benzophenone as the internal standard. The quantum yields of appearance for (*E*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (**25a**) and (*Z*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (**25b**) were determined to be 0.058 and 0.064, respectively.

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Supplementary Material Available: Tables of crystal data collection parameters, positional parameters, interatomic distances, bond angles, and anisotropic and isotropic temperature factors for **6** and direct quantum yield results for **1** and **2** (8 pages). Ordering information is given on any current masthead page.

Competitive Catalysis and Quenching by Amines of Photo-Smiles Rearrangement as Evidence for a Zwitterionic Triplet as the Proton-Donating Intermediate

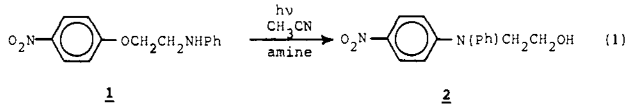
Gene G. Wubbels,* Bradley R. Sevetson, and Houston Sanders

Contribution from the Department of Chemistry, Grinnell College, Grinnell, Iowa 50112.

Received July 5, 1988

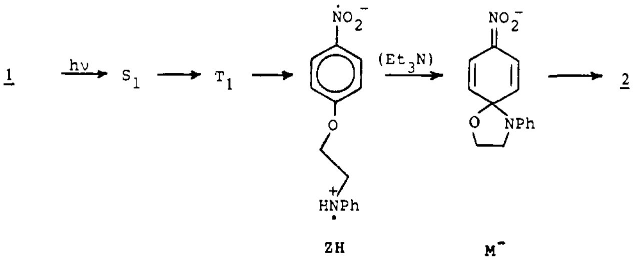
Abstract: Ten amine bases are observed to catalyze the photo-Smiles rearrangement of $4\text{-}O_2NC_6H_4OCH_2CH_2NHPh$ in acetonitrile. Plots of (quantum yield)$^{-1}$ vs [amine]$^{-1}$ are linear for all ten bases, but the intercepts representing limiting quantum yields range from a low of 1.81 ($\Phi_{\text{lim}} = 0.55$) for pyridine to a high of 16.3 ($\Phi_{\text{lim}} = 0.061$) for 1,4-diazabicyclo[2.2.2]octane. The differing intercepts imply that the amines quench as well as catalyze the reaction, and the linear double reciprocal plots can result only if the quenching and catalysis involve the same intermediate in the mechanism. The expected properties of zwitterion diradical, $^{-}O_2\dot{N}C_6H_4OCH_2CH_2\dot{N}^{+}HPh$, are consistent with all findings for the proton-donating and quenchable intermediate; the N-protonated Meisenheimer complex does not appear to be an intermediate leading to photoproduct. The reaction is sensitized by a triplet donor, is not quenched by triplet energy acceptors having E_T in the range of 50–60 kcal/mol, but is quenched by 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide ($E_T \sim 40$ kcal/mol). The derived rate constants for deprotonation by the amines make a nonlinear plot according to the Brønsted Catalysis Law. The Brønsted β reaches 0.6 in the strength-dependent regime, and the plot shows a maximal rate of 10^9 M^{-1} s^{-1} at a pK_a (acetonitrile) of 14, which corresponds closely to the predicted pK_a of the zwitterion diradical. The amine quenching mechanisms proposed involve electron exchange for tertiary amines and hydrogen abstraction–electron transfer for primary amines.

The photo-Smiles rearrangement of 2-(4-nitrophenoxy)-1-anilinoethane (**1**) (eq. 1) reported by Mutai and co-workers[1-4] interests us because the reaction is "accelerated" by triethylamine and is regioselective for the attachment para to the nitro group. In contrast, photo-Smiles rearrangement of 2-(nitrophenoxy)-ethylamine,[5-7] which is general base catalyzed, requires attachment of the rearranging side chain meta to the nitro group. We have concluded[6,8] as have Mutai and co-workers[9,10] that this regioselectivity difference reflects a mechanistic difference, the latter reaction proceeding by heterolytic nucleophilic attack while the former proceeds by intramolecular electron transfer and radical coupling.

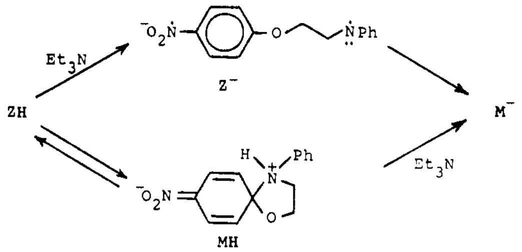


(1)

Scheme I



Scheme II



Nanosecond flash photolysis studies of the photorearrangement of **1** by Mutai and co-workers[2] established several mechanistic features, as shown by Scheme I. Involvement of the nitrophenyl

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(1) Mutai, K.; Kanno, S.; Kobayashi, K. *Tetrahedron Lett.* **1978**, 1273–76.

(2) Yokoyama, K.; Nakagaki, R.; Nakamura, J.; Mutai, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2472–75.

(3) Mutai, K.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 462–65.

(4) Mutai, K.; Yokoyama, K.; Kanno, S.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1112–15.

(5) Wubbels, G. G.; Halverson, A. M.; Oxman, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 4848–49.

(6) Wubbels, G. G.; Celander, D. W. *J. Am. Chem. Soc.* **1981**, *103*, 7669–70.

(7) Wubbels, G. G.; Halverson, A. M.; Oxman, J. D.; DeBruyn, V. H. *J. Org. Chem.* **1985**, *50*, 4499–4504.

(8) Wubbels, G. G. *Acc. Chem. Res.* **1983**, *16*, 285–92.

(9) Mutai, K.; Kobayashi, K.; Yokoyama, K. *Tetrahedron* **1984**, *40*, 1755–59.

(10) (a) Mutai, K.; Nakagaki, R.; Tukada, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2066–71. (b) Mutai, K.; Nakagaki, R. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3663–64.

(11) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

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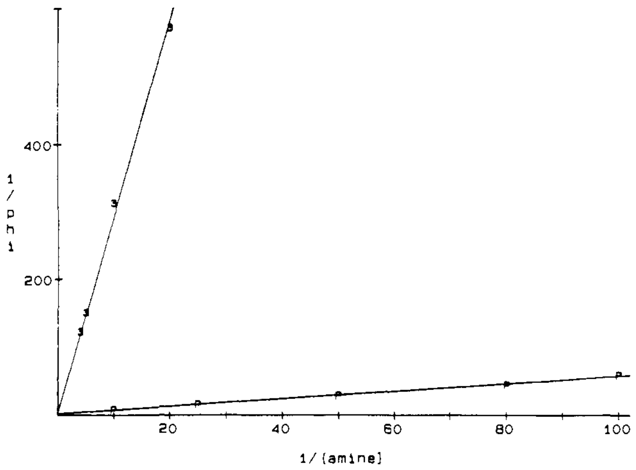

Figure 1. Effect of reciprocal pyridine (–P–) and 3-chloropyridine (–3–) concentrations on the reciprocal quantum yield of photo-Smiles rearrangement of **1** in acetonitrile.

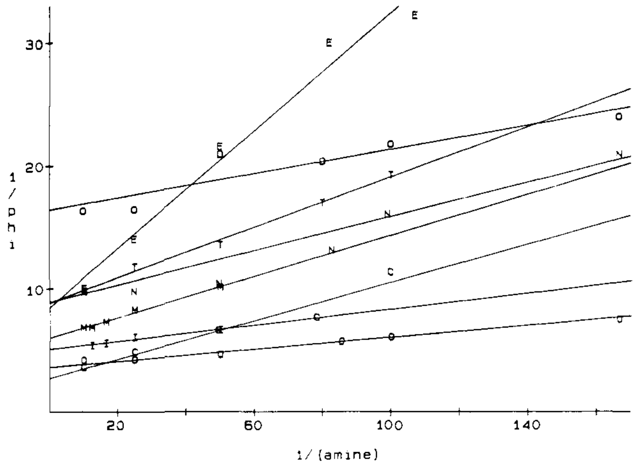

Figure 2. Effect of reciprocal concentrations of collidine (–C–), ethanolamine (–O–), imidazole (–I–), morpholine (–M–), *n*-butylamine (–N–), *tert*-butylamine (–T–), triethylamine (–E–), and 1,4-diazabicyclo-[2.2.2]octane (–D–) on the reciprocal quantum yield of photo-Smiles rearrangement of **1** in acetonitrile.

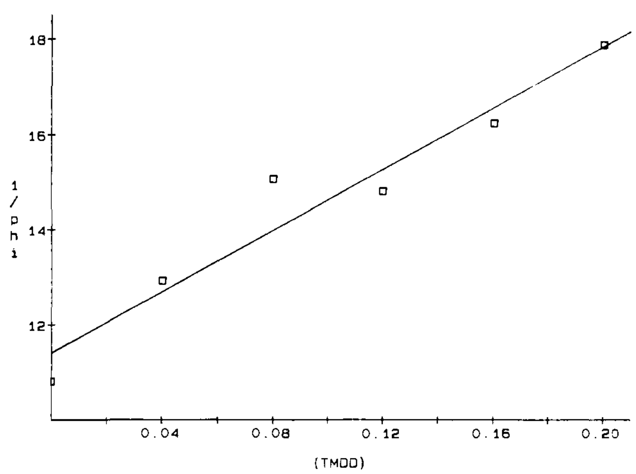

Figure 3. Stern–Volmer plot for quenching of 0.1 M pyridine-catalyzed photo-Smiles rearrangement of **1** by 3,3,4,4-tetramethyl-1,2-diazetin 1,2-dioxide (TMDD).

ether triplet was inferred from the nature of the excitation and the high intersystem crossing rate of nitroaromatics. The initial excited state reacts within the duration of the laser shot (10 ns). The species ZH and M^- were inferred from transient absorption spectra. ZH showed a lifetime of 65 ns in neat acetonitrile, 25 ns with 0.1 M Et_3N, and 20 ns with O_2 at saturation; M^- showed a lifetime of milliseconds. It was shown by various means that Et_3N increased the efficiency of the photorearrangement, but quantum yield measurements were not reported.

These studies left open the identity of the proton-donating intermediate. Assuming that ZH was accurately identified, we wished to determine how Et_3N shortened its lifetime while increasing the transient absorbance presumably caused by M^-. Two possibilities involving ZH and MH as proton donor are shown in Scheme II. We wished also to measure the efficiencies of deprotonation for bases of different strengths, the overall efficiencies, and the loci of inefficiency in the photoreaction.

We report herein those measurements and evidence that the reaction involves a zwitterionic triplet as the proton-donating intermediate.

Results

Figure 1 shows the variation in quantum yield for various concentrations of pyridine and 3-chloropyridine, and Figure 2 shows data for eight other amine bases. The data for each amine make a straight line in a double reciprocal plot, yet each of the extrapolated intercepts is unique. Were each amine acting solely as a base catalyst, the intercepts (which correspond to infinite base concentration) should be identical. That they are not implies that the amines are quenching as well as catalyzing. These are phenomenological conclusions that do not assume a particular mechanism.

We conducted several additional tests of the behavior of the photoreaction. Solutions of **1** were irradiated exhaustively with each of the amine catalysts, and the progress of reactions was monitored by scans of the electronic spectrum (550 to 250 nm). In all cases, isosbestic points appeared at 339 and 285 nm, and the final spectrum was identical with that of **2**.[2] These findings imply that the chemistry is clean for all the amine catalysts investigated. Irradiation of **1** for 4 h in pure acetonitrile caused no loss of absorbance of **1** at 303 nm. We calculate that the maximum efficiency of uncatalyzed photo-Smiles rearrangement of **1** is 0.0006 and conclude that uncatalyzed photorearrangement virtually does not occur.

These reaction solutions were not degassed. Mutai has reported[2] that the presence of O_2 reduces the efficiency of the photoreaction and also shortens the lifetime of ZH. We established that the quantum yields of photorearrangement at 0.10 M *n*-butylamine for air-saturated and deoxygenated solutions were indistinguishable by our measurement method (±5%). This implies that the oxygen quenching effect becomes negligible at high base concentration and that the lines of Figures 1 and 2 at low base concentrations are affected by oxygen quenching. This matter is taken account of in our calculations (see below).

The involvement of the triplet state in this reaction has been suggested[2] but never directly tested. We found that the quantum yield of triplet-sensitized photo-Smiles rearrangement of **1** (1.54×10^{-4} M) in the presence of 0.10 M ethanolamine is 53% of the directly irradiated efficiency; N_2-purged solutions were used for this experiment, and 4-methoxyacetophenone at 0.113 M was the sensitizer, which absorbed 90% of the incident light. Triplet quenchers such as 1-methylnaphthalene, *cis*-piperylene, 2,5-dimethyl-2,4-hexadiene, and *trans*-stilbene (triplet energies[11] of 59.6, 57, 56, and 50 kcal/mol, respectively) at concentrations up to 0.10 M had no effect on the efficiency of the 0.10 M pyridine-catalyzed reaction at 350 nm. However, 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide (TMDD, $E_T \cong 40$ kcal/mol)[12,13] did quench this reaction; the Stern–Volmer plot is shown in Figure 3. This implies that the reaction involves a quenchable triplet of energy less than 50 kcal/mol but greater than about 40 kcal/mol.

Discussion

That amines both catalyze and quench the photoarrangement provides mechanistic insight. The quenching by amines is obvious from the differing intercepts in Figures 1 and 2. At whatever stage the amines catalyze by abstracting a proton, if the process involved

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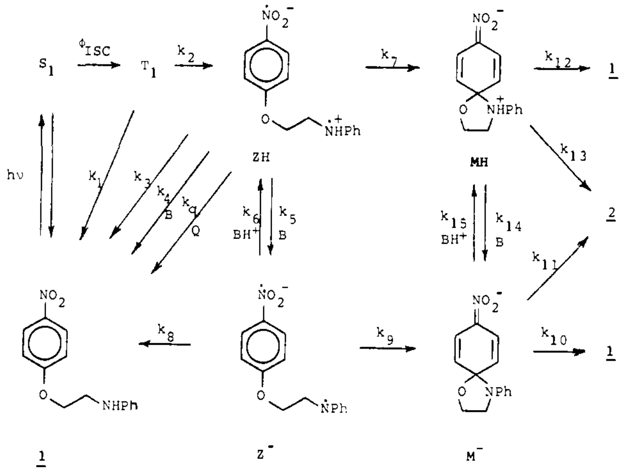
(12) Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077–78.
(13) Singh, P.; Ullman, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 3018–19.

Table I. Kinetic Data on Amine Catalysis and Quenching of **1** in Acetonitrile

amine	slope	intercept	Φ_{lim}	$10^{-9}k_4$, $M^{-1}\,s^{-1}$	$10^{-9}k_5$, $M^{-1}\,s^{-1}$	log k_4	log k_5	pK_a(AN)[a]	IP,[b] eV
3-chloropyridine[c]	29	(1.8)	(0.55)	0.00028	0.0011	5.45	6.04	10.00	9.85
pyridine	0.56	1.81	0.55	0.015	0.057	7.18	7.75	12.33	9.60
collidine	0.07	2.76	0.36	0.38	0.41	8.58	8.61	14.90	9.20
ethanolamine	0.025	3.56	0.28	1.9	1.3	9.28	9.11	17.53	9.87
imidazole	0.032	5.11	0.20	2.6	1.0	9.41	9.00	14.50	8.78
morpholine	0.085	6.04	0.17	1.2	0.38	9.08	8.57	16.60	8.88
triethylamine	0.24	8.51	0.12	0.66	0.13	8.82	8.12	18.46	8.07
tert-butylamine	0.10	8.84	0.11	1.6	0.31	9.21	8.49	18.14	9.25
n-butylamine	0.070	8.93	0.11	2.4	0.46	9.38	8.66	18.26	9.34
DABCO	0.050	16.34	0.061	6.6	0.64	9.82	8.80	18.29	7.51

[a] Values of pK_a of conjugate acids in acetonitrile at 25 °C taken from ref 18; values for collidine, imidazole, and 3-chloropyridine are estimated from ref 18. [b] Values taken from: Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311. Ramsey, B. G.; Walker, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 3314. Leavell, S.; Steichen, J.; Franklin, J. L. *J. Chem. Phys.* **1973**, *59*, 4343. Domelsmith, L. N.; Houk, K. N. *Tetrahedron Lett.* **1977**, 1981. Cradock, S.; Findlay, R. H.; Palmer, M. H. *Tetrahedron* **1973**, *29*, 2173. [c] Values in parentheses stem from an assumed intercept.

Scheme III



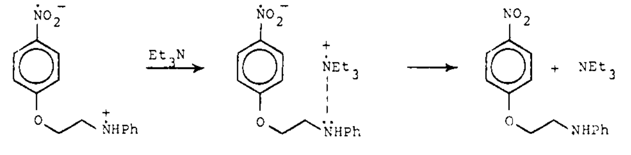
solely catalysis, each of the intercepts corresponding to infinite amine concentration would be identical. If fact the intercepts differ by nearly an order of magnitude (cf. pyridine at 1.81 and DABCO at 16.3).

We propose the mechanism involving species Z^- shown in Scheme III for this base-catalyzed photorearrangement. The reciprocal quantum yield expression for this pathway is given by eq 2. Since there is no uncatalyzed rearrangement, MH, if formed, does not form photoproduct (via k_{13}). ZH could decay, therefore, via k_7 and k_{12} (as well as k_3), which would alter eq 1 by replacing k_3 with $(k_3 + k_7)$. Equation 2 assumes that there is no inefficiency at stages Z^- and M^-, i.e. that $k_8 \ll k_9$ and $k_{10} \ll k_{11}$, and that

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{ISC}}}\left(1 + \frac{k_1}{k_2}\right) + \left(1 + \frac{k_4}{k_5} + \frac{k_3}{k_5[\text{B}]}\right) \qquad (2)$$

the deprotonation is irreversible $(k_8 + k_9) \gg k_6[\text{BH}^+]$. That pyridine causes almost no quenching, and that the inefficiencies at the stages T_1, Z^-, and M^- must be slight is indicated by the intercept of 1.81 for pyridine. This corresponds to a limiting quantum yield of 0.55, which is close to the estimated quantum yield of intersystem crossing (0.7 ± 0.2).[14] The absence of inefficiency also supports the assumption that the deprotonation is practically irreversible; if it were not, a relatively weak base such as pyridine (see below) could not attain high efficiency at any concentration. Irreversible deprotonation means that the catalysis is general base rather than specific base catalysis, but that distinction is not very significant for this case. The rate constants k_4 and k_5 can be extracted from the experimental data and eq 2 by setting $\Phi_{\text{isc}} = 0.7$, $k_2 \gg k_1$, and $k_3 = 3.2 \times 10^7$ s^{-1}.[15]

Scheme IV



The results are given in Table I, which also lists the pK_a's of the ammonium or pyridinium ions in acetonitrile and the gas-phase ionization potentials for the amines.

The data for 3-chloropyridine were difficult to obtain, requiring long irradiation times even at high catalyst concentrations. Since the extrapolation to the intercept was long and uncertain, we assigned the plot the intercept of pyridine in order to extract rate data. The two values dependent upon the assumed intercept are therefore given in parentheses in Table I.

Equation 2 predicts that each of the amines, despite the evident quenching, should give a linear plot of Φ^{-1} vs $[\text{amine}]^{-1}$, and this prediction agrees with the facts. None of the amines gave a plot that was even approximately linear when plotted according to Stern–Volmer quenching kinetics (Φ^{-1} vs [amine]). The unique feature of Scheme III that rationalizes these outcomes is the assignment of the locus of quenching as the same as the locus of catalysis. No other arrangement yields a quantum yield expression showing linear dependence of Φ^{-1} on $[\text{amine}]^{-1}$. Considering the candidate proton donor intermediates, ZH and MH, we can see no plausible means whereby amines could "quench" (cause reversion of MH to **1**) a closed-shell σ-complex such as MH. On the other hand, ZH presents the plausible quenching pathway that is shown in Scheme IV for Et_3N. That the quenching and catalysis must coincide at one intermediate provides strong evidence that the proton donor is ZH rather than MH.

That the mechanistic interpretations of Scheme III and eq 2 are appropriate is evidenced by the rate constants obtained for k_4 and k_5 (Table I). Rate constants for proton transfer for hydrogen bonding acids and bases such as amines and aminium ions would be expected to approach maximal values in the range of 10^8 to 10^9 M^{-1} s^{-1} in acetonitrile.[16] The pK_a in water of the aniline cation radical, 7.0 ± 0.1,[17] provides a good model for the cation radical portion of ZH. Since the aqueous pK_a values of a great variety of alkylammonium, anilinium, and pyridinium ions are higher by 7.5 ± 1 in acetonitrile,[18] the pK_a of ZH in acetonitrile may be estimated to be 14.5 ± 1. Eight of the ten amines in Table I have pK_a's equal to or greater than this value and would be expected to abstract a proton from ZH at the predicted maximum rate, as observed.

The data of Table I for this general base catalyzed reaction can be used to construct a plot according to the Brønsted Catalysis

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(14) For discussions, see: (a) Wubbels, G. G.; Kalhorn, T. F.; Johnson, D. E.; Campbell, D. *J. Org. Chem.* **1982**, *47*, 4664–70. (b) Wubbels, G. G.; Susens, D. P.; Coughlin, E. B. *J. Am. Chem. Soc.* **1988**, *110*, 2538–42.

(15) This is the calculated lifetime from data in ref 2 for ZH in air-saturated acetonitrile.

(16) Robinson, B. H. In *Proton Transfer Reactions*; Caldin, E.; Gold, V., Eds.; Wiley: New York, 1975; p 139.

(17) Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2016–26.

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Law (eq 3), which is shown in Figure 4. The data at the lower

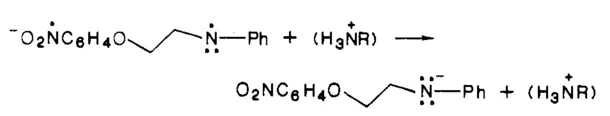
$$\log k_H = \beta pK_a + C \qquad (3)$$

rates are insufficient to give much confidence in the observed slope (β) of 0.6; it is likely that the plot in this region actually approaches unity. It is clear that the plot is nonlinear. The upper limit of about 10^9 M^{-1} s^{-1} is reached at a pK_a of 14, which corresponds closely to the predicted pK_a of ZH. This observation of Eigen-type behavior[19] of the base catalysis, with a break point at a pK_a of 14, is impressive evidence in support of the proposed mechanism. The pK_a of the alternative acid, MH, is less accessible, but the rule of thumb for similar Meisenheimer-type adducts with two or three nitro groups on the cyclohexadienide moiety is that the pK_a is about three units less than that of the corresponding alkyl anilinium cation.[20] This yields an aqueous pK_a estimate for MH in the range of 2.5 ± 1, which would be about 10 in acetonitrile. This is clearly inconsistent with the break point observed in the Brønsted plot.

Involvement of the excited singlet state of **1** in the intramolecular electron transfer leading to ZH is possible because the rapid intersystem crossing rate ($\sim 10^{11}$ s^{-1}) expected for the nitroaromatic[21] is of the same order as that expected for the electron transfer. We have demonstrated elsewhere[22] with an experiment involving α-cyclodextrin complexation that in water the intramolecular electron transfer in **1** does not depend on π-orbital overlap of the two aromatic groups; the transfer proceeds by electron tunnelling through the σ bonds. The rates for similar electron transfers in other systems are estimated at $\geq 10^{11}$ s^{-1}.[23] That the triplet of the nitrophenyl ether (E_T = 60 kcal/mol)[24] is not quenchable by four energy acceptors in the range of E_T = 50–60 kcal/mol implies that it reacts too fast to be intercepted. This is consistent with Mutai's observation[2] that the triplet reacts to give ZH so rapidly that it cannot be detected with a nanosecond apparatus. Since the triplet lifetime of 4-nitroanisole is on the order of microseconds in acetonitrile, k_1 should be around 10^6 s^{-1}; we conclude that $k_2 \gg k_1$ and that there is virtually no inefficiency at the T_1 stage.

That TMDD (E_T ~40 kcal/mol) quenches the pyridine-catalyzed reaction and that quenchers having $E_T \geq 50$ kcal/mol have no effect implies that a second triplet of energy well below 50 kcal/mol occurs on the pathway. TMDD is a specific triplet quencher, having been shown to be a feeble singlet acceptor as well as a feeble electron acceptor.[12] The only prospects for this triplet are ZH and Z^-. Of these, ZH is the only reasonable possibility because Z^- appears to be energetically close to or in an electronic ground state, as argued below.

If one considers the electronic transition shown in eq 4, the



(4)

energy level, relative to **1**, of the ion pair at the right can be estimated from the pK_a of **1** and that of H_3N^+R. Since the pK_a of (neutral) aniline in water (27) would be increased by 15–20 units in acetonitrile,[18] according to $\Delta G° = -RT \ln K$, the ion pair in acetonitrile lies some 38 to 45 kcal/mol above **1** and H_2NR. Since Z^- is generated from ZH by H_2NR in an approximately thermoneutral reaction, and ZH lies about 40 kcal/mol above **1** (see below), the energy change for eq 4 must be in the range of −2 to 5 kcal/mol. This implies that the most plausible decay pathway for Z^- in the absence of a proton source is cyclization (k_9). This analysis supports our earlier conclusion that the inefficiency at the Z^- stage must be slight ($k_9 \gg k_8$).

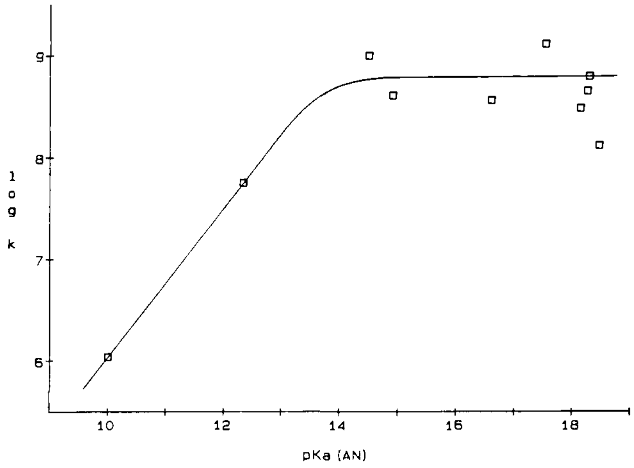


Figure 4. Brønsted Catalysis Law plot for amine catalysis of photo-Smiles rearrangement of **1** in acetonitrile (data from Table I).

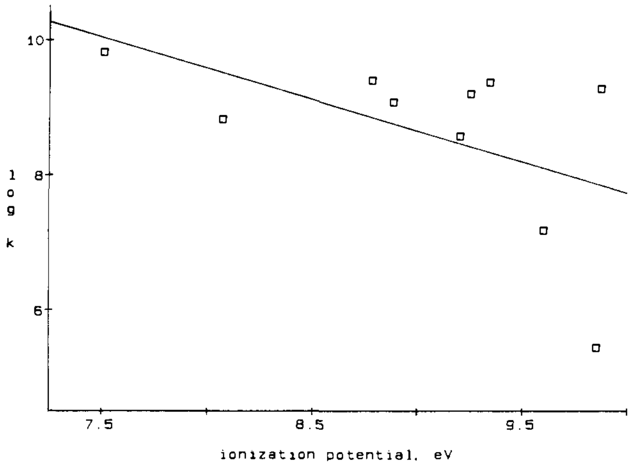


Figure 5. Effect of amine ionization potential on the rate of quenching by amines of photo-Smiles rearrangement of **1** in acetonitrile (data from Table I).

Kinetic analysis of the quenching by TMDD of ZH yields the result in eq 5 for the slope/intercept ratio. Substituting the values

$$\text{slope/intercept} = k_q/(k_3 + k_4[B] + k_5[B]) \qquad (5)$$

of the constants for pyridine at 0.10 M reveals that $k_q = 6.4 \times 10^7$ M^{-1} s^{-1}, which is substantially below the diffusion rate constant. If indeed TMDD quenches ZH by the electron exchange mechanism, the quenching data of Singh and Ullman[13] for TMDD suggest that the triplet energy is about 40 kcal/mol.

That the quenching of ZH by amines involves some degree of charge transfer from the amine is shown by Figure 5. The slopes of the plot (-0.92 ± 0.52 mol/eV) indicates that k_4 decreases very roughly an order of magnitude for each 20-kcal increase of gas-phase ionization energy. Closely analogous quenching by amines has been reported recently for the singlet intramolecular charge transfer state of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN).[25] The primary interaction, invoked on the basis of steric influence of amine substituents, was exciplex formation involving the amine lone pair of electrons and the valence hole on the nitrogen of the excited state. Such a step is likely to be the first step of Scheme IV. The electron hole site of the twisted intramolecular charge transfer state of DMABN is highly congested, and the observed steric effect of amine substituents is not surprising. For ZH, however, we expect much less steric hindrance to approach of a nitrogen lone pair.

Given these differences, we find excellent agreement between the quenching rate constants for amines and those reported by Wang,[25] who also used acetonitrile as solvent. The least sterically

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(21) Ohtani, H.; Kobayashi, T.; Suzuki, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 43–47.

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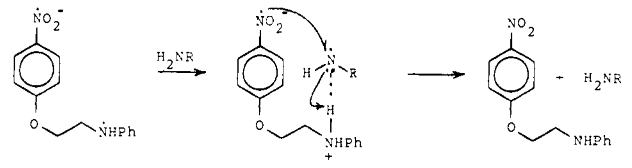
(24) Brinen, J. S.; Singh, B. *J. Am. Chem. Soc.* **1971**, *93*, 6623–29.

(25) Wang, Y. *Chem. Phys. Lett.* **1985**, *116*, 286–91.

Scheme V



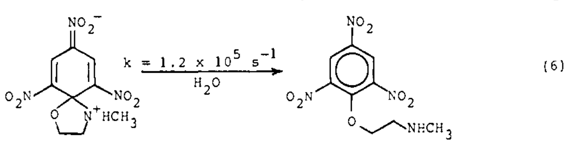
encumbered amine studied by Wang, 1-azabicyclo[2.2.2]octane (ABCO), was the fastest quencher (1.4×10^9 M^{-1} s^{-1}); the fastest quenching we observe is for 1,4-diazabicyclo[2.2.2]octane (DABCO) at 6.7×10^9 M^{-1} s^{-1}. DABCO is sterically virtually identical with ABCO but is easier to oxidize in the gas phase by 0.52 eV. Triethylamine quenched DMABN singlet at 1.1×10^8 M^{-1} s^{-1}, and it quenches triplet ZH at 6.6×10^8 M^{-1} s^{-1}. That the latter is a factor of 6 faster than for DMABN but about a factor of 5 slower than one would expect based on its ionization potential suggests that ZH exerts a modest steric requirement on the primary quenching interaction.

The most puzzling aspect of Figure 5 is the fast quenching rates for the primary amines. These average only three times slower than that for DABCO, which is about 2 eV easier to oxidize, and they are 2.4 to 10 times *faster* than the rate for triethylamine, which is 1.2 to 1.8 eV easier to oxidize. Moreover, whereas ethanolamine and 3-chloropyridine have nearly identical ionization potentials, ethanolamine quenches at 6800 times the rate of 3-chloropyridine. For comparison, tertiary amines quench triplet benzophenone by an electron transfer interaction at rates 10 to 60 times faster than do primary amines.[26]

These findings suggest that a quenching mechanism in addition to that of Scheme IV occurs for primary amines. A plausible pathway is shown in Scheme V. Precedent for the initial hydrogen abstraction step is available in the conclusion[26] that primary and secondary amines react with triplet benzophenone by donation of an N–H hydrogen atom in a transition state having some charge transfer character.

An interesting concomitant of our mechanistic interpretation is that MH must be totally incapable of forming **2**, even in the presence of 0.1 M base catalyst that would remove its proton at a diffusion-controlled rate. In other words, MH must have a lifetime of much less than a nanosecond; its decay path is k_{12}, which must be at least 10^{10} s^{-1}. We attribute the inefficiency of the system in the absence of amines mainly to this process. What precedent exists for this claim?

Bernasconi has shown that expulsion of alkoxide ions and amines from anionic Meisenheimer complexes is remarkably fast and strongly dependent on the basicity of the leaving group.[20] For example, eq 6 proceeds with $k = 1.2 \times 10^5$ s^{-1}. Applying the estimate[27] that removing one conjugating ortho nitro group accelerates the expulsion by 4×10^4, the loss of two ortho nitro groups would put k_{12} in the range of 10^{14} s^{-1}. This does not yet correct for the effect of *N*-phenyl in place of *N*-methyl, which would create an additional acceleration on the order of 10^4 to 10^5. We regard this as strong evidence that MH, even in the presence of base, should indeed be totally incapable of giving **2**.



(6)

Experimental Section

Electronic spectra were recorded with a Beckman 5260 spectrophotometer. Quantum yields were measured with 313-nm light from a 75W xenon lamp (PRA No. ALH215) and a 200-mm monochromator (Jobin Yvon H-10) with solutions in a thermostated cell compartment (PRA No. C103) at 25 °C. Occasional irradiations were carried out in cuvettes with 350-nm light in a Rayonet reactor.

Acetonitrile was from Matheson, Coleman, and Bell and toluene was from Aldrich; both were HPLC grade. Nitrogen gas was prepurified, and 1,4-diazabicyclo[2.2.2]octane (DABCO) from Aldrich was used as received. Each of the other amines was the highest grade available commercially and each was distilled prior to use. 4-Methoxyacetophenone (Eastman) was twice recrystallized from ether. TMDD was prepared by a literature procedure[12] and recrystallized from methanol.

2-(4′-Nitrophenoxy)-1-anilinoethane (1). 2-(4-Nitrophenoxy)ethyl tosylate[28] (45.85 g, 0.136 mol) was heated for 1.5 h at 125 °C with distilled aniline (185 mL), and the aniline was removed by steam distillation after addition of excess aqueous Na_2CO_3. The product was filtered and recrystallized twice from ether [26.6 g; 75.7%; mp 106–106.5 °C (lit.[29] mp 103–104 °C)].

Quantum Yields. Reaction solutions were 5.0×10^{-5} M in **1** and were irradiated in 1.00-cm cuvettes at 313 nm. For the amines transparent at 303 nm (λ_{max} for **1**), reaction progress was monitored at that wavelength ($\epsilon_{reactant} = 13600$; $\epsilon_{product} = 2100$). Reactions of amines absorptive at 303 nm were monitored by product appearance at 390 nm ($\epsilon = 21000$). The two methods gave identical results where both could be used. Each quantum yield represents the average of a pair of identical solutions; these values typically agreed to within ± 5% of the mean. Solutions were not optically opaque at 313 nm, and corrections were applied for light transmission. The actinometer was Aberchrome 540 in toluene,[30] which was used daily to monitor the photon flux.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We also acknowledge gratefully the support of the National Science Foundation (Grant CHE-8605343). NSF support for purchase of the UV-vis spectrophotometer is also appreciated. We appreciate the interest of Prof. Henry Shine in this work and his suggestions for the synthesis of **1**.

Registry No. 1, 25836-86-6; 2-(4-nitrophenoxy)ethyl tosylate, 22483-44-9; aniline, 62-53-3; 3-chloropyridine, 626-60-8; pyridine, 110-86-1; collidine, 29611-84-5; ethanolamine, 141-43-5; imidazole, 288-32-4; morpholine, 110-91-8; triethylamine, 121-44-8; *tert*-butylamine, 75-64-9; *n*-butylamine, 109-73-9; DABCO, 280-57-9.

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