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Registry No. 4, 140438-51-3; 20, 140438-52-4; 22, 62399-28-4; 2-azabutadiene, 38239-27-9; BH_3, 13283-31-3; ethylene, 74-85-1; acrylonitrile, 107-13-1; vinyl chloride, 75-01-4; vinyl alcohol, 557-75-5; acetylene, 74-86-2; cyanoacetylene, 1070-71-9; dicyanoacetylene, 1071-98-3.

Photocyclization of 4-(Dialkylamino)-2-aryl-1-butenes

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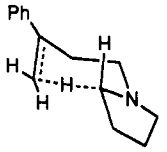
Irradiation of 4-(dialkylamino)-2-aryl-1-butenes gave cyclization products, 3-methyl-3-arylpyrrolidines, in high yields. These styrylamines formed fluorescent intramolecular exciplexes, but studies based on Stern–Volmer quenching for the fluorescence and the photoreaction suggested that the emissive exciplexes did not participate in the photoreaction.

Photochemical hydrogen abstraction by acyclic alkenes is quite rare[1] in contrast to the fact that some cyclic alkenes undergo such reaction[2] as with carbonyl compounds.[3] This fact may be attributed to the presence of competitive processes such as *E–Z* isomerization. Hornback et al. reported very inefficient type II analogous reaction of styrenes.[4] On the other hand, some acyclic alkenes undergo efficient hydrogen abstraction from electron donors such as amines. Lewis et al. reported photoaddition of secondary or tertiary amines to singlet-excited stilbene via hydrogen transfer.[5] Intermolecular photoaddition of amines to styrenes has also been reported.[6] These photoreactions of stilbene and styrenes have been reported to proceed via proton transfer from charge transfer exciplexes or ion pairs produced by single-electron transfer. Recently, Lewis et al. reported photocyclization of ω-(styrylamino)alkanes which proceeded via hydrogen transfer from the NH group to the olefinic carbons.[7] This reaction has also been explained in terms of proton transfer of intramolecular exciplexes although emission from the exciplexes was not observed. In relation to our studies on photochemical reactions of styrenes bearing a nitrogen-containing functional group,[8] we report here facile photocyclization of α-[(dialkylamino)ethyl]styrenes **1**.[9] This cyclization proceeds via hydrogen abstraction from the C–H group by the olefinic carbon in distinction from the above-mentioned cyclization of ω-(styrylamino)alkanes. This reaction provides a useful method for the synthesis of some pyrrolidines and is of interest mechanistically since these styrylamines show emission from intramolecular exciplexes.

Chart I

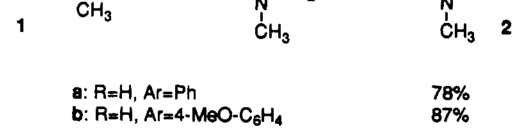


Results and Discussion

The unsaturated amines **1** can be easily prepared by the Wittig reaction of the corresponding Mannich bases.

Photochemical Reactions. When 4-(dimethylamino)-2-phenyl-1-butene (**1a**) in hexane was irradiated with a low-pressure mercury lamp, 1,3-dimethyl-3-phenylpyrrolidine (**2a**) was obtained in 72% yield. The structure of **2a** was determined on the basis of elemental analysis and spectral data. The ^1H- and ^{13}C-NMR spectra showed the presence of a methyl group on a nitrogen atom and that on a quaternary carbon and the absence of olefinic carbons. The formation of **2a** is readily explained in terms of intramolecular hydrogen abstraction by the terminal olefinic carbon and subsequent cyclization of the resulting diradical. Irradiation of 4-methoxyphenyl and 4-biphenylyl derivatives **1b** and **1c** also gave the corresponding cyclization products **2b** and **2c** in high yields, whereas a 4-cyanophenyl derivative **1d** was unreactive toward photolysis and prolonged irradiation resulted in the formation of an intractable mixture. Meanwhile, irradiation of 5-(dimethylamino)-3-phenyl-2-pentene (**1e**), which has a trisubstituted double bond, underwent facile photocyclization.

The reactions of **1a** and **1b** were found to be singlet reactions because they were neither sensitized by xanthone nor quenched by 1,3-pentadiene.



a: R=H, Ar=Ph	78%
b: R=H, Ar=4-MeO-C_6H_4	87%
c: R=H, Ar=4-Ph-C_6H_4	63%
d: R=H, Ar=4-CN-C_6H_4	0%
e: R=Me, Ar=Ph	82%

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[9] Photoreaction of **3b** has been briefly mentioned in a preliminary report: Aoyama, H.; Arata, Y.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1381. The low yields of the products reported in the paper are apparently due to the secondary decomposition. See the Experimental Section.

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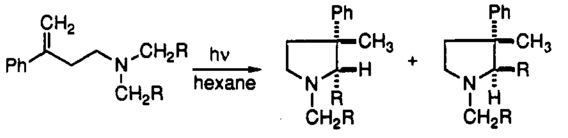
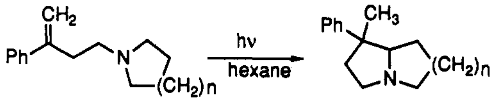
In the case of diethylamino or dibenzylamino derivative **3a** or **3b**, the product was a mixture of two stereoisomers. The isomers, **4b-*cis*** and **4b-*trans***, could be separated by chromatography, whereas **4a-*cis*** and **4a-*trans*** were not completely separated.



3 **4-*cis*** **4-*trans***

a: R=Me 36% 54%
b: R=Ph 28% 24%

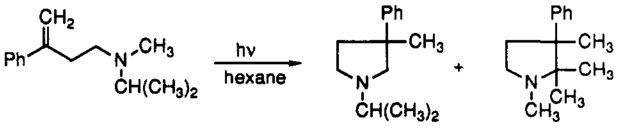
Cyclic amines **5a** and **5b** afforded bicyclic compounds **6a** and **6b** on irradiation in good yields. In these cases, a single product was obtained. Although pyramidal inversion of amines takes place rapidly at room temperature, the ring junction of **6a** should be cis because an alternative trans configuration is energetically unfavorable.[10] The phenyl group of **6a** was found to be cis to the bridgehead methine hydrogen because a strong NOE effect was observed between the phenyl hydrogens and the methine hydrogen. The stereospecificity may be explained in terms of syn C–H addition to the double bond[7] via a sterically favorable chair-form-like transition state (Chart I).[11] Meanwhile, the stereochemistry of **6b** is not clear since in the case of 6–5 fused rings the stability of cis isomers is not so different from that of trans isomers.[10]



5 **6**

a: n=1 73%
b: n=2 84%

Photolysis of an *N*-methyl-*N*-isopropyl derivative **7** yielded two products **8** and **9** formed by hydrogen abstraction from the methyl group and the isopropyl group, respectively. The result of this reaction is quite different from that of the intermolecular photoreaction of stilbene with diisopropylmethylamine in which methyl hydrogens are selectively abstracted.[5] The lack of regioselectivity in the cyclization of **7** is, however, not unreasonable. The selective methyl hydrogen abstraction in the intermolecular reaction has been explained in terms of stereoelectronic effects[5] in the transition state in which the C–H bond being broken overlaps with the nitrogen nonbonding orbital. However, in the seven-membered cyclic transition state of the intramolecular reaction of **7**, effective overlap of these orbitals is sterically forbidden (see Chart I).



7 **8**: 46% **9**: 42%

In connection with photoreactions of the aminostyrenes, those of styrenes having an alkylthio group were also examined. Sulfides are electron donors which are weaker than secondary amines but stronger than primary amines.[12] 4-(Alkylthio)-2-phenyl-1-butene **10a–c** showed emission from the intramolecular exciplexes as with the aminostyrenes (vide infra), but photolysis of **10a–c** yielded only intractable mixtures.

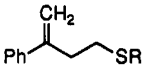
Table I. Fluorescence Spectra of 1

compd	solvent	λ_{max} (nm)	$\Delta\nu^a$ (10^{15} s^{-1})
1a	hexane	380 (303)[b]	2.01
	THF	435, 470	
	MeCN	490	
1b	hexane	322 (320)[b]	
	THF	322, 415	
	MeCN	325, 472	
1c	hexane	328, 385 (328)[b]	1.36
1d	hexane	410 (310)[b]	2.36

[a] $\Delta\nu = \nu_{00} - \nu_{max}$. ν_{00}: the 00 band of emission from the S state of 1 (that for the S_1 state of the corresponding 2-arylpropene was used instead in the case of 1a and 1d). ν_{max}: ν_{max} of the exciplex emission. [b] λ_{max} of the corresponding 2-arylpropene.

Table II. Solvent Dependence of Quantum Yields for Photoreaction of 1a and 1b

	quantum yields		
compd	hexane	THF	MeCN
1a	0.30	0.04	0.006
1b	0.32	0.089	0.016



10a: R=Et
b: R=Pr^i
c: R=CH2Ph

Exciplex Emission. Styrenes form singlet exciplexes with tertiary amines, and photoaddition of the amines to the styrenes has been presumed to proceed via the exciplexes as described above.[6,7] Photoaddition of amines to stilbene has also been proposed to proceed from exciplexes.[5] The fluorescence spectra of **1a**, **1c**, and **1d** (Table I) clearly showed the formation of intramolecular exciplexes. The charge-transfer character of the exciplexes was indicated by the solvent effects on the emission maxima. The stabilization energy due to charge transfer interaction in the exciplex can be estimated on the basis of the emission maximum of the exciplex and the 0–0 band in the emission from the S_1 state (the locally excited state).[13] The values ($\Delta\nu$) are shown in Table I. The 4-methoxyphenyl derivative **1b** did not show exciplex emission in hexane but showed only the emission from the S_1 state. This finding indicates that formation of the exciplex from the S_1 state of **1b** is energetically unfavorable in the nonpolar solvent. The degrees of charge transfer stabilization in the intramolecular exciplexes of the aminostyrenes are in the following order: **1b** < **1c** < **1a** < **1d**. This order is reasonable because (a) the electron affinity of an excited molecule is correlated with the energy of the HOMO in the ground state[6b] and (b) the energy of the HOMO is raised by electron-donating substituents and lowered by electron-withdrawing substituents.[14]

Solvent and Substituent Effects. As Table II clearly shows, the efficiencies of photoreactions of the aminostyrenes are high in hexane and the increase of the polarity

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[14] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976; p 120.

Table III. Stern–Volmer Plots for Photoreaction and Fluorescence of 1a and 1b

compd (process)	solvent	$k_q\tau$, M^{-1}	Φ_0/Φ[a]
1a (photoreaction)	hexane	11	1.11
1a (exciplex emission)	hexane	*b*	1.60
1b (photoreaction)	hexane	21	
1b (S_1 emission)	hexane	20	
1b (photoreaction)	THF	15	1.15
1b (S_1 emission)	THF	13	
1b (exciplex emission)	THF	*b*	2.60

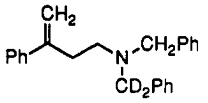
[a] Φ_0/Φ at 1.00×10^{-2} M biacetyl concentration. [b] The Stern–Volmer Plots were not linear.

of the solvent reduces the quantum yields of the photoreactions. The 4-methoxystyrene **1b** which did not show exciplex emission in hexane underwent efficient photoreaction in the solvent, whereas the 4-cyanostyrene **1d** which formed the most stable exciplex among the aminostyrenes studied here was photochemically unreactive.

Stern–Volmer Experiments. In order to examine the intermediacy of the emissive exciplexes in the photoreactions, Stern–Volmer plots for the emissions and for the photoreactions were carried out using biacetyl as a quencher. Biacetyl has a low singlet energy (65 kcal/mol)[15] and can quench both the S_1 and the exciplex emissions. Although biacetyl possesses weak absorptions in the range of 250–500 nm, the internal filter effects on incident light for the photoreactions were negligible, and those for the emissions (<8%) could be corrected by use of the extinction coefficients. Stern–Volmer plots for the photoreactions were linear, but those for the S_1 emissions were slightly curved upward at high biacetyl concentrations even after the correction for internal filter effects on the incident light. This slight curvature is attributable to the weak internal filter effects by biacetyl on the emitting light. The Stern–Volmer coefficients were obtained on the basis of the plots at low quencher concentrations. On the other hand, the Stern–Volmer plots for the exciplexes (**1a** in hexane and **1b** in THF) were substantially curved upward. This observation is understandable because the two consecutively formed excited states (the S_1 state and the exciplex) are both quenchable.[16]

The quenching behavior (Φ_0/Φ) for the exciplex emission from **1a** in hexane is quite different from that for the photoreaction. Meanwhile, the Stern–Volmer coefficient for the S_1 emission of **1b** in hexane is in accord with that for the photoreaction. These findings are inconsistent with the reaction mechanism via the exciplexes. Next, the photoreaction and the emission of **1b** in THF was studied. This styrylamine exhibits both the emission from the S_1 state and that from the exciplex on excitation in THF as shown in Table I. The two emissions showed different quenching behavior, and the Stern–Volmer coefficient for the photoreaction is in accord with that for the S_1 emission within the experimental error, but not with that for the exciplex emission.

Although it is impossible to obtain definitive evidence for the mechanism from the data based only on steady-state kinetics, the result of the present experiments suggests the possibility that the emissive exciplexes are not reactive intermediates. The photoreactions might take place directly from the S_1 states. However, styrenes in the S_1 states do not undergo efficient hydrogen abstraction except for the reactions with electron donors. Further, the deuterium isotope effect measured by use of **3b-*d*$_2$** was small ($\Phi_H/\Phi_D = k_H/k_D = 1.5$) as in the case of hydrogen (or proton) transfer via exciplexes or contact ion pairs.[5]



3b-d$_2$

These facts suggest that charge-transfer interactions play some role in the facile hydrogen transfer. In any event, careful analysis of lifetime data based on laser flash photolysis is essential to determine the mechanism of this photoreaction.

Experimental Section

Melting points are not corrected. Distillation was effected on a rotary distillation apparatus (only oven temperature is given).

General Procedure for Preparation of Aminostyrenes. 1-Aryl-3-(dialkylamino)propan-1-one (15 mmol) which is prepared by the Mannich reaction was dissolved in THF (20 mL) and was added under argon to a cold THF solution (200 mL, 0 °C) of the phosphorous ylide prepared from triphenylmethylphosphonium bromide (17 mmol) and butyllithium. After the solution had been stirred for 1 h at room temperature, methanol (5 mL) and water (200 mL) were added. The aqueous layer was extracted with benzene, and the combined organic layer was washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$, and evaporated. The styryl amine was isolated by flash chromatography on silica gel, eluting with hexane–acetone–triethylamine.

4-(Dimethylamino)-2-phenyl-1-butene (1a): bp 100 °C (5 Torr); mp (picrate) 126–127 °C; IR ($CHCl_3$) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (6 H, s, NMe_2), 2.3–2.7 (4 H, m, CH_2CH_2), 5.09 (1 H, d, J = 1.0 Hz, =CH), 5.30 (1 H, d, J = 1.0 Hz, =CH), 7.2–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 33.8, 45.5, 58.8, 113.1, 126.0, 127.4, 128.3, 141.0, 146.6; UV λ_{max} (hexane) 237 nm (ϵ = 8940). Anal. Calcd for $C_{18}H_{20}N_4O_6$ (picrate): C, 53.46; H, 4.98; N, 13.85. Found: C, 53.39; H, 5.00; N, 13.78.

4-(Dimethylamino)-2-(4-methoxyphenyl)-1-butene (1b): bp 85 °C (2 Torr); mp (picrate) 99–100 °C; IR ($CHCl_3$) 1610 and 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (6 H, s, NMe_2), 2.3–2.9 (4 H, m, CH_2CH_2), 3.75 (3 H, s OMe), 5.00 (1 H, d, J = 1.0 Hz, =CH), 5.23 (1 H, d, J = 1.0 Hz, =CH), 6.83 (2 H, m, aromatic), 7.35 (2 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 33.8, 43.4, 55.0, 58.9, 111.4, 113.6, 127.0, 133.3, 145.8, 159.1; UV λ_{max} (hexane) 253 nm (ϵ = 12600). Anal. Calcd for $C_{19}H_{22}N_4O_6$ (picrate): C, 52.53; H, 5.10; N, 12.90. Found: C, 52.47; H, 5.23; N, 12.90.

4-(Dimethylamino)-2-(4-biphenylyl)-1-butene (1c): mp (picrate) 98–100 °C; IR ($CHCl_3$) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.26 (6 H, s, NMe_2), 2.3–2.7 (4 H, m, CH_2CH_2), 5.12 (1 H, d, J = 1.0 Hz, =CH), 5.38 (1 H, d, J = 1.0 Hz, =CH), 7.2–7.6 (9 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 33.7, 45.5, 58.8, 113.1, 126.4, 127.0, 127.3, 128.7, 139.8, 140.2, 140.6, 146.0; UV λ_{max} (hexane) 270 nm (ϵ = 21600). Anal. Calcd for $C_{24}H_{24}N_4O_6$ (picrate): C, 60.00; H, 5.03; N, 11.66. Found: C, 60.16; H, 5.03; N, 11.50.

4-(Dimethylamino)-2-(4-cyanophenyl)-1-butene (1d): mp (picrate) 141.5–143 °C; IR ($CHCl_3$) 2240 and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (6 H, s, NMe_2), 2.2–2.8 (4 H, m, CH_2CH_2), 5.26 (1 H, s, =CH), 5.42 (1 H, s, =CH), 7.42–7.91 (4 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 33.1, 45.2, 58.2, 96.1, 111.2, 116.3, 126.2, 126.7, 128.2, 128.5, 128.7, 131.9, 132.2, 144.8, 145.3; UV λ_{max} (hexane) 256 nm (ϵ = 9200). Anal. Calcd for $C_{19}H_{19}N_5O_6$ (picrate): C, 55.81; H, 5.15; N, 13.02. Found: C, 55.81, H, 5.18; N, 12.97.

4-(Dimethylamino)-3-phenyl-2-pentene (1e) was a ca. 6:4 mixture of *E* and cis isomers: bp 100 °C (3 Torr); IR ($CHCl_3$) 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58 and 1.80 (3 H in total, each d, Me), 2.17 and 2.25 (6 H in total, each s, NMe_2), 2.2–2.8 (4 H, m, CH_2CH_2), 5.58 and 5.79 (1 H in total, each q, =CH), 7.0–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.4, 27.8, 37.2, 45.1, 57.9, 58.3, 122.0, 123.5, 125.7, 126.1, 126.3, 128.2, 138.3, 139.4, 140.4, 142.6. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found (for a mixture of the isomers): C, 82.24; H, 10.19; N, 7.24.

4-(Diethylamino)-2-phenyl-1-butene (3a): bp 70 °C (2 Torr); mp (picrate) 73–74 °C; IR ($CHCl_3$) 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (6 H, t, J = 7.3 Hz, Me), 2.54, (4 H, q, J = 7.3 Hz, NCH_2), 2.3–2.7 (4 H, m, CH_2CH_2), 5.08 (1 H, br s, =CH), 5.29 (1 H, d,

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[15] Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973.

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J = 1.5 Hz, =CH), 7.2–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 11.9, 33.0, 47.0, 52.1, 113.0, 126.0, 127.3, 128.2, 141.1, 147.0. Anal. Calcd for $C_{20}H_{24}N_4O_7$ (picrate): 55.55; H, 5.59; N, 12.96. Found: C, 55.49; H, 5.69; N, 12.93.

4-(Dibenzylamino)-2-phenyl-2-butene (3b): IR ($CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.4–2.8 (4 H, m, CH_2CH_2), 3.57 (4 H, s, NCH_2 × 2), 4.98 (1 H, d, *J* = 1.3 Hz, =CH), 5.25 (1 H, d, *J* = 1.3 Hz, =CH), 6.9–7.7 (15 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 33.0, 52.5, 58.3, 113.1, 126.7, 127.2, 128.1, 128.2, 128.7, 139.7, 140.8, 146.5; UV λ_{max} (hexane) 238 nm (ε = 10 000).

1-(3-Phenyl-3-butenyl)pyrrolidine (5a): bp 70 °C (2 Torr); mp (picrate) 101.5–102.5 °C; IR ($CHCl_3$) 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.7–1.9 (4 H, m, CH_2CH_2), 2.4–2.8 (8 H, m, NCH_2CH_2C= and NCH_2 × 2), 5.10 (1 H, d, *J* = 1.0 Hz, =CH), 5.30 (1 H, d, *J* = 1.0 Hz, =CH), 7.2–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 23.4, 34.8, 54.1, 55.6, 113.1, 125.9, 127.4, 128.2, 140.8, 146.4. Anal. Calcd for $C_{20}H_{22}N_4O_6$ (picrate): C, 55.81; H, 5.15; N, 13.02. Found: C, 55.82; H, 5.24; N, 13.02.

1-(3-Phenyl-3-butenyl)piperidine (5b): bp 70 °C (2 Torr); mp (picrate) 114.5–115.5 °C; IR ($CHCl_3$) 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2–1.8 (6 H, m, $CH_2CH_2CH_2$), 2.2–2.9 (8 H, m, N-CH_2CH_2C= and NCH_2 × 2), 5.09 (1 H, d, *J* = 1.0 Hz, =CH), 5.30 (1 H, d, *J* = 1.0 Hz, =CH), 7.2–7.4 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 24.2, 25.8, 35.7, 46.6, 54.5, 113.1, 126.0, 127.4, 128.3, 140.9, 146.9. Anal. Calcd for $C_{21}H_{24}N_4O_6$ (picrate): C, 56.75; H, 5.44; N, 12.61. Found: C, 56.42, H, 5.48; N, 12.84.

4-(Methylisopropylamino)-2-phenyl-1-butene (7): bp 70 °C (2 Torr); mp (picrate) 83–84 °C; IR ($CHCl_3$) 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (6 H, d, *J* = 6.8 Hz, Me), 2.24 (3 H, s, NMe), 2.3–2.8 (4 H, m, CH_2CH_2), 2.80 (1 H, sep, *J* = 6.8 Hz, methine), 5.08 (1 H, d, *J* = 1.0 Hz, =CH), 5.30 (1 H, d, *J* = 1.0 Hz, =CH), 7.2–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 18.0, 34.3, 37.1, 52.7, 53.5, 112.9, 126.0, 127.3, 128.2, 141.1, 147.0. Anal. Calcd for $C_{20}H_{24}N_4O_6$ (picrate): C, 55.55; H, 5.59; N, 12.96. Found: C, 55.47; H, 5.68; N, 12.90.

Synthesis of 4-(Alkylthio)-2-phenyl-1-butene. The Wittig reaction of 3-(alkylthio)-1-phenylpropan-1-one which was prepared by the reaction of phenyl vinyl ketone with a thiol in the presence of triethylamine was carried out as in the case of the synthesis of the aminostyrenes 1.

4-(Ethylthio)-2-phenyl-1-butene (10a): bp 100 °C (1 Torr) (bath temp); IR ($CHCl_3$) 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (3 H, t, *J* = 7.3 Hz, Me), 2.52 (2 H, q, *J* = 7.3 Hz, SCH_2), 2.5–2.8 (4 H, m, CH_2CH_2), 5.10 (1 H, d, *J* = 1.5 Hz, =CH), 5.31 (1 H, d, *J* = 1.5 Hz, =CH), 7.1–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 14.8, 25.9, 30.4, 35.8, 113.2, 126.1, 127.5, 128.3, 140.5, 146.9. Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.38. Found: C, 74.59; H, 8.48.

4-(Isopropylthio)-2-phenyl-1-butene (10b): bp 100 °C (1 Torr); IR ($CHCl_3$) 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (6 H, d, *J* = 6.4 Hz, Me × 2), 2.6–2.8 (4 H, m, CH_2CH_2), 2.91 (1 H, sep, *J* = 6.4 Hz, methine), 5.10 (1 H, d, *J* = 1.0 Hz, =CH), 5.31 (1 H, d, *J* = 1.0 Hz, =CH), 7.2–7.4 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 23.3, 29.2, 34.7, 35.9, 113.0, 125.9, 127.4, 128.2, 140.4, 146.9. Anal. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79. Found: C, 75.54; H, 8.85.

4-(Benzylthio)-2-phenyl-1-butene (10c): bp 60 °C (10^{-3} Torr); IR ($CHCl_3$) 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.4–2.8 (4 H, m, CH_2CH_2), 3.69 (2 H, s, SCH_2), 5.04 (1 H, d, *J* = 1.0 Hz, =CH), 5.28 (1 H, d, *J* = 1.0 Hz, =CH), 7.2–7.3 (10 H, m, Ph). Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13. Found: C, 80.35; H, 7.27.

General Procedure for Preparative Photoreactions. A hexane solution (50 mL) of a styryl amine (300 mg) in a quartz tube was purged with argon and irradiated with a low-pressure mercury lamp (a Rayonet photochemical reactor, RPR 2537 A) for 1–3 h. After removal of the solvent, the residue was chromatographed on silica gel using hexane–acetone–triethylamine.

In the case of **3b**, irradiation was done by use of a high-pressure mercury lamp (1000 W) with a filter (a NaBr–Ag_2SO_4 solution)[17] in order to avoid secondary decomposition of the products.

1,3-Dimethyl-3-phenylpyrrolidine (2a): bp 60 °C (2 Torr); mp (picrate) 155–156 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (3 H, s, 3-Me), 1.7–3.0 (4 H, m, CH_2CH_2), 2.38 (3 H, s, NMe), 2.76 (2 H, s, 2-CH_2), 7.1–7.3 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 30.9, 40.4, 42.7, 46.2, 56.1, 77.0, 125.5, 125.8, 128.1, 150.4. Anal. Calcd for $C_{18}H_{20}N_4O_7$ (picrate): C, 53.46; H, 4.98; N, 13.85. Found: C, 53.35; H, 5.03; N, 13.90.

1,3-Dimethyl-3-(4-methoxyphenyl)pyrrolidine (2b): bp 90 °C (2 Torr) (bath temp); mp (picrate) 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (3 H, s, 3-Me), 1.8–3.0 (4 H, m, CH_2CH_2), 2.37 (3 H, s, NMe), 2.72 (2 H, s, 2-CH_2), 3.74 (3 H, s, OMe), 6.81 (2 H, m, aromatic), 7.22 (2 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 30.8, 40.6, 42.7, 45.5, 55.0, 56.1, 70.3, 113.4, 126.7, 142.5, 157.4. Anal. Calcd for $C_{19}H_{22}N_4O_8$ (picrate): 52.53; H, 5.10; N, 12.90. Found: C, 52.33; H, 5.16; N, 12.78.

1,3-Dimethyl-3-(4′-biphenylyl)pyrrolidine (2c): ^{1}H NMR ($CDCl_3$) δ 1.48 (3 H, s, 3-Me), 1.8–3.0 (4 H, m, CH_2CH_2), 2.40 (3 H, s, NMe), 2.80 (2 H, s, 2-CH_2), 7.2–7.6 (9 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 30.7, 40.5, 42.7, 46.0, 56.2, 70.2, 126.3, 126.9, 127.0, 128.7, 138.5, 141.0, 149.5.

3-Ethyl-1-methyl-3-phenylpyrrolidine (2e): bp 100 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.64 (3 H, t, *J* = 7.7 Hz, Me), 1.6–3.2 (8 H, m, methylenes), 2.47 (3 H, s, NMe), 7.0–7.4 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 9.0, 34.9, 36.8, 42.3, 50.3, 54.9, 65.8, 125.4, 126.1, 127.7, 146.3. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48, H, 10.12; N, 7.40. Found: 82.50; H, 10.06; N, 7.38.

2,3-Dimethyl-1-ethyl-3-phenylpyrrolidine (4a) was a mixture of two stereoisomers (cis and trans): bp 70 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.56 (1.2 H, d, *J* = 6.4 Hz, 2-Me-*cis*), 0.97 (1.8 H, d, *J* = 6.3 Hz, 2-Me-*trans*), 1.12 (1.2 H, t, *J* = 7.2 Hz, CH_2CH_3-*cis*), 1.13 (1.8 H, t, *J* = 7.2 Hz, CH_2CH_3-*trans*), 1.35 (1.8 H, s, 3-Me-*trans*), 1.40 (1.2 H, s, 3-Me-*cis*), 1.8–3.3 (7 H, m, methines and methylenes), 7.1–7.4 (5 H, m, Ph). Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found (for a mixture of the isomers): C, 82.83; H, 10.56; N, 6.89.

2,3-Diphenyl-1-benzyl-3-methylpyrrolidine (4b) was a mixture of two stereoisomers, and they could be separated by chromatography on silica gel.

4b-*cis*: mp (picrate) 153–154 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (3 H, s, Me), 1.8–3.4 (4 H, m, CH_2CH_2), 3.01 and 3.86 (2 H, ABq, *J* = 13 Hz, benzylic), 3.45 (1 H, s, methine), 6.4–7.2 (10 H, m, Ph), 7.2–7.9 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 26.6, 38.9, 49.7, 51.8, 58.1, 80.6, 124.9, 125.3, 125.8, 126.5, 126.7, 127.1, 127.7, 128.0, 128.3, 128.4, 138.6, 139.7, 146.0. Anal. Calcd for $C_{30}H_{28}N_4O_7$ (picrate): C, 64.74; H, 5.07; N, 10.06. Found: C, 64.55; H, 5.11; N, 10.07. **4b-*trans***: mp (picrate) 189–192 °C; ^{1}H NMR ($CDCl_3$) δ 1.13 (3 H, s, Me), 1.5–3.45 (4 H, m, CH_2CH_2), 3.08 and 3.98 (2 H, ABq, *J* = 13 H, benzylic), 3.73 (1 H, s, methine), 6.6–7.95 (15 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 23.4, 40.6, 48.9, 52.5, 58.6, 81.2, 125.8, 126.7, 126.8, 126.9, 127.2, 127.6, 127.8, 128.0, 128.1, 128.4, 128.9, 129.7, 138.8, 139.9, 148.2. Anal. Calcd for $C_{30}H_{28}N_4O_7$ (picrate): C, 64.74; H, 5.07; N, 10.06. Found: C, 64.40; H, 5.09; N, 9.80.

1-Aza-4-methyl-4-phenylbicyclo[3.3.0]octane (6a): bp 100 °C (2 Torr); mp (picrate) 159–160 °C; ^{1}H NMR ($CDCl_3$) δ 1.42 (3 H, s, Me), 1.9–3.2 (8 H, m, methylenes), 3.6–4.0 (2 H, m, NCH_2), 4.4–4.6 (1 H, br t, methine),[18] 7.0–7.5 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 24.8, 26.6, 27.8, 40.4, 47.3, 52.1, 54.8, 73.8, 125.4, 127.2, 128.9, 144.8. Anal. Calcd for $C_{20}H_{22}N_4O_7$ (picrate): C, 55.81; H, 5.15; N, 13.02. Found: C, 55.97; H, 5.20; N, 12.90.

1-Aza-7-methyl-7-phenylbicyclo[4.3.0]nonane (6b): bp 110 °C (2 Torr) (bath temp); mp (picrate) 161–162 °C; ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (11 H, m, methine and methylenes), 1.39 (3 H, s, Me), 3.1–3.4 (2 H, m, NCH_2), 7.0–7.4 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 24.3, 24.4, 25.0, 25.6, 40.5, 46.9, 54.5, 75.1, 125.6, 126.3, 128.1, 149.2. Anal. Calcd for $C_{21}H_{24}N_4O_7$ (picrate): C, 56.75; H, 5.44; N, 12.61. Found: C, 56.42; H, 5.47; N, 12.30.

1-Isopropyl-3-methyl-3-phenylpyrrolidine (8) and 1,2,2,3-tetramethyl-3-phenylpyrrolidine (9) could not be separated. Characteristic signals of **8**: ^{1}H NMR ($CDCl_3$) δ 1.11 and 1.12 (each d, *J* = 6.4 Hz, iPr), 2.89 (s, 2-CH_2). Characteristic signals of **9**: ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 2-Me), 1.04 (s, 2-Me), 2.24 (s, NMe). Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found (for a mixture of the isomers): C, 82.46; H, 10.38; N, 6.90.

Stern–Volmer Plot for the Reaction of 1a or 1b. Irradiation was performed in a merry-go-round apparatus (Rayonet Photochemical Reactor-RPR 2537A). The samples in quartz tubes were purged with argon. After irradiation the degree of reaction was determined by the UV absorption spectroscopy. Before and after

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[17] Schönberg, A. *Preparative Organic Photochemistry*, Springer: New York, 1968; p 491.

[18] The assignment was confirmed by the H–C COSY spectrum.

irradiation, the samples were placed in the dark because biacetyl absorbs visible light and may undergo photochemical reaction. The concentrations of the styrylamines were 3.5 mmol/dm^3 (**1a**) and 1.5 mmol/dm^3 (**1b**) and those of biacetyl were 5–20 mmol/dm^3. The consumption of biacetyl during irradiation was negligible.

Stern–Volmer Plot for the Fluorescence of 1a or 1b. The samples were purged with argon. The extinction coefficients of the styrylamines and biacetyl at the excitation wavelength (254 nm) are as follows: **1a**, ϵ_{254} = 5600; **1b**, ϵ_{254} = 12 600; biacetyl, ϵ_{254} = 14.

Quantum Yield Determination. Hexanone actinometry was used. Irradiation was performed with the Rayonet photochemical reactor. The samples in quartz tubes were purged with argon. After irradiation the degree of reaction was determined by the NMR spectroscopy.

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Supplementary Material Available: ^{1}H NMR spectra of **1g** and **2c** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Correlation of Solvolytic Reactivities of 1,1,1-Trifluoro-2-phenyl-2-propyl, 1-*tert*-Butyl-1-phenylmethyl, and Some Related Tosylates[†]

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Solvolysis of 1,1,1-trifluoro-2-phenyl-2-propyl tosylate (**3**), 2,2,2-trifluoro-1-(4′-methylphenyl)ethyl tosylate (**4**), 1-*tert*-butyl-1-phenylmethyl tosylate (**5**), 1-*tert*-butyl-1-(3′-chlorophenyl)methyl tosylate (**6**), and 1-(3′,5′-dichlorophenyl)-2,2,2-trifluoro-1-phenylethyl tosylate (**7**) in a variety of solvents were found to give log $k - Y_{\mathrm{OTs}}$ plots with significant deviations from linearity (R = 0.95–0.98). The data points for those measured in aqueous acetone always showed depression from the line, whereas those measured in nonnucleophilic solvents were on the line. On the other hand, **3**, **4**, **6**, and **7** all showed excellent linear relationships ($R > 0.99$) for log k against log k(**5**). Additional evidence for the limiting S_N1 mechanism in the solvolysis of **5** was given. Similar to the previous work (refs 11–13) a new Y_{BnOTs} scale based on the solvolysis rates of **5** for correlating the solvolytic reactivity of benzylic tosylates involving charge delocalizations to the aryl moiety in the cationic transition states was then proposed. The advantages of using this new Y scale of solvent ionizing powers were discussed. The importance of solvent nucleophilicities in the solvolysis of primary benzylic tosylate **8** and unhindered deactivating secondary benzylic tosylates **9** and **10** was confirmed.

In 1948 the Grunwald–Winstein equation (1) was stated to define the first scale of empirical solvent ionizing power (Y) based on the solvolytic rate constants of *tert*-butyl chloride.[1] Multiparameter equations, such as (2),[2] were

$$\log (k/k_0) = mY \qquad (1)$$

$$\log (k/k_0) = mY + lN \qquad (2)$$

then introduced to accommodate the effect of the solvent nucleophilicity. Later studies indicated the use of 1- or 2-adamantyl tosylate as a better reference for defining the solvent ionizing power.[3,4] Moreover, the necessity of using different Y_X scales to correlate the solvolytic reactivity of substrates containing different leaving groups (X) was first shown by Bentley and co-workers.[5] A variety of Y_X scales based on 1- or 2-substituted adamantanes have thus been developed[6] and have been generally considered as an important set of solvent parameters for the understanding of the correlation of solvolytic reactivities.[7] The observation of dispersed log $k - Y_X$ plots due to the rate constants measured in nonnucleophilic solvents, such as those that have been noted in the cases of *tert*-butyl halides[5,8] and 2-(trifluoromethyl)-2-propyl triflate,[9] has been considered as an useful probe for detecting nucleophilic solvent assistance.[10]

On the other hand, we recently demonstrated the advantage of using a new Y_{BnCl} scale based on 2-aryl-2-chloroadamantane **1a**[11] over the Y_{Cl} based on 1-chloroadamantane (**2**)[5] to describe the solvent ionizing power of a large number of solvents for correlating the solvolytic reactivity of tertiary benzylic chlorides by eq 1. A similar approach has also been found to be successful for benzylic bromides[12] and *p*-nitrobenzoates[13] by employing the corresponding 2-aryl-2-adamantyl derivatives **1b** and **1c**, re-

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[†] Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

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