Photochemical Addition of Tertiary Amines to Stilbene. Stereoelectronic Control of Tertiary Amine Oxidation

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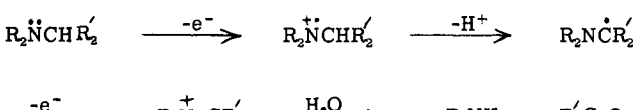
The photochemical addition reactions of seven nonsymmetrical tertiary amines with singlet *trans*-stilbene are described. Addition of methyldiisopropylamine or isopropyldimethylamine is highly selective for formation of the least substituted α-amino radical, whereas addition of several less highly branched amines is relatively nonselective. The product isotope effect for *tert*-butylmethyl(trideuteriomethyl)amine is 2.2 ± 0.2. Product selectivity is determined by the orientation of deprotonation of an aminium radical intermediate by the stilbene radical anion. Selective oxidation results from a stereoelectronic effect which is most evident when one or more alkyl group is highly branched.

Amine oxidation is a ubiquitous process which can be effected by a variety of chemical one-electron oxidants,[1] electrochemically,[2] photochemically,[3] and enzymatically.[4] The electrochemical oxidation of tertiary amines has been extensively investigated and is believed to occur by the mechanism indicated in eq 1.[5] The initial one-electron



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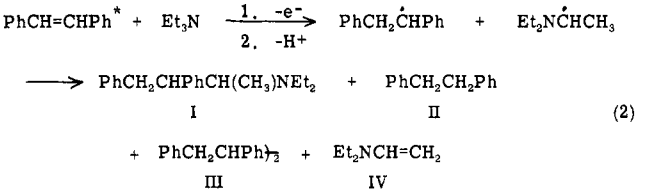
oxidation yields a planar animium radical which is deprotonated to yield an α-amino radical. A second one-electron oxidation produces an immonium ion, which is readily hydrolyzed to yield a secondary amine and a carbonyl compound. Oxidation of nonsymmetrical amines, e.g., R_2NR', can give two different α-amino radicals and hence two dealkylation products. Smith and Mann[2a] reported in 1969 that electrochemical oxidation of ethyldiisopropylamine resulted in highly selective cleavage of the ethyl group. Selective oxidation of the less substituted alkyl group has subsequently been reported for chemical, electrochemical, and photochemical oxidation of several highly branched tertiary amines.[1-3] Selectivity has been attributed to both steric and kinetic acidity effects. In contrast, the oxidation of less substituted amines such as dimethyl-*n*-alkylamines has been reported to be nonselective, a result in accord with neither a simple steric nor a kinetic acidity effect.

We have reported that the reaction of singlet *trans*-stilbene with tertiary amines in polar aprotic solvents yields stilbene–amine adducts I and other products (II–IV) expected from cross termination and autotermination of 1,2-diphenylethyl and α-amino radicals (eq 2).[6] The



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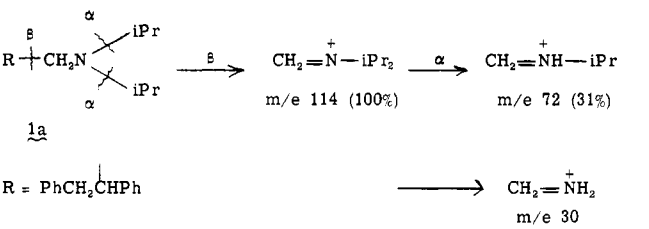
mechanism of this reaction involves the same first two steps as electrochemical amine oxidation, namely, one-electron transfer followed by proton transfer. The second oxidation step does not occur due to the absence of a suitable oxidant. We report here an investigation of the photochemical reactions of *trans*-stilbene with a number of nonsymmetrical tertiary amines, the results of which serve to elucidate the origin of amine oxidation selectivity.

Results

Stilbene–Amine Adducts. Irradiation of a degassed acetonitrile solution of *trans*-stilbene and diisopropylmethylamine (1) leads to the formation of a single adduct, **1a**, which was isolated and characterized by its ^1H NMR



and mass spectra and by conversion to the methiodide salt. The absence of both an *N*-methyl singlet in the NMR spectrum and a *m/e* 58 fragment in the mass spectrum (vide adduct **2b**) provided conclusive evidence for the formation of **1a**. Trialkylamines are known to undergo mass spectral fragmentation by cleavage of the weakest β–γ bond with concomitant or subsequent α cleavage.[7] The α-cleavage process of the intermediate immonium ion is accompanied by hydrogen transfer to nitrogen and is greatly facilitated by α-branching (Me ≪ Et < *i*-Pr).

As previously reported,[6a] stilbene and ethyldiisopropylamine (2) yield adducts **2a** (mixture of diastereo-

(1) (a) Smith, P. A. S.; Loeppky, R. N. *J. Am. Chem. Soc.* **1967**, *89*, 1147. (b) Deno, N. C.; Fruit, R. E. *Ibid.* **1968** *90*, 3502. (c) Audeh, C. A.; Lindsay-Smith, J. R. *J. Chem. Soc. B* **1970**, 1280. (d) Audeh, C. A.; Lindsay-Smith, J. R. *Ibid.* **1971**, 1741. (e) Lindsay-Smith, J. R.; Mead, L. A. V. *J. Chem. Soc., Perkin Trans. 2* **1973**, 206.

(2) (a) Smith, P. J.; Mann, C. K. *J. Org. Chem.* **1969**, *34*, 1821. (b) Portis, L. C.; Bhat, V. V.; Mann, C. K. *Ibid.* **1970**, *35*, 2175. (c) Masui, M.; Sayo, H. *J. Chem. Soc. B* **1971**, 1593. (d) Lindsay-Smith, J. R.; Masheder, D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 47.

(3) (a) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973** *73*, 141. (b) Bartholomew, R. F.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 2347. (c) Bartholomew, R. F.; Brimage, D. R. G.; Davidson, R. S. *Ibid.* **1971**, 3482. (d) Cohen, S. G.; Stein, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6542. (e) Ojanpera, S.; Parola, A.; Cohen, S. G. *Ibid.* **1974**, *96*, 7379. (f) Bellas, M.; Bryce-Smith, D.; Clarke, M. T.; Gilbert, A.; Klunkin, G.; Krestonosich, S.; Manning, C.; Wilson, S. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2571. (g) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1980**, *102*, 1751.

(4) Kapeller-Adler, R. "Amine Oxidases and Methods for Their Study"; Wiley-Interscience: New York, 1970.

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

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

(7) Beynon, J. H.; Saunders, R. A.; Williams, A. E. "The Mass Spectra of Organic Molecules"; Elsevier: Amsterdam, 1968; p 529.

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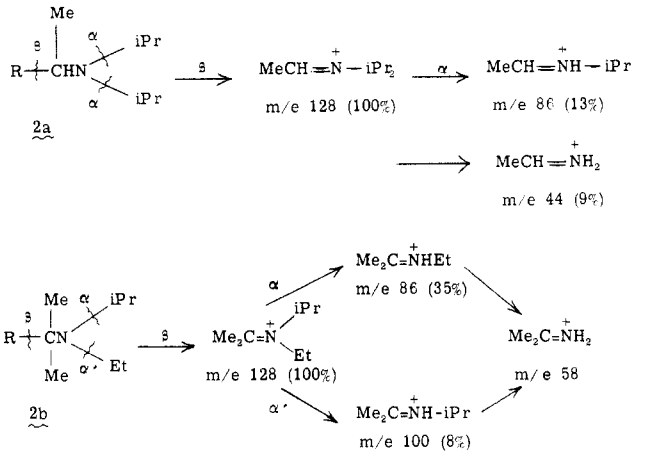
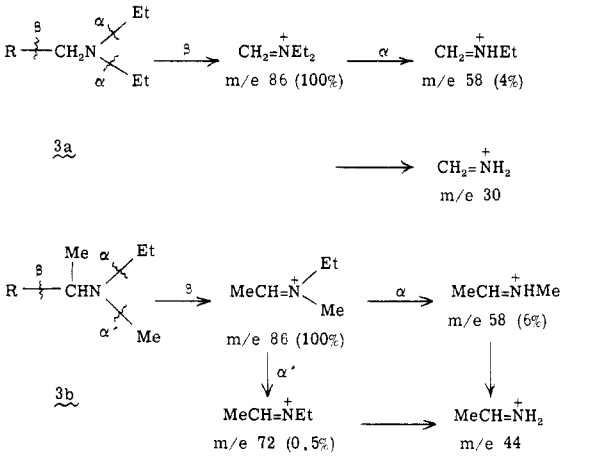
mers) and **2b**. These adducts can be separated by ana-



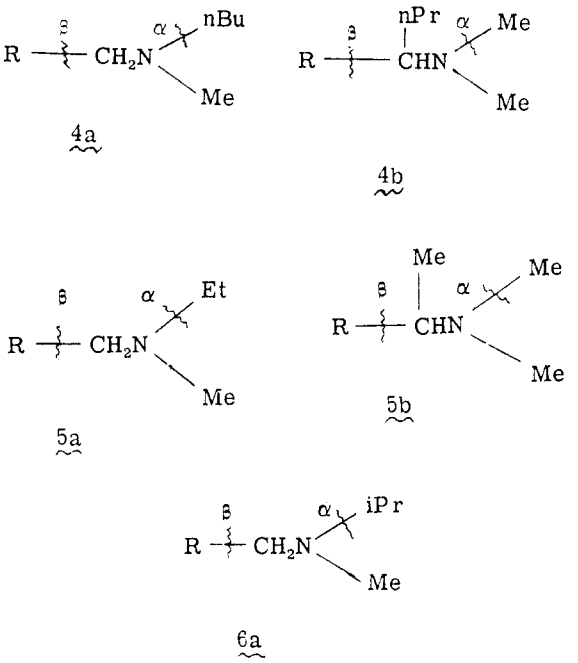
lytical gas chromatography (GC) and their structures readily assigned by mass spectral analysis. The immonium ion fragment from the major adduct **2a** yields a single α-cleavage fragment, whereas the immonium ion from the minor adduct **2b** forms two α-cleavage fragments (note that the α/α' ratio is 4.4).

Irradiation of stilbene with diethylmethylamine yields adducts **3a** and **3b** (mixture of diastereomers) which are



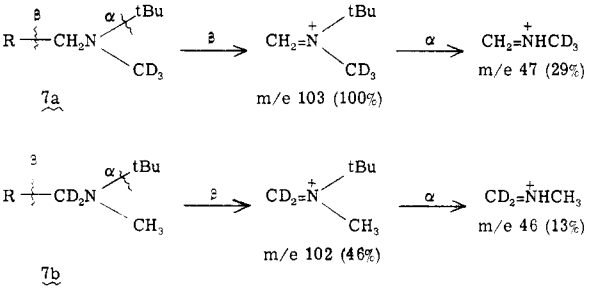
partially resolved by GC. Structure assignments are based on the massgrams shown in Figure 1. The total-ion (TI) plot gives the same product ratio of **3a/3b** as flame-ionization GC. The m/e 86 and 58 plots give smaller **3a/3b** ratios, whereas the m/e 30 plot gives a larger ratio. The relative propensity toward α-cleavage allows assignment of structure **3a** to the major adduct. This assignment is supported by the observation of a small m/e 72 fragment in the mass spectrum of **3b** but not **3a** (note that the α/α' ratio is >10).

Irradiation of stilbene with *n*-butyldimethylamine yields three adducts. The major adduct **4a** displays a β-cleavage fragment (m/e 100, 100%) and an α,β-cleavage fragment (m/e 44, 5%); however, the two minor adducts display only a β-cleavage fragment (m/e 100). Since the two minor adducts are formed in the same yield and have similar mass spectra, they are assumed to be the diastereomers of **4b**. Similarly, the major adduct **5a** from stilbene and ethyldimethylamine displays both a β-cleavage (m/e 72, 100%) and an α,β-cleavage (m/e 44, 6%) fragment, whereas the minor adduct **5b** (mixture of diastereomers) displays only a β-cleavage fragment. Irradiation of stilbene with isopropyldimethylamine yielded only one adduct by GC analysis. The mass spectrum of this adduct displays both β-cleavage (m/e 86, 100%) and α,β-cleavage (m/e 44,



15%) fragments, supporting the assignment of structure **6a** to this adduct. A previously reported second adduct[3g] proved, upon closer scrutiny, to be the adduct of stilbene with a secondary amine, isopropylmethylamine, present as an impurity in the isopropyldimethylamine. It is possible that a small amount of a second stilbene–isopropyldimethylamine adduct is formed but not resolved from **6a** by analytical GC. The absence of a m/e 72 fragment in the mass spectrum of the stilbene–amine adduct indicates that a second adduct can account for no more than 10% of the total adduct.

Irradiation of stilbene with *tert*-butylmethyl(trideuteriomethyl)amine yielded one stilbene–amine adduct fraction by analytical GC. Mass spectral analysis indicated the formation of **7a** and **7b**. The ratios m/e 103/102 and



m/e 47/46 provide a product ratio of **7a/7b** of 2.2 ± 0.2. Integration of the *tert*-butyl vs. *N*-methyl region of the NMR spectrum of the isolated stilbene–amine adducts provides a product ratio of **7a/7b** of 2.3 ± 0.2.

The percentage of stilbene–amine isomers of type **a** and **b** obtained with amines 1–7 is summarized in Table I along with the **a/b** product ratios statistically corrected for the number of equivalent abstractable α-protons.

Quantum Yields. Quantum yields for formation of *cis*-stilbene, stilbene–amine adducts I, diphenylethane II, and tetraphenylbutane III from *trans*-stilbene (0.01 M) with five tertiary amines (1.0 M) are given in Table II. The use of a 90% acetonitrile–10% diethyl ether mixed solvent was necessitated by the low solubility of triisopropylamine in acetonitrile. Quantum yields for formation of I–III increase with increasing amine concentration, whereas the value for *cis*-stilbene formation decreases. Limiting values for triethylamine obtained by extrapo-

Table I. *trans*-Stilbene–Amine Adduct Yields and Ratios

no.	amine	% a	% b	cor a/b ratio[a]
1	diisopropylmethyl	>95	<5[b]	>20
2	ethyldiisopropyl	92	8	12
3	diethylmethyl	63	37	2.3
4	*n*-butyldimethyl	86	14	2.0
5	ethyldimethyl	84	16	1.8
6	isopropyldimethyl	>95	<5[b]	>20
7	*tert*-butylmethyl-(trideuteriomethyl)	69	31	2.2

[a] Statistically corrected for the number of equivalent abstractable α-protons. Average of two or more determinations; limits of error ±10%. [b] Not detected by analytical GC.

lating data[6a] for 0.1–1.0 M amine concentrations are included in Table II. By use of the quantum yield for *cis*-stilbene formation as a measure of unquenched singlet *trans*-stilbene, the extent of quenching by 1.0 M amine is ca. 40% for trimethylamine, 90% for triisopropylamine, and 65% of the other three amines in Table II. Stilbene–amine adduct yields increase with increasing solvent polarity, as previously observed for stilbene with triethylamine.[6a] Relative yields for adduct formation vs. solvent dielectric constant are shown in Figure 2 for stilbene with three tertiary amines. The yields of stilbene–amine adducts are the same in dry or wet (3% H_2O) acetonitrile or in acetonitrile containing 5% methanol. No stilbene–amine adduct was observed upon prolonged photolysis of stilbene with triisopropylamine or with Dabco (1,4-diazabicyclo[2.2.2]octane).

Fluorescence Studies. Stern–Volmer constants for quenching of *trans*-stilbene fluorescence by several tertiary amines in hexane and acetonitrile solution are given in Table III. Exciplex fluorescence with a band maximum at ca. 23 000 cm^{-1} was detected for four of the tertiary amines investigated. The relative intensity of exciplex fluorescence increased in the order *n*-butyldimethylamine < triethylamine < ethyldiisopropylamine < diisopropylmethylamine. Increasing solvent polarity causes a red shift of the exciplex fluorescence maximum and a reduction in exciplex fluorescence intensity.[6] Relative intensities of exciplex fluorescence vs. solvent dielectric constant are shown in Figure 2 for stilbene with three amines.

Discussion

We have previously reported that quenching of *trans*-stilbene fluorescence by tertiary amines occurs via the reversible formation of a charge-transfer-stabilized exciplex intermediate (Scheme I).[6] In nonpolar solvents, the exciplex may dissociate (k_{-e}), fluoresce (k_{fx}), undergo nonradiative decay (k_{dx}), or undergo intersystem crossing to yield triplet stilbene and ground-state amine (k_{tx}).[8] Ac-

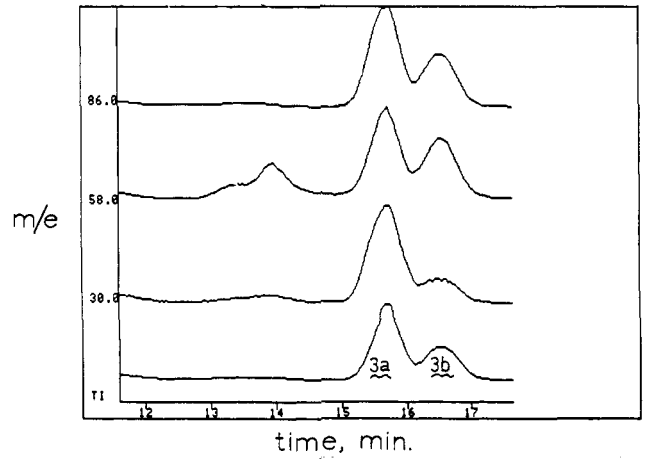


Figure 1. Total-ion and mass chromatograms for stilbene–diethylmethylamine adducts **3a** and **3b**. Total-ion chromatogram shows impurities with retention time below 15 min to be insignificant.

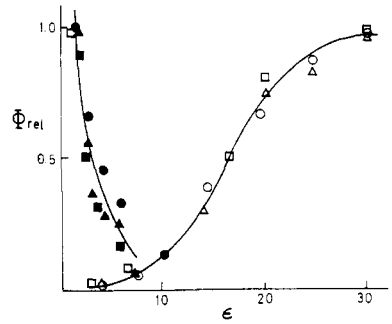
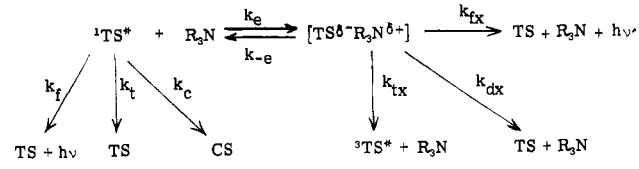
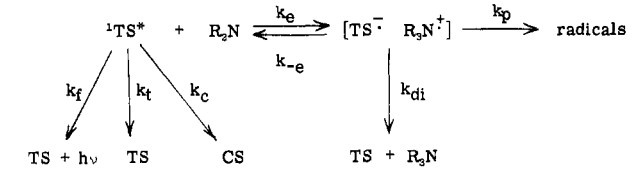


Figure 2. Relative quantum yields for exciplex fluorescence (filled symbols) and addition product formation (open symbols) vs. solvent dielectric constant for *trans*-stilbene with diisopropylmethylamine (○), ethyldiisopropylamine (△), and triethylamine (□) in hexane–ethyl acetate and ethyl acetate–acetonitrile mixed solvents.

Scheme I. Exciplex Formation and Decay in Nonpolar Solvent



Scheme II. Radical Ion Pair Formation and Decay



cording to this mechanism, the rate constant for fluorescence quenching in nonpolar solvents is given by eq 3.

Table II. Quantum Yields for Product Formation from *trans*-Stilbene with Tertiary Amines[a]

amine	Φ_{CS}	Φ_I	Φ_{II}	Φ_{III}	Φ_{II}/Φ_{III}
trimethyl	0.26	0.014	0.006	0.013	0.5
triethyl	0.17 (<0.01)[b]	0.059 (0.12)[b]	0.038 (0.063)[b]	0.021	1.8
diisopropylmethyl (1)	0.16	0.22	0.012	0.033	0.4
ethyldiisopropyl (2)	0.15	0.11	0.11	0.034	3.2
triisopropyl	0.055	<0.005	0.007	<0.005	>1

[a] Values for degassed solutions of *trans*-stilbene (10^{-2}/M) and amine (1.0 M) in 90% acetonitrile–10% diethyl ether mixed solvent: relative error ±10%, absolute error ±20%. [b] Values extrapolated to infinite amine concentration.

$$k_q = k_e\left(\frac{k_{fx} + k_{dx} + k_{tx}}{k_{-e} + k_{fx} + k_{dx} + k_{tx}}\right) \quad (3)$$

The values of $k_q\tau$ in Table III increase continuously with amine electron-donor ability, as expected for the formation of a charge-transfer-stabilized exciplex.[6] The relative intensity of stilbene–amine exciplex fluorescence first increases and then decreases with amine donor ability (Me_2N-*n*-Bu < Et_3N < *i*-Pr_2NMe > *i*-Pr_2NEt > *i*-Pr_3N). Thus the exciplex formation and decay pathways (Scheme I) may be subject to steric as well as electronic effects. The association constants for ground-state amine–boron trifluoride complexes display the opposing effects of inductive stabilization and steric repulsion ($MeNH_2$ < Me_2NH > Me_3N > Et_3N).[9]

In polar solvents, the radical ion-pair state is of lower energy than the fluorescent exciplex.[6] Thus as solvent polarity is increased (Figure 2), the fluorescence characteristic of the exciplex is replaced by the chemistry characteristic of the radical ion pair proton transfer followed by free-radical combination and disproportionation (eq 2). Fluorescence quenching in polar solvents can be described by Scheme II, according to which the rate constant for fluorescence quenching is given by eq 4. A small but finite

$$k_q = k_e\left(\frac{k_p + k_{di}}{k_{-e} + k_p + k_{di}}\right) \quad (4)$$

isotope effect is observed for fluorescence quenching of stilbene by *tert*-butyldimethylamine in acetonitrile solution (Table III). Proton transfer (k_p) is the only decay process which can display a primary isotope effect. The observation of an isotope effect on k_q requires that exciplex formation be reversible, in accord with our previous conclusions which were based on the temperature dependence of stilbene fluorescence quenching by triethylamine.[6] The absence of an observable isotope effect in hexane soluton indicates that proton transfer does not occur, in accord with the failure to observe photoproducts. The low quantum yield for *cis*-stilbene formation extrapolated to infinite amine concentration (Table II) indicates that the triplet state of stilbene is not efficiently populated from the radical ion pair in acetonitrile solution.[8]

Proton transfer from an aminium radical to the stilbene radical anion produces an α-amino radical and the 1,2-diphenylethyl radical. The nonsymmetric amines **1–7** can form two distinct α-amino radicals. The plethora of reactions available to the two free-radical pairs formed from stilbene and diethylmethylamine are shown in Scheme III (autotermination of α-amino radicals has been omitted). Both cage pairs **a** and **b** may undergo diffusion (k_{ea}, k_{eb}), back hydrogen atom transfer (k_{ra}, k_{rb}) to regenerate the starting materials, and combination to yield adducts **5a** and **5b** (k_{ca}, k_{cb}). Pair **b** can also undergo disproportionation (k_{db}) to yield diphenylethane and an enamine, whereas pair **a** cannot. The corresponding homogeneous cross termination processes can occur following diffusion from the cage. Autotermination of 1,2-diphenylethyl yields stilbene and diphenylethane (k_d) or tetraphenylbutane (k_c).

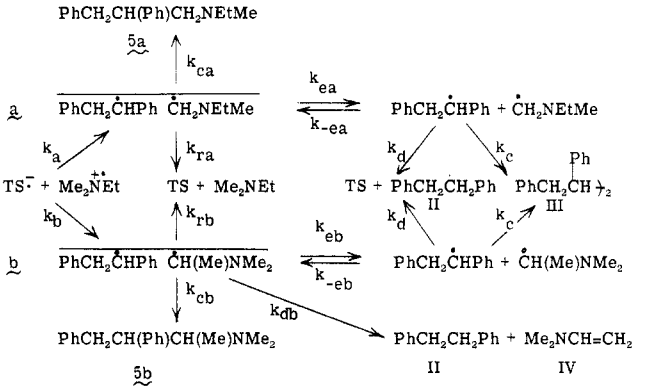
The quantum yield data in Table II allow partial analysis of the complex kinetics of Scheme III. The α-amino radical from trimethylamine cannot yield diphenylethane by cross disproportionation with 1,2-diphenylethyl. Thus all of the diphenylethane found in the reaction of stilbene with trimethylamine must be formed

Table III. Fluorescene Quenching of *trans*-Stilbene by Tertiary Amines

amine	$k_q\tau$, M^{-1} [a] hexane	$k_q\tau$, M^{-1} [a] acetonitrile	$^{ex}\nu_{max}$, cm^{-1} [b]
trimethyl	1.6		
diethylmethyl (**3**)	2.1		
triethyl	2.2	2.8	22 700
tert-butyldimethyl	2.6	2.3	
tert-butylmethyl(trideuteriomethyl) (**7**)	2.5	1.5	
diisopropylmethyl (**1**)	3.6		23 000
ethyldiisopropyl (**2**)	3.9	4.9	23 000
triisopropyl	7.9		
Dabco		8.6	

[a] Slopes of linear Stern–Volmer plots for fluorescence quenching of *trans*-stilbene (10^{-4} M) by tertiary amines (0.1–1.0 M) in degassed solution: corelation coefficients >0.98. [b] Exciplex fluorescence maxima for 1.0 M tertiary amine in hexane solution.

Scheme III. Radical Pair Termination Reactions



by autodisproportionation of 1,2-diphenylethyl. The observed value of the ratio of II/III is $k_d/k_c = 0.5 \pm 0.1$ and is in reasonable agreement with the data of Gibian and Corley[10] for thermolysis of azo compounds when extrapolated to 25 °C. The α-amino radical from triethylamine can undergo cross disproportionation and displays a higher II/III ratio (=1.8). If the "excess" diphenylethane comes from cross disproportionation (k_{db}), then the quantum yield for cross disproportionation is 0.027. Comparison of this value with that for adduct formation provides a cross combination/disproportionation ratio (k_{cb}/k_{db}) = 2.2. Thus a diphenylethyl–α-amino-1-ethyl radical pair is twice as likely to combine as disproportionate. Due to the occurrence of cross disproportionation for α-aminoethyl radicals but not α-aminomethyl radicals, the product ratios of **a**/**b** in Table I may overestimate the kinetic preference k_a/k_b for deprotonation of the less substituted alkyl group (Scheme III). For example, correction of the **a**/**b** product ratio for amine **5** for selective disproportionation of radical pair **b** lowers the value of k_a/k_b from 1.8 to 1.2. The low selectivity for amines **3–5** and the small deuterium isotope effect for amine **7** are consistent with the small extent of bond breaking expected in a nonselective process.

In contrast to the low selectivity of product formation observed for amines **3–5**, the methylisopropylamines **1** and **6** form methyl adducts exclusively. The failure of these amines and triisopropylamine to yield isopropyl adducts could reflect either inefficient radical pair formation or inefficient radical pair combination. The low quantum yields for the formation of diphenylethane (Φ_{II}) from

(8) Lewis, F. D.; Simpson, J. T. *J. Phys. Chem.* **1979**, *83*, 2015.
(9) Brown, H. C.; Taylor, M. D. *J. Am. Chem. Soc.* **1947**, *69*, 1332.
(10) Gibian, M. J.; Corley, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 4178.

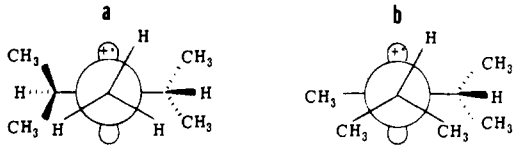
Table IV. Selectivity of Amine Oxidation by Various Reagents[a]

amine	$Fe(CN)_6^{-3}$ [b]	anodic[c]	Ph_2CO*[d]	benzene*[e]	stilbene*
ethyldimethyl		0.83		2.0	1.8
butyldimethyl		0.91,[f] 1.6			2.0
diethylmethyl	4.1[g]				2.3
isopropyldimethyl		1.0		2.7	>20
diisopropylmethyl	>20[h]		2.1		>20
ethyldiisopropyl		>20, 8.8[i]	2.2		12

[a] Ratio of oxidation products from the less vs. the more substituted alkyl group corrected for the number of equivalent α-hydrogens. [b] Data from ref 1c,e. [c] Data from ref 2. [d] Data from ref 3b,d. [e] Data from 3f. [f] Dimethylpropylamine. [g] Di-*n*-butylmethylamine. [h] Di-*sec*-butylmethylamine. [i] Dicyclohexylmethylamine.

stilbene and amine 1 or triisopropylamine (Table II) indicate that neither radical pair diffusion nor cross disproportionation to yield diphenylethane and enamine are significant reaction pathways. Exclusive radical-pair disproportionation to yield starting materials could explain the observed results; however, it seems highly improbable that radical-pair diffusion and cross disproportionation to yield diphenylethane and enamine should occur for the α-aminoethyl radical but not the α-aminoisopropyl radical. Thus we conclude that the low yield of products derived from α-aminoisopropyl radicals is due to inefficient radical-pair formation.

The selectivity of tertiary amine oxidation obtained with several different oxidizing agents is summarized in Table IV. The selectivity for methyl vs. alkyl oxidation by ferricyanide, electrochemically, and by the singlet state of stilbene is seen to increase with increasing α branching. Only with isopropylamines is highly selective oxidation observed. The deprotonation of a planar aminium radical may be considered to be analogous to the deprotonation of a carbonium ion in the second step of an E1 elimination reaction. The requirement of overlap between the half-vacant nitrogen p orbital and the incipient carbon radical p orbital gives rise to a stereoelectronic effect on aminium radical deprotonation. This effect is most evident for highly substituted amines such as diisopropylmethylamine. The conformation necessary for methyl deprotonation (**a**)



is clearly of lower energy than that for isopropyl deprotonation (**b**). It is, in fact, difficult for a space-filling model to attain conformation **b** and even more difficult for the triisopropylaminium radical to attain the conformation necessary for deprotonation. Space-filling models of the aminium radicals for the first three amines in Table IV reveal much smaller differences between the conformations required for deprotonation of methyl vs. alkyl. It is, of course, possible that a small stereoelectronic effect serves to counterbalance the greater product stability of the more substituted free radical. We have, in fact, observed highly selective formation of the more substituted α-amino radical from several tertiary amines of the type Me_2NCH_2G, where G is a radical-stabilizing group with minimal steric requirements.[11] Base strength may also influence the orientation of tertiary amine oxidation and account for the differences between the oxidizing agents in Table IV. Increasing base strength is known to increase the yield of the less substituted alkene in E1 elimination reactions.[13,14]

It is possible that substituents on stilbene which alter its electronic demand might change the selectivity of amine oxidation. Wagner[15] has recently observed such an effect for the deprotonation of the *p*-cymene radical cation by the trifluoroacetophenone radical anion within an exciplex.

Experimental Section

Materials. *trans*-Stilbene (Aldrich) was recrystallized from benzene and from 95% ethanol. Trimethylamine (Eastman), triethylamine (Eastman), and ethyldiisopropylamine (Aldrich) were fractionally distilled prior to use. Most other amines were synthesized from commercially available primary or secondary amines by the N-methylation procedure of Clarke et al.[16] Obtained in this manner were diisopropylmethylamine [bp 109–112 °C (760 nm)], diethylmethylamine [bp 62–64 °C (760 mm)], *tert*-butyldimethylamine [bp 77–78 °C (760 mm)], *n*-butyldimethylamine [bp 88–90 °C (760 mm)], isopropyldimethylamine [bp 61–62 °C (760 mm)], and ethyldimethylamine [bp 34–36 °C (760 mm)]. Triisopropylamine was synthesized by the method of Kuffner and Koechlin,[17] bp 139 °C (760 mm). *tert*-Butylmethyl(trideuteriomethyl)amine was synthesized by following the method of Peterson et al.[18] Reaction of 10 g of methyl-d_3 iodide (Stohler Isotope, 99.5% isotopic purity) with 11.3 g of *N*-benzylidene-*tert*-butylamine gave 4.5 g (70%) of *tert*-butylmethyl-d_3-amine: bp 69 °C (760 mm); ^1H NMR δ (CCl_4) 1.03 (9 H, s), 1.68 (1 H, s). Methylation of this amine (2.9 g) by the method of Clarke et al.[16] yielded 2.0 g (60%) of *tert*-butylmethyl(trideuteriomethyl)amine: bp 78 °C (760 mm); ^1H NMR δ ($CDCl_3$) 1.03 (9 H, s), 2.15 (3 H, s).

General Procedures. Methods for preparative photolyses and quantum yield determinations have been previously described.[6] Irradiated solutions were analyzed by GC with a Hewlett-Packard 5750 dual-flame gas chromatograph using either a 5% SF-96 on Chromosorb G or a 7% Apiezon L–2% potassium hydroxide on Chromosorb W column. The latter column was more effective for separating isomeric stilbene–amine adducts. Mass spectra were recorded on a Hewlett-Packard 5985 mass spectrometer using an ionizing voltage of 70 eV. Molecular ions of the stilbene–amine adducts could not be detected even at lower ionizing voltages. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrophotometer and NMR spectra on a Perkin-Elmer R20B spectrometer.

Irradiation of Stilbene and Diisopropylmethylamine. A solution of 2.25 g (0.05 mol) of *trans*-stilbene and 14.4 g (0.5 mol) of diisopropylmethylamine in 250 mL of acetonitrile was irradiated for 19 h. Removal of the volatile material followed by thick-layer chromatography (Quanta PLQF 1000, ethyl acetate) of the residual oil afforded a pure sample of *N,N*-diisopropyl-2,3-diphenylpropylamine (**1a**): ^1H NMR δ ($CDCl_3$) 0.95 (12 H, d, J = 7 Hz), 2.5–3.5 (7 H, m), 7.0–7.1 (10 H, m).

A sample of **1a** was refluxed in methyl iodide for 1 h and yielded, upon cooling, the crystalline methiodide salt: mp 203–204 °C (hexane/ethyl acetate); NMR δ ($CDCl_3$) 1.3 (12 H, dd), 2.7

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(3 H, s), 2.9–4.4 (7 H, m), 7.3 (10 H, m). Anal. Calcd for $C_{22}H_{32}NI$: C, 60.41; H, 7.37; N, 3.20; I, 29.01. Found: C, 60.45; H, 7.54; N, 3.21; I, 28.59.

Irradiation of Stilbene and *tert*-Butyldimethylamine. A solution of 1 g (0.056 mol) of *trans*-stilbene and 6 g (0.59 mol) of *tert*-butyldimethylamine in 100 mL of acetonitrile was irradiated for 18.5 h. Removal of the volatile material followed by thick-layer chromatography (hexane) of the residual oil afforded a pure sample of *N*-*tert*-butyl-*N*-methyl-2,3-diphenylpropylamine: ^{1}H NMR δ ($CDCl_3$) 1.0 (9 H, s), 2.2 (3 H, s), 2.3–3.5 (5 H, m), 7.0 (10 H, m).

Irradiation of Stilbene and *tert*-Butylmethyl(trideuteriomethyl)amine. A solution of 0.9 g (0.1 mol) of *trans*-stilbene and 0.52 g (1.0 mol) of *tert*-butylmethyl(trideuteriomethyl)amine in 5 mL of acetonitrile was irradiated for 7.5 h. Removal of the volatile material followed by thick-layer chromatography (ethyl acetate) of the residual oil afforded a mixture of the isomers *N*-*tert*-butyl-*N*-(trideuteriomethyl)-2,3-diphenylpropylamine (**7a**) and *N*-*tert*-butyl-*N*-methyl-1,1,3-trideuterio-2,3-diphenylpropylamine (**7b**): ^{1}H NMR δ ($CDCl_3$) 1.00 (s, $C(CH_3)_3$), 2.19 (s, NCH_3), 2.67–3.03 (m), 7.13–7.25 (m, aromatic).

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Registry No. **1**, 10342-97-9; **1a**, 76233-27-7; **2**, 7087-68-5; **2a** (isomer 1), 76233-28-8; **2a** (isomer 2), 76233-29-9; **2b**, 76233-30-2; **3**, 616-39-7; **3a**, 76233-31-3; **3b** (isomer 1), 76233-32-4; **3b** (isomer 2), 76233-33-5; **4a**, 76233-34-6; **4b** (isomer 1), 76233-35-7; **4b** (isomer 2), 76233-36-8; **5a**, 76233-37-9; **5b** (isomer 1), 76233-38-0; **5b** (isomer 2), 76233-39-1; **6a**, 76233-40-4; **7**, 52688-93-4; **7a**, 76233-41-5; **7b**, 76233-42-6; *trans*-stilbene, 103-30-0; trimethylamine, 75-50-3; triethylamine, 121-44-89; *tert*-butyldimethylamine, 918-02-5; butyldimethylamine, 927-62-8; isopropyldimethylamine, 996-35-0; ethyldimethylamine, 598-56-1; triisopropylamine, 3424-21-3; dabco, 280-57-9; **1a** methyl iodide, 76250-81-2.

Photochemical Reactivity of Keto Amidines. Type I Rearrangement to Aminocyclopropyl Isocyanates and Photochemical Generation of Bisisocyanates from Bichromophoric Systems

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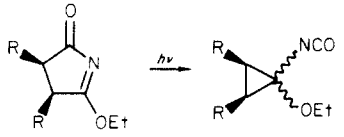
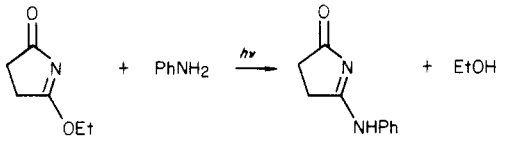
The photochemical rearrangement of 2-aminopyrrolin-5-ones and bis(2-aminopyrrolin-5-ones) to aminocyclopropyl isocyanates and bis(aminocyclopropyl isocyanates) is described. Specifically, 2-(dimethylamino)pyrrolin-5-one (**3**), 2-(methylphenylamino)pyrrolin-5-one (**4**), 1,4-bis[(5-oxopyrrolin-2-yl)methylamino]-2-butyne (**6**), and 1,4-bis[(5-oxopyrrolin-2-yl)phenylamino]-2-butyne (**8**) photochemically rearrange in 80 to 90% yield to (dimethylamino)cyclopropyl isocyanate, (methylphenylamino)cyclopropyl isocyanate, 1,4-bis[(isocyanatocyclopropyl)methylamino]-2-butyne, and 1,4-bis[(isocyanatocyclopropyl)phenylamino]-2-butyne, respectively, isolated as dimethylurea derivatives **9**, **10**, **13**, and **14**. The aminopyrrolinones were prepared by the addition of secondary amines to 2-ethoxypyrrolin-5-one (**1**).

We have previously described the Norrish Type I rearrangement of 2-ethoxypyrrolin-5-ones to ethoxycyclopropyl isocyanates.[1] The reaction displays a high degree of stereospecificity[2] and can be used as a synthetic method for the preparation of bicyclo[*n*.1.0] systems.[3] The ethoxycyclopropyl isocyanate is potentially a synthetically useful structural unit. It is a cyclopropanone equivalent and has been used in the synthesis of the natural product coprine.[4]



At the time Comstock and Wheeler reported the synthesis of 2-ethoxypyrrolin-5-one (**1**), they also noted that it reacted with aniline to give 2-anilinopyrrolin-5-one (**2**).[5]



1 **2**

We have observed that **1** similarly reacts with secondary amines and that the resulting aminopyrrolinones, unlike the ethoxypyrrolinones, are stable to water and other moderate nucleophiles. The ethoxypyrrolinones rapidly react with atmospheric moisture and hydrolyze to the imides from which they were synthesized.

We now report the photochemical rearrangement of 2-aminopyrrolin-5-ones to aminocyclopropyl isocyanates and the photochemical rearrangement of bis(aminopyrrolinones) to bisisocyanates. Because of the stability of the aminopyrrolinone system to nucleophiles, this latter reaction might be useful for the in situ photochemical generation of a cross-linking agent for polyurethane and

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