6b/6a** and the relative yield are lower in the polar hydroxylic solvent methanol than in acetonitrile. The temperature dependence of the product ratios has also been determined for *t*-**6** (Table VI). Decreasing the temperature results in an increase in the regioselectivity of adduct formation, but a decrease in the efficiency of addition vs isomerization. Since both *t*-**6** and *c*-**6** yield adducts **6a** and **6b** with similar yields, the occurrence of isomerization should not reduce the preparative yield or regioselectivity of preparative low-temperature irradiation.

The stereochemistry of the *N*-methyl-2-phenylpiperidine formed upon irradiation of *t*-**6**-*N*-*d* and *c*-**6**-*N*-*d* was determined by means of ^{1}H NMR analysis. Deuterium incorporation occurs exclusively at C-3, as expected for an addition mechanism similar to that for addition of singlet stilbene and secondary amines (Scheme I).[3] In the case of *t*-**6**-*N*-*d*, only the piperidine $\mathbf{6b}_{ax}$ in which the deuterium is axial (cis to phenyl) can be detected. In the case of *c*-**6**-*N*-*d*, both the piperidine $\mathbf{6b}_{ax}$ and its diastereomer $\mathbf{6b}_{eq}$ are formed in an ca. 3:1 ratio. GC-MS analysis confirmed the incorporation of 1.0 deuterium in the piperidine ring of **6b** and the absence of deuterium incorporation in the pyrrolidine ring of **6a** or in the vinyl group of recovered *t*-**6**.



$\mathbf{6b}_{ax}$ $\mathbf{6b}_{eq}$

The effect of increasing the bulk of the *N*-alkyl group was also investigated for the 5-phenyl-4-penten-1-amines **9** and **10**. Irradiation of the *N*-isopropylamine **9** in acetonitrile solution followed by column chromatography results in the formation of **9b** (65%) and 5-phenylpentanal (**18**) (15%). GC-MS analysis of the irradiated solution prior to chromatography indicates that the imine

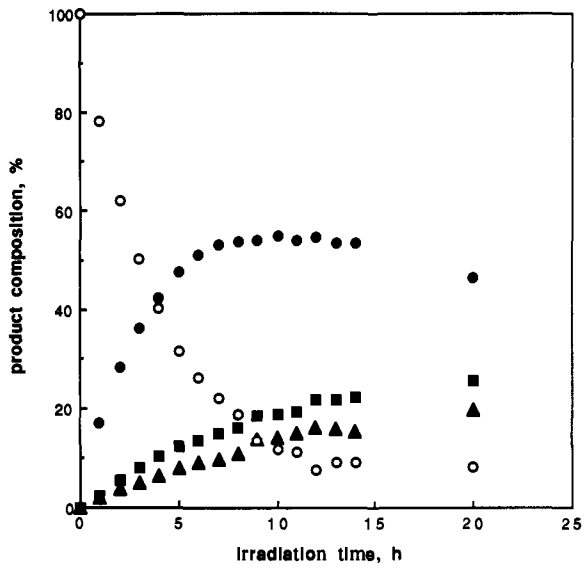
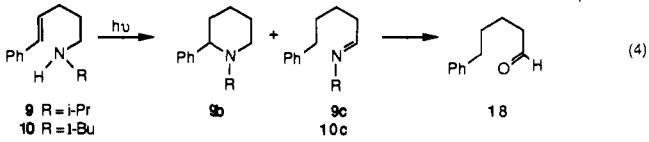


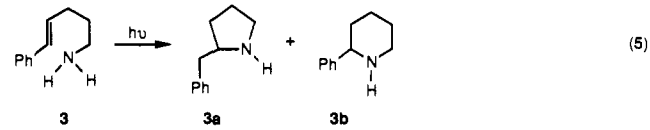
Figure 1. Conversion of *trans*-5-phenyl-4-penten-1-amine (**3**, ○) to its cis isomer (●) and to adducts **3a** (▲) and **3b** (■).

9c is a primary product of the photochemical reaction and undergoes hydrolysis to yield the aldehyde **18** (eq 4). No evidence was obtained by GC-MS for the formation of *N*-isopropyl-2-benzylpyrrolidine. Irradiation of the *N-tert*-butylamine **10** followed by chromatography results in essentially quantitative formation of the aldehyde **18**. No evidence was obtained by GC-MS for the formation of either piperidine or pyrrolidine products from **10**. The aldehyde **18** obtained from the irradiation of **10**-*N*-*d* was analyzed for deuterium content (>95% based upon GC-MS analysis) and location (>90% at C-4 based upon ^{13}C NMR analysis). Thus the formation of **18** from **10**-*N*-*d* occurs via regioselective transfer of the *N*-*d* to the β-carbon. Furthermore, when **10**-*N*-*d* is recovered after ca. 50% conversion to products and analyzed for deuterium content and location by GC-MS and by ^1H NMR spectroscopy, no H–D exchange of the vinyl protons can be detected.



(4)

Irradiation of the primary styrylamine **3** in acetonitrile solution results in both isomerization and intramolecular addition to yield a mixture of **3a** and **3b** (eq 5). In contrast to the results for the



(5)

secondary amine *t*-**6**, isomerization is more efficient than addition in the case of **3** as seen in Figure 1. The ratio of adducts **3b**/**3a** is also smaller (ca. 1.4) than is the case for *t*-**6**. The absence of upward or downward curvature in the plots of yield vs time indicates that **3a** and **3b** are formed from *t*- and *c*-**3** with comparable efficiencies.

Discussion

Styrene Photophysics and Photoisomerization. The photophysics of styrene and its alkyl derivatives both in the vapor phase[15] and in solution[8-12] has been the subject of several previous investigations. The measured lifetimes reported in Table I for **1**, *t*-**2**, and *c*-**2** are in agreement with the longest of the values reported in the literature. The lifetime and fluorescence quantum yield for *c*-**2** are significantly lower than those for *t*-**2**; however, the values of k_f for both isomers are similar to that of **1**. The relatively long singlet lifetimes of the styrenes (compared to the stilbenes) and the absence of temperature-dependent fluorescence quantum yields have been attributed to a large barrier for twisting about the alkene double bond in the lowest singlet state.[9] In contrast, the triplets of *t*-**2** and *c*-**2** undergo essentially activationless isomerization with quantum yields of 0.5.[17,18]

The inefficient isomerization of *t*-**2** and *c*-**2** (Table I) might reflect either slow singlet isomerization or inefficient intersystem crossing, followed by triplet-state isomerization. The rate constant for singlet-state isomerization $k_i = 2.5 \times 10^6$ and 1.4×10^7 s^{-1} can be calculated from the measured values of τ_s and Φ_i ($k_i = \Phi_i \tau s^{-1}$) for *t*-**2** and *c*-**2**, respectively. Assuming a normal preexponential for alkene isomerization (log A = 13.8), values of E_a = 10 and 9 kcal/mol can be estimated for *t*-**2** and *c*-**2**, somewhat smaller than the calculated value of 16 kcal/mol for **1**.[19] A slightly lower barrier might have been expected for *c*-**2** vs *t*-**2** on the basis of greater nonbonded repulsion. Barriers of this magnitude would be consistent with the observed absence of temperature-dependent fluorescence for **1**.[9] The measured values of Φ_i for direct (288 nm, Table I) and triplet-sensitized isomerization of *t*-**2** and *c*-**2** provide an upper limit for the quantum yield for intersystem crossing, $\Phi_{isc} < 0.06$ ($\Phi_{isc} = 2\Phi_i$). This value is similar to those estimated by Zimmerman et al.[20] for several 1-phenylcycloalkenes, but it is distinctly lower than those estimated for **1** and 1-phenylbutene by Bonneau.[10] If the triplet mechanism applies, rate constants for intersystem crossing (k_{isc}) are double the calculated values of k_i.

Quenching of Styrene Fluorescence and Isomerization by Amines. Tertiary amines have been reported to quench the fluorescence of several styrenes.[11] Rate constants were observed to increase with increasing solvent polarity, increasing styrene electron affinity, and decreasing amine oxidation potential, in accord with an electron transfer quenching mechanism. Exciplex fluorescence was observed in cyclohexane but not in acetonitrile solution. The electrochemical reduction of styrenes (−2.46 and −2.54 V vs SCE for **1** and *t*-**2**, respectively[21]) and oxidation of alkylamines (0.78 V for Et_3N[22]) in nonaqueous solution are highly irreversible. None-the-less, reasonable agreement is obtained between the observed values of λ_{max} for exciplex fluorescence (Table I) and values calculated by using the empirical relationship (eq 6) derived by Weller.[23] Values for the free energy of electron transfer, ΔG_{et}, in nonpolar solvent can also be calculated from the redox potential and singlet energies of the styrenes (E_s = 4.22 eV) by using eq 7, also derived by Weller.[23] The values for singlet **1** with Et_3N

$$E_{max} = E_D^{ox} - E_A^{rdn} - 0.15 + 0.1 \text{ eV} \quad (6)$$

$$\Delta G_{et} = E_D^{ox} - E_A^{rdn} - {}^1E^* - 0.06 \text{ eV} \quad (7)$$

and Et_2NH ($E_{1/2}$ = 1.01 V vs SCE[22]) are ΔG = −0.62 and −0.29, respectively. The observation of rate constants near the rate of diffusion for styrene fluorescence quenching by these amines is consistent with the proposed exergonic electron transfer quenching mechanism. The somewhat lower quenching rate constants for singlet *t*-**2** vs **1** or *c*-**2** may reflect its higher reduction potential.[24]

(15) (a) Rockley, M. G.; Salisbury, K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1582. (b) Steer, R. P.; Swords, M. D.; Crosby, P. M.; Phillips, D.; Salisbury, K. *Chem. Phys. Lett.* **1976**, *43*, 461. (c) Ghiggino, K. P.; Hara, K.; Salisbury, K.; Phillips, D. *J. Chem. Soc., Faraday Trans. 2* **1978**, 607.

(16) Reports of significantly shorter lifetimes for *t*-**2**[8] and 1-phenylbutene[10] vs styrene appear to be spurious.

(17) Caldwell, R. A.; Sovocool, G. W.; Peresie, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 1496.

(18) Arai, T.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2204.

(19) Bendazzoli, G. L.; Orlandi, G.; Palmieri, P.; Poggi, G. *J. Am. Chem. Soc.* **1978**, *100*, 392.

(20) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1974**, *96*, 7821.

(21) Chodowski, J.; Giovanoli-Jakubaczak, T. *Rocz. Chem.* **1967**, *41*, 273.

(22) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

(23) (a) Weller, A. *Z. Phys. Chem.* (*Wiesbaden*) **1982**, *130*, 129. (b) Weller, A. *Z. Phys. Chem.* (*Wiesbaden*) **1982**, *133*, 93.

(24) We were able to observe the irreversible reduction of *c*-**2** but not *t*-**2** in dimethyl sulfoxide solution.

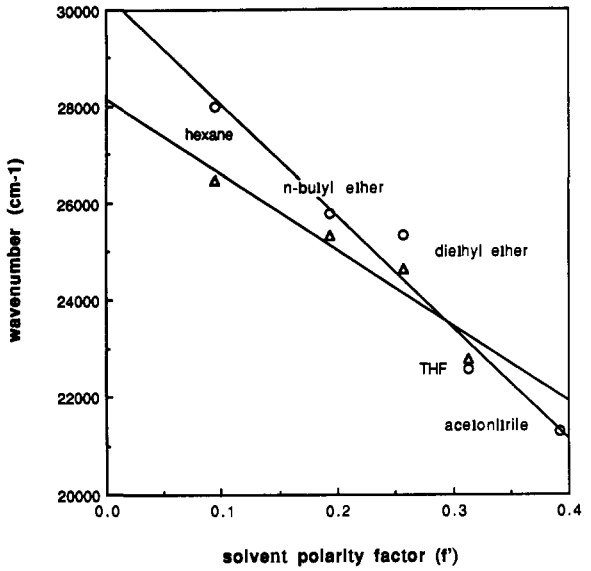


Figure 2. Plot of exciplex emission maxima for *trans*-*N*,*N*-dimethyl-4-phenyl-3-buten-1-amine (**12**, ○) and *trans*-*N*,*N*-dimethyl-5-phenyl-4-penten-1-amine (**13**, △) vs Lippert's solvent polarity factor, according to eq 8.

While the oxidation potentials of primary amines have not been measured in solution, a value in excess of 1.5 V is expected on the basis of the effect of N-alkylation upon amine ionization potentials.[25] Thus electron-transfer quenching of the styrenes by primary amines is expected to be endergonic, in accord with the low observed rate constant for fluorescence quenching of **1** by $BuNH_2$.

The values of τ_s and Φ_f for the styrylamines **3**–**15** are all lower than the values for *t*-**2** and *c*-**2** (Table I), presumably as a consequence of intramolecular electron-transfer quenching of the singlet styrene chromophore by the ground-state amine. There is ample precedent for the formation of fluorescent intramolecular arene–tertiary amine exciplexes[26] as well as one report of exciplex fluorescence from an α-linked styrylamine.[27] The effect of solvent polarity upon the exciplex fluorescence maxima of **12** and *t*-**13** is similar to that observed by Van der Auweraer et al.[26] for the intramolecular exciplexes of ω-phenyl-α-(*N*,*N*-dimethylamino)-alkanes. Plots of the emission maxima vs solvent polarity (f') using Lippert's equation[28] (eq 8, in which n is the refractive index of

$$f' = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/2(2n^2 + 1) \qquad (8)$$

the solvent and ϵ is its dielectric constant) are shown in Figure 2. From the slopes and an estimated solvent cavity radius of 5 Å, values of the exciplex dipole moment μ = 20.0 and 13.6 D are obtained for the exciplexes of **12** and *t*-**13**, respectively. These values are similar to those for phenylaminoalkanes of similar alkane chain length.[26a] The larger dipole moment for **12** vs *t*-**13** presumably reflects a larger separation of charge due to the more restricted conformational mobility of **12**. On the basis of the variation in exciplex fluorescence maxima, the trend in exciplex stability follows the order intermolecular > *c*-**13** ~ *t*-**13** > **12**.

The values of τ_{ex} for the fluorescent intramolecular exciplexes of **12**, *t*-**13**, and *c*-**13** (Table III) are all significantly longer than the lifetimes of the residual monomer (Table I). This indicates that intramolecular exciplex formation is essentially irreversible, in accord with the large negative value of ΔG_{et} for the quenching of styrenes by trialkylamines. If it is assumed that intramolecular electron-transfer quenching of the singlet styrene chromophore by all of the secondary and tertiary amines is irreversible and that the styrene singlet lifetime is otherwise unaffected by the alkylamino group, the rate constants for intramolecular electron transfer (k_{et}) can be calculated from the residual monomer lifetime of the styrylamine and the lifetime of *t*-**2** or *c*-**2** (τ_0) with eq 9. The resulting values of k_{et} are reported in Table VII.

Table VII. Rate Constants for Intramolecular Electron-Transfer Quenching[a]

secondary amine	$10^{-9}k_{et}$, s^{-1}	tertiary amine	$10^{-9}k_{et}$, s^{-1}
5	1.3	**12**	6.5
t-**6**	1.8	*t*-**13**	2.8
c-**6**	2.3	*c*-**13**	>2
7	0.53	**14**	0.58
8	0.27	**15**	0.21
9	1.8		
10	1.8		

[a] Calculated from the lifetime data in Table I with eq 9.

$$k_{et} = \tau_s^{-1} - \tau_0^{-1} \qquad (9)$$

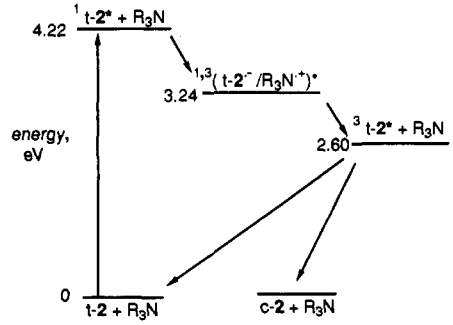
The values of k_{et} for secondary amines and tertiary amines with the same alkane chain length separating the two chromophores are similar, except in the case of the C_2 chain (**5** vs **12**). This parallelism supports the assumption that irreversible electron-transfer quenching occurs for the secondary as well as the tertiary amines. The decrease in k_{et} with increasing chain length is expected for intramolecular electron-transfer quenching.[26] The larger value for **12** vs **5** may reflect the larger driving force for the through-space interaction with a tertiary vs secondary amine, which may dominate for the very short (C_2 and C_1) alkane chains. The larger value for *c*-**6** vs *t*-**6** may also reflect the larger driving force for reduction of a *cis*- vs *trans*-styrene.[24] The values of k_{et} for **9** and **10** are the same as that for *t*-**6**. Thus the rate constant for intramolecular electron-transfer quenching is independent of the bulk of the N-alkyl group, as is the case for the intermolecular quenching of singlet *trans*-stilbene by tertiary amines.[3] All of the values of k_{et} in Table VII are significantly larger than those previously reported for linked arene–*N*,*N*-dimethylaniline systems.[29] The large values of k_{et} are consistent with previous reports that the singlet arene lifetimes of linked arene–trialkylamines are too short to measure at room temperature with a conventional single photon counting apparatus.[26]

In the case of styrylamines for which both τ_s and Φ_f values are available, the calculated values of k_f are comparable to or somewhat larger than those for *t*-**2**. Thus the radiative decay rate for the unquenched styrene-like emission is unchanged (in the case of the tertiary amines) or slightly increased (in the case of the primary and secondary amines) by the linked amino group. Neither monomer nor exciplex fluorescence is observed in the case of the 3-phenyl-2-propen-1-amines **4** and **11**. A similar absence of fluorescence was reported by Chandross and Thomas[30] for α- and β-(dimethylamino)methylnaphthalenes and attributed to through-space interaction of the arene and amino frontier orbitals.

In the cases of styrylamines for which τ_s and Φ_i values are available, rate constants for singlet-state isomerization (k_i) or intersystem crossing (k_{isc}, triplet-state isomerization mechanism) can be calculated. Assuming either a singlet-state or triplet-state mechanism, the calculated values of k_i or k_{isc} for *t*-**6** and **7** are 2 to 3 times larger than those for *t*-**2** and the values for **12** and *t*-**13** are over 100 times larger! Thus exciplex formation results in an increased rate of styrene isomerization or intersystem crossing. Unimolecular isomerization of the styrene anion radical

(25) Watanabe, K.; Mottl, J. *J. Chem. Phys.* **1957**, *26*, 1773.
(26) (a) Van der Auweraer, M.; De Schryver, F. C.; Gilbert, A.; Wilson, S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 227. (b) Van der Auweraer, M.; Gilbert, A.; De Schryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4007. (c) Van der Auweraer, M.; Gilbert, A.; De Schryver, F. C. *Nouv. J. Chim.* **1980**, *4*, 153. (d) Van der Auweraer, M.; Swinnen, A. M.; De Schryver, F. C. *J. Chem. Phys.* **1982**, *77*, 4110. (e) Swinnen, A. M.; Van der Auweraer, M.; De Schryver, F. C.; Windels, C.; Goedeweeck, R.; Vannerem, A.; Meeus, F. *Chem. Phys. Lett.* **1983**, *95*, 467. (f) Swinnen, A. M.; Van der Auweraer, M.; De Schryver, F. C.; Nakatani, K.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1987**, *109*, 321.
(27) Aoyama, H.; Arata, Y.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1381.
(28) Lippert, E. *Z. Naturforsch.* **1955**, *109*, 541.
(29) Okada, T.; Saito, T.; Mataga, N.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 331.
(30) Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, *9*, 393.

Scheme II



is unlikely to account for enhanced isomerization as the rotational barrier should be larger in the anion radical than in the singlet state. It seems more likely that exciplex formation provides an alternative pathway leading to the formation of styrene triplet, namely exciplex intersystem crossing and return electron transfer to generate the locally excited styrene triplet (Scheme II).[31] While the singlet energy of *t*-**2** (4.22 eV) is well above that of the singlet exciplex of **12** and *t*-**13** (3.47 and 3.28 eV, respectively), the triplet energy of *t*-**2** (2.60 eV[17]) is significantly lower than that of the singlet or triplet exciplex.

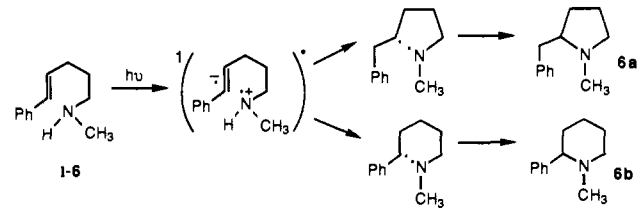
Rate constants for singlet exciplex intersystem crossing can be calculated from the measured values of Φ_i and τ_{ex} ($k_{isc} = 2\Phi_i\tau_{ex}^{-1}$). The resulting values for **12** and *t*-**13** are $k_{isc} = 2.2 \times 10^7$ and 2.3×10^7 s^{-1}, respectively, somewhat smaller than the value for the intermolecular exciplex of *trans*-stilbene with Et_3N ($k_{isc} = 4.9 \times 10^7$ s^{-1}).[31] Okada et al.[4] have reported that the rate constant for intersystem crossing of the pyrene–*N*-ethylaniline exciplex is much larger than that for the pyrene–*N*,*N*-dimethylaniline exciplex (ca. 10^8 vs 10^6 s^{-1}) and attribute this difference to N–H–pyrene hydrogen bonding in the secondary amine exciplex. A similar difference in the intersystem crossing rate constants for the secondary vs tertiary styrylamine exciplexes would explain our failure to observe exciplex fluorescence from the secondary styrylamines as well as the low quantum yields for intramolecular addition. The failure of triplet sensitization to effect styrene–amine addition indicates that it is a singlet-state process.

Intramolecular Hydrogen Transfer. Comparison of the products of inter- vs intramolecular photochemical styrene–amine reactions (eq 2 vs 3) reveals several important differences between these reactions. Among these is the significantly higher yield of intra- vs intermolecular adduct formation of secondary amines in cases where 2, 3, or 4 methylenes separate the styryl and amino groups (Table IV). In addition, the intramolecular addition reaction displays lower or even inverted regioselectivity when compared to the intermolecular reaction. The formation of products resulting from reductive dimerization of the styrene chromophore is not observed in the intramolecular reactions, and photoreduction is only observed for secondary amines with bulky *N*-alkyl groups (eq 4). Perhaps even more striking is the photochemical stability of tertiary styrylamines. These and other characteristics of the intramolecular styrene–amine reaction can be attributed to steric and stereoelectronic effects upon the formation and behavior of biradical intermediates. These effects are dependent upon the length of the polymethylene chain connecting the styryl and amino groups and the bulk of the *N*-alkyl group.

The formation of two regioisomeric adducts from the styrylamines **5**–**7** is attributed to the occurrence of N–H transfer to both the α- and β-carbon of the styrene double bond as shown in Scheme III for the reaction of *t*-**6**. In view of the low quantum yields for total intramolecular adduct formation (Table IV) it is possible that the initially formed biradical intermediates disproportionate to reform ground-state styrylamine in competition with cyclization to form adducts. If this were the case, then the observed adduct ratios might reflect biradical behavior rather than the competition between N–H transfer to the α- vs β-carbon. Two lines of evidence indicate that this is not likely to be the case. First,

(31) Lewis, F. D.; Simpson, J. T. *J. Phys. Chem.* **1979**, *83*, 2015.

Scheme III



irradiation of neither *t*-**6**-*N*-*d* nor **10**-*N*-*d* results in H–D exchange of the vinyl protons of the recovered starting material. This would necessitate that disproportionation occur with retention of stereochemistry in the biradical intermediate, a requirement seemingly at odds with the observation of nonstereospecific cycloaddition of *c*-**6**-*N*-*d* (vide infra). Second, biradical disproportionation is observed in the case of the styrylamines **9** and **10** (eq 4); however, the products are the imines **9c** and **10c**. Thus we conclude that the product ratios reported in Table IV reflect the regioselectivity of the N–H transfer process.

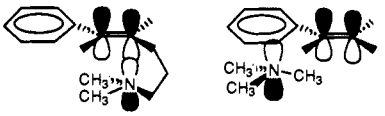
The preferential formation of a benzyl vs secondary radical would be expected on thermodynamic grounds and is the predominant process in the case of the intermolecular reaction (eq 2) and intramolecular reactions of styrylamines **4**, **5**, and **8**. In the case of **6**, N–H transfer to C-β is favored in polar solvents while transfer to C-α is slightly favored in nonpolar solvents. Transfer of N–H to C-α is favored for all solvents in the case of **7**. We assume that the competition between C-α vs C-β transfer is determined by the relative heights of the very small activation barriers leading to the formation of biradical intermediates from either a single exciplex intermediate or multiple minima separated by even smaller barriers. This model is consistent with the increase in regioselectivity and decrease in relative yield for cycloadduct formation with decreasing reaction temperature (Table VI) and increasing solvent polarity (Table V). Both decreasing the reaction temperature and increasing the solvent polarity should stabilize the exciplex intermediate and selectively disfavor the formation of the product of the higher barrier process. Since no information is currently available concerning the geometry of either the styryl–amine exciplex or the transition states for N–H transfer,[32] we can only speculate that the occurrence of C-α transfer must result from an increase in the barrier for C-β transfer in some of the intramolecular reactions as a consequence of the energetics of polymethylene chain folding. C-α transfer does not occur to an appreciable extent either when the chain length is too short to allow effective C-α–H–N overlap (as in the case of **4**) or sufficiently long so as to not conformationally bias the N–H transfer process (as in the case of **8**). A further indication that the regioselectivity of N–H transfer is dependent upon exciplex geometry is provided by the observation that an α-linked secondary 3-styrylpropylamine undergoes regiospecific C-β transfer.[33]

The competition between C-α vs C-β N–H transfer is dependent upon the bulk of the amino group as well as the polymethylene chain length. In the case of the primary styrylamine **3**, the ratio of cyclization products (eq 5, **3a**/**3b** = 1.4) indicates that the N–H transfer process is less regioselective than in the case of the secondary styryl-*N*-methylamine *t*-**6** (**6a**/**6b** = 2.4). In the case of the secondary styryl-*N*-isopropylamine **9** only the piperidine product **9b** is observed, indicative of regiospecific C-β N–H transfer. In the case of the styryl-*N*-*tert*-butylamine **10** deuterium-labeling studies indicate that N–D transfer occurs regiospecifically to C-β. Inspection of molecular models fails to indicate an increase in nonbonded interactions for the transition state leading to C-α vs C-β transfer upon increasing the bulk of the N-alkyl substituent. In view of the previously described effects of temperature and solvent polarity upon N–H transfer regioselectivity, it seems more likely that decreasing amine ionization

(32) See, however, ref 26 for the geometry of arene–tertiary amine exciplexes and ref 4 for a proposed geometry of an arene–secondary amine exciplex.

(33) Reddy, G. D., unpublished results.

Scheme IV



potential in the series N–H > N–CH_3 > N–$CH(CH_3)_2$ > N–$C(CH_3)_3$[25] results in the formation of a more stable exciplex which undergoes more selective C-β transfer.

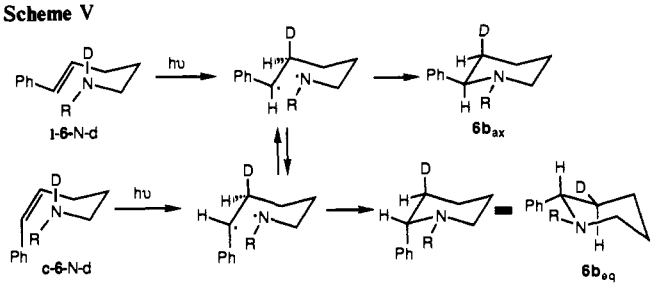
The failure of the tertiary styrylamines **11–15** to undergo intramolecular addition was at first surprising in view of the occurrence of the analogous intermolecular reaction (eq 1) and of the intramolecular reactions of some α-linked styryl-*N*,*N*-dibenzylamines[27] and ω-phenyl(*N*,*N*-dimethylamino)alkanes.[34] There has been a previous report of the occurrence of intramolecular phenanthrene–amine addition for secondary amines and not for tertiary amines.[35] However, no explanation was given for the failure of the tertiary amine to undergo intramolecular addition. We suspect that the occurrence of inter- but not intramolecular α-C–H transfer from tertiary amines to singlet styrene is a consequence of exciplex geometry. The location of the amino group in the intramolecular exciplexes is constrained by the polymethylene chain to the vicinity of the styrene double bond. The resulting exciplex geometries do not allow for concomitant orbital overlap and α-C–H transfer from the amine cation radical to the styrene anion radical. In contrast, location of the amine over the benzene ring in the intermolecular exciplex would permit such simultaneous overlap to occur (Scheme IV).

Behavior of the Biradical Intermediates. The higher preparative yields for intra- vs intermolecular styrene–amine adduct formation and the absence of photoreduction and reductive dimerization products for the secondary styrylamines **5–7** are plausibly the consequence of differences in the behavior of the biradical vs radical pair intermediates formed in these reactions. By analogy to our earlier studies of stilbene–amine photochemical reactions (Scheme I),[3] formation of the styrene–amine adduct **17** (eq 2) is proposed to occur via the in-cage combination of the (1-phenylpropyl)diethylaminyl radical pair. 1-Phenylpropane can be formed either via the disproportionation of this radical pair or the reaction of 1-phenylpropyl following cage escape. The reductive dimer 3,4-diphenylhexane is presumed to be formed via the combination of two 1-phenylpropyl radicals. In view of the high reported combination/disproportionation ratio for this radical (9.3 at 118 °C in benzene solution[36]), autodisproportionation can account for only a small fraction of the 1-phenylpropane formed. On the basis of our earlier studies,[3,5] 1-phenylpropane formation plausibly occurs predominantly via the in-cage disproportionation of the (1-phenylpropyl)diethylaminyl radical pair.

The higher yield of adduct formation and the absence of reductive dimer formation for the intra- vs intermolecular styrene–secondary amine addition reactions were anticipated on the basis of the inability of the alkyl and aminyl radicals to diffuse apart when connected by a polymethylene chain. Two modes of disproportionation are available to the biradical intermediates: hydrogen abstraction by nitrogen to regenerate the styrylamine and hydrogen abstraction by the carbon-centered radical to generate an *N*-alkylimine. Negative evidence concerning the former mode was presented in the context of regioselective biradical formation. The later mode is in fact observed in the case of the styryl-*N*-isopropylamine **9** and is the predominant reaction in the case of the biradical intermediate formed from the styryl-*N*-*tert*-butylamine **10**. The decrease in the biradical cyclization/disproportionation ratio with increasing bulk of the *N*-alkyl group is consistent with the steric effect anticipated for radical pair combination.[37]

Further information about the biradical cyclization process is provided by the stereochemistry of N–D addition in the case of

Scheme V



t-**6**-*N*-*d* and *c*-**6**-*N*-*d*. ^{1}H NMR analysis of the piperidine product establishes that *t*-**6** yields only $\mathbf{6b_{ax}}$, the product of stereospecific syn N–H addition to the *trans*-styrene double bond. Stereospecific N–H addition to the *cis*-styrene double bond would be expected to yield $\mathbf{6b_{eq}}$; however, *c*-**6** yields an ca. 3:1 mixture of the diastereomeric piperidines $\mathbf{6b_{ax}}$ and $\mathbf{6b_{eq}}$. This result is indicative of partial rotational equilibration of the 1,6-biradical intermediate prior to cyclization (Scheme V). Preferential formation of piperidine $\mathbf{6b_{ax}}$ presumably reflects a lower energy for the cyclization transition state in which the phenyl group is equatorial rather than axial. The formation of ca. 25% $\mathbf{6b_{eq}}$ from *c*-**6**-*N*-*d* indicates that rotational equilibrium is not fully established prior to cyclization.

Concluding Remarks. The photophysical and photochemical behavior of styrylaminoalkanes is dependent upon the length of the polymethylene chain separating the chromophores, the degree of N-alkylation, and the reaction environment (solvent and temperature). Following the generation of the locally excited styrene singlet state upon the absorption of light, the rate of the subsequent intramolecular electron transfer quenching process is determined by the amine oxidation potential and the polymethylene chain length. In the case of the exciplex intermediates formed from primary and secondary styrylamines, N–H transfer to either C-α or C-β of the styrene double bond generates two regioisomeric biradical intermediates, which can either cyclize or disproportionate. The regioselectivity of N–H transfer is dependent upon both the polymethylene chain length and the bulk of the *N*-alkyl substituent, while disproportionation is observed only with bulky *N*-alkyl substituents. The exciplex intermediates formed from tertiary styrylamines are fluorescent and undergo enhanced styrene isomerization, but fail to undergo styrene–amine addition. The conformational limitations placed upon the intramolecular styrene–amine exciplex geometry by the connecting polymethylene chain are believed to be responsible for the failure of the tertiary amines to undergo α-C–H transfer and for the unusual regioselectivity of N–H transfer observed for some of the secondary amines.

The formation of intramolecular styrene–amine adducts ranging in ring size from four to eight (eq 3) establishes the synthetic potential of this photochemical reaction. Extention to even larger ring sizes is limited only by the requirement that intramolecular exciplex formation compete with decay of the styrene singlet. High conversions of reactant to product in preparative reactions are possible due to the absorption of Pyrex-filtered light ($\lambda > 300$ nm) by the styrene chromophore, but not by the styrene–amine adducts. In cases where two regioisomeric adducts are formed, some control of regioselectivity can be realized by the appropriate choice of solvent and reaction temperature. The stereochemistry of N–H addition to β-substituted styrenes can be predicted on the basis of ring formation via a rotationally equilibrated biradical intermediate. Applications of this reaction to the synthesis of polycyclic and macrocyclic amines are currently being explored in our laboratories.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on Varian EM 390 and XLA 400 spectrometers with TMS as an internal standard. ^{13}C NMR spectra were recorded on a Jeol FX 270 spectrometer with $CDCl_3$ as the reference and the solvent. UV-visible absorption spectra were measured with a Hewlett-Packard 8452 A diode array spectrometer. Mass spectra were determined with a Hewlett-Packard 5985 GC/VG70-250SE MS system using an ionizing voltage of 70 eV. Fluores-

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cence spectra were measured on a Perkin-Elmer MPF-44A spectrometer. Fluorescence quantum yields were determined relative to styrene (ϕ_f = 0.24)[9] for solutions of matched absorbance (0.1) at the excitation wavelength (270 nm). Fluorescence lifetimes were measured with two different single photon counting apparatuses, one with a gated arc lamp (PTI-LS1, time resolution ca. 0.5 ns) and the other with a mode-locked dye laser (time resolution ca. 50 ps[13b]). The preparative scale irradiations were carried out in Rayonet reactor fitted with RPR 3000 lamps. All the reactions were carried under dry N_2 in Pyrex tubes. Quantum yield measurements were carried out on an optical bench (at 288 nm), and light intensities were determined with *trans*-stilbene actinometry.[38] Irradiated mixtures were analyzed on a Hewlett-Packard 5890 A gas chromatograph equipped with a 10 m × 0.53 mm glass column packed with polydimethylsiloxane for the analysis of photoproducts. The chromatograph is equipped with flame ionization detector.

Materials. Solvents were all spectral grade. Acetonitrile (Aldrich) and dichloromethane (Aldrich) were distilled over calcium hydride prior to use. Benzene (Aldrich) containing benzophenone indicator was distilled over sodium metal. Hexane (Aldrich), cyclohexane (Mallinkrodt), and methyl alcohol (Aldrich) were distilled prior to use. Styrene and *cis*- and *trans*-1-phenylpropene (Aldrich) were >98% pure by GC analysis and were used without further purification.

***trans*-*N*-Methyl-3-phenyl-2-propen-1-amine (4).** The secondary amine was prepared in three steps starting from cinnamic acid (Aldrich). To 1 g of cinnamic acid 1.1 equiv of thionyl chloride was added and refluxed until the evolution of HCl gas ceased (approximately 90 min). The excess thionyl chloride was removed at reduced pressure and the residue dissolved in 5 mL of dry benzene transferred in to a dropping funnel, and added dropwise to a mixture of 20 mL of benzene, 10 mL of diethyl ether, 2 g of ice, 0.5 mL of 40% aqueous methylamine (Aldrich), and 0.9 g of anhydrous K_2CO_3 at 0 °C over a period of 30 min. The reaction mixture was stirred overnight at room temperature. The organic layer separated and was dried over $MgSO_4$, and the solvent was removed to provide the amide (90%). Reduction of the amide with lithium aluminum hydride[39] afforded **4** as a colorless oil in 95% yield. ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.35 (m, 2 H), 3.0 (d, 2 H), 2.2 (s, 3 H). IR (chloroform) 3250 cm^{-1}.

***trans*-*N*-Methyl-4-phenyl-3-buten-1-amine (5).** Styrylacetic acid (2.0 g) (Aldrich) was converted to the amide as above. Reduction of the amide with triethyloxonium tetrafluoroborate[40] provided **5** as a colorless oil in 50% yield. ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.35 (m, 2 H), 2.6 (m, 4 H), 2.35 (s, 3 H).

***trans*-*N*-Methyl-5-phenyl-4-penten-1-amine (6).** Alkylation of diethyl malonate (26.2 g) with cinnamyl chloride (25 g, Aldrich) afforded the corresponding diester[41] in ~75% yield. The diester was refluxed at 180 °C for 6 h in the presence of sodium chloride in aqueous dimethyl sulfoxide[42] solution to yield the monoester (75%). Part of the monoester was converted into amide (95%) on standing for 3 days in a saturated methanolic solution of methylamine in the presence of sodium methoxide.[43] LAH reduction of the amide resulted in the formation of **6** as a colorless oil in 95% yield. ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.35 (m, 2 H), 2.60 (t, 2 H), 2.66 (s, 3 H), 2.3 (m, 2 H), 1.60 (q, 2 H). IR (chloroform) 3250 cm^{-1}. HRMS 175.1354 (obsd) and 175.1360 (calcd).

***trans*-*N*-Methyl-6-phenyl-5-hexen-1-amine (7).** The monoester (2.0 g), prepared as in **6**, was hydrolyzed under basic conditions to 5-phenyl-4-pentenoic acid by refluxing in 20 mL of 10% KOH in methanol and 1 mL of water for 2 h. The acid was treated with 1.1 equiv of thionyl chloride and refluxed for 1.5 h and added dropwise to a solution of excess diazomethane in diethyl ester at −5 °C and left overnight at room temperature. Removal of the solvent under reduced pressure provided quantitative yield of the diazoketone. The diazoketone is subjected to Wolff rearrangement in dioxane following the procedure reported[44] for the preparation of homologous acids and quenched with methylamine to provide the secondary amide in 50% yield. The amide is reduced with LAH to the amine **7** as above. ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.35 (m, 2 H), 2.6 (m, 2 H), 2.5 (s, 3 H), 2.4 (m, 2 H), 1.5 (m, 4 H). IR (chloroform) 3250 cm^{-1}.

***trans*-*N*-Methyl-7-phenyl-6-hepten-1-amine (8).** The monoester (2.0 g) employed in the preparation of **6** was reduced with LAH to the primary alcohol. The primary alcohol was converted to the chloride in 60% yield by refluxing with 1.1 equiv of thionyl chloride. Alkylation of diethyl malonate with this chloride followed by a sequence of reactions similar to the one reported for **6** provided **8** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.35 (m, 2 H), 2.6 (t, 2 H), 2.5 (s, 3 H), 2.4 (m, 2 H), 1.5 (m, 6 H). IR (chloroform) 3250 cm^{-1}. HRMS (*m/e*) 203.1659 (obsd) and 203.1673 (calcd).

Preparation of Tertiary Amines (11–15).[45] The preparation of **13** is typical for all tertiary amines from the corresponding secondary amines. To a stirred solution of 100 mg of secondary amine and 0.5 mL of 37% aqueous formaldehyde in 5 mL of acetonitrile was added 100 mg of sodium cyanoborohydride in portions. The reaction mixture was stirred for 15 min and glacial acetic acid was added dropwise until the solution tested neutral. Stirring was continued for an additional 45 min while maintaining the pH near neutrality. The solvent was evaporated under reduced pressure, and 5 mL of aqueous 2 N KOH was added to the residue. The resulting mixture was extracted with diethyl ether and dried over $MgSO_4$, and the solvent was evaporated in vacuo to give ~100 mg (>90%) of tertiary amine as a colorless oil. All the compounds were characterized by ^{1}H NMR and mass spectra. **11**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.35 (m, 2 H), 3.02 (d, 2 H), 2.3 (s, 6 H). MS (*m/e*) 161 (M^+). **12**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.35 (m, 2 H), 2.35 (m, 4 H), 2.25 (s, 6 H). MS (*m/e*) 175 (M^+). **13**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.35 (m, 2 H), 2.3 (m, 4 H), 2.2 (s, 6 H), 1.6 (qui, 2 H). MS (*m/e*) 189 (M^+). **14**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.35 (m, 2 H), 2.25 (br s, 10 H), 1.5 (m, 4 H). MS (*m/e*) 203 (M^+), 84 (40), 58 (100). **15**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.35 (m, 2 H), 2.25 (br s, 10 H), 1.5 (m, 6 H). MS (*m/e*) 217 (M^+), 160 (20), 91 (28), 70 (100).

Preparation of Cis Isomers (*c*-6 and *c*-13). A 0.01 M solution of *t*-**6** or *t*-**13** in dry acetonitrile was irradiated in the presence of Michler's ketone in a Rayonet reactor fitted with RPR 3500 lamps. The photolysis was stopped after reaching the photostationary state consisting of ca. 75% cis isomer. The solvent was removed and the residue repeatedly column chromatographed on silica gel (20% methanol in chloroform) to provide the cis isomer in more than 98% purity based on GC analysis. *c*-**6**: ^{1}H NMR ($CDCl_3$) δ 7.3 (br s, 5 H), 6.4 (dt, 1 H), 5.7 (m, 1 H), 2.6 (t, 2 H), 2.45 (s, 3 H), 2.4 (q, 2 H), 2.0, 1.65 (qui, 2 H). *c*-**13**: ^{1}H NMR ($CDCl_3$) δ 7.3 (br s, 5 H), 6.4 (dt, 1 H), 5.7 (m, 1 H), 2.3 (m, 4 H), 2.25 (s, 6 H), 1.6 (qui, 2 H).

Preparation of 3, 9, and 10. 5-Phenyl-4-pentenoic acid obtained in the preparation of **7** was converted in to **3**, **9**, and **10** following a similar procedure as used in the preparation of **4** except the amines used were ammonium hydroxide, isopropylamine, and *tert*-butylamine, respectively. **3**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 6.4 (m, 2 H), 2.7 (t, 2 H), 2.2 (q, 2 H), 1.6 (qui, 2 H), 1.65 (br s, 2 H, NH_2). MS (*m/e*) 161 (M^+), 144 (42), 129 (75), 91 (40). **9**: ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.4 (m, 2 H), 2.8 (sep, 1 H), 2.7 (t, 2 H), 2.35 (q, 2 H), 1.65 (q, 2 H), 1.0 (d, 6 H). **10**: ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.4 (m, 2 H), 2.7 (t, 2 H), 2.3 (q, 2 H), 1.6 (q, 2 H), 1.2 (s, 9 H).

Preparation of Deuterated Amines *t*-6-*N*-*d*, *c*-6-*N*-*d*, and 10-*N*-*d*. The deuterated amines were prepared by stirring a mixture of amine (100 mg) and 1 mL of D_2O under nitrogen atmosphere for 24 h. The D_2O was then removed under vacuo and fresh D_2O was added again and stirred for an additional 24 h. The sequence was repeated at least three times, and isotopic purity was confirmed by mass spectral analysis.

Photolysis. All analytical irradiations were carried out on 0.01 M solutions of styrylamines contained in Pyrex test tubes that had been purged with dry N_2 gas for 10–15 min using a Rayonet reactor fitted with RPR 3000 lamps. After 10–15 min of irradiation (less than 20% conversion) the samples were analyzed for product formation by means of gas chromatography. The preparative irradiations were carried out in acetonitrile solution under conditions similar to those for analytical reactions except for the conversion, which typically went to a maximum of 95%. Evaporation of the solvent under reduced pressure and column chromatography (silica gel, 5% methyl alcohol in either dichloromethane or chloroform) yielded the pure adducts in most cases. All the major adducts from each of the secondary amines and the minor adduct from **6** were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. The remaining minor adducts were tentatively identified from their mass spectral fragmentation patterns. The structure assigned to the major adduct from **4** was also confirmed by comparison of its ^{1}H NMR spectrum and GC retention time with those of an independently synthesized sample of 1-methyl-2-phenylazitidine.[46] The chemical shifts and high-resolution mass spectra of the adducts are as follows. **4a**: MS (*m/e*) 147

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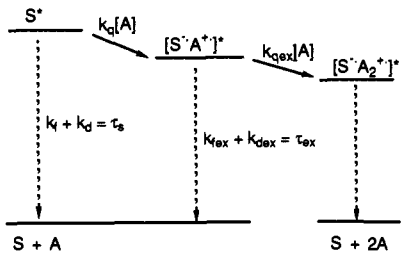
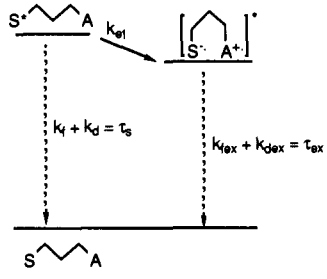
Scheme VI



Scheme VII



(M^+), 120 (100), 91 (15). **4b**: ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 5 H), 3.72 (t, 1 H), 3.35 (m, 1 H), 2.75 (m, 1 H), 2.24 (s, 3 H), 2.12 (m, 2 H). MS (*m/e*) 147 (M^+), 118 (100), 104 (54). **5a**: HRMS: 161.1178 (obsd) and 161.1204 (calcd). **5b**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 3.3 (m, 1 H), 3.2 (m, 1 H), 2.25 (m, 1 H), 2.2 (s, 3 H), 1.8 (m, 2 H). HRMS (*m/e*) 161.1181 (obsd) and 161.1204 (calcd). The other fragments are 132, 84 (100). **6a**: ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 3.1 (m, 3 H), 2.6–2.1 (m, 3 H), 2.33 (s, 3 H), 1.6 (m, 4 H). ^{13}C NMR δ 140.0 (s), 129.1 (d), 128.1 (d), 125.9 (d), 67.8 (d), 57.4 (t), 40.7 (q, t), 30.9 (t), 21.7 (t). HRMS 175.1349 (obsd) and 175.1362 (calcd). Other fragments are 91 (9), 84 (100). **6b**: ^{1}H NMR ($CDCl_3$, TMS) δ 7.2–7.4 (m, 5 H), 3.04 (d, 1 H), 2.75 (dd, 1 H), 2.1 (m, 1 H), 1.99 (s, 3 H), 1.8 (m, 1 H), 1.7 (m, 3 H), 1.6 (m, 4 H), 1.35 (m, 1 H). ^{13}C NMR δ 144.8 (s), 128.7 (d), 127.4 (d), 126.9 (d), 71.1 (d), 57.6 (t), 44.5 (q), 35.9 (t), 26.2 (t), 25.0 (t). MS (*m/e*) 175 (M^+), 118 (33), 98 (100). HRMS 175.1353 (obsd), 175.1362 (calcd). **7a**: ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 3.35 (dd, 1 H), 3.2 (m, 1 H), 3.02 (m, 1 H), 2.9 (m, 1 H), 2.5 (m, 1 H), 2.2 (s, 3 H), 1.7 (m, 6 H). ^{13}C NMR δ 141.0 (s), 123.6 (d), 122.5 (d), 121.9 (d), 121.0 (d), 67.0 (d), 50.89 (t), 39.84 (t), 31.22 (q), 23.52 (t), 22.4 (t), 21.0 (t). MS (*m/e*) 189 (M^+), 160, 146, 132, 118, 112, 91. HRMS 189.1507 (obsd) and 189.1517 (calcd). **7b**: MS (*m/e*) 189 (M^+, 2), 98 (100), 91 (25). HRMS 189.1504 (obsd) and 189.1517 (calcd). **8a**: MS (*m/e*) 203 (M^+), 160, 104, 91. HRMS 203.1673 (obsd) and 203.1673 (calcd). **8b**: MS 203 (M^+), 160. HRMS 203.1668 (obsd) and 203.1673 (calcd). **9b**: ^{1}H NMR ($CDCl_3$) δ 7.1–7.4 (m, 5 H), 3.3 (dd, 1 H), 2.9 (m, 1 H), 2.8 (sep, 1 H), 1.5–1.8 (m, 5 H), 1.3 (m, 1 H), 0.97 (d, 3 H), 0.75 (d, 3 H). ^{13}C NMR δ 144.0 (s), 128.0 (d), 127.1 (d), 126.3 (d), 47.9 (d), 43.8 (d), 36.9 (t), 36.0 (t), 25.2 (t), 21.0 (q), 11.7 (q). **10c**: MS (*m/e*) 217 (M^+), 202 (100), 160, 140, 91, 84. **18**: ^{1}H NMR ($CDCl_3$) δ 9.7 (s, 1 H), 7.1–7.3 (m, 5 H), 2.6 (t, 2 H), 2.42 (t, 2 H), 1.6 (m, 4 H). ^{13}C NMR δ 202.4 (s), 141.8 (s), 128.3 (d), 43.7 (t), 35.6 (t), 30.8 (t), 21.7 (t). The aldehyde (**18**) isolated from **10-*N*-*d*** contains deuterium exclusively at the C-4 carbon (30 ppm) based on the coupling between carbon and deuterium. Integration of the two benzylic protons in ^{1}H NMR does not show any decrease, indicating there is no deuterium incorporation at C-5 (benzylic). MS (*m/e*) 162 (M^+), 91 (100). IR (chloroform) 1730 cm^{-1} (C=O stretch).

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Appendix I

Analysis of the fluorescence decay curves is based on the kinetic schemes for intermolecular exciplex formation and intramolecular exciplex formation shown in Schemes VI and VII, respectively. In all cases the monomer fluorescence monitored at 308 nm exhibits monoexponential decay (experimentally verified) with an amplitude >0.97 for the major component. Time-resolved exciplex emission monitored at 410 nm was analyzed by a least-squares-fitting procedure assuming a multiexponential decay law. It was found that an increase in the number of exponentials beyond two did not improve the fit. Since the lifetime of the rising and major decaying components did not change upon addition of a third component, we interpret these components as the lifetime of the styrene monomer and of the exciplex, respectively. The styrene monomer lifetimes obtained in this fashion for styrylamines **12** and *t*-**13** (0.10 and 0.32 ns, respectively) are in good agreement with those obtained from the decay time of the monomer fluorescence (Table I). Since the amplitudes of additional components in the 410-nm emission were always below 0.05 we conclude that emission occurs either from a single exciplex geometry or multiple geometries with equal decay times. The simplified kinetic analysis of Scheme VII is appropriate in either case.