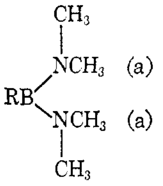
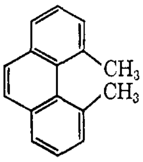
in normal amides (*e.g.*, 18 kcal/mol in formamide,[22] one of the amides where nitrogen has been shown[21] to be pyramidal).

Equally, of course, this argument suggests that observable free carbanions should be planar; for such ions can exist as independent entities only if the corresponding stabilization is very large. Recent studies[23] suggest that the pK_A's of simple paraffins are >70; the carbanion from a hydrocarbon acid as weak as toluene ($pK_A \sim 30$) must therefore have a net resonance stabilization of the order of 50 kcal/mol.

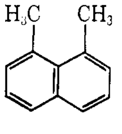
One point of interest in this connection is the curious line broadening shown by certain of our aminoboranes, as described at the end of the preceding section. This seems to imply that in compounds of the type $RB(NMe_2)_2$, the hydrogen atoms of one pair of methyl groups tend to become nonequivalent at very low temperatures. The only explanation that occurs to us is hindered rotation about the corresponding NCH_3 bonds. If the nitrogen atoms in aminoboranes are indeed pyramidal, as the arguments given above imply strongly, then there may be a conformational barrier to rotation of each methyl group of the order of 3 kcal/mol.[24] Furthermore, in the favored near-planar structure XII, the *cis*-methyls (a) will be pressed close together; mechanical interference between them will tend to make them rotate like a pair of meshed gear wheels, further increasing the effective barrier to rotation about the NCH_3 bonds. The two effects together could well be enough to bring about the observed broadening, this being assigned to the signal due to the hindered *cis*-methyls; for even at −145° the lines in question had merely broadened and not split. The barrier to nonequivalence of the methyl protons must therefore be very low, of the order of 5 kcal/mol.



XII



XIII



XIV

On the off chance that the barriers might be predominantly mechanical, rather than conformational, we examined the nmr spectra of two hydrocarbons, XIII and XIV, in which analogous interference exists. However in both cases the methyl signals remained sharp down to the lowest temperatures studied (−145°). It is, of course, well known that there is virtually no conformational barrier to rotation of methyl in methyl derivatives of aromatic hydrocarbons (*e.g.*, toluene); if the observed broadening in VIIIa, VIII, and IX is due to hindered NCH_3 rotation, a large part of the barrier must therefore be conformational in origin.

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[22] B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).

[23] A. Streitwieser, W. C. Langworthy, and J. J. Braumann, *J. Am. Chem. Soc.*, **85**, 1761 (1963).

[24] D. R. Lide, *Ann. Rev. Phys. Chem.*, **15**, 233 (1964).

The Photoreduction of Fluorenone

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Abstract: The photoreduction of fluorenone has been investigated by kinetic methods supplemented by flash photolysis. We have confirmed the previously noted lack of photoreactivity of fluorenone with isopropyl alcohol and found negligible reactivity with toluene and methylcyclohexane. Fluorenone is photochemically reduced in the presence of tri-*n*-butylstannane to give fluorenone pinacol. The reaction proceeds, at least for the most part, from the triplet state of fluorenone. Primary, secondary, and tertiary amines which possess α-hydrogens all photoreduce the fluorenone triplet state in both benzene and acetonitrile solvents. The fluorescence of fluorenone is quenched by the amines with an efficiency which is inversely proportional to their ionization potentials, and the efficiency of quenching is greater in acetonitrile than in benzene. These data support an electron-transfer mechanism for fluorescence quenching, although flash irradiation failed to provide conclusive evidence for this mechanism. The quantum yield of the reaction is also decreased at high amine concentration by those amines which are effective at quenching fluorescence. In at least the reaction of fluorenone with triethylamine in benzene, kinetic evidence is presented for the possibility of some singlet reaction. Flash photolysis has been employed to determine the character and lifetimes of some of the transients produced upon irradiation of fluorenone in solution.

The photochemistry of fluorenone has received relatively little attention. Yang[1] has found only very slow photocycloaddition to trimethylethylene and that the photoreduction of fluorenone by alcohols does not proceed at a measurable rate.[2] By contrast, Singer and Davis[3,4] have found that the fluorenone triplet undergoes very facile photochemical addition to ketenimines with rate constants to the order of 10^8 l. mol^{-1} sec^{-1}. Kinetic evidence for a reactive singlet state has been found in the photocycloaddition of

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[1] N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

[2] (a) N. C. Yang, private communication. (b) Note: A study of the photoreduction of fluorenone by triethylamine has been published shortly after completion of this manuscript and has been brought to our attention by a referee: S. G. Cohen and J. B. Guttenplan, *Tetrahedron Letters*, 5353 (1968).

[3] L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158 (1967).

[4] L. A. Singer and G. A. Davis, *ibid.*, **89**, 941 (1967).

Table I. Isolated Products in the Photoreduction of Fluorenone

Wt of fluorenone, g	Reducing agent (g)	Solvent (ml)	Irrad time, hr	% **1** isolated	% **2** isolated	% unreacted fluorenone recvd
1.00	Triethylamine (**3**) (1)	Benzene (50)	4	41	Trace[a]	45
1.00	Triethylamine (**3**) (1)	Acetonitrile (250)	28	Trace[a]	35	20[d]
0.65	N,N-Dimethylbenzylamine (**4**) (1)	Benzene (30)	17	91	0	2
0.50	Diethylamine (**5**) (1)	Benzene (50)	20	0[b]	12	75
1.00	Diethylamine (**5**) (1)	Acetonitrile (50)	31	0	12	82
1.00	Diisopropylamine (**6**) (1)	Benzene (50)	12	Trace[a]	17	65[c]
0.50	Cyclohexylamine (**7**) (1)	Benzene (30)	32	12	Trace[a]	68
0.50	α-Methylbenzylamine (**8**) (1)	Benzene (30)	32	15	Trace[a]	80
1.00	α-Methylbenzylamine (**8**) (1)	Acetonitrile (10)	48	2	0	95
0.65	Tri-*N*-butylstannane (**9**) (1.5)	Benzene (20)	3	75	0	18
0.50	Solvent	2-Propanol (50)	64	0	0	97
0.50	Solvent	Toluene (50)	64	0	0	94

[a] Trace amounts of products were indicated by analytical thin layer chromatography of one or more chromatographic fractions. [b] In another run of this reaction 8% of 9-fluorenyl alcohol (**2**) was isolated along with 8% of pinacol (**1**) and 78% of fluorenone. [c] In addition, 15% of a roughly 50:50 mixture of fluorenone and 9-fluorenyl alcohol was obtained, in one chromatography fraction. [d] In addition, 20% of a mixture of 9-fluorenyl alcohol, fluorenone, and a trace of pinacol was obtained in one chromatography fraction.

fluorenone to dimethyl(N-cyclohexyl)ketenimine.[5] The ketenimine has also been found to deactivate the fluorenone singlet to the ground state in competition with reaction.

Some disagreement exists as to the configuration of the lowest excited states of fluorenone. While criteria usually employed to distinguish between $\pi\pi^*$ and $n\pi^*$ singlet states do not give unequivocal results for fluorenone, Yoshihara and Kearns[6] and Kuboyama[7] offer strong evidence for a $\pi\pi^*$ lowest singlet. Discrepancies in experimental findings make it difficult to determine the energy and nature of the lowest triplet state of fluorenone.[1,6–10]

We have undertaken a kinetic and flash photolytic study of the reactivity of fluorenone toward photoreduction by a variety of reducing agents in an attempt to further elucidate the excited-state chemistry and properties of this ketone.

Results and Discussion

Isolation of Photoproducts. Several preparative-scale reactions of fluorenone with potential photoreducing agents were run in both benzene and acetonitrile solutions. The reducing agents investigated include tri-*n*-butylstannane, isopropyl alcohol, toluene, and primary, secondary, and tertiary amines. Irradiations were performed using a GE BH-6 Hg lamp filtered with a 7380 Corning cut-off filter which allows irradiation only of the first absorption band of fluorenone. The reactant solutions were contained in Pyrex test tubes and were flushed with nitrogen prior to reaction. Chromatography on silica gel was employed to isolate the products after photolysis, which were then identified by melting point and ir and nmr spectra (see Experimental Section for details). The only isolated reduction products were found to be fluorenone pinacol (**1**) and 9-fluorenyl alcohol (**2**). By contrast, Cohen and Guttenplan[2b] have isolated a cross-coupling product between the 9-hydroxy-9-fluorenyl and 1-diethylamino-1-ethyl radicals in the reaction of fluorenone with triethylamine. The oxidation products of the amines were not characterized. Table I summarizes the reaction conditions, per cent yields of reduction products, and material balance for these reactions.

Reversibility of Pinacol Formation. The 9-fluorenyl alcohol (**2**) isolated from certain of the reactions summarized in Table I almost certainly arises from thermal cleavage of the product pinacol by reaction with the amine present. In one experiment 0.10 g of pinacol was heated with 0.2 *M* diethylamine in benzene for 40 hr. Products were separated by preparative thin layer chromatography and 0.043 g (43%) of fluorenone and 0.048 g (48%) of 9-fluorenyl alcohol were isolated. The reaction is quite general and these products have been found to arise by uv and thin layer analysis in the reactions of the pinacol with 50% solutions of amines **3**, **5**, **6**, and **8** in benzene and with amines **3**, **5**, and **8** in acetonitrile. The growth of the 380-mμ fluorenone peak was followed as the reactions proceeded.

As expected, reaction rates were faster in acetonitrile than in benzene and the order of amine reactivity in both solvents is secondary > tertiary > primary.

Fortunately, the reverse reactions are not sufficiently fast to interfere noticeably with the photochemical kinetics in benzene discussed below, although some uncertainty is introduced in the kinetics run in acetonitrile at the higher amine concentrations.

Flash Photolysis. Fluorenone Transients Produced in Benzene and Acetonitrile. We have subjected 0.0012 *M* fluorenone solutions in benzene and acetonitrile to flash irradiation in which the decay of the resulting transients were monitored as a function of time at selected wavelengths. Figure 1 shows the first-order decay of the transients produced in these two solvents. In benzene solution the transient absorption spectrum showed a broad peak centered at about 600 mμ, and a higher intensity system of three split peaks centered at about 430 mμ as well as an absorption beginning at about 360 mμ and increasing to lower wavelengths. A similar spectrum was found in acetonitrile. In benzene, the transient decays with a lifetime of 60 μsec and with a lifetime of 29 μsec in acetonitrile. These transients

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(5) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *J. Am. Chem. Soc.*, **91**, 897 (1969).

(6) K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, **45**, 1991 (1966).

(7) A. Kuboyama, *Bull. Chem. Soc. Japan*, **37**, 1540 (1964).

(8) P. Pesteil, A. Zmerli, and M. Barbaron, *Compt. Rend.*, **239**, 255 (1954).

(9) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(10) A. Heller and E. Wasserman, *J. Chem. Phys.*, **42**, 949 (1965).

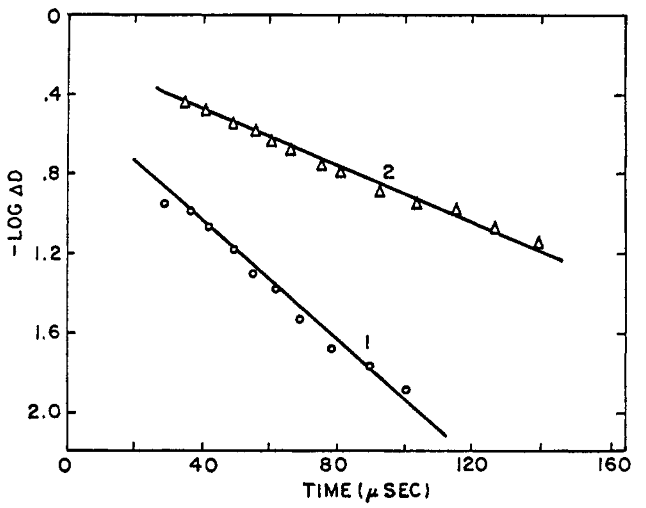

Figure 1. First-order decay of transients produced in the flash irradiation of 0.0012 *M* fluorenone in benzene, ○, curve 1, and in acetonitrile, △, curve 2.

disappear completely in the presence of oxygen. We believe this transient may be the fluorenone triplet state; however, the lifetime of this transient is in very serious disagreement with the lifetime of 6.7×10^{-7} sec determined for the fluorenone triplet state by kinetic quenching experiments.[11] Further work is needed to clarify this point, and we will defer calculations based on the triplet lifetime until such work is completed.

Photoreduction by Tri-*n*-butylstannane. Fluorenone is efficiently and cleanly photoreduced to its corresponding pinacol by reaction with tri-*n*-butylstannane. The quantum yield as a function of stannane concentration for this reaction in benzene solution was determined by benzophenone–benzhydrol actinometry as described in the Experimental Section.

The data are plotted conventionally as reciprocal quantum yield against reciprocal concentration in Figure 2. Fairly good linearity is found over the concentration range investigated.[12] The first excited singlet state of fluorenone is probably not the major reactive state since the fluorescence of fluorenone is quenched only by 15% by 1.0 *M* stannane. At this concentration of stannane, the quantum yield of photoreduction is 0.71. Thus, at least 79% of the reaction at this concentration is occurring from a state other than than the fluorescent singlet. We assume that this state is the fluorenone triplet. The simple mechanism consistent with our data is given in Scheme I.

Scheme I

$$\mathrm{F_0} \xrightarrow{h\nu} \mathrm{F^1} \tag{1}$$

$$\mathrm{F^1} \xrightarrow{k_d{}^1} \mathrm{F_0} + \Delta \text{ and } h\nu' \tag{2}$$

$$\mathrm{F^1} \xrightarrow{k_{isc}} \mathrm{F^3} \tag{3}$$

$$\mathrm{(Bn)_3SnH} + \mathrm{F^3} \xrightarrow{k_r{}^3} \mathrm{FH}\cdot + \mathrm{(Bu)_3Sn}\cdot \tag{4}$$

$$\mathrm{F^3} \xrightarrow{k_d{}^3} \mathrm{F_0} + \Delta \tag{5}$$

$$2\mathrm{FH}\cdot \longrightarrow \mathrm{(FH)_2} \tag{6}$$

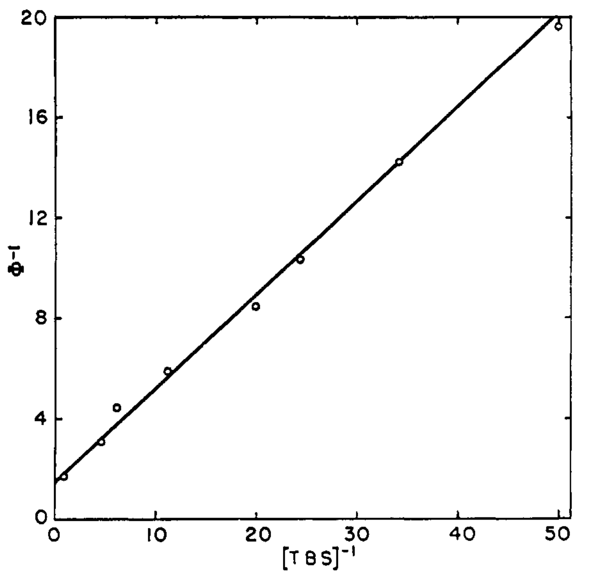

Figure 2. Plot of reciprocal quantum yield of fluorenone disappearance *vs.* reciprocal concentration for the reaction of fluorenone with tri-*n*-butylstannane in benzene.

The kinetic expression[13] based on this mechanism is

$$\frac{1}{\Phi} = \frac{1}{a} + \frac{k_d{}^3}{ak_r{}^3[\mathrm{(Bn)_3SnH}]} \tag{7}$$

where a is the fractional population of the reactive (triplet) state, known to be 0.93 for fluorenone in benzene.[14] Our intercept of about 1.2 is in satisfactory argeement with this. The slope term in eq 7 is identified with the ratio of rate constants for deactivation and reaction of the triplet state, $k_d{}^3/k_r{}^3$. The slope seen in Figure 2 is 0.4 *M;* thus, the rate constant for reaction, $k_r{}^3$, is comparable with the rate constant for triplet deactivation, $k_d{}^3$. The rate constant for deactivation of the fluorenone triplet in benzene solution has been found to be 1.8×10^6 sec^{-1} based on kinetic quenching experiments.[3,13] However, flash irradiation of fluorenone in benzene produces a transient which decays with a first-order rate constant of 1.7×10^4 sec^{-1} (see above). The great discrepancy between these rate constants does not permit us to assign a unique value to either $k_d{}^3$ or $k_r{}^3$ at this time.

We wish simply to note here that tributylstannane is considerably less reactive as a reducing agent than certain of the amines described below.

Reaction Kinetics of Fluorenone with Amines. The reaction of fluorenone with amines shows somewhat more complicated kinetic behavior than that found for the tributylstannane reduction. The quantum yield *vs.* amine concentration data for six amines in benzene solution are plotted in Figure 3. The plot shows that three distinct types of kinetic behavior are found for primary, secondary, and tertiary amines, respectively. It will therefore be convenient to discuss these reactions separately.

Reactions with Tertiary Amines. Both triethylamine (**3**) and N,N-dimethylbenzylamine (**4**) exhibit linear behavior except at high (0.1–0.3 *M*) amine concen-

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(11) This value was determined by assuming a rate constant of 2×10^9 l. mol^{-1} sec^{-1} for quenching of the fluorenone triplet state by di-*t*-butylnitroxide; see ref 3.

(12) Linearity in a plot such as shown in Figure 2 is consistent with reactivity of only *one* excited state. It does not provide a sensitive test for such reactivity, however, and we cannot on this basis disqualify the possibility of some singlet reactivity.

(13) For a discussion of photochemical kinetics see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, and references therein.

(14) From the Ph.D. thesis of A. A. Lamola, California Institute of Technology, Pasadena, 1965.

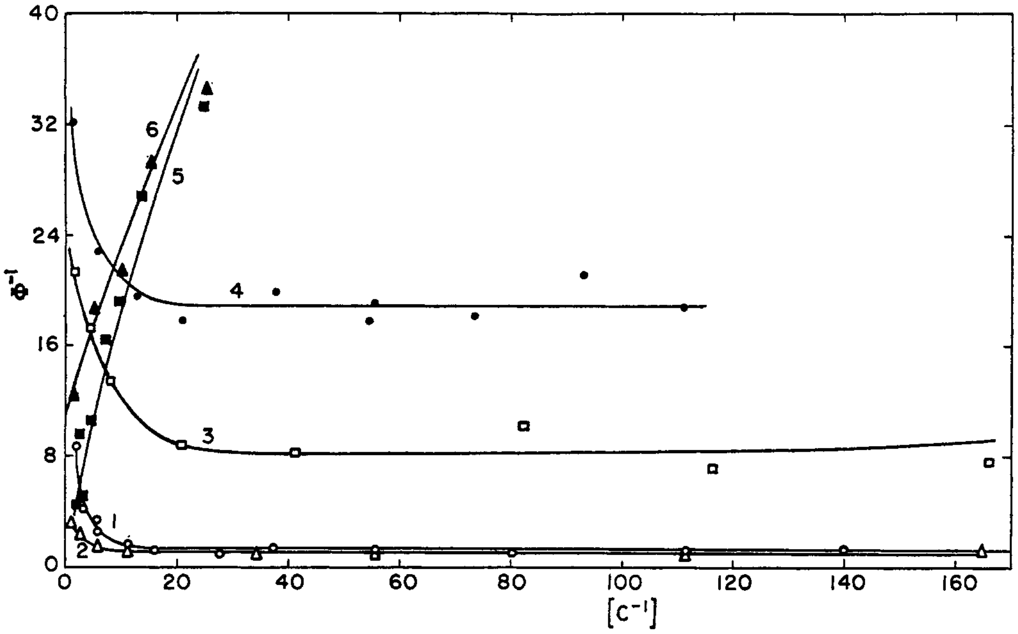

Figure 3. Plot of reciprocal quantum yield against reciprocal concentration for the reactions of fluorenone with triethylamine, ○, curve 1; N,N-dimethylbenzylamine, △, curve 2; diethylamine, □, curve 3; diisopropylamine, ●, curve 4; cyclohexylamine, ■, curve 5; and α-methylbenzylamine, ▲, curve 6.

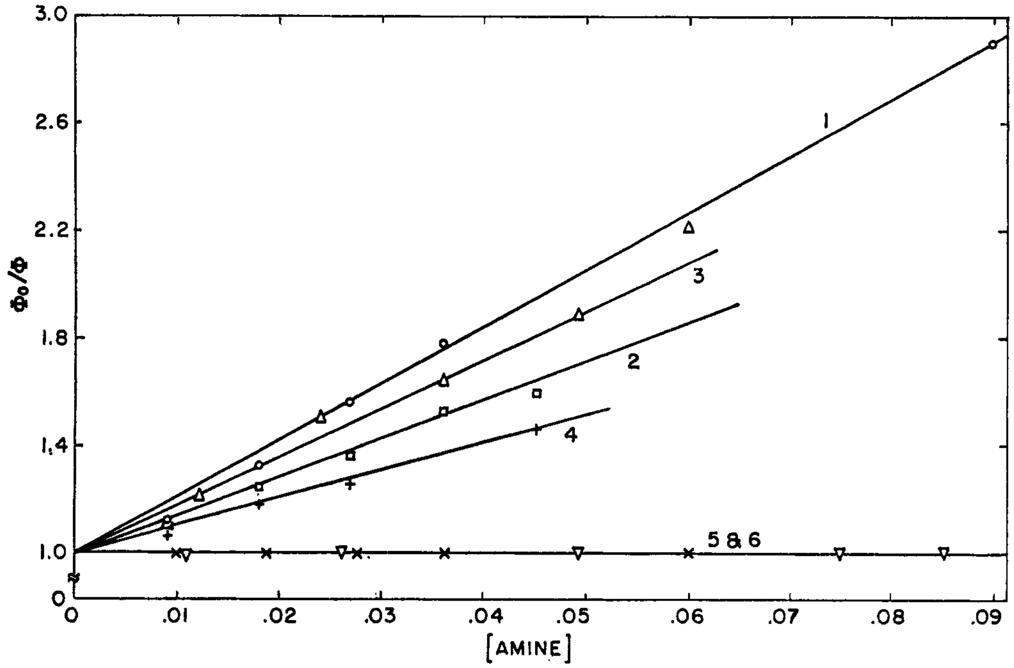

Figure 4. Stern–Volmer plots for the quenching of fluorenone fluorescence in benzene by triethylamine, ○, curve 1, slope 28.0 M^{-1}; □, curve 2, slope 14.4 M^{-1}; diethylamine, △, curve 3, slope 18.2 M^{-1}; diisopropylamine, +, curve 4, slope 10.6 M^{-1}; cyclohexylamine, ▽, curve 5, slope ~0; and α-methylbenzylamine, ×, curve 6, slope ~0.

trations, where the quantum yield of reduction falls off with increasing amine concentration. The linear portions of these curves are determined by the reaction of a long-lived excited state, almost certainly the fluorenone triplet.[15] The first excited singlet state cannot be the reactive state for this reaction at low amine concentrations, since the fluorescence of fluorenone is quenched by only 17 and 13% by amines **3** and **4**, respectively, at 0.01 *M* amine (see Figure 4), while the quantum yield of reaction in both cases is greater than 0.7 at this amine concentration.

The upward curvature (corresponding to a fall off in quantum yield) at high tertiary (and secondary) amine concentration seen in Figure 3 is due to the deactivation of the excited singlet state of fluorenone by interaction with the amines. These amines quench the fluorescence of fluorenone as the Stern–Volmer plots in Figure 4 show. This quenching effect is not due to ground-state charge-transfer formation between fluorenone and the amines. Absorption spectra taken of fluorenone with

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(15) A similar study of quantum yield *vs.* triethylamine concentration has been undertaken by Cohen and Guttenplan[2b] and very similar results were obtained. Their solvent, however, was cyclohexane, while ours is benzene. We therefore do not wish to try to explain small discrepancies in numerical values obtained in our respective studies.

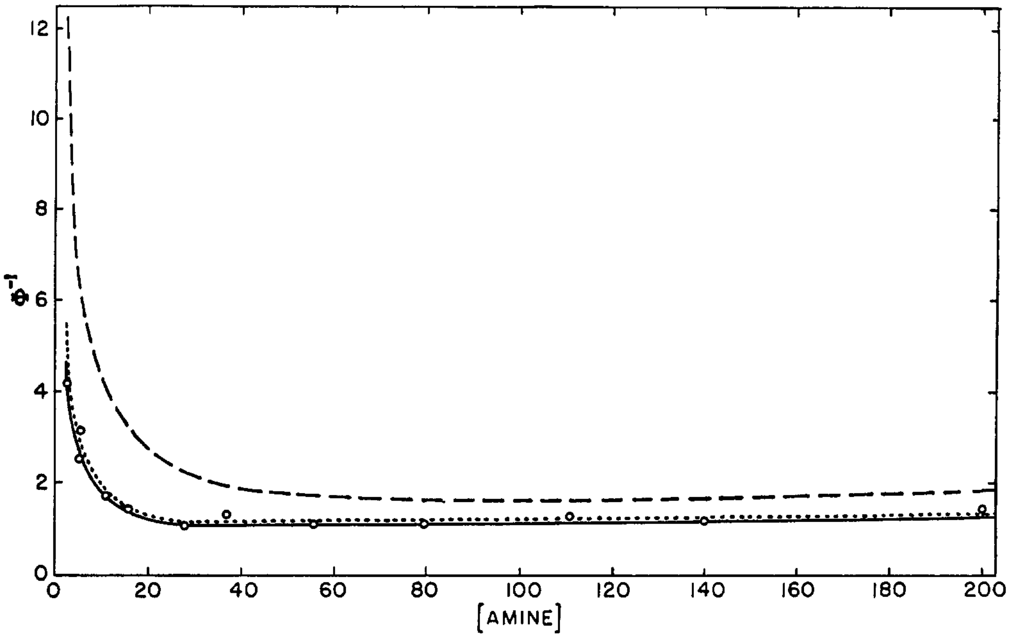

Figure 5. Reciprocal quantum yield of reduction *vs.* reciprocal triethylamine concentration. Heavy line, experimental curve; dashed line, semitheoretical curve using the experimental Stern–Volmer slope of 28.0 M^{-1}. Dotted lines, semitheoretical curve fitted to the experimental points using a Stern–Volmer slope of 8.9 M^{-1}.

higher concentrations of these amines than those used in the kinetic experiments are identical with the summed spectra of fluorenone and the long-wavelength tail of the amine.

These experiments establish the mechanistic steps for the reaction of fluorenone with tertiary amines shown in Scheme II.[16] The kinetic expression based on this mechanism is given in eq 14.

Scheme II

$$F_0 \longrightarrow F^1 \tag{8}$$

$$F^1 \xrightarrow{k_{isc}} F^3 \tag{9}$$

$$F^1 \xrightarrow{k_d{}^1} F_0 + \Delta \text{ or } h\nu\cdot \tag{10}$$

$$\text{Am} + F^1 \xrightarrow{k'_d{}^1} \text{Am} + F_0 + \Delta \tag{11}$$

$$\text{Am} + F^3 \xrightarrow{k_r{}^3} \text{(free radicals)} \tag{12}$$

$$F^3 \xrightarrow{k_d{}^3} F_0 + \Delta \tag{13}$$

$$\frac{1}{\Phi} = \left[\frac{k_{isc} + k_d{}^1 + k'_d{}^1(\text{Am})}{k_{isc}}\right] + \left[\frac{k_{isc} + k_d{}^1 + k'_d{}^1(\text{Am})}{k_{isc}}\right]\frac{k_d{}^3}{k_r{}^3(\text{Am})} \tag{14}$$

In the absence of quenching by the amine (eq 11 in Scheme II) eq 14 is identical with eq 7 written for the stannane reaction above. The extrapolated intercept of the linear portion of curves 1 and 2 (Figure 3) should therefore equal the reciprocal of triplet population of fluorenone. This intercept is quite close to 1 for amines **3** and **4**, in satisfactory agreement with the triplet population of 0.93 found for fluorenone.[14]

Reactions with Secondary Amines. The secondary amine reactions (curves 3 and 4, Figure 3) show kinetic behavior very similar to that found for the tertiary amines, except that the intercepts of the extrapolated straight-line portions of the plots deviate considerably from the reciprocal of the triplet population of fluorenone. We postulate that the intercepts of 7.5 and 19 for the diethylamine and diisopropylamine reactions, respectively, are due to a deactivation of the fluorenone triplet by the amine which competes with triplet reaction. We feel this to be the only reasonable step in accord with the kinetic results, though we can only guess at this time as to a possible mechanism for this deactivation. The mechanism of these secondary amine reactions would thus be identical with that shown above for the tertiary amines (Scheme II) except that the additional step $F^3 + \text{Am} \rightarrow F_0 + \text{Am} + \Delta$ (rate constant $k'_d{}^3$) would be included. This mechanism leads to kinetic eq 15. This equation may be used to

$$\frac{1}{\Phi} = \left(\frac{k'_d{}^3}{k_r{}^3} + 1\right)\left[\frac{k_{isc} + k_d{}^1 + k'_d{}^1(\text{Am})}{k_{isc}}\right] + \left[\frac{k_{isc} + k_d{}^1 + k'_d{}^1(\text{Am})}{k_{isc}}\right]\frac{k_d{}^3}{k_r{}^3(\text{Am})} \tag{15}$$

calculate the fraction $k'_d{}^3/k_r{}^3$, *i.e.*, the ratio of the rate constants for triplet deactivation and triplet reaction. For the diethylamine reaction, the extrapolated intercept is 7.5; thus, $k'_d{}^3/k_r{}^3 = 6.0$ *M*, while for diisopropylamine the intercept is close to 19, so that $k'_d{}^3/k_r{}^3 = 16.8$ *M*. We are presently in no position to comment on the difference between these intercepts.

Reactions with Primary Amines. Kinetic plots for the reactions of cyclohexylamine and α-methylbenzylamine with fluorenone are shown in curves 5 and 6 of Figure 3. Both show apparent linearity with a little or no rate fall-off at high concentration. The data for these very slow reacting amines are not good enough to allow an accurate determination of the intercept. The quantum yields do not fall off with increasing amine concentration, as expected, since these primary amines do not quench the fluorescence of fluorenone as shown

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(16) This mechanism is almost identical with that proposed for the photocycloaddition of fluorenone to ketenimines; see ref 3.

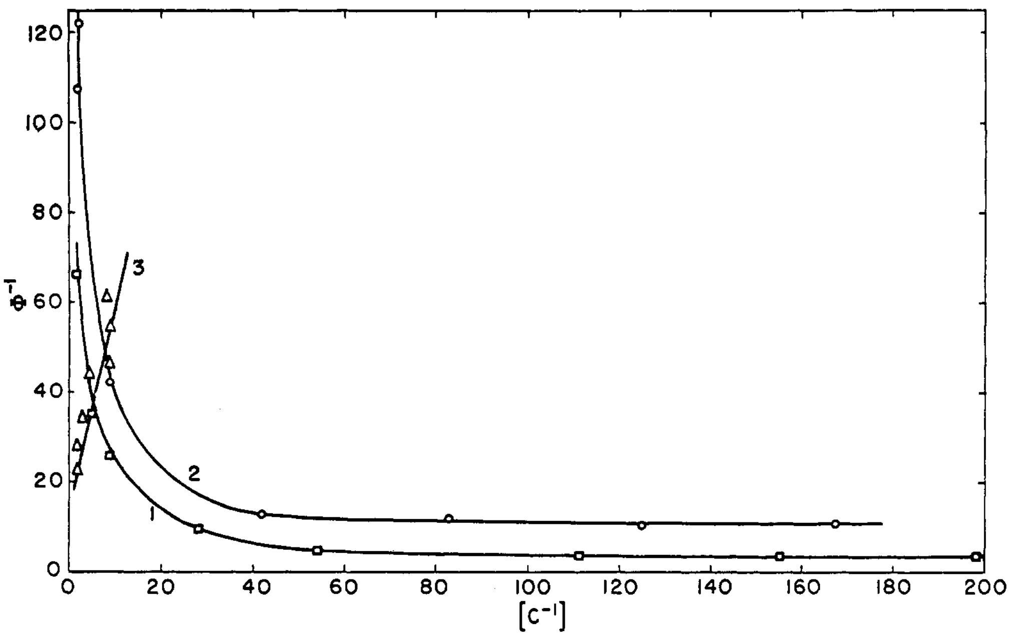

Figure 6. Reciprocal quantum yield *vs.* reciprocal concentration for the reduction of fluorenone by amines in acetonitrile by triethylamine, □, curve 1; diethylamine, ○, curve 2; and cyclohexylamine, △, curve 3.

in curves 5 and 6 of Figure 4. We are also not able to assign a multiplicity to the state responsible for these reactions; however, we feel that it is probably the triplet by analogy with the secondary and tertiary amine reactions. In any event, it is clear that triplet reactivity is at least two orders of magnitude lower for the primary than for either the secondary or tertiary amines, as indicated by the relative magnitudes of the slopes for the plots in Figure 3.

The Possibility of Reaction from the Fluorenone Singlet State. Although the excited singlet state of fluorenone cannot be the reactive state at low amine concentration, as shown by kinetic analysis above, the possibility that the singlet does undergo *some* reaction at high amine concentration has not been disqualified. Good evidence that some singlet reaction may be occurring in *at least* the triethylamine reaction has in fact been obtained by comparing the rate constant for *fluorescence* quenching by the amine with the rate constant for *reaction* quenching by the amine.

The slopes of the Stern-Volmer plots of Figure 4 are identified with the quantity τk_q, where τ is the lifetime of the fluorescent state, and k_q is the rate constant for quenching that state. Now,

$$\tau = \frac{1}{k_{\mathrm{isc}} + k_d{}^1} \tag{16}$$

where $k_{\mathrm{isc}} + k_d{}^1$ are the rate constants for the unimolecular processes which deactivate the fluorenone singlet; but for fluorenone $k_d{}^1 = 0.07k_{\mathrm{isc}}$ since intersystem crossing occurs with an efficiency of 93%. Therefore,

$$\tau = \frac{1}{1.07k_{\mathrm{isc}}} \tag{17}$$

and

$$\tau k_q = \frac{k_q}{1.07k_{\mathrm{isc}}} \tag{18}$$

For quenching of fluorenone fluorescence by triethylamine, the Stern-Volmer slope is 28.0 M^{-1} (Figure 4). Therefore, $k_q/k_{\mathrm{isc}} = 30.0\ M^{-1}$.

Now, eq 14, which describes the mechanism for tertiary amine reactions in Scheme II, may be written as shown in eq 19. But $(k_{\mathrm{isc}} + k_d{}^1)/k_{\mathrm{isc}}$ is simply the

$$\frac{1}{\Phi} = \left[\left(\frac{k_{\mathrm{isc}} + k_d{}^1}{k_{\mathrm{isc}}}\right) + \left(\frac{k'_d{}^1(\mathrm{Am})}{k_{\mathrm{isc}}}\right)\right] + \left[\left(\frac{k_{\mathrm{isc}} + k_d{}^1}{k_{\mathrm{isc}}}\right) + \left(\frac{k'_d{}^1(\mathrm{Am})}{k_{\mathrm{isc}}}\right)\right]\left(\frac{k_d{}^3}{k_r{}^3(\mathrm{Am})}\right) \tag{19}$$

reciprocal of the fractional intersystem crossing undergone by fluorenone in benzene solution, which is 1.07. The term $k_d{}^3/k_r{}^3$ is the experimental slope term, which is 0.0022 from Figure 5.[17] Now, if the only mode of fluorescence quenching is deactivation by the mechanism written as step 11 of Scheme II, then k_q should equal $k'_d{}^1$, and $k'_d{}^1/k_{\mathrm{isc}}$ should equal k_q/k_{isc}. It should therefore be possible to reproduce the experimental plot by calculating Φ^{-1} for a series of triethylamine concentrations. The experimental and theoretical plots are shown in the continuous and dashed curves in Figure 5. A major discrepancy between these plots is obvious; fluorescence quenching is therefore more efficient than reaction quenching, and thus an important mode of fluorescence quenching results in reaction.

We may, however, fit the theoretical curve to the experimental curve quite well using a value of 8.9 M^{-1} for the Stern-Volmer slope rather than the experimental value of 28.0 M^{-1}. This plot is shown in the dotted curve, Figure 5. Therefore, only 32% of the fluorescence quenching can be attributed to the excited

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(17) Accurate determination of the slope of the linear portion of curve 1, Figure 5, is obviously quite difficult. The quantum yields calculated using eq 19, however, are quite insensitive to differences in the magnitude of this small slope. Similarly, small inaccuracies in the determination of the fraction of intersystem crossing undergone by fluorenone[14] will have little effect. The major determinant of the semitheoretical curve at high concentration is the magnitude of the Stern-Volmer fluorescence quenching slope.

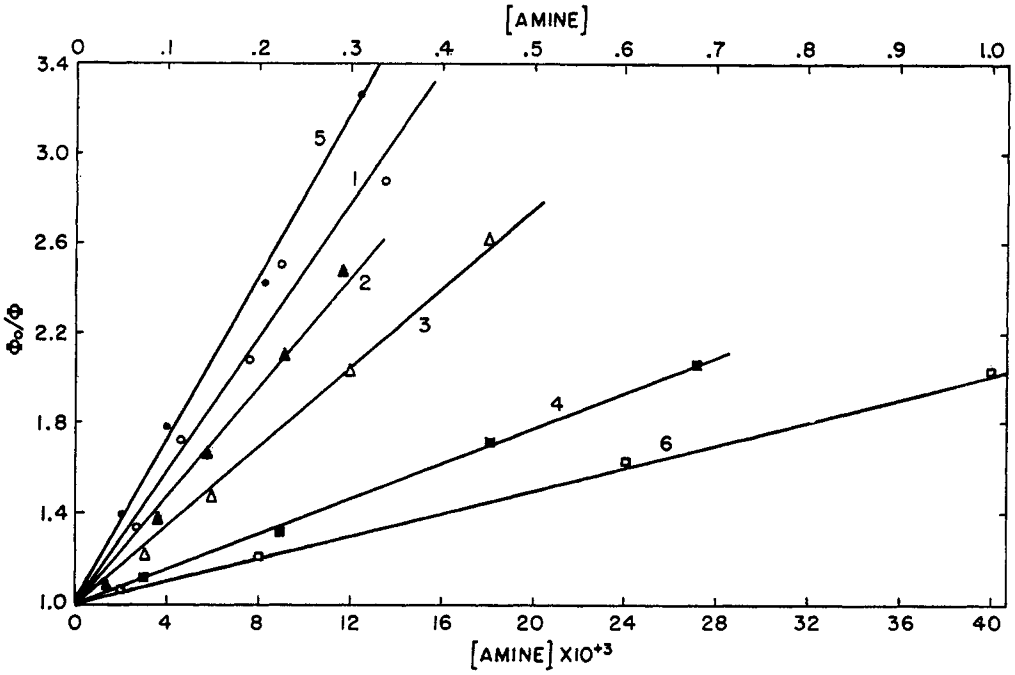

Figure 7. Stern–Volmer plots for the quenching of fluorenone fluorescence in acetonitrile by triethylamine, ○, curve 1, slope 147 M^{-1}; dimethylbenzylamine, ▲, curve 2, slope 122 M^{-1}; diethylamine, △, curve 3, slope 66 M^{-1}; diisopropylamine, ■, curve 4, slope 38.7 M^{-1}; cyclohexylamine, ●, curve 5, slope 7.4 M^{-1}; and α-methylbenzylamine, □, curve 6, slope 1.0 M^{-1}. Bottom scale for curves 1–4, top scale for curves 5 and 6.

singlet → ground state deactivation as written in step 11 of Scheme II. The other 68% may be due to singlet reaction, or to crossing of the fluorenone singlet to the reactive triplet induced by collision with the amine,[18,19] or to some combination of these steps. Our kinetic data do not permit distinguishing between these possibilities.

The Mechanism of Singlet Deactivation by Amines. The relative positions of the absorption spectra of fluorenone and the amines clearly do not allow for singlet–singlet energy transfer with resulting excitation of the amine. The deactivation of the fluorescent state of fluorenone must therefore occur by some other mechanism. Additional information concerning this mechanism was sought by running several reactions in the polar solvent acetonitrile. Kinetics were determined exactly as for the benzene runs. Plots of Φ^{-1} *vs.* c^{-1} for the reactions of amines **3**, **5**, and **7**, are shown in Figure 6. While it is seen that the general features of these plots parallel the corresponding data in benzene, two differences are apparent. First, the extrapolated intercepts of the linear portions of these curves are higher than those found in benzene, at least for the reactions of amines **3** and **5**. The extent to which this is due to a lower fractional intersystem crossing in acetonitrile,[20] to faster cleavage of the product pinacol by the amine to regenerate fluorenone,[21] and to more efficient deactivation of the fluorenone triplet by these amines in acetonitrile is not at all clear.

Second, we may note that the deactivation of the fluorenone singlet state by amines **3** and **5** is much more efficient in acetonitrile than in benzene. This behavior is paralleled, as expected, by much larger Stern–Volmer fluorescence quenching constants in the polar solvent. Emission quenching data in acetonitrile are shown in Figure 7. It may be observed that the emission-quenching ability of the amines follows the order tertiary > secondary > primary. In benzene solution, it is also apparent that secondary and tertiary amines are much better quenchers of fluorenone fluorescence than are primary amines. We have found that this trend is generally true for alkylamines and that aniline and its N-substituted derivatives are also effective quenchers.[22]

A corrolation may be made between the ionization potential of the amine and its ability to quench fluorenone fluorescence. The relevant data are shown in Table II. Assuming the ionization potentials of these amines parallel their reduction potentials in solution, we have good evidence for an electron-transfer mechanism of singlet-state quenching. Such interaction has previously been observed by Leonherdt and Weller[19] in a study of the quenching of perylene fluorescence by amines in acetonitrile.

Flash photolysis was employed in order to gain additional evidence for an electron-transfer mechanism. We hoped in this way to detect the absorption spectrum of the fluorenone radical anion. A 0.0012 *M* solution of fluorenone in a 10:1 mixture of acetonitrile and

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(18) This has been suggested as the mechanism of the fluorescence quenching of perylene by triethylamine and other amines in benzene solution; see ref 19.

(19) H. Leonherdt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 74.

(20) We have found that the intensity of fluorenone fluorescence in acetonitrile is 2.8 times that in benzene: unpublished data, L. A. Singer and G. A. Davis. A lower triplet population in the former solvent is thus a real possibility.

(21) Kinetics of the reverse reaction yielding 9-fluorenyl alcohol and fluorenone from fluorenone pinacol show that the rate of this reaction with the higher concentrations of amines **3** and **5** may be somewhat competitive with the rate of photoreduction in acetonitrile.

(22) In these experiments, the fluorescence of fluorenone solutions in benzene was visually observed in the presence of 10% by volume of amines. The results are therefore qualitative. The amines investigated in this way are given in Table II.

Table II

Amine	Ionization pot., eV	Quenching of fluorenone emission[a]	Stern–Volmer slopes, M^{-1}	
			Benzene	Acetonitrile
Aniline	7.69 ± 0.03[b]	+		
N-Methylaniline	7.34 ± 0.03[b] 7.6[e]	+		
N,N-Dimethylaniline	7.14 ± 0.03[b] 7.3[e]	+		
N,N-Diethylaniline	7.15	+		
N,N-Dimethylbenzylamine	*g*	+	14.4	122
Triethylamine	7.85 ± 0.07[c]	+	28.0	147
Diethylamine	8.44 ± 0.01[c]	+	18.2	66
Diisopropylamine	*h*	+	10.6	38.7
Cyclohexylamine	*h*	−	0	7.4
α-Methylbenzylamine	*i*	−	0	1.0
n-Propylamine	9.17 ± 0.04[d]	−		
Isopropylamine	9.5 ± 0.2[f]	−		
n-Butylamine	9.19 ± 0.04[d]	−		
Pyridine	9.5[f]	−		

[a] The symbol + signifies complete or almost complete quenching of fluorenone emission determined as described in ref 19. The symbol − indicates little or no fluorescence quenching determined in the same way. [b] A. N. Terenin and F. I. Vilesov, *Dokl. Akad. Nauk SSR*, **115,** 744 (1957). [c] J. Collin, *Can. J. Chem.*, **37,** 1053 (1959). [d] J. D. Morrison and A. J. Nicholson, *J. Chem. Phys.*, **20,** 1021 (1952). [e] J. Czekalla and G. Briegleb, *Z. Elektrochem.*, **63,** 6 (1959). [f] V. I. Vedeneyer, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martin's Press, New York, N. Y., 1966. [g] Ionization potential not available, but is probably similar to that given for triethylamine. [h] Reliable ionization potential not available, but is probably similar to that given for diethylamine. [i] Ionization potential not available but is probably similar to 8.64 eV for benzylamine; see footnote *b*.

triethylamine was flashed and the transient absorption was monitored at selected wavelengths. Only a very weak transient absorption was seen which followed apparent first-order decay kinetics with a lifetime of roughly 3.5×10^{-3} sec. The absorption maximum of the transient was in the neighborhood of 460 mμ. The transient absorbed too weakly, however, to offer convincing evidence that the fluorenone radical anion is produced in this irradiation.

Reactivity of the Fluorenone Triplet State. The lack of reactivity of fluorenone with 2-propanol and toluene would seem to provide evidence that the lowest triplet state of fluorenone is of the $\pi\pi^*$ configuration,[23,24] as indicated to be by Yoshihara and Kearns.[6] The low reactivity of this ketone toward photocycloaddition to olefins,[2] which we have recently confirmed,[25] also lends weight to this conclusion. The relative slowness of reaction with tri-*n*-butylstannane exhibited by 2-acetonaphthone and 1-naphaldehyde, which are known to possess $\pi\pi^*$ lowest excited triplets[24] is similarly observed in the fluorenone reaction described above.

The order of amine reactivity is also interesting, with primary amines exhibiting much lower reactivity than either the secondary or tertiary amines. This may be due to the difference in number of α-hydrogens possessed by the respective amines,[26] and to steric hindrance factors, but we are inclined to give serious consideration to the mechanism proposed by Cohen and Cohen[27] for the photoreduction of *p*-aminobenzophenone by amines involving internal electron-transfer stabilization of the transition state for hydrogen atom transfer. This stabilization should be more effective for amines of lower ionization potential. Cohen and Baumgarten[28] have also studied the photoreduction of benzophenone by amines. Unfortunately, their data are not amenable to direct comparison with ours.

While many uncertainties still remain concerning the detailed mechanism of the fluorenone photoreduction, it is clear that the high reactivity of fluorenone with amines and ketenimines, in contrast to its low reactivity with alcohol and olefins, suggests an important role for the basic nitrogen atom in the reactant molecule.

Experimental Section

Materials. Benzene (Mallinckrodt analytical reagent) was distilled over P_2O_5 through a 5-ft glass-bead column and a center fraction was taken. Acetonitrile (Fisher Certified) was purified by distillation through the same column after first drying with a Linde Molecular Sieve. Toluene (Fisher Certified) was purified in the same way. Methylcyclohexane (Matheson Coleman and Bell Spectrograde) was used without further purification, as was isopropyl alcohol (Burdick and Jackson) "Distilled in Glass." Benzophenone and benzhydrol (both Matheson Coleman and Bell reagents) were twice recrystallized from ether–petroleum ether (bp 30–60°) mixtures prior to use. Fluorenone (Aldrich) was recrystallized three times from a chloroform–hexane mixture. Amines **3**, **5**, **6**, and **7** were fractionally distilled through a 4-in. vacuum-jacketed glass helices column, while amines **4** and **8** were purified by vacuum distillation using the same apparatus. The amines were all purchased from various commercial sources. Tri-*n*-butylstannane was prepared by $LiAlH_4$ reduction of the tin chloride after the method of Van der Kerk and Luitjen[29] and subsequently purified by fractional vacuum distillation.

Isolation and Identification of Photoreduction Products. One gram or less of fluorenone along with the reducing agent was dissolved in either benzene or acetonitrile contained in a Pyrex test tube of appropriate size. The solutions were then flushed for 5 min with purified nitrogen and quickly stoppered. Irradiations were performed using an air-cooled GE BH-6 Hg lamp filtered by a 7380 Corning glass cut-off filter. The photolyses were conducted under the time and concentration conditions specified in Table I. After reaction the crude mixtures were stripped of solvent and volatile products on a rotary evaporator. The oily residue was then chromatographed using a silica-gel column. The pinacol (**1**) and 9-fluorenyl alcohol (**2**) products were eluted with 50% ether

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(23) F. Bergmann and Y. Hirshberg, *J. Am. Chem. Soc.*, **65,** 1429 (1943).

(24) G. S. Hammond and P. A. Leermakers, *ibid.*, **84,** 207 (1962).

(25) Unpublished data, G. A. Davis and J. D. Gresser.

(26) No reaction occurs when fluorenone is irradiated in the presence of *t*-butylamine; thus α-hydrogens are probably abstracted in a primary step: unpublished data, G. A. Davis and J. D. Gresser.

(27) S. G. Cohen and J. I. Cohen, *J. Am. Chem. Soc.*, **89,** 164 (1967).

(28) S. G. Cohen and R. Baumgarten, *ibid.*, **89,** 3471 (1967).

(29) G. J. M. Van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.* (London), 7, 369 (1957).

in petroleum ether. These fractions were preceded by unreacted fluorenone.

The composition of the chromatographed fractions was determined with the aid of a Beckman IR-8 infrared spectrometer and nmr spectra were taken on a Varian T-60 instrument.[30] In some cases recrystallization of fractions was found necessary to give sharp melting points.

Fluorenone pinacol (**1**), mp 188–189°; lit.[31] 190–192°, was identified by its ir peaks at 2.8, 2.9, 3.25–2.40, 6.22, 6.91, 7.45, 7.80, 9.60, 10.65, 10.70, 11.3 μ in $CHCl_3$. Its nmr spectrum taken in $CDCl_3$ showed a complex multiplet, δ 6.8–7.4, and a small singlet at δ 3.22 in an integrated ratio of 8:1. Identification of 9-fluorenyl alcohol, mp 155–156°, lit.[32] 153°, was based on its ir spectrum in $CHCl_3$ which showed peaks at 2.8, 2.95, 3.25–3.40, 6.91, 7.30, 8.45, and 9.82 μ, and its nmr spectrum in $CDCl_3$ which showed a complex multiplet at δ 7.2–7.7 and a singlet at δ 5.50, again in an 8:1 area ratio.

Photochemical Kinetics. Kinetic data were determined in the following way. Four milliliters of the solution to be irradiated was placed in a 1-cm rectangular Beckman quartz uv cell fitted with a cylindrical stem. Oxygen was expelled by flushing the solution with purified nitrogen and the cell was then quickly stoppered. The absorbance of the fluorenone peak at 380 mμ was recorded using a Beckman DK spectrometer. A voltage-stabilized GE BH-6 lamp was focused into a Bausch and Lomb monochromator to isolate the 366-mμ band. The transmitted band was focused onto the reactant solution. After irradiation for timed intervals the fluorenone absorbance was recorded. For each concentration of reducing agent a minimum of five points was used to construct a per cent reaction *vs.* time plot. Good linearity was generally obtained for up to 25% reaction. Initial rates as a function of time were obtained by multiplying the slopes by the initial fluorenone concentration. These rates were then converted to quantum yields by comparison with the rate of disappearance of benzophenone irradiated in vacuum-degassed benzene solutions containing 1.0 *M* benzhydrol, as previously described.[3] The benzophenone concentration was adjusted so that the same amount of light was absorbed at 366 mμ by both the actinometer and the fluorenone solutions. Actinometry was performed at several intervals throughout a series of kinetic experiments, and the rate of benzophenone consumption was found to be constant to within a 10% error for all runs.

In order to ensure that deoxygenation by nitrogen flushing was sufficiently efficient, several fluorenone reductions were run in ampoules deoxygenated by three freeze–thaw cycles and sealed under high vacuum. The rates of reaction of fluorenone with tri-*n*-butylstannane at 0.20 *M* and with triethylamine at 0.018 *M* were found to be well within 10% of the rates found in the nitrogen flushed ampoules.

Emission Experiments. All emission quenching experiments were performed using the emission attachment to the Beckman DK spectrometer. The Hg-exciting light was filtered to pass only the 366- and 313-mμ lines. The quartz solution ampoules in all cases contained 0.10 *M* fluorenone along with the appropriate concentration of amine in benzene or acetonitrile. The solutions were deoxygenated by N_2 flushing prior to taking spectra. Stern–Volmer plots were constructed by dividing the peak height of emission in ampoules containing no quencher by the peak height for quenched emission and plotting as a function of quencher concentration. No new emission bands or other changes in the emission spectrum of fluorenone were observed in the presence of any of the amines.

Absorption Spectra. Evidence for charge-transfer interaction between fluorenone and the amines was sought by taking the absorption spectrum of fluorenone in benzene and acetonitrile between 500 and 320 mμ with and without added amines. No change was seen in the spectrum of fluorenone at 0.003 *M* in the presence of amines **3**, **5**, and **7** at 0.72 *M* concentration which could not be accounted for by simple addition of the fluorenone and amine spectra.

Flash Photolysis Experiments. The flash apparatus is described in detail elsewhere.[33] Solutions were made up in 6- or 9-cm path length Pyrex optical cells, and degassed through six freeze–thaw cycles to less than 10^{-6} mm on a high-vacuum line and flame sealed. The solutions containing amines were made up in "tipsy-tubes" as described by Tyler, *et al.*,[34] which allowed for refilling the cell under vacuum after each flash.

The cells were wrapped in a blue plastic Roscolene filter no. 963 which passes light between 350 and 530 mμ (T_{max} = 410 mμ). Samples were flashed at a constant input energy of 900 J. Decay curves were measured after this time by oscilloscope displays at selected wavelengths. Changes in optical density as a function of time were found with the aid of a Gerber GDDRS-3B-2 data reduction system and plotted to conform to first- or second-order kinetics.

Reversibility of Pinacol Formation. In a stoppered test tube 0.10 g of fluorenone pincaol (**1**) was dissolved in 1 ml of a 1:1 mixture of diethylamine and benzene. The solution was heated at 40° for 20 hr. Preparative thin layer chromatography was employed to isolate the reaction products which were identified as 0.043 g (43%) of fluorenone and 0.048 g (48%) of 9-fluorenyl alcohol by melting point and nmr spectra.

The rate of this reverse reaction was measured by heating 0.003 *M* solutions of the pinacol in benzene or acetonitrile containing 0.2 *M* amine. The production of fluorenone was followed after various times as the solutions were heated to 40° by the increase in absorbance of the fluorenone peak. The reactions of amines **3**, **5**, **6**, and **8**, in benzene and of **3**, **5**, and **8** in acetonitrile were followed in this way.

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[30] We wish to thank Miss Virginia Mai for facilitating our use of this instrument at Massachusetts Institute of Technology.

[31] M. Gomberg and W. E. Bachman, *J. Am. Chem. Soc.*, **49**, 236 (1927).

[32] H. Hoch, *et al.*, *Chem. Ber.*, **83**, 227 (1956).

[33] (a) P. A. Schnieper, Records, Northeast Electronics Research and Engineering Meetings, 1965, p 158; (b) A. M. Halpern and K. Weiss, *J. Phys. Chem.*, in press.

[34] W. M. Moreau, T. A. Tyler, and K. Weiss, *J. Chem. Educ.*, **43**, 435 (1966).