Intramolecular Photoaddition of Secondary α-(Aminoalkyl)styrenes

Frederick D. Lewis,* Dario M. Bassani, and G. Dasharatha Reddy

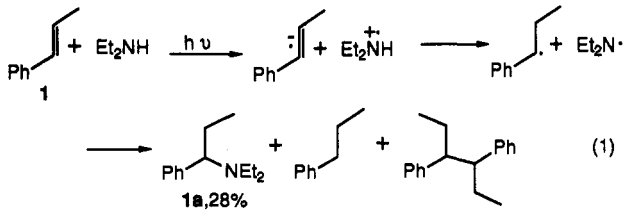
Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Received March 30, 1993•

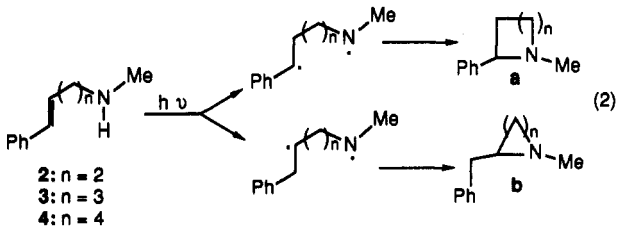
The photophysical and photochemical behavior of a series of α-[(*N*-methylamino)alkyl]styrenes with two to four methylenes separating the styryl and amino groups and an (aminoalkyl)indene have been investigated and the results compared to those for the intermolecular reaction of α-methylstyrene with diethylamine. Both inter- and intramolecular quenching of styrene fluorescence by the amine is observed, indicative of electron-transfer quenching as the initial step in these reactions. The resulting exciplex undergoes regioselective N–H proton transfer to styrene C-β yielding a biradical, in the case of the intramolecular reaction, and a radical pair, in the case of the intermolecular reaction. Biradical or radical pair combination yields styrene–amine addition products. The conformation of the intermediate exciplex is proposed to control the regioselectivity of the intramolecular N–H proton transfer process.

Introduction

Irradiation of styrenes or stilbenes in the presence of secondary amines results in the formation of N–H adducts accompanied by reduction products.[1-4] The mechanism proposed for the formation of addition and reduction products from β-methylstyrene (**1**) and diethylamine is outlined by eq 1.[2c] Electron transfer quenching of the



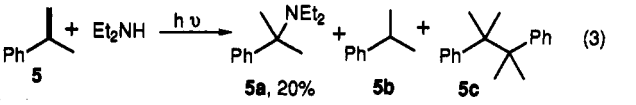
styrene singlet by diethylamine followed by regioselective proton transfer to styrene C-β yields a radical pair which can combine yielding **1a**, disproportionate, or diffuse part. We have recently reported that intramolecular analogs of these reactions afford high preparative yields of nitrogen heterocycles in the case of several β-[(*N*-methylamino)-alkyl]styrenes and *o*-[(*N*-methylamino)alkyl]stilbenes.[2,5] The regioselectivity of these intramolecular addition reactions was found to be dependent upon the length of the polymethylene chain connecting the styrene or stilbene and the amine. For example, the ratios of C_α/C_β adducts from the β-(aminoalkyl)styrenes **2–4** in hexane solution are **2a/2b** = 2.9:1, **3a/3b** = 0.9:1 and **4a/4b** = 0.8:1, respectively (eq 2). This chain-length dependence was attributed to the occurrence of intramolecular proton transfer via least-motion pathways from the lowest energy folded conformation of the singlet exciplex intermediate.



We report here the results of our investigation of the intermolecular reaction of α-methylstyrene (**5**) with diethylamine and the intramolecular reactions of several α-[(*N*-methylamino)alkyl]styrenes **6–8** and of the 1-(aminoalkyl)indene **9**. In all of these reactions regioselective intramolecular addition occurs with C–N bond formation at styrene C_α. These results serve both to extend the scope of the intramolecular styrene–amine photoaddition reaction and to further establish the relationship between exciplex conformation and the regioselectivity of C–N bond formation.

Results and Discussion

Photochemical Reactions. Irradiation of a deoxygenated hexane solution of **5** and diethylamine (0.01 and 0.1 M, respectively) with Pyrex-filtered light results in the formation of the adduct **5a** and the reduction products **5b** and **5c** in approximately equal amounts (eq 3). The



ultraviolet absorption spectrum of **5** displays an allowed transition at 242 nm (ε = 14100) and a shoulder at 285 nm (ε = 50) extending to ca. 300 nm, both assigned to π,π* transitions.[2c] The products do not absorb above 290 nm, permitting high conversions in preparative irradiations. The optimum yield of **5a** as determined by GC analysis is 20%, somewhat lower than that obtained for addition of **1** with diethylamine (eq 1). Irradiation in acetonitrile solution results in more rapid product formation, but similar product yields and ratios.

The (aminoalkyl)styrenes **6–8** and the (aminoalkyl)-indene **9** were prepared by standard procedures as described in the Experimental Section. The *gem*-dimethyl

• Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Susumu, T.; Hida, S.; Takamuku, S.; Sakurai, H. *Nippon Kagaku Kaishi* **1984**, 152.

(2) (a) Lewis, F. D.; Reddy, G. D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1989**, *111*, 6465. (b) Lewis, F. D.; Reddy, G. D. *Tetrahedron Lett.* **1990**, *31*, 5293. (c) Lewis, F. D.; Reddy, G. D.; Schneider, S.; Gahr, M. *J. Am. Chem. Soc.* **1991**, *113*, 3498. (d) Lewis, F. D.; Reddy, G. D.; Bassani, D.; Schneider, S.; Gahr, M. *J. Photochem. Photobiol. A: Chem.* **1992**, *65*, 205. (e) Lewis, F. D.; Reddy, G. D.; Bassani, D. M. *Pure Appl. Chem.* **1992**, *64*, 1271.

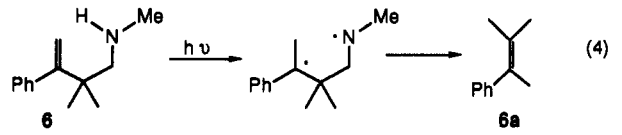
(3) Kawanisi, M.; Matsunaga, K. *J. Chem. Soc. Chem. Commun.* **1972**, 313.

(4) (a) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991. (b) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152.

(5) Lewis, F. D.; Reddy, G. D. *Tetrahedron Lett.* **1992**, *33*, 4249.

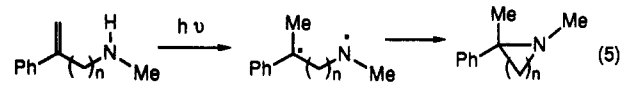
0022-3263/93/1958-6390$04.00/0

substituents in 6 were introduced to prevent isomerization of the double bond during purification. The absorption spectra of 6–8 are similar to that of 5 with enhanced absorption at short wavelength due to the amine. Irradiation of 6 (0.01 M) in hexane or acetonitrile solution results in the formation of the elimination product 6a in ca. 50% yield, as determined by GC analysis (eq 4). Also



6 6a (4)

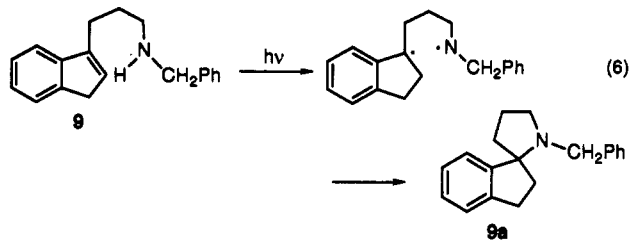
formed were two unidentified products whose mass spectra displayed the same molecular ion as that of 6. Irradiation of 7 under analogous conditions results in the formation of a single product 7a in 80% optimum yield by GC analysis (eq 5). Similarly, irradiation of 8 results in the formation



7: n = 3
8: n = 4

7a: n = 3
8a: n = 4 (5)

of a single product 8a in 75% optimum yield (eq 5). The photochemical behavior of the (aminopropyl)indene 9 was also investigated. The *N*-benzyl sustituent was used in place of *N*-methyl to simplify synthesis and purification. Irradiation of 9 (0.01 M) in hexane solution results in the formation of a single product 9a in 70% yield based on GC analysis (eq 6). All photoproducts were isolated by column



9 9a (6)

chromatography and their structures assigned on the basis of their spectral data (see Experimental Section).

Mechanistic Studies. Both of the methylstyrenes 1 and 5 display strong fluorescence in deoxygenated hexane solution.[2,7] The slope of linear Stern–Volmer plots for fluorescence intensity quenching by added diethylamine and the measured singlet lifetimes provide approximate rate constants for singlet quenching which are nearly equal to the rate constant for diffusion in hexane solution (Table I).[8] Quenching of singlet styrenes by secondary and tertiary amines is proposed to occur via an electron transfer mechanism.[2,4] The slightly larger rate constant for diethylamine quenching of 5 vs 1 may reflect its slightly higher singlet energy and/or lower reduction potential.[9,10]

(6) Values for the singlet lifetimes are similar to those previously reported by 1[2c] and 5.[7]

(7) Crosby, P. M.; Salisbury, K. *J. Chem. Soc. Chem. Commun.* **1975**, 477.

(8) Lewis, F. D.; Bassani, D. M. *J. Photochem. Photobiol. A: Chem.* **1992**, *66*, 43.

(9) The singlet energies of 1 and 5 are estimated to be 98 and 100 kcal/mol, respectively, from their absorption and fluorescence spectra. The oxidation potentials of 1 and 5 are −2.30 and −2.15 V vs ferrocecene in acetonitrile solution.

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

Table I. Fluorescence Lifetimes and Rate Constants for Inter- and Intramolecular Fluorescence Quenching and Quantum Yields for Intramolecular Addition[a]

styrene	τ_S, ns	$10^{10}k_q$[b]	Φ_{addn}[c]
5	1.9	1.8	
6	<0.2	>5	
7	<0.2	>5	0.19
8	0.4	2.0	0.23
1	11.6	0.41	
2	0.73	1.3	0.024
3	0.51	1.8	0.011
4	1.6	0.53	0.050

[a] Data for 1–4 from ref 1c. [b] Bimolecular rate constant for fluorescence quenching by diethylamine or unimolecular rate constant for intramolecular quenching in deoxygenated hexane solution. [c] Quantum yield for product formation in deoxygenated hexane solution.

Both the fluorescence intensity and lifetime for the (aminoalkyl)styrenes 6–8 are substantially smaller than for 5, presumably a consequence of intramolecular electron-transfer quenching.[2c] In the case of 8 the lifetime of the weak residual styrene-like fluorescence is 0.4 ns, while the lifetimes of the very weak fluorescence from 6 and 7 are shorter than the time resolution of our instrmentation (ca. 0.2 ns). Approximate rate constants for intramolecular quenching can be estimated from the residual monomer lifetime (τ_S) and the lifetime of 5 (τ_5, eq 7).

$$k_{et} = \tau_s^{-1} - \tau_5^{-1} \quad (7)$$

The resulting values of k_{et} are reported in Table I along with our previously reported results for 2–4.[2c] As is the case for intermolecular quenching of 5 vs 1, larger rate constants are observed for the α-linked vs β-linked (aminoalkyl)styrenes. Neither intermolecular nor intramolecular quenching of the singlet styrenes by secondary amines results in red-shifted fluorescence which might be attributed to an exciplex intermediate. Exciplex fluorescence is observed for the corresponding tertiary α- and β-(aminoalkyl)styrenes.[2c,11,12]

As in the case of the β-(aminoalkyl)styrenes 2–4, intramolecular addition for 6–9 is proposed to occur via electron transfer followed by proton transfer, yielding the singlet biradical intermediates shown in eqs 4–6. The 1,4-biradical intermediate formed from 6 undergoes fragmentation to yield 6a. Cyclization of the 1,4-biradical intermediate would yield an azetidine, which may be among the unidentified minor products. The 1,5-biradical intermediates formed from 7 and 9 cyclize to yield the pyrrolidine 7a and the unusual spiropyrrolidine 9a,[13] respectively, in good preparative yield. The formation of fragmentation products from 1,4-biradicals but only cyclization products from 1,5-biradicals finds precedent in the behavior of the triplet biradical intermediates formed upon γ- and δ-hydrogen abstraction by aryl alkyl ketones.[14] The 1,6-biradical intermediate formed from 8 cyclizes to yield the piperidine 8a. We anticipate that irradiation of α-(aminoalkyl)styrenes with longer styrene–amine linkers would yield medium-ring nitrogen hetero-

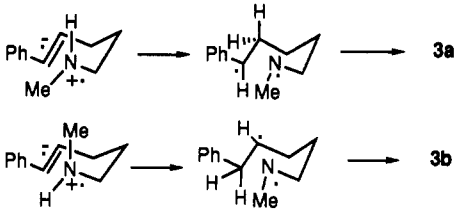
(11) Aoyama, H.; Sugiyama, J.; Yoshida, M.; Hatori, H.; Hosomi, A. *J. Org. Chem.* **1992**, *57*, 3037.

(12) Lewis, F. D.; Reddy, G. D.; Bassani, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 6468.

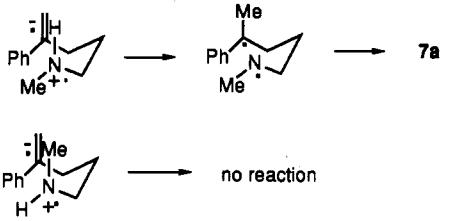
(13) For previous reports of the synthesis of this ring system see: (a) Oppolzer, W.; Pfenninger, E.; Keller, K. *Helv. Chim. Acta* **1973**, *56*, 1807. (b) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.

(14) (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.

Scheme I



Scheme II



cycles, with the product ring size being limited by the kinetics of intramolecular electron-transfer quenching and the behavior of the resulting benzyl–aminyl biradical intermediates. Preparatively useful yields of azetidines might also be obtained from less-substituted α-(aminoethyl)styrenes.

The N–H proton transfer process occurs regioselectively to styrene C_β in both hexane and acetonitrile solution to yield tertiary benzyl–aminyl biradicals in preference to primary alkyl–aminyl biradicals in the case of the α-(aminoalkyl)styrenes and indene (eqs 4–6). In the case of the β-(aminoalkyl)styrenes N–H proton transfer occurs to both C_α and C_β resulting in the formation of mixtures of secondary benzyl–aminyl biradicals vs secondary alkyl–aminyl biradicals (eq 2).[2] The quantum yields for product formation are much higher in the case of the α-vs β-(aminoalkyl)styrenes, indicative of larger rate constants for exciplex proton transfer to the terminal C_β of the α-(aminoalkyl)styrenes vs the internal C_β or C_α of the β-(aminoalkyl)styrenes. While N–H proton transfer might be expected to be more rapid and selective in the case of the α- vs β-(aminoalkyl)stilbenes, product stability control cannot account for the preferential formation of **3b** vs **3a** and **4b** vs **4a** in cyclohexane solution (eq 2).

We previously proposed that the formation of the two regioisomeric adducts from **2–4** resulted from exciplex conformational control of N–H proton transfer. On the basis of their extensive experimental and computational studies of [(*N*,*N*-dimethylamino)alkyl]arene singlet exciplexes, De Schryver, Van der Auweraer, and co-workers[15] have suggested that in nonpolar solvents these exciplexes adopt compact folded conformations which maximize Coulombic attraction while minimizing nonbonded interactions in the polymethylene chain. By analogy to their suggestions, the exciplex of **3** was proposed to adopt a chair-like conformation in which the N–H is either axial or equatorial.[2d] Least-motion proton transfer of the axial N–H to styrene C-β would lead to the formation of **3a**, while least-motion proton transfer of the equatorial N–H to styrene C-α would lead to the formation of **3b** (Scheme I). Folding of the exciplexes of **6–8** with maximum overlap between nitrogen and styrene C_α would place the N–H above either styrene C_β or the phenyl ipso position, as shown for **7** in Scheme II. A least-motion pathway for proton transfer is available in the former conformation, but not in the latter. Thus proton transfer to C_α in the exciplexes of **6–8** may be conformationally as well as energetically unfavorable.

Both inter- and intramolecular photoaddition of styrene with tertiary amines result in addition of the amine α-C–H to styrene.[1–4,11,12] In contrast, N–H addition occurs to the exclusion of α-C–H addition for secondary amines. Kinetically favored N–H vs α-C–H proton transfer is consistent with the observation of exciplex fluorescence for the intramolecular styrene–tertiary amine exciplexes, but not for the styrene–secondary amine exciplexes. The intramolecular photoaddition reactions of α- and β-[(*N*,*N*-dimethylamino)alkyl]styrenes are highly dependent upon the point of attachment (α vs β), alkyl chain length, and solvent polarity.[12] These effects are also attributed to conformational control of exciplex proton transfer. The differences in behavior observed for secondary vs tertiary (aminoalkyl)styrenes are not observed in the photochemical reactions of secondary and tertiary β-aminopropiophenones, both of which are reported to undergo α-C–H addition to the carbonyl group.[16] The origins of these differences require further investigation.

Experimental Section

General Methods. NMR spectra were recorded in $CDCl_3$ solution using a Gemini 300 or Varian XLA 400 spectrometer with TMS as an internal standard. High-resolution mass spectra were determined with a Hewlett-Packard 5985 GC/VG70-250SE MS system using an ionizing voltage of 70 eV. Ultraviolet absorption spectra were obtained using a Hewlett-Packard 8452 diode-array spectrophotometer. Steady state fluorescence spectra were obtained using a Perkin-Elmer MPF-44A spectrometer. Fluorescence lifetimes were measured using a PTI-LS1 single photon counting apparatus (time resolution ca. 0.2 ns). The method of analysis of the fluorescence decay curves has previously been described.[8]

Preparative-scale irradiations were carried out under nitrogen in Pyrex test tubes using a Rayonet reactor fitted with RPR 3000 lamps. Acetonitrile solutions (0.01 M (aminoalkyl)styrene) were irradiated to >95% conversion of starting material. Products were isolated by either preparative thick-layer chromatography or column chromatography followed in some cases by bulb-to-bulb distillation. Quantum yield measurements were carried out on an optical bench (200-W Xenon-Mercury high pressure lamp and 0.25-m high-intensity monochromator at 281 nm) with conversions limited to 10%. Light intensities were determined using *trans*-stilbene actinometry.[17] Irradiated solutions were analyzed by gas chromatography (Hewlett-Packard 5890 equipped with a flame ionization detector) with 10 × 0.53 mm fused silica column coated with polymethylsiloxane.

Materials. α-Methylstyrene (Aldrich) and diethylamine (Aldrich) were distilled prior to use. Ethyl benzoylacetate (Aldrich), 3-benzoylpropionic acid (Aldrich), 4-benzoylbutyric acid (Aldrich), and 2-indanone (Aldrich) were used without further purification. Spectrograde hexane and acetonitrile (Aldrich) were used as received.

***N*,*N*-Diethyl-2-phenylpropan-2-amine (5a).** Photolysis of 0.01 M solution of α-methylstyrene and 0.1 M diethylamine resulted in the formation of **5a**, cumene, and bicumyl in a ca. 1:1:1 ratio by GC. A sample of **5a** was obtained as an oil by thick-layer chromatography: ^1H NMR ($CDCl_3$) δ 7.6 (m, 2 H), 7.33 (m, 2 H), 7.22 (m, 1 H), 2.50 (q, 4H, J = 7.2 Hz), 1.38 (s, 6

(15) (a) Van der Auweraer, M.; Swinnen, A. M.; De Schryver, F. C. *J. Chem. Phys.* **1982**, *77*, 4110. (b) Swinnen, A. M.; Van der Auweraer, M.; De Schryver, F. C. *J. Photochem.* **1985**, *28*, 315. (c) Van der Auweraer, M. *Acad. Anal.* **1986**, *48*, 27. (d) Van der Auweraer, M.; Grabowski, Z. R.; Rettig, W. *J. Phys. Chem.* **1991**, *95*, 2083.

(16) (a) Roth, H. J.; El Raie, M. H.; Schrauth, T. *Arch. Pharmaz.* **1974**, *307*, 584. (a) Abdul-Baki, A.;Rotter, F.; Schrauth, T.; Roth, H. J. *Arch Pharmaz.* **1978**, *311*, 341.

(17) Lewis, F. D.; Johnson, D.E. *J. Photochem.* **1977**, *7*, 421.

H), 1.06 (t, 6 H, J = 7.2 Hz); MS (m/e) 191 (M^+, 21%), 176 (100), 148 (10), 119 (62); IR (film) 2976, 1649 cm^{-1}; HRMS 191.1674 (calcd), 191.1674 (obsd).

***N*,2,2-Trimethyl-3-phenyl-3-buten-1-amine (6).** Ethyl benzoylacetate (5 g, 26 mmol) was sequentially alkylated with methyl iodide using potassium carbonate in acetone and sodium in ethanol as base. To a stirred suspension of methyl triphenylphosphonium bromide (6.0 g, 17 mmol) and 50 mL of dry benzene in a three-necked flask fitted with reflux condenser, addition funnel, and a septum was added *n*-butyllithium (1 equiv) dropwise from a syringe at room temperature. The resulting yellow solution was stirred for 15 min and the keto ester (3.2 g, 14 mmol) was added dropwise from the addition funnel while heating the reaction mixture. The reaction was stirred at reflux temperature for 5 h and for an additional 10 h at room temperature prior to addition of 50 mL of water and extraction of the mixture twice with 50 mL of benzene. The organic layer was dried over sodium sulfate and the solvent removed by rotary evaporation. The residue was purified by column chromatography (silica gel, 30% chloroform in hexane as eluant) providing the styryl ester as an oil in 60% yield: ^1H NMR ($CDCl_3$) δ 7.1–7.3 (m, 5 H), 5.33 (s, 1 H), 5.16 (s, 1 H), 4.11 (q, 2 H, J = 7.2), 1.39 (s, 6 H), 1.18 (t, 3H, J = 7.2). The styryl ester was converted to the secondary amine in 56% overall yield via the amide using standard methods, as previously described, and isolated by an oil by column chromatography:[2c] ^1H NMR ($CDCl_3$) δ 7.1–7.4 (m, 5 H), 5.21 (s, 1 H), 4.93 (s, 1 H), 2.44 (s, 3 H), 2.42 (s, 2 H) 1.13 (s, 6 H); IR (film) 3406, 1649 cm^{-1}; MS (m/e) 189 (M^+, 18%), 174 (5), 146 (49), 129 (37), 115 (31), 103 (23), 91 (40), 77 (38), 44 (100); HRMS 189.1517 (calcd) and 189.1505 (obsd).

2-Methyl-3-phenyl-2-butene (6a). Irradiation of **6** in acetonitrile solution afforded three products by gc analysis. Thick-layer chromatography of the irradiated solution afforded a sample of the short retention time product **6a** as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.1–7.35 (m, 5 H), 1.96 (s, 3 H), 1.81 (s, 3 H), 1.6 (s, 3 H); MS (m/e) 146 (M^+, 74%), 131 (100), 91 (47), 77 (19).

***N*-Methyl-4-phenyl-4-penten-1-amine (7).** 3-Benzoylpropionic acid (5 g, 28 mmol) in 50 mL of anhydrous ethyl alcohol and 0.5 mL of concentrated sulfuric acid were refluxed for 12 h. The reaction mixture was cooled, the alcohol removed by rotary evaporation, and 50 mL of diethyl ether was added. The ether solution was washed with 50 mL of 5% aqueous KOH solution and water and dried over magnesium sulfate, and the solvent was removed providing the keto ester in 95% yield. The keto ester (2.8 g, 14 mmol) was converted to the styryl ester in 65% yield using the procedure described above: ^1H NMR ($CDCl_3$) δ 7.22–7.42 (m, 5 H), 5.31 (s, 1 H), 5.1 (s, 1 H), 4.12 (q, 2 H, J = 6.5 Hz), 2.84 (t, 2 H, J = 7.6 Hz)), 2.49 (t, 2 H, J = 7.6 Hz)), 1.25 (t, 3 H, J = 6.5 Hz). The styryl ester was converted to the amide in 95% yield and the amide reduced to the amine in 90% yield, as previously described.[2c] Purification by column chromatography afforded **7** as a colorless oil in 53% overall yield from 3-benzoylpropionic acid: ^1H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 5.27 (s, 1 H), 5.07 (s, 1 H), 2.60 (t, 2 H, J = 7.6 Hz), 2.26 (t, 2 H, J = 7.6 Hz), 2.41 (s, 3 H), 1.50 (quintet, 2 H, J = 7.6 Hz); IR (film) 3286, 2976, 1625 cm^{-1}; MS (m/e) 175 (M^+, 4%), 57 (89), 44 (100); HRMS 175.1361 (calcd), 175.1365 (obsd).

1,2-Dimethyl-2-phenylpyrrolidine (7a). Irradiation of **7** in acetonitrile solution followed by preparative thick-layer chromatography afforded **7a** in 80% isolated yield: ^1H NMR ($CDCl_3$) δ 7.2–7.5 (m, 5 H), 3.10 (m, 1 H), 2.70 (m, 1 H), 2.12 (s, 3 H), 1.84–2.00 (m, 4 H), 1.33 (s, 3 H); IR (film) 2976, 2785, 1496, 1450 cm^{-1}; MS (m/e) 175 (M^+, 4%), 160 (15), 57 (100), 44 (100); HRMS 175.1361 (calcd), 175.1364 (obsd).

***N*-Methyl-5-phenyl-5-hexen-1-amine (8).** This compound was prepared from 4-benzoylbutyric acid by the same reaction sequence as described for the preparation of **7**: ^1H NMR ($CDCl_3$) δ 7.2–7.45 (m, 5 H), 5.2 (s, 1 H), 5.06 (s, 1 H), 2.54 (m, 4 H), 2.40 (s, 3 H), 1.50 (m, 4 H). IR (film) 3372, 2936, 1632 cm^{-1}; MS (m/e) 189 (M^+, 45%), 158 (30), 143 (29), 91 (18), 70 (100); HRMS 189.1517 (calcd), 189.1518 (obsd).

1,2-Dimethyl-2-phenylpiperidine (8a). Irradiation of **8** in acetonitrile solution followed by preparative thick-layer chromatography afforded **8a** in 75% yield. ^1H NMR ($CDCl_3$) δ 7.56 (m, 2 H), 7.31 (m, 2 H), 7.2 (m 1 H), 3.75 (m, 1 H), 3.55 (m 1 H), 1.95 (s, 3 H), 2.45–2.75 (m, 6 H), 1.36 (s, 3 H); IR (film) 2936, 2792, 1496, 1450 cm^{-1}; MS (m/e) 189 (M^+, 28%), 174 (100), 160 (18), 146 (18), 112 (52); HRMS 189.1517 (calcd), 189.1520 (obsd).

***N*-Benzyl-3-(1-indenyl)propylamine (9).** A solution of 2-indanone (5 g, 38 mmol) in 10 mL of ethanol was added to 1 equiv of sodium in ethanol at 45 °C and the reaction mixture stirred for 15 min prior to addition of 1 equiv of 3-bromopropionitrile over a period of 30 min. The resulting solution was stirred at reflux temperature for 8 h and cooled, the solvent removed by rotary evaporation at reduced pressure, 50 mL of water added, and the solution extracted with diethyl ether. The organic layer was dried over magnesium sulfate, the solvent removed, and the residue purified by column chromatography (silica gel, 15% dichloromethane in hexane), providing 1-(cyanoethyl)-2-indanone in 80% yield. This compound (5.6 g, 30 mmol) was reduced with 1.5 equiv of sodium borohydride in 50 mL of methanol. The reaction mixture was stirred for 3 h and neutralized with acetic acid, and the solvent was removed under reduced pressure. The resulting residue was extracted with diethyl ether and dried over magnesium sulfate, and the solvent was removed affording 1-(cyanoethyl)-2-indanol in 90% yield. This compound (4.9 g, 26 mmol) and 1.1 equiv of *p*-toluenesulfonic acid in 100 mL of benzene was refluxed for 24 h while removing water as an azeotropic mixture. Removal of the solvent followed by distillation under vacuum (bp 123 °C at 0.1 mm) afforded 1-(cyanoethyl)indene in quantitative yield. A solution of 3 g of the 1-(cyanoethyl)indene in 10 mL of dry ether was added to a suspension of 1 equiv of lithium aluminum hydride in 20 mL of dry ether at room temperature while stirring. The reaction mixture was refluxed overnight and cooled, and the excess lithium aluminum hydride was decomposed by slow addition of cold water. The ether layer was dried over magnesium sulfate and the solvent removed to yield 2.2 g of primary amine (80%). A solution of primary amine (0.5 g, 2.9 mmol) and 1 equiv of freshly distilled benzaldehyde in 10 mL of methyl alcohol was stirred at room temperature for 2 days and cooled to 0 °C, and 1.1 equiv of sodium borohydride was added in portions while stirring. The stirring was continued for 2 h and the solution neutralized with acetic acid. Extraction of the reaction mixture with diethyl ether after removing the methanol yielded **9** as a colorless oil (0.45 g, 59%) in 33% overall yield from 2-indanone: ^1H NMR ($CDCl_3$) δ 7.2–7.6 (m, 9 H), 6.2 (br s, 1 H), 3.85 (s, 2 H), 3.28 (br s, 2 H), 2.70 (t, 2 H), 2.58 (t, 2 H), 1.9 (quintet, 2 H); MS (m/e) 263 (M^+, 6%), 170 (6), 133 (54), 120 (60), 104 (11), 91 (100); HRMS 263.1674 (calcd), 263.1678 (obsd).

***N*-Benzyl-2,3-dihydrospiro[1*H*-indene-1,2′-pyrrolidine] (9a).** Irradiation of **9** in acetonitrile solution followed by preparative thick-layer chromatography afforded **9a** in 70% yield: ^1H NMR ($CDCl_3$) δ 7.1–7.5 (m, 9 H), 3.3 (AB quartet, 2 H, J = 13 Hz), 3.0 (m, 1 H), 2.9 (m, 2 H), 2.5 (m, 1 H), 2.22 (m, 1 H), 2.0 (m, 1 H), 1.85 (m, 4 H); ^{13}C NMR 147.4 (s), 144.1 (s), 141.2 (s), 128.8 (d), 128.6 (d), 127.9 (d), 127.1 (d), 127.0 (d), 125.0 (d), 124.1 (d), 76.2 (s), 53.9 (t), 51.3 (t), 39.9 (t), 30.4 (t), 30.4 (t), 22.1 (t); MS (m/e) 263 (M^+, 33%), 234 (83), 172 (22), 144 (24), 128 (18), 91 (100), 77 (8), 65 (18).

Acknowledgment. Financial support for this research has been provided by the National Science Foundation (CHE-8922835).

Supplementary Material Available: Copies of ^1H NMR spectra (9 pages). This material is contained in 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.