A partial substitution of CO by the electrophilic reagent[29] is followed by an attack on CO by the nucleophilic N of the diazo unit. An η^2-C,N bonded unit, like that shown in D, may then insert another functional group, giving a larger metallacycle (complex VI). We feel that the formation of the trinuclear unit comes from the reaction of the preformed complex VI with $Cp_2Ti(CO)_2$ by a reaction similar to that observed in related titanium-ureylene complexes.[27] The proposed sequence indicates the preeminent role played by the presence of an available orbital on titanium in all the insertion steps depicted. This view seems to exclude that reaction 7 can be justified as arising from a fundamental one-electron reducing process of the diazo molecule requiring Ti(II) → Ti(III) oxidation, vs. the coordination of the diazo ligand to the metal involving a formal two-electron change in the oxidation state of the metal for both model complexes.

In conclusion, it would appear that vanadocene could be a highly versatile reagent for coordinating various functional groups, whereas titanocene, generated from $Cp_2Ti(CO)_2$, can promote the most elementary transformations of the same functional groups or small molecules.

Acknowledgment. We thank CNR (Rome) for financial support.

Registry No. I, 12129-51-0; II, 80679-13-6; III, 80679-14-7; IV, 80878-08-6; VI, 80679-06-7; VII, 75309-44-3; cp_2V, 1277-47-0.

Supplementary Material Available: Tables of thermal parameters for complexes II and IV (Tables III and VI) and fractional atomic coordinates for hydrogen atoms for complex IV (Tables IV and V) and listings of factor structures amplitudes for complexes II and IV (32 pages). Ordering information is given on any current masthead page.

Photochemical Addition of Tertiary Amines to Stilbene. Free-Radical and Electron-Transfer Mechanisms for Amine Oxidation

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Abstract: Several amines of structure Me_2NCH_2R, where R = $CH{=}CH_2$, CO_2Et, $C{\equiv}CCH_3$, and $C{\equiv}CH$, but not Ph, react with the singlet state of *trans*-stilbene in hexane solution to yield adducts of structure $PhCH_2CHPhCHRNMe_2$. In acetonitrile solutions, these adducts are accompanied by variable amounts of adducts of structure $PhCH_2CHPhCH_2NMeCH_2R$. Both types of adduct are formed by cross combination of 1,2-diphenylethyl-α-aminoalkyl radical pairs. The mechanism of radical-pair formation is concluded to be solvent dependent. In nonpolar solvents, hydrogen atom transfer selectively yields a merostabilized α-aminoalkyl radical. In polar solvents, a sequential electron-transfer, proton-transfer mechanism yields both α-aminoalkyl radicals.

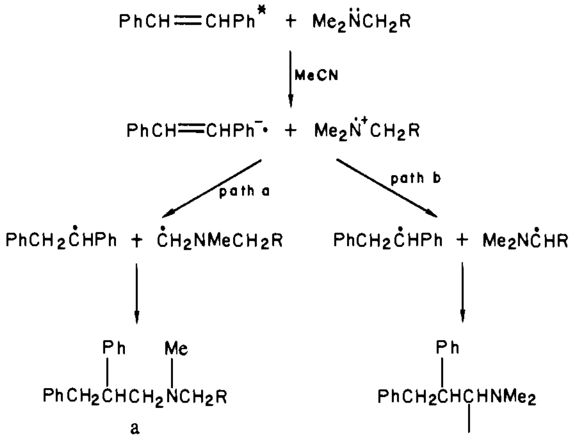
The abstraction of a hydrogen atom from tertiary amines can be effected chemically, electrochemically, photochemically, and enzymatically.[1] Several of these reactions are known to occur via one-electron oxidation to yield a planar aminium radical followed by deprotonation to yield an α-aminoalkyl radical (eq 1).[2] One characteristic of this mechanism is an increase in

$$R_2\ddot{N}CH_2R' \xrightarrow{-e} R_2\dot{N}^+CH_2R' \xrightarrow{-H^+} R_2N\dot{C}HR' \qquad (1)$$

reaction yield or rate with increasing solvent polarity. For example, singlet *trans*-stilbene and ethyldiisopropylamine form an unreactive fluorescent exciplex in nonpolar solvents (τ = 19 ns in hexane solution) but react efficiently to yield a diphenylethyl-α-aminoalkyl radical pair in polar solvents.[2,3] A second characteristic of this mechanism is stereoelectronic control of the deprotonation step.[4] For example, the reaction of singlet *trans*-stilbene with with ethyldimethylamine (**1**) yields 84% of adduct **a** and 16% of adduct **b** via the mechanism shown in Scheme I (R = CH_3).[1] The selective formation of the less substituted of two possible α-aminoalkyl radicals is consistent with a product-determining proton-transfer process but not with a simple hydrogen atom transfer process.

Amines processing π-electron-acceptor α-substituents are capable of forming exceptionally stable free radicals as a consequence of "merostabilization" (also known as "captodative stabilization").[5]

Scheme I



Formation of merostabilized radicals from several α-substituted amines has been reported for hydrogen atom abstraction by *tert*-butoxy radicals[5] but not for electrochemical or photochemical oxidation of these amines. It thus appeared of interest to determine whether the reaction of singlet *trans*-stilbene with such amines yields the less substituted α-aminoalkyl radical, as observed for

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(1) For leading references, see: Lewis, F. D.; Ho, T.-I.; Simpson, J. T. *J. Org. Chem.* **1981**, *46*, 1077-1082.

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(5) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917-932.

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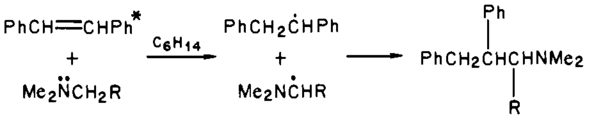
Table I. Quantum Yields and Fluorescence Quenching Constants for the Reaction of *trans*-Stilbene with Tertiary Amines

compd	R^a	$\sigma_I{}^b$	E_{D/D^+}, V^c	ΔG_{ET}, eV^d	$k_q\tau$, M^{-1} ^{e}	$10^2\Phi_b$-$(C_6H_{14})^f$	$10^2\Phi_a$-(MeCN)	$10^2\Phi_b$-$(MeCN)^f$
1	$CH_3{}^g$	−0.04			1.9 (1.4)	<0.1	2.6	0.20
2	H^g	0	0.76	−0.57	1.6	<0.1	1.4	
3	Ph	0.10	0.90	−0.43	1.6 (1.9)	<0.1	4.0	1.2
4	$CH{=}CH_2$	0.09	0.92	−0.41	1.3	0.76	2.1	0.27
5	CO_2Et	0.34	0.96	−0.37	0.87	0.90	0.93	0.98
6	$C{\equiv}CCH_3$	0.34	1.01	−0.32	0.68	11	0.28	1.9
7	$C{\equiv}CH$	0.35	1.23	−0.10	0.60 (0.68)	4.3	<0.1	1.2

[a] From Me_2NCH_2R. [b] Values from: Charton, M. *J. Org. Chem.* 1964, *29*, 1222–1227. [c] Oxidation potentials vs. SCE in acetonitrile solution. [d] Free energy for electron transfer calculated from eq 3. [e] Slope of linear Stern–Volmer plot in hexane solution. Values in parentheses are for acetonitrile solution. [f] Mixture of diastereomers. [g] Data from ref 1.

other trialkyl amines,[1] or the merostablized radical. We now report that several amines of structure Me_2NCH_2R where R = $CH{=}CH_2$ (**4**), CO_2Et (**5**), $C{\equiv}CCH_3$ (**6**), $C{\equiv}CH$ (**7**), and *N*-methylisoindoline (**8**) react selectively with singlet *trans*-stilbene in nonpolar solvents to yield the product **b** derived from the merostabilized radical via a hydrogen atom transfer mechansim (eq 2).[6] In polar solvents, both hydrogen atom transfer and/or electron-transfer, proton-transfer mechanisms operate. The hydrogen atom transfer process, like the previously investigated proton-transfer process,[1] is subject to stereoelectronic control.



$$PhCH{=}CHPh^* + Me_2\ddot{N}CH_2R \xrightarrow{C_6H_{14}} PhCH_2\dot{C}HPh + Me_2N\dot{C}HR \longrightarrow PhCH_2\underset{R}{\underset{|}{\overset{\overset{Ph}{|}}{C}H}}\,CHNMe_2 \quad (2)$$

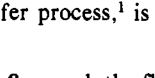
b

R = CH_3 (**1**), H (**2**), Ph (**3**), $CH{=}CH_2$ (**4**), CO_2Et (**5**), $C{\equiv}CCH_3$ (**6**), $C{\equiv}CH$ (**7**)

Results

Amines **1–8** quench the fluorescence of *trans*-stilbene in fluid solution. Stern–Volmer quenching constants ($k_q\tau$) obtained in hexane and acetonitrile solution are given in Table I. The short singlet lifetime of *trans*-stilbene (50–100 ps) necessitates the use of high amine concentrations (0.1–1.0 M) in order to observe fluorescence quenching. Assuming a stilbene singlet lifetime of 90 ps,[7] quenching rate constants (k_q) ranging from 6×10^9 M^{-1} s^1 for amine **7** to 2×10^{10} M^{-1} s^{-1} for amine **1** are calculated. Weak exciplex fluorescence with a band maximum of 23 000 cm^{-1} was detected from stilbene and **3** in nonpolar solvents.

Irradiation of *trans*-stilbene and amines **1–3** in hexane solution results in the formation of *cis*-stilbene and stilbene dimers, but no stilbene–amine adducts. In contrast, irradiation of *trans*-stilbene and amines **4–8** in hexane solution results in the formation of type **b** stilbene–amine adducts (eq 2) as the only amine-containing product, along with *cis*-stilbene, phenanthrene, 1,2-diphenylethane, and 1,2,3,4-tetraphenylbutane (see Experimental Section). Type **b** adducts are obtained as a mixture (ca. 1:1) of diastereomers, which in the case of adducts **5b–7b** are partially resolved by analytical GC. Attempts at physical separation were unsuccessful. Structures of adducts **4b–7b** were assigned on the basis of ^1H NMR, IR, and mass spectra and by analogy to previously characterized stilbene–amine adducts.[1,2] Adduct **8b**, obtained from the reaction of *trans*-stilbene and N-methylisoindoline (**8**), could not be isolated by the chromatographic method used for other stilbene–amine adducts. Its structure is tentatively assigned on the basis of its mass spectrum.



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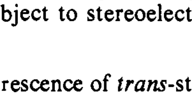

8b

Table II. Quantum Yields for Formation of 1,2-Diphenylethane and 1,2,3,4-Tetraphenylbutane[a]

compd	R^b	$\Phi_{PhCH_2CH_2Ph}$	$\Phi_{PhCH_2CH(Ph)CH(Ph)CH_2Ph}$
2	H	0.006	0.013
3	Ph	0.003	0.012
7	$C{\equiv}CH$	0.001	<0.001

[a] Values for degassed acetonitrile solutions containing 0.5 M stilbene and 1.0 M amine. [b] From Me_2NCH_2R.

Irradiation of *trans*-stilbene and amines **1–8** in acetonitrile solution results in the formation of type **a** and/or type **b** adducts as well as *cis*-stilbene and the other stilbene-containing products obtained in hexane solution. The reactions of stilbene with amines **1** and **2** have previously been described.[1,2] Type **a** adducts are the major amine-containing products from the reaction of stilbene and amines **3–5** in acetonitrile solution. Adducts **3a–5a** have been isolated and characterized by their ^1H NMR, IR, and mass spectra. Minor adducts **4b** and **5b** were identified by comparison of GC retention time and mass spectral fragmentation with samples isolated from hexane irradiation. The structure of minor adduct **3a** was tentatively assigned on the basis of its mass spectrum. Type **b** adducts are the major products from the reaction of stilbene and amines **6–8** in acetonitrile as well as in hexane. No type **a** adduct is detected by analytical GC for the reaction of stilbene with amines **7** or **8**. A minor adduct was detected by analytical GC for the reaction of stilbene and amine **6** and is tentatively identified as **6a** on the basis of its mass spectrum.

Yields of stilbene–amine adducts extrapolated to zero conversion are much lower for *cis*-stilbene than for *trans*-stilbene. The apparent absence of *cis*-stilbene reaction with amines is consistent with its very short singlet lifetime.[8]

Irradiation of *trans*-stilbene and *N,N*-dimethylglycine-α-*d* ethyl ester yields the monodeuterated adducts **5a** and **5b**. Comparison of the *m/e* 131 and 130 abundances in the mass spectra of adduct **5b** provides the ratio of $^1H/^2H$ transfer in acetonitrile ($k_H/k_D = 1.53 \pm 0.05$) and in hexane ($k_H/k_D = 2.24 \pm 0.07$).

Quantum yields for the formation of adducts from *trans*-stilbene (0.05 M) and amines **1–7** (1.0 M) in hexane and acetonitrile are given in Table I. Quantum yields were determined on solutions irradiated to <60% conversion of *trans*-stilbene to *cis*-stilbene and <5% conversion of total stilbene to photoproducts. Incomplete quenching of singlet *trans*-stilbene by 1.0 M amine and absorption of part of the incident light by *cis*-stilbene will cause the measured quantum yields to be less than the true efficiency of the addition process. The quantum yield for reaction of *trans*-stilbene and amine **7** in acetonitrile solution was determined at several amine concentrations. The resulting Stern–Volmer plot (Figure 1) has an intercept of 4 and a slope of 7, from which a limiting quantum yield (100% singlet quenching) of 0.2 and a Stern–Volmer quenching constant (intercept/slope = $k_q\tau$) of 0.6 are calculated.[2] The Stern–Volmer constants obtained by fluorescence quenching (Table I) and product formation (Figure 1) are in excellent agreement. Quantum yields for the formation of 1,2-diphenyl-

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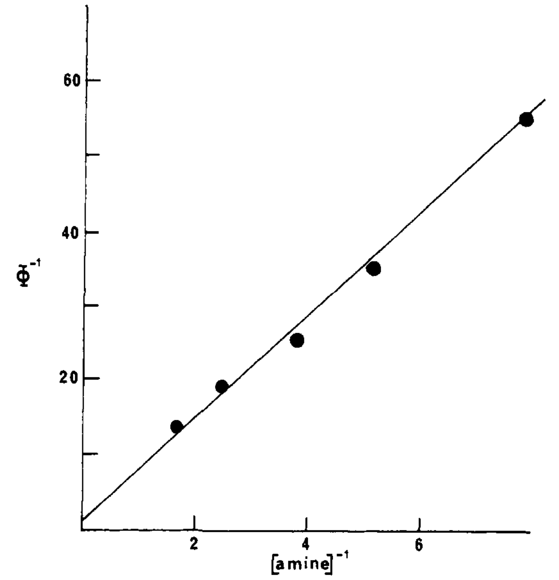

Figure 1. Dependence of adduct quantum yield upon concentration of *N*,*N*-dimethylpropargylamine (**7**) in hexane solution.

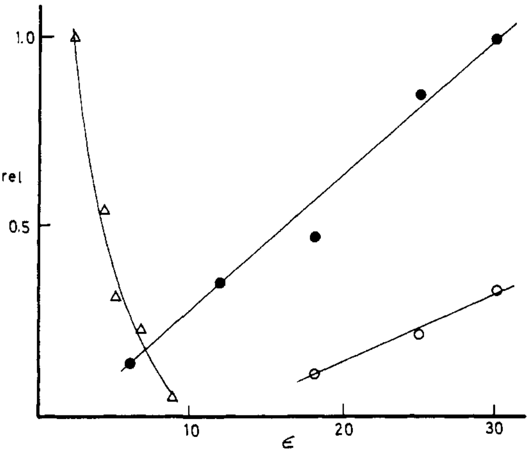

Figure 2. Relative quantum yields for exciplex fluorescence (△) and the formation of adducts **3a** (●) and **3b** (○) from *trans*-stilbene and *N*,*N*-dimethylbenzylamine (**3**) vs. solvent dielectric constant in hexane–ethyl acetate and ethyl acetate–acetonitrile mixed solvents. $\epsilon = \sum_i \epsilon_i V_i$, where ϵ_i and V_i are the dielectric constants and volume fraction of component i.

ethane and 1,2,3,4-tetraphenylbutane from stilbene and amines **2**, **3**, and **7** in acetonitrile solution are given in Table II. Reactions of amines **4**–**7** in hexane solution gave amounts of these products too low to measure ($\Phi < 10^{-3}$). The effect of varying solvent polarity upon stilbene–amine adduct quantum yields is shown in Figures 2–4. Also shown in Figure 2 is the solvent dependence of the fluorescence intensity from the exciplex of *trans*-stilbene and amine **3**.

Oxidation potentials of amines **2**–**7** were measured by cyclic voltammetry in acetonitrile solution vs. Ag/AgI and are reported in Table I vs. SCE.

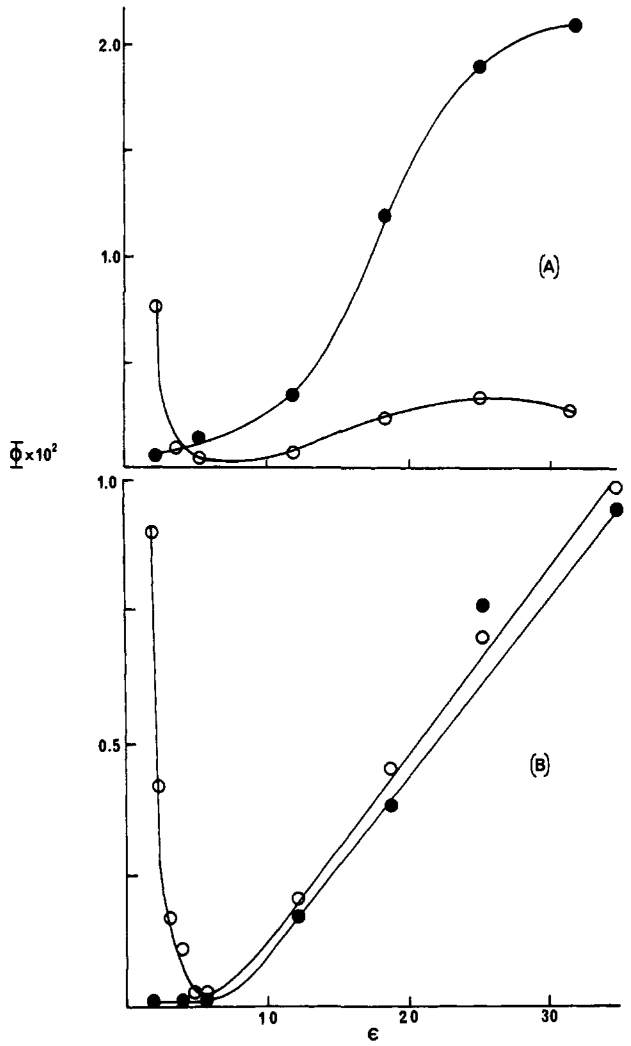

Figure 3. (A) Quantum yields for the formation of adducts **4a** (●) and **4b** (○) from *trans*-stilbene and *N*,*N*-dimethylallylamine (**4**). (B) Quantum yields for the formation of adducts **5a** (●) and **5b** (○) from *trans*-stilbene and *N*,*N*-dimethylglycine ethyl ester (**5**) vs. solvent dielectric constant.

Discussion

The Stern–Volmer constants ($k_q\tau$) for quenching of *trans*-stilbene fluorescence by amines **1**–**7** decrease as the oxidation potential of the amine increases (Table I). The dependence of $k_q\tau$ on E_{D/D^+} is indicative of the formation of a charge-transfer-stabilized exciplex in which singlet stilbene is the electron acceptor and the amine is the electron donor.[8] The approximate free energy for electron transfer from amine to singlet stilbene in acetonitrile solution can be calculated by using Weller's equation (eq 3),[9] where E_s and $E_{A^-/A}$ are the singlet energy (3.53 eV) and

$$\Delta G_{ET} = -E_S - E_{A^-/A} + E_{D/D^+} - e_0^2/\epsilon a \qquad (3)$$

reduction potential (−2.26 V) of *trans*-stilbene,[10] E_{D/D^+} is the measured amine oxidation potential, and the last term is the ionic attraction (ca. 0.06 V). The calculated values of ΔG_{ET} in acetonitrile solution (Table I) are moderately exergonic. Rate constants for singlet quenching (k_q) calculated from the measured $k_q\tau$ values and the reported singlet lifetime of *trans*-stilbene are near or equal to the rate of diffusion in hexane solution (2×10^{10} M^{-1} s^{-1}), as expected for exergonic electron-transfer quenching.[9] The absence of a good linear correlation between either $k_q\tau$ values or amine oxidation potentials (E_{D/D^+}) and the electron-withdrawing ability of the group R (σ_I) (Table I) is not surprising as the group R can interact directly with singlet stilbene or the electrode surface in addition to exerting an inductive effect on the nitrogen nonbonding electrons.

Previous investigations of the photochemical reactions of singlet *trans*-stilbene with trialkyl amines established the formation of a singlet exciplex between stilbene and amines in nonpolar solvents.[1-3] These exciplexes decay by radiative and intersystem crossing pathways but fail to undergo chemical reactions. In polar solvents, the radical ion pair state is of lower energy than the exciplex. Thus as solvent polarity is increased, the fluorescence characteristic of the exciplex is replaced by the chemistry characteristic of the radical ion pair, namely, proton transfer followed by free-radical termination (Scheme I).

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(9) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

(10) Lewis, F. D.; Hoyle, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 3779–3786.

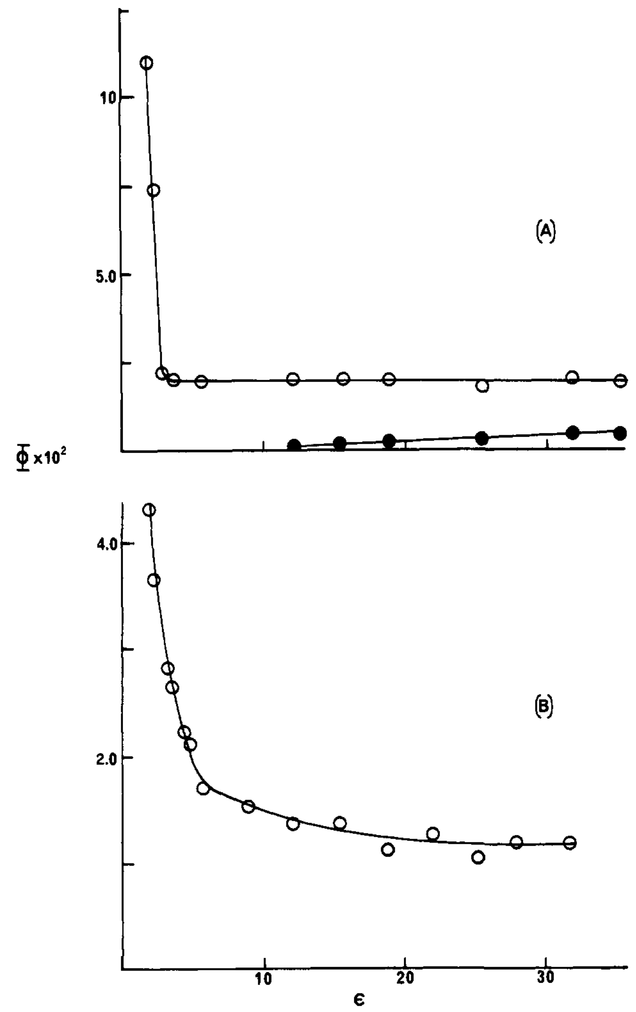


Figure 4. (A) Quantum yields for formation of adducts **6a** (●) and **6b** (○) from *trans*-stilbene and 1-(dimethylamino)-2-butyne (**6**). (B) Quantum yields for the formation of adduct **7b** (○) from *trans*-stilbene and *N*,*N*-dimethylpropargylamine (**7**) vs. solvent dielectric constant.

The behavior of *trans*-stilbene and *N*,*N*-dimethylbenzylamine (**3**), as shown in Figure 2, is entirely consistent with this model. The yields of both stilbene–amine adducts **3a** and **3b** are negligible in nonpolar solvents and increase with increasing solvent polarity. The product ratio **3a**/**3b** is independent of solvent polarity and displays a slighlty larger than statistical preference for product formation via the less substituted α-aminoalkyl radical (Scheme I, path a). It is assumed that the product ratio reflects the relative rates of methyl (path a) vs. benzyl (path b) deprotonation.[1] Statistical deprotonation for the aminium radical of **3** has also been observd for electrochemical oxidation of **3** in the presence of strong bases.[11-13]

The most striking feature of our results is the selective formation of the stilbene–amine type **b** adducts derived from the merostabilized radicals in hexane solution (eq 2 and Table I). The increase in Φ_b with increasing amine oxidation potential for amines **1–6** and the rapid decrease in Φ_b with small increases in solvent polarity (Figures 3 and 4) are incompatible with an electron-transfer, proton-transfer mechanism for α-aminoalkyl radical formation. By analogy to the formation of merostabilized radicals upon reaction of amines with *tert*-butoxy radicals,[5] hydrogen atom transfer via a singlet encounter complex or exciplex is the most plausible mechanism for the formation of the diphenylethyl-merostabilized radical pair in nonpolar solvents (eq 2).

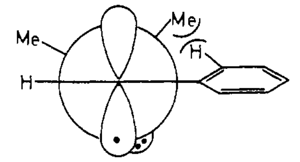
Table III. Singly Occupied π-Orbital Coefficients for α-Aminoalkyl Radicals

		coefficient			
compd	R[a]	N	C_α	C_β	C_γ
1	CH_3	0.450	−0.812	−0.011	
2	H	0.491	−0.848		
3	Ph (in plane)	0.425	−0.720	−0.074[b]	0.295[c]
	(out of plane)	0.430	−0.828	−0.084[b]	−0.101[c]
4	$CH{=}CH_2$	0.429	−0.742	−0.059	0.483
5	CO_2Et	0.461	−0.747	−0.134	0.461[d]
7	$C{\equiv}CH$	0.439	−0.761	−0.034	0.443

[a] From Me_2NCHR. [b] Ipso carbon. [c] Ortho carbon. [d] Carbonyl oxygen.

The stability of merostabilized α-aminoalkyl radicals $Me_2N\dot{C}HR$ should be dependent upon both the resonance stabilization energy and the π-acceptor ability of group R.[5] Orbital coefficients for the singly occupied π orbital obtained from INDO calculations are given in Table III.[14] For radical **3**, results are given for radical conformations with the phenyl ring coplanar and orthogonal to the $N–C_\alpha–C_\beta$ plane. As expected, the former conformation results in greater delocalization of the unpaired electron (smaller C_α coefficient) than the latter conformation. The C_α coefficients for radicals **3–7** are all substantially smaller than the values for radicals **1** and **2**. The absence of any obvious correlation between the C_α or N coefficients and either σ_I (Table I) or the resonance stabilization energies of substituted methyl radicals (R = Ph > $CH{=}CH_2$ > $C{\equiv}CH$ > CO_2Et)[15] indicates that both factors are important in determining the stability of merostabilized radicals. It is interesting to note that the marked preference for C_α vs. C_γ coupling of the diphenylethyl radical with the (dimethylamino)allyl and (dimethylamino)propargyl radicals is consistent with the larger C_α vs. C_γ SOMO coefficients (Table III). Nonsymmetrical allyl radicals normally display a preference for terminal rather than internal coupling.[16]

The failure of amine **3** to yield a type **b** adduct in hexane solution plausibly results from steric inhibition of resonance in the intermediate α-aminoalkyl radical. The Newman projection shown below illustrates the nonbonded interaction between a



N-methyl group and an ortho hydrogen of the phenyl group for a radical conformation with the phenyl ring coplanar with the $N–C_\alpha–C_\beta$ plane. Rotation of the phenyl ring would relieve the nonbonded interaction but reduce the delocalization of the α-aminoalkyl radical (Table III). The formation of a type **b** adduct from *N*-methylisoindoline (**8**) and singlet *trans*-stilbene in hexane solution provides strong evidence for a stereoelectronic effect on hydrogen atom transfer. The nonbonded interactions present in radical **3** are removed by incorporation of one *N*-alkyl group and the phenyl group into the five-membered ring of amine **8**.

The efficiency of type **b** adduct formation in hexane solution is determined by several factors: (a) exciplex stability, which is roughly related to amine oxidation potential; (b) the stereoelectronic effect on hydrogen atom transfer; (c) the stability of the radical pair (Table III); (d) the efficiency of radical pair combination. The relative rates of radical pair combination vs. dif-

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(11) The ratio of methyl/methylene oxidation of amine **3** is reported to be dependent upon base strength[12] and solvent.[13]

(12) Barry, J. E.; Finkelstein, M.; Mayeda, E. A.; Ross, S. D. *J. Org. Chem.* **1974**, *39*, 2695–2699.

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fusion in acetonitrile can be estimated from the quantum yields for formation of adducts (Table I) vs. 1,2,3,4-tetraphenylbutane (Table II), the major product of 1,2-diphenylethyl radical autotermination.[1] For amines **2** and **3**, which form α-aminomethyl radicals, the efficiencies of cage combination and diffusion are comparable, whereas for amine **7**, which forms a merostabilized radical, cage combination is much more efficient than diffusion. The low quantum yields for 1,2,3,4-tetraphenylbutane formation from the reactions of stilbene with amines **4–7** in hexane solution indicate that the preference for radical cage combination vs. diffusion is a property of all the merostabilized radicals investigated. This conclusion is consistent with the known ability of merostabilized radicals to serve as efficient free-radical scavengers.[5]

We have identified two limiting mechanisms for the reaction of singlet *trans*-stilbene with tertiary amines. In polar solvents, reaction normally occurs via electron transfer from amine to singlet stilbene (when $\Delta G_{ET} < 0$) to form a radical ion pair which then undergoes proton transfer to yield a free-radical pair (Scheme I).[2] The orientation of deprotonation of nonsymmetrical amines is governed by kinetic acidity, which is subject to stereoelectronic control.[1] In nonpolar solvents a singlet stilbene–amine encounter complex or exciplex can react via hydrogen atom transfer to yield a radical pair (eq 2) only when an exceptionally stable α-aminoalkyl radical is formed. The formation of type **b** adducts of amines **4–7** in polar solvent could occur via either a hydrogen atom and/or proton-transfer mechanism. The solvent dependence of Φ_b for propargyl amines **6** and **7** (Figure 4) is suggestive of predominant hydrogen atom transfer even in polar solvents. Values of Φ_b decrease rapidly with increasing solvent polarity for $\epsilon < 5$ but show little change in more polar solvents. This behavior is analogous to that observed by Lewis and Hoyle[10] for the solvent dependence of diphenylvinylene carbonate–2,5-dimethyl-2,4-hexadiene exciplex cycloaddition and is consistent with Mataga's[17,18] proposal that the energy of an exciplex decreases rapidly with increasing solvent polarity in nonpolar solvents but decreases only slightly in more polar solvents. The solvent dependence of Φ_b for amines **3–5** (Figures 2 and 3) is indicative of predominant proton transfer in polar solvents. The continuous increase in Φ_b and constant Φ_b/Φ_a ratio with increasing solvent polarity ($\epsilon > 10$) provide the principal evidence for this conclusion. Additional evidence for the formation of type **b** adducts via proton transfer in polar solvents is provided by the increasing ratio of type **b**/type **a** adducts with increasing electron-withdrawing ability of the group R ($CH_3 < CH{=}CH_2 < CO_2Et$). The kinetic acidity of the methylene vs. methyl protons of the aminium radical would be expected to increase in this order. Further evidence for a solvent-induced change in mechanism for the formation of adduct **5b** is provided by the difference in deuterium isotope effects for hexane ($k_H/k_D = 2.2$) vs. acetonitrile ($k_H/k_D = 1.5$) solutions.

One final aspect of the solvent-dependent behavior of amines **1–5** deserves comment, namely, the inefficiency of either exciplex and/or radical ion processes for solvents with $\epsilon \sim 5$–10 (Figures 2 and 3). A possible explanation for this common occurrence[2,18] is that radical ion pairs are formed in these solvents (thus precluding exciplex reactions or fluorescence); however, solvent stabilization of the radical ion pair is insufficient to allow proton transfer or other chemical processes to compete with decay to ground state reactants via back electron transfer.[19]

The orientation of oxidation of amines **1–8** may prove to be a useful chemical probe of radical vs. one-electron-transfer mechanisms for amine oxidation. The mechanism of oxidation of amino acids and propargyl amines (e.g., **5–7**) is of special interest in view of their roles as substrates and suicide inhibitors, respectively, for amine oxidase enzymes.[20,21] An electron-transfer, proton-transfer mechanism has recently been proposed for amine oxidation by mitochondrial monoamine oxidase.[21,22] Further investigation of selective amine oxidation are in progress in our laboratory.

Experimental Section

General Procedures. Quantum yields were determined by using the published value for addition of *trans*-stilbene and 1.0 M triethylamine (0.052)[1] as a secondary standard. Samples contained in 7-mm o.d. Pyrex test tubes were degassed by bubbling with purified nitrogen and irradiated on a merry-go-round apparatus with monochromatic 313-nm light isolated from the output of a Hanovia medium-pressure mercury lamp by means of a potassium chromate filter solution. Irradiated samples were analyzed by using a Hewlett-Packard 5750 dual flame detector gas chromatograph with a 7% Apiezon L-2% potassium hydroxide on Chromosorb W 6 ft × $^1/_8$ in. column.[23] Fluorescence spectra were recorded on a Perkin-Elmer MPF 44A spectrophotometer, NMR spectra were recorded on a Varian CFT 20 spectrometer, IR spectra were recorded on a Perkin-Elmer 283 spectrometer, and mass spectra were recorded on a Hewlett-Packard 5985 mass spectrometer using an ionizing voltage of 70 eV or chemical ionization (methane). Molecular ions of most stilbene–amine type **a** or **b** adducts were not detected when an ionizing voltage of 20 eV was used.

The oxidation potentials of amines **3–7** were measured by cyclic voltammetry in acetonitrile vs. Ag/AgI in a three-electrode cell using Pt working and auxiliary electrodes. The measurements were computer controlled and were run at a scan rate of 1 V/s. The solutions contained 0.1 M tetra-*n*-butylammonium perchlorate and 10^{-3} M amine and were deoxygenated by bubbling with nitrogen prior to measurement. The working electrode was polished before every run. Values of the peak potential for irreversible one-electron oxidation are reported vs. SCE.

The coordinates of the atoms for the INDO calculations were determined from published bond lengths and angles.[24] The calculations were performed on the Northwestern University CDC Cyber 170/730 computer system.

Materials. *trans*-Stilbene (Aldrich) was recrystallized from benzene and from 90% ethanol. Dimethylallylamine (Eastman), (dimethylamino)acetonitrile (Pfaltz and Bauer), dimethylglycine ethyl ester (Eastman), dimethylpropargylamine (Aldrich), and dimethylbenzylamine (Aldrich) were fractionally distilled prior to use. 1-(Dimethylamino)-2-butyne was prepared from dimethylpropargylamine by the method of Brandsma.[25] Isoindoline was prepared by the method of Dubois et al.[26] and converted to *N*-methylisoindoline by the method of Clarke et al.[27] This amine proved less stable to oxidation than the other tertiary amines investigated and was used immediately following distillation. Acetonitrile (Burdick and Jackson) was distilled from calcium hydride immediately prior to use, hexane (Aldrich, reagent) was distilled successively from sulfuric acid, potassium carbonate, and phosphorus pentoxide, and ethyl acetate (Aldrich, gold label) was used as received.

***N,N*-Dimethylglycine-*α-d* Ethyl Ester.** A solution of lithium diisopropylamide (0.4 M) in dry tetrahydrofuran was cooled to −78 °C. To this rapidly stirred solution, 0.9 equiv of *N,N*-dimethylglycine ethyl ester in tetrahydrofuran was added dropwise over a period of 10 min.[28] Th solution was warmed to 0 °C and stirred for 2 h and then quenched with 1.5 equiv of D_2O. The resulting mixture was filtered through a short silica gel column and the solvent removed. Vacuum distillation of the residual oil gave a 77% yield of *N,N*-dimethyglycine-*α-d* ethyl ester: bp (35 torr) 57–58 °C; ^1H NMR ($CDCl_3$) δ 2.74 (t, 3 H), 3.82 (s, 6 H), 4.63 (s, 1.4 H), 5.68 (q, 2 H). NMR integration and mass spectra analysis indicated that 63 ± 2% monodeuteration was achieved. Incomplete incorporation of deuterium has been attributed to an unusual protonation mechanism during the quenching process.[29]

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Table IV. Mass Spectral Data for Stilbene–Amine Adducts

adduct, *m/e* (%)	β,γ cleavage, *m/e* (%)	α cleavage, *m/e* (%)
3a, 315 (0%)	$CH_2{=}\overset{+}{N}MeCH_2Ph$, 134 (100%)	$Ph\overset{+}{C}H_2$, 91 (80%)
3b, 315 (0%)	$Me_2\overset{+}{N}{=}CHPh$, 134 (100%)	$Me\overset{+}{N}H{=}CHPh$, 120 (58%)
4a, 265 (1%)	$CH_2{=}\overset{+}{N}MeCH_2CH{=}CH_2$, 84 (100%)	$CH_2{=}\overset{+}{N}HMe$, 44 (3%)
4b, 265 (0%)	$Me_2\overset{+}{N}{=}CHCH{=}CH_2$, 84 (100%)	none
5a, 311 (0%)	$CH_2{=}\overset{+}{N}MeCH_2CO_2Et$, 130 (100%)	$CH_2{=}\overset{+}{N}HMe$, 44 (9%)
5b, 311 (0%)	$Me_2\overset{+}{N}{=}CHCO_2Et$, 130 (100%)	$Me\overset{+}{N}H{=}CHCO_2Et$, 116 (26%)
6a, 277 (0%)	$CH_2{=}\overset{+}{N}MeCH_2C{\equiv}CCH_3$, 96 (100%)	$CH_2{=}\overset{+}{N}HMe$, 44 (10%)
6b, 277 (0%)	$Me_2\overset{+}{N}{=}CHC{\equiv}CCH_3$, 96 (100%)	none
7b, 263 (1%)	$Me_2\overset{+}{N}{=}CHC{\equiv}CH$, 82 (100%)	none
8b, 313 (1%)	132 (100%)	none
314 (100%)[a]	132 (96%)	none

[a] Chemical ionization.

Preparative Irradiation. Solutions of *trans*-stilbene (0.9 g, 0.05 M) and tertiary amine (2.0 M) in 100 mL of hexane or acetonitrile solvent were purged with dry nitrogen and irradiated for 9–25 h with a Hanovia medium-pressure mercury lamp in a water-cooled Pyrex lamp well. Reactions were monitored by GC and terminated after ca. 90% conversion of stilbene. In a typical reaction, irradiation of stilbene and *N,N*-dimethylallylamine (**4**) yielded, after removal of solvent and unreacted amine under vacuum, 0.99 g (110% based on stilbene) of a light yellow oil. This oil was subjected to flash column chromatography on 200 g of silica gel (Davidson Chemical 950) with 1–10% ethyl acetate–hexane as the elutant and with monitoring by analytical GC. The order of elution and GC retention (5% SF 96 on Chromosorb G) were the same. Obtained in this fashion were 1,2-diphenylethane (6%),[30] two reduction products of stilbene or phenanthrene which were not fully characterized but which contain no nitrogen (24% and 18%),[31] recovered stilbene (11%), phenanthrene (18%),[30] and adduct **4b** (11%). The remaining 12% consists of several minor products (total = 4%) and uneluted material.

Characterization of Stilbene–Amine Adducts. All adducts were obtained as pale yellow oils of >90% purity by GC analysis. The adducts resisted attempts to induce crystallization and decomposed within several days of isolation at 0 °C and rapidly upon heating or attempted distillation. Adduct **8b** was unstable to the conditions of column chromatography. Attempts to convert several of the adducts to quaternary ammonium salts[1] with methyl iodide or picric acid were unsuccessful, as were attempts to convert adduct **7b** to a silver acetylide salt and adduct **5b** to an acid salt by alkaline ester hydrolysis. All type **b** adducts are formed as 1:1 mixtures of diastereomers which were partially resolved by GC but unresolved by column or thick-layer chromatography or HPLC. The IR spectra of all isolated adducts displayed the same aliphatic C–H and multiple bond stretching frequencies as the reactant amines. The NMR spectra of the isolated adducts are described below. Structures of the unisolated adducts are tentatively assigned on the basis of the mass spectral data reported in Table IV. Adducts display characteristic cleavage of the weakest β–γ bond to yield the principal immonium ion fragment along with variable amounts of its α-cleavage products.[1,2] The α-cleavage fragments were used to distinguish between type **a** and type **b** adducts.

***N*-Methyl-*N*-benzyl-2,3-diphenylpropylamine (3a)** was obtained from the reaction of stilbene and *N,N*-dimethylbenzylamine (**3**) in acetonitrile solution in 6% isolated yield; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3 H), 2.5–3.2 (m, 5 H), 3.51 (s, 2 H), 7.1 (m, 15 H).

***N*-Allyl-*N*-methyl-2,3-diphenylpropylamine (4a)** was obtained from the reaction of stilbene and *N,N*-dimethylallylamine (**4**) in acetonitrile solution in 30% isolated yield; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 3 H), 2.8 (m, 7 H), 5.0 (m, 2 H), 5.7 (m, 1 H), 7.1 (m, 10 H); IR (film, cm^{-1}) 1615.

3-(Dimethylamino)-4,5-diphenyl-1-pentene (4b) was obtained from the reaction of stilbene and *N,N*-dimethylallylamine (**4**) in hexane solution in 11% isolated yield as a mixture of diastereomers; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 6 H), 2.9–3.3 (m, 3 H), 5.2–5.6 (m, 3 H), 7.1 (m, 10 H); IR (film, cm^{-1}) 1605.

***N*-Methyl-*N*-(2,3-diphenylpropyl)glycine ethyl ester (5a)** and ***N,N*-dimethyl-1,2-diphenylethylglycine ethyl ester (5b)** were obtained from the reaction of stilbene and *N,N*-dimethylglycine ethyl ester (**5**) in acetonitrile solution in isolated yields of 20% and 6%, respectively; (**5a**) ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3 H), 2.37 (s, 3 H), 2.9 (m, 3 H), 3.22 (s, 2 H), 4.13 (q, 2 H), 7.1 (m, 10 H); (**5b**) the presence of two diasteromers complicates the appearance of the ^{1}H NMR spectrum. The *N*-methyl proton signal appears as two singlets at δ 2.21 and 2.47. The ethyl group signals appear as two triplets at δ 0.89 and 1.35 and two quartets at δ 3.78 and 4.25. The remainder of the spectrum consists of multiplets centered at δ 3.1 (4 H) and 7.1 (10 H); IR (film, cm^{-1}) 1740.

4-(Dimethylamino)-5,6-diphenyl-2-hexyne (6b) was obtained as a mixture of diastereomers from the reaction of stilbene and 1-(dimethylamino)-2-butyne (**6**) in hexane solution in 25% isolated yield; ^{1}H NMR ($CDCl_3$) δ 1.90 (d, 3 H J = 2.1 Hz), 2.07 (s, 6 H), 2.90 (d, 1 H, J = 2.1 Hz), 3.3–3.6 (m, 3 H), 6.70–7.17 (m, 10 H) for one diastereomer and δ ($CDCl_3$) 1.60 (d, 3 H, J = 2.1 Hz), 2.21 (s, 6 H), 2.90 (d, 1 H, J = 2.1 Hz), 3.3–3.6 (m, 3 H), 6.74–7.17 (m, 10 H) for the other diastereomer; IR (film, cm^{-1}) 2220.

3-(Dimethylamino)-4,5-diphenyl-1-pentyne (7b) was obtained as a mixture of diasteromers from the reaction of stilbene and dimethylpropargylamine (**7**) in hexane solution in 10% isolated yield. The *N*-methyl proton NMR appeared as two singlets at δ 2.11 and 2.29. The acetylenic proton appeared as two doublets at δ 2.05 and 2.29 (J = 2.3 Hz). The remainder of the spectrum consists of multiplets centered at δ 3.1 (4 H) and 7.1 (10 H); IR (film, cm^{-1}) 3320, 2100.

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Registry No. 3, 103-83-3; **3a**, 80800-25-5; **4**, 2155-94-4; **4a**, 80800-26-6; **4b**, isomer 1, 80800-27-7; **4b**, isomer 2, 80800-28-8; **5**, 33229-89-9; **5a**, 80800-29-9; **5b**, 80800-30-2; **6**, 2588-78-5; **6b**, isomer 1, 80800-31-3; **6b**, isomer 2, 80800-32-4; **7**, 7223-38-3; **7b**, isomer 1, 80800-33-5; **7b**, isomer 2, 80800-34-6; **8**, 33804-84-1; **8b**, 80800-35-7; *trans*-stilbene, 103-30-0.

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(31) NMR spectra indicated partial reduction of one of the aromatic nuclei and the absence of *N*-methyl protons.