

Photoreduction by Amines

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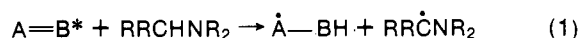
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I. Introduction

A. Scope of the Reaction

Most of the reactions to be described may be indicated schematically as those of a photoexcited unsaturated compound with an amino compound in solution, leading to abstraction of α -hydrogen from the amino compound and formation of two radicals



The radicals may lead to the several possible combination and disproportionation products. Generally disproportionation does not occur in photoreduction of aromatic carbonyl compounds by amines in nonpolar media, and high yields of pinacols may be obtained. The amine-derived radical may also donate a second reducing group to a molecule of unsaturated compound in its ground state, leading to a maximum theoretical quantum yield of two for photoreduction of the unsaturated compound. The oxidation product of the amine, so formed, may undergo hydrolysis, leading in high yields from primary amine to carbonyl compound, from secondary and tertiary amines to carbonyl compounds and primary and secondary amines respectively. The unsaturated compounds may be drawn from many classes of organic compounds, ketones, aldehydes, quinones, nitro compounds, and aromatic hydrocarbons, heterocyclic compounds, and dyes. Detailed quantitative studies have been carried out with ketones, while study of the other classes of compounds is in a more preliminary state.

Photoreduction of carbonyl compounds by amines differs importantly from photoreduction of these compounds by alcohols. Although the photoreduction of certain ketones and aldehydes by alcohols has been known and studied for many years,¹ and leads to useful synthesis of pinacols and hydrols,² it should be noted that the reac-

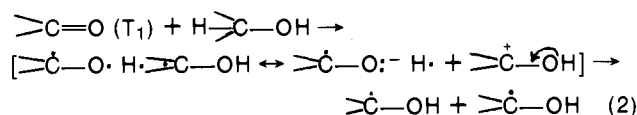
(1) G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900); **34**, 1530, 1537 (1901).

(2) W. E. Bachman, *J. Amer. Chem. Soc.*, **55**, 391 (1933).

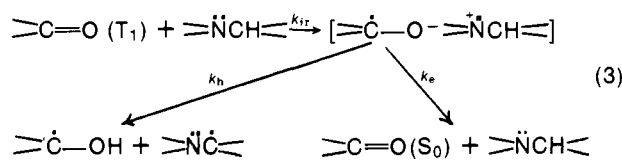
tion is not of general applicability³ and that many, perhaps most, aromatic ketones are not photoreduced by alcohols. For example, fluorenone, xanthone, aminobenzophenones, α - and β -naphthyl carbonyl compounds, and generally the many compounds with low-lying π, π^* and charge-transfer triplet states are not photoreduced efficiently by alcohols. On the other hand, recent studies indicate that conditions may be found under which all these compounds, and nearly all aromatic carbonyl compounds except, perhaps, those containing certain reactive ortho substituents, may be photoreduced by amines which contain α hydrogen, and generally most efficiently by such tertiary amines. Yet a comprehensive review³ in 1958 reported only one such reaction, light-induced addition of amino acid esters to *p*-nitrobenzaldehyde,⁴ apparently proceeding by combination of the initially formed radicals.

B. Nature of the Reaction

The marked difference between the photoreductive reactivity of alcohols and amines may arise from a fundamental, but sometimes subtle, difference in mechanism. In reduction by alcohols the excited triplet⁵ carbonyl attacks hydrogen on carbon α to the hydroxyl in preference to more distant hydrogen, and this abstraction is facilitated by electron donation by the oxygen in a polar contribution to the transition state⁶ (eq 2). Although the nitro-



gen of amines might behave similarly, reduction by amines appears to proceed, generally, by rapid initial interaction at the nonbonding electrons of the heteroatom,⁶ k_{ir} , leading to a charge-transfer complex.^{6b,7} The rate of this interaction may be expected to increase with increasing electron availability, with decreasing ionization potential. This is followed either by transfer of α -hydrogen and formation of the radicals, k_h , or by spin inversion and charge destruction, leading to quenching, k_e (eq 3).



While a substantial part of the barrier to abstraction of hydrogen may be overcome in the initial efficient charge-transfer interaction, this process also allows for subsequent quenching and failure of the reaction to achieve the maximum quantum yield of 2, which may be achieved in photoreduction of the more restricted group of ketones by alcohols. With values of k_{ir} being very high, quantum yields for photoreduction by amines will be determined by the relative value of k_e and k_h . If α -hydrogen is not present in the structure, $k_h = 0$, and such amines act as quenchers only. The broad effectiveness and varied structure of amines make possible many sig-

nificant studies of the effects of structure and conditions on reactivity and quenching. The effects of the properties of the unsaturated compounds may be studied—whether the excited singlet or triplet undergoes reaction, and what the effects of $n-\pi^*$, $\pi-\pi^*$ or CT character of the excited state and of the excited state energies and ground state reduction potentials may be. The effects of structure and oxidation potential of amine may be studied—with aliphatic and aromatic amines, and primary, secondary, tertiary, and bridgehead bicyclic amines. The polarity and structure of solvent are also found to be important, in influencing reactivity and quenching and affecting light-absorbing transients, intersystem crossing efficiency, and ease of formation and stability of the initial charge-transfer complex.

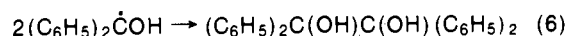
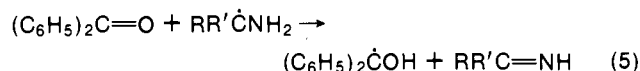
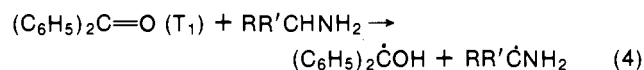
II. Photoreduction of Benzophenone and Sodium 4-Benzoylbenzoate

A. By Neat Amines and in Nonpolar Solvents

1. Rates and Products

A preliminary study^{8a} showed rapid photoreduction of benzophenone by primary and secondary aliphatic amines which contain the $>CHNH-$ group, leading to benzpinacol and imines in nearly quantitative yields. Primary amines, $RR'CHNH_2$, led to the imine $RR'CH=NCHRR'$; secondary amines, $RR'CHNHR''$, led to $RR'C=NR''$. The reactions proceed rapidly in dilute solution in hydrocarbon, do not require excess amine,^{8b} and have practical synthetic value.

Hydrolysis of the imines leads to 50% oxidative deamination of the primary amine and to oxidative degradation of the secondary amine to carbonyl compound and primary amine. Photoreduction by primary amines was similar or faster in rate than by 2-propanol; photoreduction by secondary amines was about half as fast. *tert*-Butylamine showed low reactivity, comparable to that of aliphatic hydrocarbons and 0.2 as great as 2-propanol, indicating the importance of α -CH as compared with NH. A tertiary amine, triethylamine, also showed similar low reactivity, pointing at first^{8a} to the importance of NH. However, dilution of tertiary amines with benzene led to increased rates, comparable to that with 2-propanol, indicating that NH is not required for high reactivity. Secondary amines also showed increased reactivity on dilution with hydrocarbon. Photoreduction of benzophenone by secondary and tertiary amines is accompanied by formation of light-absorbing transients and by-products,⁷ which are formed less in dilute benzene solution, and this may account for the increase in rate on dilution. The photoreduction by primary amines did not appear to lead substantially to light-absorbing transients, and the rate was neither increased nor decreased by modest dilution with hydrocarbon. The overall reactions in the case of primary and secondary amines were formulated analogously to those with primary and secondary alcohols.^{8b}



(3) A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, p 112.

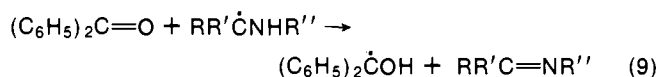
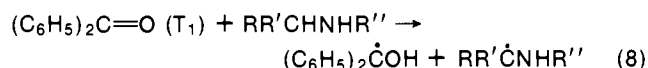
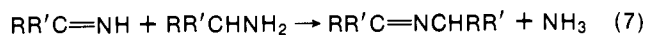
(4) E. Bergmann, H. Bendas, and C. Resneck, *J. Chem. Soc.*, 2564 (1953).

(5) G. S. Hammond and W. M. Moore, *J. Amer. Chem. Soc.*, **81**, 6334 (1959).

(6) (a) S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89**, 164 (1967); (b) *J. Phys. Chem.*, **72**, 3782 (1968).

(7) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

(8) (a) S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **87**, 2996 (1965); (b) **89**, 3471 (1967).



Donation of a second reducing group from amine-derived radical to ground state ketone (eq 5 and 9) leads to a maximum quantum yield of 2 for reduction of ketone to pinacol. Many of the free radical reactions are reversible, but they occur largely in the indicated direction under the kinetically controlled conditions of the usual photoreduction.

2. Quantum Yields and Kinetic Constants

The quantum yield for photoreduction of benzophenone by 2-butylamine, determined by ferrioxalate actinometry, was 1.1 at 334 and 366 nm.⁷ Quantum yields for photoreduction by secondary and tertiary amines, *N*-methyl- and *N,N*-dimethyl-2-butylamine, were lower, consistent with the lower rates, but had little significance because of absorption of light by by-products. Quenching by naphthalene of photoreduction of benzophenone by 1.0 *M* 2-butylamine led to $k_q/k_{ir} = 33$, indicating a very high value of k_{ir} , $2 \times 10^9 M^{-1} sec^{-1}$, for interaction of the excited triplet ketone with the amine, based on a diffusion-controlled quenching rate constant, $k_q = 6 \times 10^9 M^{-1} sec^{-1}$. This is about two orders of magnitude greater than the rate constant for abstraction of hydrogen by triplet benzophenone from 2-propanol. Analysis of the photoreduction between 10 and 0.1 *M* 2-butylamine led to $k_d/k_{ir} = 0.03 M$, $k_d = 6 \times 10^6 sec^{-1}$, indicating an apparent triplet decay rate constant 60-fold greater than that measured in the absence of amine.⁹

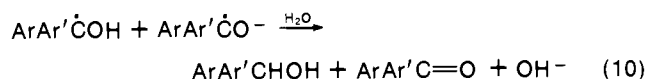
Photoreduction of benzophenone in optically active 2-butylamine led to no loss of activity in recovered 2-butylamine, indicating that disproportionation of the two initially formed radicals, regenerating starting materials, and disproportionation of amine-derived radicals to form imine and racemic amine did not occur. The absence of such reactions and of light-absorbing by-products, the very high value of k_{ir} , absolute and relative to k_d , the insensitivity to physical quenchers, and equivalent yields of imine and pinacol indicate that an explanation is required to account for the quantum yield being less than the theoretical maximum value of 2. The proposal^{6b,7} that the high value of k_{ir} is that for formation of a charge-transfer complex, and that this provides a mechanism whereby an amine may act as both a quencher and a reducing agent (eq 3), is consistent with these properties of photoreduction by amines. Photoreduction of benzophenone by 2-butylamine-*N,N*-*d*₂ and cyclohexylamine-*N,N*-*d*₂ was slightly more rapid than by the protio compounds,⁷ indicating that the quenching part of the process may involve not only the nonbonding electrons of N but also, perhaps, partial reversible transfer of N-H or N-D. Photoreduction of benzophenone by 1 and 0.7 *M* cyclohexylamine was only about 60% more rapid than by 1 and 0.7 *M* cyclohexylamine-1-*d*.⁷ With very high values of k_{ir} and high concentrations of amine, this result also indicates that quantum efficiencies for reduction by amines do not depend on k_d/k_{ir} ratios, but on the relative importance of quenching and reduction, probably in accord with eq 3.

(9) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

B. Photoreduction in Aqueous Media

1. Quantum Yields and Kinetic Constants

A quantitative kinetic study of photoreduction of benzophenone by secondary and tertiary amines in benzene could not be made because of light-absorbing by-products. Because of the proposed polar mechanism for the initial hydrogen abstraction the reactions were examined in aqueous media, and it was found that reductions by the three classes of amines proceeded rapidly without complication due to light-absorbing transients.¹⁰ This was fortuitous and fortunate, since photoreduction by alcohols in aqueous media is complicated by transients.^{8b,11} The high alkalinity of the aqueous amines apparently did not permit accumulation of by-products. The alkalinity leads to hydrols instead of pinacols; the hydrols are formed under these conditions by disproportionation reactions involving ketyl radical ions (eq 10), rather than by base-catalyzed decomposition of pinacols.^{12,13} Reduction to hydrol requires two reducing groups per molecule of ketone, and the maximum quantum yield is 1, equivalent to 2 for reduction to ketyl radical and pinacol in neutral or acid solution.



A detailed study was made of photoreduction of 0.1 *M* aromatic ketone by primary, secondary, and tertiary amines and by 2-propanol in 1:1 pyridine-water containing 0.02 *M* NaOH. Most work was done with sodium 4-benzoylbenzoate since it was reduced cleanly to the hydrol. Benzophenone led to a mixture of hydrol and pinacol, to high apparent quantum yields because of formation of pinacol, and was less suited for quantitative study. Results are summarized in Table I.¹³

Under these conditions the quantum yields are highest for tertiary amines and indicate that two reducing moieties are transferred from these amines also. The quantum yield for the primary amine, 0.55, corresponds to that observed for photoreduction in benzene.⁷ Low and variable quantum yields observed with secondary amines reflect variations in relative values of k_e and k_h . Photoreduction by the amines shows low sensitivity to concentrations of amine, $\varphi_{lim} \sim \varphi_{obsd}$, especially low sensitivity of tertiary amines to diffusion-controlled quencher, with values of k_{ir} approaching diffusion control, and variations in the apparent unimolecular deactivation constant, k_d . Photoreduction of 4-benzoylbenzoic acid by triethylamine in benzene, leading to much light-absorbing by-product, was examined by analysis at 1600 cm^{-1} . The decreasing rates were extrapolated to zero reaction, leading to an initial quantum yield of 1.5, essentially equivalent to that observed in the aqueous medium.¹³

2. Products

The photoreductions in aqueous media lead efficiently to oxidative cleavage of amines, *i.e.*, from 2-butylamine quantitatively to 2-butanone, from triethylamine to high yields of acetaldehyde and diethylamine, from *N,N*-dimethyl-2-butylamine to >80% formaldehyde, *N*-methyl-2-butylamine, and very little 2-butanone, and from *N,N*-

(10) S. G. Cohen, N. M. Stein, and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 521 (1968).

(11) S. G. Cohen and J. I. Cohen, *Isr. J. Chem.*, **6**, 757 (1968).

(12) N. M. Stein, Ph.D. Thesis, Brandeis University, 1970.

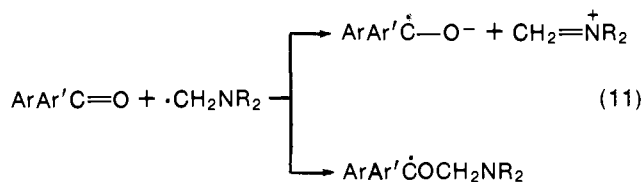
(13) S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, **93**, 6542 (1971).

TABLE I. Photoreduction of Sodium 4-Benzoylbenzoate (SBB) and Benzophenone (B) in 1:1 Pyridine-Water, 0.02 M NaOH

Ketone	Reducing agent	ϕ_{obsd}^a	ϕ_{lim}^b	k_d/k_{IR}^c M	k_q/k_{IR}^d M ⁻¹	$k_{\text{IR}}, M^{-1} \text{sec}^{-1}$	k_d, sec^{-1}
SBB	2-BuNH ₂	0.50	0.55	0.10	44	6.3×10^7	6.3×10^6
SBB	2-BuNHMe	0.27	0.28	0.03	16	1.6×10^8	4.8×10^6
SBB	2-BuNMe ₂	0.75	0.76	0.01	3	9.3×10^8	1.0×10^7
SBB	Et ₃ N	0.68	0.70	0.02	4	6.0×10^8	1.3×10^7
SBB	2-PrOH	0.42	1.0	1.65	1700	1.7×10^6	2.8×10^6
B	2-BuNH ₂	1.13	1.18	0.03	170	1.7×10^7	5.3×10^5
B	2-PrOH			0.10	2000	1.5×10^6	1.5×10^5

^a Quantum yields at 334 nm for SBB, 344 for B, 1 M reducing agent. ^b Quantum yields extrapolated to "infinite" concentration of reducing agent. ^c From effects of 0.05–1.0 M reducing agent on rates of reduction. ^d From quenching by naphthalene at 1 M reducing agent, $k_q = 3 \times 10^9 M^{-1} \text{sec}^{-1}$.

dimethylbenzylamines to *N*-methylbenzylamines and no benzaldehydes. Cleavage at the least substituted carbon generally predominated. Primary and secondary amines may cleave by hydrolysis of the imines formed by reactions 5 and 7. Tertiary amines may cleave by hydrolysis of an enamine, and vinyl-diethylamine was characterized as the product of photoreduction by triethylamine in benzene.¹³ The highly preferred abstraction from methyl groups is also followed by transfer of a second reducing group to ground state ketone and may lead to an immonium ion or to an addition product, both of which may be hydrolyzed to the observed products (eq 11).



Reactions analogous to those of eq 11 may also occur when all the alkyl groups are larger than methyl. The order of the values of k_{IR} , tertiary > secondary > primary, and the apparent steric effects indicate that photoreduction of aromatic ketones by amines provides a useful procedure for stepwise dealkylation of amines, particularly for demethylation of tertiary amines.¹³

C. Quenching of Phosphorescence of Benzophenones

Values of k_{IR} for interaction of triplet ketones with amines and other reactants may also be obtained in benzene solutions at room temperature from the effects of the reactants on the intensity of the phosphorescence emission of the ketone and application of the Stern-Volmer expression (eq 12). Values of k_{IR} , based on $\tau_0 = 6.5 \times 10^{-6} \text{sec}$, determined by flash photolysis under the same conditions of solvent and temperature,¹⁴ are summarized in Table II.¹⁵

$$I_0/I = 1 + \tau_0 k_{\text{IR}}[\text{Q}] \quad (12)$$

The values for 2-butylamine and 2-propanol are very similar to those obtained by naphthalene quenching of photoreduction by these compounds,^{7,11} lending support to the values obtained for the other amines, which cannot be studied accurately by photoreduction under these conditions. *tert*-Butylamine has a fairly high value of k_{IR} , lacks α -H and is a quencher, and retards photoreduction by 2-butylamine¹³ and by 2-propanol,¹⁵ consistent with eq 3, $k_{\text{H}} \sim 0$. Values of k_{IR} increase in the order primary

(14) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).

(15) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837 (1970).

TABLE II. Interaction of Quenchers with Benzophenone Triplet

Quencher	$k_{\text{IR}}, M^{-1} \text{sec}^{-1}$
2-Butylamine	2.5×10^8
<i>tert</i> -Butylamine	7.0×10^7
<i>N</i> -Methyl-2-butylamine	1.4×10^9
Triethylamine	2.3×10^9
<i>p</i> -Cyanodimethylaniline	2.0×10^9
Dimethylaniline	2.7×10^9
<i>p</i> -Methyldimethylaniline	4.3×10^9
2-Propanol	1.8×10^6

< secondary < tertiary aliphatic amine, approaching diffusion control, as was found in the aqueous system.¹³ Values of k_{IR} are four to ten times larger than in the aqueous system. Despite the polar character of the interaction, hydrogen bonding to the n electrons of the amine may decrease the rates in water. The rates with 2-propanol are the same in water and benzene, consistent with direct abstraction of α -H. The *N,N*-dimethylanilines show very high values of k_{IR} , consistent with low ionization potentials. The rate constant is decreased by an electron-withdrawing substituent and increased by electron donation.

D. Reactions with Aromatic Amines

1. Photoreduction

Photoreduction of benzophenone by *N,N*-dimethylaniline and by *N*-methyldiphenylamine in benzene involves abstraction of hydrogen from methyl and leads to benzpinacol and the cross-coupling products, and from dimethylaniline to methylaniline.¹⁶ The demethylation probably arises from presence of water.¹³ These photoreductions also showed low sensitivity to quenching by naphthalene, $k_q/k_{\text{IR}} < 10$, and greater sensitivity to ferric chelates but substantially less than that of photoreduction by alcohols, supporting the charge-transfer mechanism.¹⁷

2. ESR Studies

ESR studies characterized the diphenylhydroxymethyl radical in photoreduction of benzophenone by dimethylaniline and by triethylamine,^{18,19} and indicated strong hydrogen bonding between the ketyl radical and the aliphatic amine.¹⁹ Irradiation of benzophenone and dimethyli-

(16) (a) R. S. Davidson, *Chem. Commun.*, 575 (1966); (b) R. S. Davidson and P. F. Lambeth, *ibid.*, 1265 (1967).

(17) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 511 (1968).

(18) R. S. Davidson, P. F. Lambeth, J. F. McKellar, P. H. Turner, and R. Wilson, *Chem. Commun.*, 732 (1969).

(19) R. S. Davidson and R. Wilson, *J. Chem. Soc. B*, 71 (1970).

line in 2-methyltetrahydrofuran at 77°K led to the ketyl and amine derived radicals, observed spectrally. The esr spectrum might indicate two photochemically formed unstable radicals which lie close together and form a combined triplet state.²⁰ Complex formation between amine and ground state ketone was proposed.

Benzophenone ketyl radical anion was characterized by esr in photoreduction of the ketone in aqueous and ethanolic isobutylamine and *tert*-butylamine.²¹ Radical intermediates formed from the donors during the photoreduction of benzophenone by alcohols, amines, phenols, sulfides, thiols, ethers, hydrocarbons, and amides have been trapped by *tert*-nitrosobutane, and resulting nitroxide radicals have been characterized *in situ* by esr.²²

3. Quenching

Aromatic amines which lack transferable α -hydrogen were quenchers for photoreduction of benzophenone by benzhydrof; tri-*p*-tolylamine, $k_q/k_r = 525$, was more efficient than triphenylamine, $k_q/k_r = 44$, and the efficiency of the latter was increased to $k_q/k_r = 620$ by change in solvent from benzene to acetonitrile. The substituent and solvent effects support the charge-transfer mechanism, and the authors described qualitatively how the relative importance of electron and hydrogen transfer might be affected by ionization potentials of the donors.¹⁷ Spectral examination after flash photolysis of benzophenone in acetonitrile in the presence of tri-*p*-tolylamine indicated the presence of the amine radical cation.¹⁸ Quenching by aromatic amines, aniline, diphenylamine, 2-naphthylamine, and *p*-toluidine, of photoreduction of benzophenone by 2-propanol has been attributed to triplet energy transfer.²³ It appears more likely that this quenching proceeds by charge transfer, perhaps accompanied by some reversible N-H hydrogen transfer.

Triplet benzophenone has been reported²⁴ to react with diphenylamine in *tert*-butyl alcohol and in acetonitrile, but not in benzene, leading in the polar solvents to 4-(*N*-phenylamino)phenyldiphenylmethanol, $C_6H_5NH-p-C_6H_4-C(C_6H_5)_2OH$, and to essentially no benzpinacol. The reaction proceeded in low quantum yield, $\varphi \sim 0.03$, was insensitive to quenching by naphthalene, $k_q/k_r = 2.5$, and was postulated to proceed *via* a close contact intermediate, such as an ion pair or exciplex, which could collapse to ground state molecules or product. Corresponding aryldiphenylmethanols were not obtained from benzophenone and triphenylamine, *N*-methyldiphenylamine, aniline, and *N,N*-dimethylaniline.²⁴

E. Further Considerations

1. Structure of Amine

Studies are in progress²⁵ on photoreduction of benzophenone and 4-benzoylbenzoate in 1:1 water-pyridine at pH 12 by amines of varied structure, open-chain, cyclic, and bicyclic bridgehead amines, primary, secondary, and tertiary monoamines, perhydrodiazines, hydrazines, and morpholines. Effects of geometrical restrictions, lone-pair

interactions and delocalization of charge, and radical character are being evaluated. Great variation in quantum yield with small variation in k_{ir} are observed consistent with eq 3. This work will be described in detail elsewhere.

2. Concentration of Amine

The dependence of quantum yield on concentration of amine and of added quencher^{13,26} is a modification of that in photoreduction by alcohol²⁷ and is indicated in eq

$$1/\varphi = 1/af + k_d/atk_{ir}[Am] + k_q(Q)/atk_{ir}[Am] \quad (13)$$

13. The factor a includes intersystem crossing quantum yield and efficiency of the thermal reaction (eq 5) and for benzophenone under these conditions has the value 2; f is the fraction of reaction of triplet with amine which leads to hydrogen abstraction, has the maximum value 1, and may correspond to $k_h/(k_h + k_e)$ (eq 3); k_{ir} is the rate constant for total reaction of triplet with amine and may be that for formation of charge-transfer complex. In absence of added quencher, the last term (eq 13) is zero, and the ratio of slope to intercept of a plot of $1/\varphi$ vs. $1/[AM]$ is k_d/k_{ir} , where k_d is an apparent unimolecular rate constant for self- and solvent-induced deactivation of triplet. With addition of diffusion-controlled quencher at constant concentration of amine, the ratio of slope to intercept of a plot of $1/\varphi$ vs. (Q) allows calculation of k_{ir} and then of k_d . An amine which is a very inefficient reducing agent may generally be studied as a quencher for reduction of a ketone by an amine in a system in which k_{ir} has been determined. The value of k_q so determined is also that of k_{ir} for the unreactive amine.

The experiments summarized in Table I were carried out largely at concentrations of amine $> \sim 0.05 M$ and the results apply to these conditions. Variations in value of k_d were observed and appear anomalous. They are high and vary with structure of amine, although they are obtained from satisfactorily linear plots of $1/\varphi$ vs. $1/(Am)$. Further studies are in progress at lower concentrations of amine.²⁸ Plots over the whole range show curvature, while linear portions of different slopes are apparently observed over wide ranges of concentrations, 5.0–0.05 and 0.05–0.005 *M*. Higher limiting quantum yields, higher slopes, and higher apparent values of k_d are observed in the high concentration range. These results do not arise from variations in efficiency of the dark reaction (eq 5) and from changes in pH, light-absorbing transients, or singlet quenching. The effect appears to arise from a higher order amine contribution, possibly from ground state ketone-amine complexation or from nucleophilic catalysis of hydrogen transfer in the charge-transfer complex. This work will be described in detail elsewhere.

3. Solvent Effects

Solvent properties may influence photoreduction by amines by affecting intersystem crossing efficiency, the importance of light-absorbing by-products, and the relative importance of quenching and hydrogen abstraction. In photoreduction of 0.1 *M* benzophenone by 1 *M* 2-butyl-

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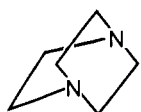
(26) S. G. Cohen, G. A. Davis, and W. D. K. Clark, *J. Amer. Chem. Soc.*, **94**, 869 (1972).

(27) W. H. Moore, G. S. Hammond, and R. B. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

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amine, the quantum yield, 1.1, was essentially unaffected as the solvent was varied from benzene to acetonitrile to aqueous pyridine.¹³ Triplet yield from excited benzophenone is solvent independent,²⁹ and light-absorbing by-products are avoided in this system. The conversion of the possible dipolar charge-transfer complex intermediate to uncharged ground state molecules or to radicals might be affected similarly by change in polarity. On the other hand, solvent effects might be masked by the high concentration of amine used in this study.

Effects of solvent and structure of amine on quantum yields of photoreduction of benzophenone at low concentrations of amine are being studied. The bridgehead bicyclic amine



1,4-diazabicyclo[2.2.2]octane (DABCO), which is a photoreducing agent for benzophenone and even for the normally unreactive *p*-aminobenzophenone⁶ in benzene solution, does not photoreduce benzophenone and is an effective quencher for it in polar solvents.²⁵ High stability of the CT complex in polar solvent may favor spin inversion and quenching over hydrogen transfer.

III. Photoreduction of Acetophenone and Related Compounds

A. Intermolecular Reactions

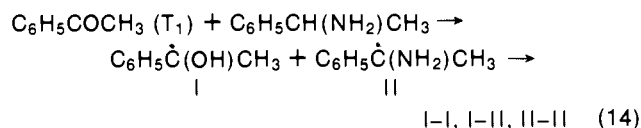
1. Products and Kinetics

Acetophenone is photoreduced by alcohols in overall reactions similar to those in the photoreduction of benzophenone.³⁰⁻³² Acetophenone, however, has low-lying n, π^* and π, π^* triplet states of similar energy^{33,34} and with increasing polarity of solvent π, π^* character may become predominant leading to lower reactivity in hydrogen abstraction.³⁵ Quantum yields for photoreduction by alcohols are somewhat lower than for benzophenone.³³ There is a larger energy gap between the n, π^* and π, π^* triplet states of benzophenone,³⁶ and solvent effects on its reactivity must probably be attributed to other factors.

Acetophenone was photoreduced readily by 1 *M* amine in benzene solution, by 2-butylamine, $\varphi \sim 1.1$, more rapidly than by α -methylbenzylamine, and in each case somewhat more rapidly than by alcohols of corresponding structure.³⁷ Photoreduction by 2-butylamine led to quantitative yields of mixed meso and *dl* acetophenone pinacols, and to the imine, *N*-2-butylidene-2-butylamine. Hydrogen abstraction and reduction of ground state ketone by the amine-derived radical, reactions similar to those written for benzophenone, probably occur (eq 4-7). The reduction was 0.7 as fast in neat 2-butylamine as in 1 *M* 2-butylamine, an effect not observed in photo-

reduction of benzophenone by this amine. Light-absorbing by-products were not observed and the decreased reactivity in neat amine may be due to greater quenching of π, π^* excited states.

Photoreduction of acetophenone and of 4-methylacetophenone by α -methylbenzylamine led to a mixture of pinacol, cross-coupling product, and diamine.³⁷ The initial abstraction in these cases leads to radicals of similar stability, both of which survive and combine (eq 14). Radicals formed by abstraction from purely aliphatic amines (and alcohols) may reduce ground state aromatic ketones, leading solely to the ketone derived radical and thence only to its pinacol.



Photoreduction of acetophenone by α -methylbenzylamine³⁷ was accompanied by formation of light-absorbing by-products, possibly products of para-para and α -para coupling,³⁸ and these were formed to a much greater extent at high concentration of amines. Rates of photoreduction thus first increased with dilution with benzene and then decreased at high dilution. Extrapolation of dilute solution values led to a limiting quantum yield $\varphi = 0.61$, $k_d/k_{iR} = 0.049$ *M*. Quenching by naphthalene led to $k_q/k_{iR} = 84$, $k_{iR} = 7 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$, $k_d = 3.5 \times 10^6 \text{ sec}^{-1}$. The high value of k_{iR} is consistent with a charge-transfer mechanism (eq 3). The maximum quantum yield for this reaction is 1, due to the stability of the amine-derived radical. The efficiency and ratio k_h/k_e are similar to those for photoreduction of benzophenone by 2-butylamine, for which the quantum yield is ~ 1.1 and the maximum theoretical value is 2. It may be noted that a charge-transfer mechanism, analogous to eq 3, is proposed for the photoreduction of trifluoroacetophenone by alkyl aromatics, the interaction of excited ketone being with a π rather than n donor, and leading to high values of k_{iR} and low quantum yields.³⁹

2. Stereochemistry

The ratio of *dl* and meso pinacols in the photoreduction of acetophenone by amines has been examined.⁴⁰ This ratio is 0.9-1.0 for several aliphatic amines and 0.8 for DABCO, as compared with 1.1 for reduction by 2-propanol and 3.0 for reduction by alkaline 2-propanol. It was suggested that the difference might arise from dimerization of the charge-transfer ion pairs. Dimerization of ketyl radicals hydrogen-bonded to amines might be a preferable explanation. Such an effect may account for asymmetric induction in photopinacolization of acetophenone in a chiral amine, (+)-1,4-bis(dimethylamino)-2,3-dimethoxybutane, acting as solvent and hydrogen donor.⁴¹ The ratio of *dl* and meso pinacols was 0.85 and the optical rotation indicated 6% *R,R* pinacol. The recovered amine showed no racemization. Such photoreduction by chiral alcohols does not lead to optically active pinacols,^{30,32,42} indicating a specific interaction of the active amine.

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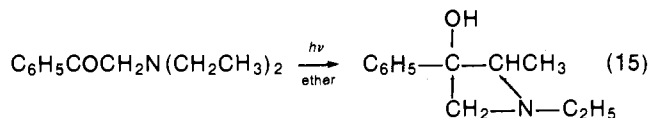
(41) D. Seebach and H. Daum, *J. Amer. Chem. Soc.*, **93**, 2795 (1971).

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B. Intramolecular Reactions

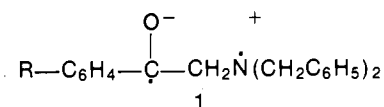
1. Dialkylphenacylamines

Dialkylphenacylamines, $C_6H_5COCH_2NR_2$ ($R = CH_3, C_2H_5, i-C_3H_7$), undergo photochemical cyclization to form the corresponding 3-hydroxyazetidines⁴³ in 9, 26, and 22% yields, respectively, (eq 15). The reaction may proceed by intramolecular hydrogen abstraction and cyclization of an intermediate biradical

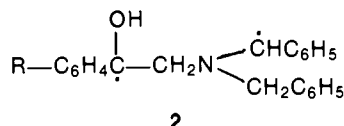


It is complicated and limited by type II cleavage to acetophenone and imine, the latter isolated as its trimer.⁴³

N,N -Dibenzylphenacylamine, $C_6H_5COCH_2N(CH_2C_6H_5)_2$, and N,N -dibenzyl-4-phenylphenacylamine undergo type II photoelimination to form acetophenone and 4-phenylacetophenone, respectively, and N -benzalbenzylamine, with similar quantum yields, 0.14 and 0.12, respectively, despite the $n-\pi^*$ excited state of the former and $\pi-\pi^*$ excited state of the latter.⁴⁴ The reactions were not quenched by 1,3-cyclohexadiene and piperylene. Reaction via a very rapidly formed zwitterion (1)



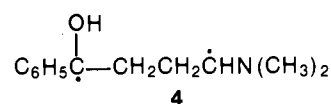
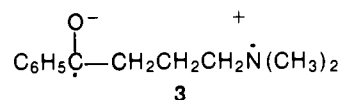
which could revert to ground state starting material or go on to a 1,4-biradical (2), analogous to eq 3, was proposed.



posed to account for the observed characteristics—reactivity of $\pi-\pi^*$ triplet and low sensitivity to quencher, accompanied by only moderate quantum yield.

2. γ -Dimethylaminobutyrophenone

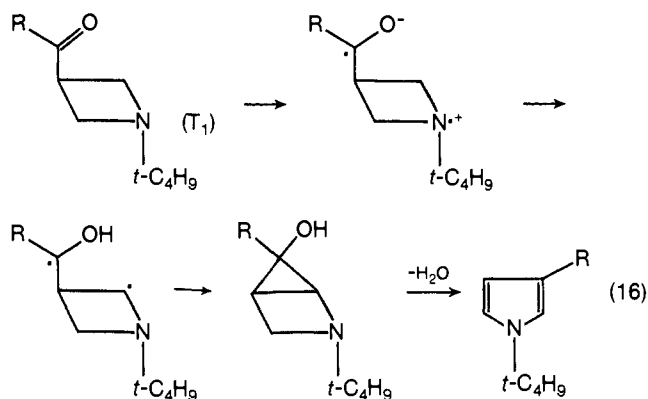
Irradiation of γ -dimethylaminobutyrophenone,⁴⁵ $C_6H_5COCH_2CH_2CH_2N(CH_3)_2$, leads to almost quantitative yield of acetophenone by type II elimination, in a reaction which has low quantum yield and yet is very insensitive to 1,3-pentadiene in benzene and acetonitrile solution. The quantum yield is higher, $\phi = 0.25$, and the sensitivity to quencher is higher in methanol, while the quantum yield is very low and the sensitivity to quencher is high in acidified methanol. Again reaction analogous to that of eq 3, via a zwitterion (3), which could revert to ground state starting material or go on to 1,4-biradical (4), was proposed. Formation of the dipole may be relatively unaffected by change of solvent from benzene to acetonitrile. Solvation may decrease the rate of zwitterion formation and increase radical formation in methanol. Protonation by acid inhibits zwitterion formation and reaction. It is also observed that two amines, triethylamine and dimethyl-*tert*-butylamine, quench type II elimination of



valerophenone with equal high efficiencies, while causing its reduction, and a charge-transfer process (eq 3) was suggested to account for these effects.⁴⁵

3. Azetidenyl and Aziridenyl Ketones

3-Aroylazetidines, irradiated in ethanol, are converted to arylpyrroles in high yield.⁴⁶ The 3-benzoyl and 3-(4-phenyl)benzoyl compounds behave similarly, the $n-\pi^*$ and $\pi-\pi^*$ triplets having similar reactivities. Quantum yields are low, ~ 0.1 , the reactions are very insensitive to quenching by piperylene, the hydrochloride salts are photochemically inert, and a rapid charge-transfer reaction, analogous to eq 3, was postulated (eq 16). The isomeric 2-azetidenyl ketone systems led to a complex mixture of photoproducts.⁴⁶



In a recent review on photochemical transformations of small ring carbonyl compounds, the photochemical properties of 2-benzoylaziridines are described.⁴⁷ The course of the reactions varies with the substituents on the aziridine ring and their steric relations and need not be reviewed here. The reactions proceed by intramolecular hydrogen transfer and may involve charge-transfer mechanisms.

IV. Biacetyl and Acetone

A. Biacetyl⁴⁸

1. Aromatic Amines

Biacetyl $n-\pi^*$ triplet undergoes efficient quenching and photoreduction by alcohol and stannane hydrogen donors, with rate constants $\sim 10^3-10^5 M^{-1} sec^{-1}$ for alcohols. Aniline, diphenylamine, triphenylamine, N,N -dimethylaniline, and N,N -diethylaniline quench the phosphorescence and fluorescence of biacetyl efficiently and do not lead to photoreduction, despite the availability of transferable α -hydrogen in the latter two compounds. Fluorescence quenching rate constants appear to be essentially diffusion controlled, $5-10 \times 10^9 M^{-1} sec^{-1}$.

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Phosphorescence quenching rate constants were 3×10^8 – $2 \times 10^9 M^{-1} \text{sec}^{-1}$, except for triphenylamine, $3 \times 10^7 M^{-1} \text{sec}^{-1}$.

2. Aliphatic Amines

Purely aliphatic secondary and tertiary amines quenched the fluorescence of biacetyl, $k_q \sim 1\text{--}8 \times 10^9 M^{-1} \text{sec}^{-1}$, and primary amines did not quench. All three classes of aliphatic amines quenched triplet phosphorescence, $k_q \sim 2\text{--}8 \times 10^7 M^{-1} \text{sec}^{-1}$. Irradiation with aliphatic amines, except DABCO, appeared to lead to photoreduction of biacetyl. Rates of quenching by amines are enhanced somewhat as solvent polarity is increased. The effect is largest on triphenylamine. Quenching by amines was proposed to proceed by a charge-transfer mechanism.⁴⁸

Efficient quenching by aromatic amines and by DABCO without photoreduction may indicate that the favorable reduction potential of the carbonyl compound and low ionization potential of these amines lead to a very stable CT complex intermediate, a situation which enhances k_e over k_h (eq 3). Quantum yields were not given for photoreduction by the aliphatic amines.

B. Acetone-Sensitized Reactions of Amides

Acylation of amines lowers the availability of the n electrons and such amides are less effective photoreducing agents than amines. They appear to be more effective than esters. Acetophenone was photoreduced slowly by *N*-acetyl- α -methylbenzylamine, $\varphi \sim 0.03$, and was not photoreduced under comparable conditions by the corresponding ester, α -methylbenzyl acetate.³⁷

There appears to be no report of photoreduction of acetone by amines. However, flash photolysis of acetone in aqueous solutions of amides led to transients which were characterized as those formed by abstraction of hydrogen by excited acetone from the amides. The acetone was reduced to the 2-hydroxy-2-propyl radical, $\text{CH}_3\text{C}(\text{OH})\text{CH}_3$, and hydrogen was abstracted mainly from the *N*-methyl group of *N*-methyl amides, and mainly from the acyl group of primary amides.⁴⁹ Irradiation of acetone in the presence of protected glycine dipeptides and glycylalanyl and glycylleucyl methyl esters led mainly to abstraction of hydrogen from the methylene group of glycine. In the presence of isobutene, 1-butene, or toluene, the glycol residues were converted to leucine, norleucine, or phenylalanine residues, respectively, in yields up to 60%,⁵⁰ and some asymmetric induction has been noted.^{51–53} The study has been extended to modification of glycine-containing polypeptides.^{52,53}

V. Photoreduction of Aminobenzophenone and Related Compounds

A. Aminobenzophenones and *o*-Hydroxybenzophenone

1. *p*-Aminobenzophenone (PAB)

m-Aminobenzophenone, *o*-Aminobenzophenone, and *o*-Hydroxybenzophenone

p-Aminobenzophenone (PAB) does not undergo pho-

to-reduction at substantial rates by alcohols, and this was attributed to its chemically unreactive $\pi\text{--}\pi^*$ or charge transfer, CT, triplet^{54,55} present in polar solvents. It was photoreduced, albeit with low quantum yield, by cyclohexane,⁵⁵ which is less reactive than alcohols in photoreducing benzophenone. This was attributed to inversion of levels, the more reactive $n\text{--}\pi^*$ triplet of PAB being more stable and present in the nonpolar solvent.⁵⁵

Study of photoreduction of PAB by amines⁶ showed exceedingly low reactivity in primary amines, probably less than in alcohols.^{6b} This was attributed to solvation or hydrogen bonding of the polar CT triplet by N and H of primary amines. It was photoreduced to the pinacol by neat diisopropylamine, $\varphi \sim 0.04$.

It was photoreduced by triethylamine to pinacol and cross-coupling products. Quantum yields, φ , varied with conditions from 0.22 to 0.57. Quantum yields were higher (i) at lower initial concentration of PAB, (ii) in solution of amine in hydrocarbon than in neat amine, and (iii) at higher light intensity. Quantum yields for photoreduction by triethylamine rose 50% as concentration of ketone decreased from 0.020 to 0.001 *M*. This effect indicates deactivation of triplet by ground state PAB with efficiency half that of a diffusion-controlled quencher. This may be accounted for by quenching by charge transfer by an aromatic amine which does not possess transferable α -hydrogen or by exciplex formation. This concentration effect was also observed in photoreduction of PAB by the secondary amine.

Quantum yields for photoreduction of 0.001 *M* PAB by triethylamine increased on dilution with cyclohexane (0.4 in neat amine, ~ 0.55 in 0.10–1.0 *M* triethylamine). Quantum yields rose similarly on dilution with benzene, while dilution with acetonitrile effectively prevented photoreduction by 1 *M* triethylamine. While it might be held⁵⁵ that hydrocarbons led to the reactive $n\text{--}\pi^*$ triplet and the dipolar solvent to the unreactive CT triplet, study of triplet yields by stilbene isomerization indicated a strong effect of solvent on efficiency of intersystem crossing.²⁹ Essentially no triplet of PAB was detected in 2-propanol; 0.06 that from benzophenone was observed in acetonitrile and about 0.3–0.4 of that from benzophenone in cyclohexane and benzene, respectively. Such yields of $n\text{--}\pi^*$ triplets in the hydrocarbons are consistent with the observed reactivity of PAB to tertiary amines in these solvents. The lower reactivity in neat tertiary amine may be due to some singlet quenching or to π,π^* character in the triplet. The low reactivity of PAB in 2-propanol may be due to absence of triplet, while in acetonitrile there may be a low yield of unreactive CT triplet.²⁹

The decrease of φ with decreasing, 1.0–0.01 *M*, concentration of triethylamine in cyclohexane is small and leads to $k_d/k_r = 0.011 M$. The effect of naphthalene, after correction for quenching by ground state ketone, leads to $k_{ir} \sim 4 \times 10^7 M^{-1} \text{sec}^{-1}$, $k_d \sim 5 \times 10^5 \text{sec}^{-1}$.

The bridgehead bicyclic diamine DABCO was also a moderately effective photoreducing agent for PAB, $\varphi \sim 0.2$, and this, combined with the other properties of photoreduction by amines, low values of k_d/k_{ir} and k_q/k_{ir} , and moderate quantum yields, led to the initial proposals that these reactions proceed by a charge-transfer interaction.^{6b,7}

m-Aminobenzophenone (MAB) was photoreduced by 1 *M* triethylamine in cyclohexane,^{6b} $\varphi \sim 0.07$ at 0.006 *M*

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(50) D. Elad and J. Sperling, *Chem. Commun.*, 655 (1968); *J. Chem. Soc. C*, 1579 (1969).

(51) D. Elad and J. Sperling, *Chem. Commun.*, 234 (1969).

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ketone as compared with $\varphi \sim 0.5$ for PAB under comparable conditions. The lower efficiency may arise from the greater importance of back-electron transfer and quenching in the CT intermediate, k_e , due to the electron-donating substituent in the meta position. Study of stilbene isomerization indicated that intersystem crossing and triplet formation was at least as efficient for MAB as for PAB.²⁹

o-Aminobenzophenone (OAB) showed little if any photoreduction by triethylamine, at most an order of magnitude less than MAB.^{6b} The *o*-amino group may lead to efficient quenching of either singlet or triplet by reversible intramolecular electron or hydrogen transfer. No triplet of OAB was detected by stilbene isomerization in 2-propanol and in benzene. That conditions may be found under which similar possible self-quenching need not occur is indicated by the photoreduction of *o*-hydroxybenzophenone by hexamethylphosphoric triamide,⁵⁶ $\varphi = 0.11$.

2. *p*-Dimethylaminobenzophenone and Bis(*p,p'*-dimethylamino)benzophenone, Michler's Ketone

Photoreduction of *p*-dimethylaminobenzophenone (DMAB) by triethylamine has been examined briefly.^{6b} The rate of photoreduction by triethylamine increases with decreasing initial concentration of DMAB, rising 25% from 0.020 to 0.001 *M* ketone, to quantum yield $\varphi \sim 0.4$.^{6b} This effect of concentration is less than that observed in the photoreduction of *p*-aminobenzophenone and indicates either less efficient formation of quenching exciplex or partial quenching and partial reduction in the interaction of triplet with ground state ketone containing transferable α -hydrogen in the *N*-methyl groups.

Evidence of such photoreduction *via* interaction of triplet with ground state ketone is seen in irradiation of the related compound, Michler's ketone (MK). This compound, like *p*-aminobenzophenone, is not photoreduced in 2-propanol but is photoreactive in cyclohexane.³³ Irradiation of Michler's ketone in benzene led⁵⁷ to abstraction of hydrogen by triplet ketone from an *N*-methyl group and coupling of the ketyl and amine-derived radicals. The reaction was retarded by ethanethiol, and in the presence of ethanethiol-*S-d* all 12 methyl hydrogens may be exchanged. Retardation of photoreduction and introduction of deuterium by action of thiols has been described for a number of systems and reviewed.⁵⁸ The limiting quantum yield for photodestruction of Michler's ketone was less than unity, indicating that self-quenching accompanied the hydrogen abstraction. From the effect of concentration of Michler's ketone on its photodestruction and from quenching by cyclohexadiene, the rate constant for triplet decay and complex formation are $k_d = 9 \times 10^6 \text{ sec}^{-1}$ and $k_c = 1.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.

A related reaction was observed in irradiation of Michler's ketone and benzophenone in 2-propanol,⁵⁹ leading to the product of coupling of the benzophenone ketyl radical and that derived from abstraction of hydrogen from an *N*-methyl group of Michler's ketone, $\varphi = 0.08$. In this case triplet Michler's ketone was formed and apparently reacted with benzophenone to form a triplet exciplex which led to the two radicals.

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(59) C. C. Wamser, G. S. Hammond, C. T. Chang, and C. Baylor, Jr., *J. Amer. Chem. Soc.*, **92**, 6362 (1970).

3. Effects of Quaternization and Protonation

Quaternization of the amino group of *p*-dimethylaminobenzophenone by methylation leads to *p*-benzoylphenyltrimethylammonium salts. These compounds have low intensity long-wavelength $n-\pi^*$ absorption bands, in place of the high-intensity $\pi-\pi^*$ or CT bands of *p*-aminobenzophenone and *p*-dimethylaminobenzophenone, and they undergo photoreduction⁶⁰ similarly to benzophenone or *p*-benzoylbenzoate ion. Irradiation in 1:1 2-propanol-water led to the quaternized pinacols, $\varphi \sim 0.6$, and in 0.5 *M* 2-propylamine in water to the quaternary ammonium-substituted benzhydrol, $\varphi \sim 0.4$. The nonquaternized aminobenzophenones are inert in these media. The quaternary ammonium ketone was also photoreduced by 0.2 and 1.0 *M* *N*-acetyl-2-propylamine, $\varphi \sim 0.2$, attack apparently occurring at C-H α to N.^{60b} Similar reactivity was observed in photoreduction of benzophenone by 2.5 *M* *N*-acetylacetamide in benzene.⁶¹

Protonation also prevents conjugation between amino and carbonyl groups in the *o*- and *p*-aminobenzophenones and leads to salts which have low intensity long-wavelength $n-\pi^*$ absorptions in place of the high intensity CT bands of the free bases. *p*-Dimethylaminobenzophenone and *o*- and *p*-aminobenzophenones are photoreduced readily by 2-propanol in the presence of hydrochloric acid, while they are photoreduced very slowly if at all by 2-propanol in the absence of acid.⁶² Such acidification may not be used to promote their photoreduction by amines, since the amines become protonated and unreactive.

B. Xanthone, 4-Phenylbenzophenone, and 4-Phenylacetophenone

1. Xanthone

Xanthone was photoreduced by *N,N*-dimethylaniline to give 56% yield of xanthopinacol.^{16b}

The oxidation by oxygen of triethylamine, di-*n*-propylamine, and *n*-propylamine, photosensitized by xanthone, fluorenone, *p*-aminobenzophenone, and 2-acetonaphthone, was interpreted as occurring by initial hydrogen abstraction from the amine by the excited ketone. The reactions were much less efficient than when sensitized by benzophenone, apparently because of lower rates of hydrogen abstraction.⁶³ Xanthone has been reported not to be photoreduced by 2-propanol,² but to be photoreduced by ethanol, methanol, dioxane, and hydrocarbons.⁶⁴ The photoreduction of xanthone by xanthone, $\varphi = 0.6$, has been described.⁶⁵

2. 4-Phenylbenzophenone and 4-Phenylacetophenone

These ketones have low-lying $\pi-\pi^*$ triplets and are not photoreduced by alcohols and hydrocarbons. They were photoreduced by di-*n*-propylamine, $\varphi = 0.2$, and high yields of the pinacols and the imine were reported.⁴⁴ Irra-

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(64) V. Zanker and E. Ehrhardt, *Bull. Chem. Soc. Jap.*, **39**, 1694 (1966).

(65) J. B. Guttenplan, Ph.D. Thesis, Brandeis University, 1970.

diations of 4-phenylbenzophenone in aqueous and ethanolic triethylamine led to the pinacol.²¹

VI. Photoreduction of Fluorenone

A. Properties of Excited Fluorenone

Fluorenone was not photoreduced by 2-propanol,² 9-fluorenol,⁶⁶ or hydrocarbons.⁶⁷ It was photoreduced by fluorene and xanthene in benzene.⁶⁵ It formed photoaddition products with olefins with low efficiency⁶⁸ and adds readily to ketenimines.⁶⁹ While assignment of configuration to the excited states is not unequivocal, evidence supports low-lying $\pi-\pi^*$ excited singlet and triplet states.⁷⁰ Quantum yields for singlet fluorescence were higher in dipolar aprotic solvents, low in hydrocarbons; intersystem crossing rates and triplet yields were lower in polar solvents, higher in hydrocarbons.^{65,71-74} These results were attributed to the effects of polarity on the stability and ordering of configurations in the singlet and triplet manifolds.⁷¹ There may be specific complex formation between the excited singlet and hydroxylic solvents⁷⁰ leading to very low triplet yields.⁷³ Triplet yields were reported to be 1.03 in cyclohexane,⁷⁴ 0.93 in benzene.^{74,75} The triplet energy is 53 kcal/mol.⁷⁰

B. Photoreduction by Aliphatic Amines

1. Effects of Concentration of Amine

Photoreduction of fluorenone by aliphatic amines has been studied in cyclohexane,^{65,66,73} benzene,⁷⁶ and acetonitrile.^{63,66,76} Photoreduction by triethylamine, neat and in cyclohexane, led to the pinacol and to the coupling product of the 9-hydroxy-9-fluorenyl and 1-diethylamino-1-ethyl radicals.⁶⁶ Photoreduction by primary, secondary, and tertiary amines in benzene and acetonitrile was reported to lead to the pinacol and to 9-fluorenol, with secondary amines and acetonitrile leading more to the fluorenol.⁷⁶ The latter may at least in part have arisen from decomposition of the pinacol during work-up.

Fluorenone was photoreduced by a primary amine, 2-butylamine, with low efficiency, $\varphi \sim 0.04$ in neat amine, $\varphi \sim 0.02$ in 0.1 *M* amine in cyclohexane.⁶⁶ Similarly, low photoreducing efficiencies, decreasing with decreasing concentration, were observed for cyclohexylamine in benzene and acetonitrile and for α -methylbenzylamine in benzene.⁷⁶

Photoreduction by a secondary amine, *N*-methyl-2-butylamine, was slightly more efficient, $\varphi \sim 0.05$ in neat amine, and this value rose to $\varphi \sim 0.13$ in 0.08 *M* amine in cyclohexane.⁶⁶ Similar results, decreasing quantum yields at high concentrations of amine, were observed in photoreduction by diethylamine in benzene and acetonitrile, and by diisopropylamine in benzene.⁷⁶

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(76) G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969).

Photoreduction by a tertiary amine, triethylamine, was slightly more efficient, $\varphi = 0.09$ in neat amine. The quantum yield rose tenfold to $\varphi = 0.9$ in 0.1 *M* amine in cyclohexane, and decreased very slowly with further dilution, $\varphi = 0.6$ at 0.02 *M* amine.⁶⁶ An inverse plot of the latter data led to a limiting quantum yield of 1.0, $k_d/k_{iR} = 0.013$ *M*; quenching by stilbene led to $k_q/k_{iR} = 140$, $k_{iR} = 1.7 \times 10^7$ *M*⁻¹ sec⁻¹ based on $k_q = 2.4 \times 10^9$ *M*⁻¹ sec⁻¹, and $k_d = 2.2 \times 10^5$ sec⁻¹.⁶⁶ A similar quenching study led to $k_{iR} = 2.2 \times 10^6$ *M*⁻¹ sec⁻¹ for reaction of fluorenone triplet with the secondary amine, *N*-methyl-2-butylamine.⁶⁶ A marked decrease in efficiency of photoreduction was also observed with increasing concentration of the triethylamine in benzene and acetonitrile, and of *N,N*-dimethylbenzylamine in benzene.⁷⁶ Decreasing efficiency of photoreduction with increasing concentration of secondary and tertiary amine was attributed at least in part to quenching of the singlet. This was supported by quenching of fluorescence of fluorenone by secondary and tertiary amine in benzene and by all three classes of amines in acetonitrile.⁷⁶ Rates of singlet quenching were highest for tertiary amines and paralleled ionization potentials.⁷⁶ Quenching of fluorenone singlet by triethylamine has been studied by others.^{71,72}

2. Effects of Medium in Photoreduction by Triethylamine

Fluorescence quantum yields, triplet yields as indicated by stilbene isomerization, and quantum yield of photoreduction of 0.005 *M* fluorenone by 0.005 *M* triethylamine have been measured as affected by solvent, and compared with the efficient reduction observed in cyclohexane.⁷³ A small quantity of acetonitrile, ~ 0.25 *M*, increases fluorescence ca. threefold, may increase triplet yield slightly, and increases photoreduction $\sim 30\%$ to $\varphi = 0.30$. The acetonitrile may favor formation of the CT complex, k_{iR} , and hydrogen transfer, k_H (eq 3). Neat acetonitrile as solvent increases fluorescence 100-fold, decreases intersystem crossing, and halves the yield of triplet and lowers the photoreduction efficiency $\sim 20\%$. 2-Propanol as solvent increases fluorescence about tenfold and lowers the triplet yield and photoreduction quantum yield to about 0.1 that found in cyclohexane.⁷³

The photoreduction of fluorenone in neat, ~ 8.6 *M*, triethylamine may be quenched by stilbene, 0.08 *M* trans-stilbene decreasing the rate $\sim 30\%$ and undergoing isomerization in the process.^{65,73} Stilbene is not a quencher for singlet fluorenone;⁷⁴ triethylamine quenches the singlet fluorescence at a diffusion-controlled rate or nearly so^{71,72} and was present in 100-fold excess over stilbene in these experiments. Stilbene may not compete with triethylamine for the singlet but may compete with it for the triplet, which it quenches at a nearly diffusion-controlled rate,⁷⁷ $k_q/k_{iR} = 140$.⁷³ It appears that while some photoreduction of the singlet in neat triethylamine⁷² may not be ruled out, a very substantial part proceeds via fluorenone triplet. The triplet may not arise by normal intersystem crossing in the presence of 8.6 *M* diffusion-controlled quencher for the singlet.⁷⁴ It may arise via a singlet fluorenone-triethylamine charge-transfer complex, which leads in part to ground state fluorenone and in part to excited triplet fluorenone. Formation of triplet by such a mechanism has been described in other systems.⁷⁸

(77) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

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3. Effects of Structure of Tertiary Aliphatic Amines

Photoreduction of fluorenone by tertiary aliphatic amines may in general be a very efficient process, due to high values of k_{1r} . It should be carried out at low concentration of amine to avoid quenching of singlet, and may be carried out with little excess of amine. Quantum yields at 0.01 *M* amine are little different from limiting quantum yields and are determined by k_h/k_e ratios and by extent of donation of a second reducing group from amine-derived radical to ground state ketone, either by reactions analogous to that of eq 11 or by formation of enamines. Isolation of the cross-coupling product⁶⁶ in reduction by triethylamine indicates that a substantial part of this amine-derived radical survives and does not donate a second reducing group to fluorenone in hydrocarbon. Quantum yields for photoreduction by 0.01 *M* tertiary amine in benzene were 0.8 for triethylamine, 1.0 for methyl-diethylamine, and 1.2 for ethyl-diisopropylamine.⁷⁹ Analysis of the hydrolyzed photoproduct from methyl-diethylamine indicated that more than 50% of the attack may take place on the methyl group. Hydrolysis of the photoproduct from ethyl-diisopropylamine led to 0.5 mol of aliphatic carbonyl compound per mole of fluorenone reduced. The acetaldehyde:acetone ratio was 9:1 indicating strongly favored abstraction of hydrogen from the less hindered position, as was observed to a lesser extent in certain abstractions by benzophenones.^{12,13}

C. Reactions with Aromatic Amines

1. Photoreduction and Quenching by Para-Substituted *N,N*-Dimethylanilines (*p*-*X*-DMA)

Fluorenone was reported to be photoreduced by dimethylaniline, leading to the pinacol, ~58% yield.^{16a}

Effects of polar substituents on photoreduction and quenching of fluorenone triplet by substituted dimethylanilines have been described,⁸⁰ and these studies have been extended,⁷⁹ Table III. For compounds which were effective photoreducing agents quantum yields at 0.01 *M* amine were determined, and values of k_{1r} were obtained by quenching by stilbene of the photoreduction. Values of k_{1r} for substituted dimethylanilines which were not efficient reducing agents were obtained from use of them as quenchers for photoreduction of fluorenone by dimethylaniline or by *p*-carboethoxydimethylaniline. In general, the effects arise from the effect of the substituent on the dimethylamino-aromatic system and not from interaction of the triplet with the substituent. Bromobenzene, phenetole, phenyl methyl sulfide, and acetanilide, each 0.01 *M*, had no effect on photoreduction of fluorenone by 0.01 *M* dimethylaniline. However when two of these inert substituents, ethoxy and acetamido, were combined in one system, quenching was observed (phenacetin, $k_q = 1.5 \times 10^7 M^{-1} \text{sec}^{-1}$).⁷⁹

A linear plot of $\log k_{1r}$ vs. σ^+ may be constructed with a high negative value of ρ , -1.83. This supports development of a positive charge at N and the charge-transfer mechanism (eq 3). For *p*-CN, σ^- fits the linear plot indicating important conjugative stabilization of the ground state amine. The value for *p*-N(CH₃)₂ lies off the plot since the rate has become almost diffusion controlled and is no longer responsive to increasingly negative σ^+ . The rate of interaction of fluorenone triplet with dimethylanil-

TABLE III. Photoreduction and Quenching of 0.003 *M* Fluorenone by *p*-XC₆H₄N(CH₃)₂ in Benzene

X	$k_{1r}, M^{-1} \text{sec}^{-1}$	Quantum yield, ϕ	
		0.01 <i>M</i> amine	ϕ_{11m}
<i>p</i> -CN	3.2×10^6	0.12	0.18
<i>p</i> -CO ₂ C ₂ H ₅	2.9×10^7	0.17	
<i>p</i> -COCH ₃	6.0×10^7	0.10	
<i>p</i> -Br	2.9×10^8	0.27	0.31
<i>p</i> -Cl	2.5×10^8	0.37	
<i>p</i> -H	4.7×10^8	0.58	0.80
<i>p</i> -CH ₃	2.6×10^9	0.71	0.76
<i>p</i> -OC ₂ H ₅	8.9×10^9	0.32	
<i>p</i> -NHCOCH ₃	5.3×10^9	<0.02	
<i>p</i> -SCH ₃	5.7×10^9	0.30	
<i>p</i> -N(CH ₃) ₂	9.5×10^9	<0.02	
<i>p</i> -NH ₂		<0.02	
<i>m</i> -OH		<0.02	

ines is sensitive to the electron-donating and withdrawing power of the substituents, values of k_{1r} in Table III varying by more than three orders of magnitude.

The dependence of fluorenone on electron availability may arise from its low triplet energy and favorable reduction potential. Benzophenone and *p*-aminobenzophenone with greater, more favorable, triplet energies and higher, less favorable, reduction potentials show very small variation of k_{1r} with polarity of substituent in dimethylanilines.⁷⁹ Their reactions may depend less upon electron availability and show more hydrogen abstraction character, although this too has a polar contribution.⁷ Abstraction of hydrogen from substituted toluenes⁶⁷ shows a dependence on σ^+ , $\rho = -1.16$, and quenching of luminescence of biacetyl by phenols and anilines shows dependence on σ^\pm , with ρ values ranging from -0.33 to -1.15.⁸¹

While values of k_{1r} rise smoothly with electron donation by the substituent, quantum yields for photoreduction rise initially from *p*-CN, $\phi = 0.12$, to a maximum at *p*-CH₃, $\phi = 0.71$, and then fall with further electron availability (Table III). Electron-attracting substituents may favor electron return and quenching in the CT complex, k_e (eq 3), while excess electron availability may lead to a stable long-lived CT complex, in which spin inversion and quenching may be favored over hydrogen transfer, k_h . Substituents which lead to the highest values of k_{1r} may lead to no photoreduction and to very efficient quenching. The *p*-NH₂ and *m*-OH substituents may lead to quenching by their own interactions. The *p*-Br substituent may lower quantum yield relative to *p*-Cl by a heavy atom effect in the CT complex.

Effects of concentration of amine (<0.02 *M*) on quantum yields, studied for four compounds, led to the limiting quantum yields indicated in Table III. At high concentrations, marked decrease in quantum yields was observed, presumably due to singlet quenching. Values of k_d were obtained and found to vary, $1.7\text{--}6.0 \times 10^5 \text{sec}^{-1}$, and were lower for amines with lower values of k_{1r} .⁷⁹

2. Photoreduction by *N,N*-Dialkylanilines

Effects of structure of alkyl groups in *N,N*-dialkylanilines on photoreduction of fluorenone in benzene have been studied and results are summarized in Table IV.⁷⁹

Values of k_{1r} , measured by quenching by stilbene, show little variation with changes in structure of the alkyl

(79) G. H. Parsons, Jr., and S. G. Cohen, unpublished results, supported by the U. S. Atomic Energy Commission.

(80) S. G. Cohen and G. H. Parsons, Jr., *J. Amer. Chem. Soc.*, **92**, 7603 (1970).

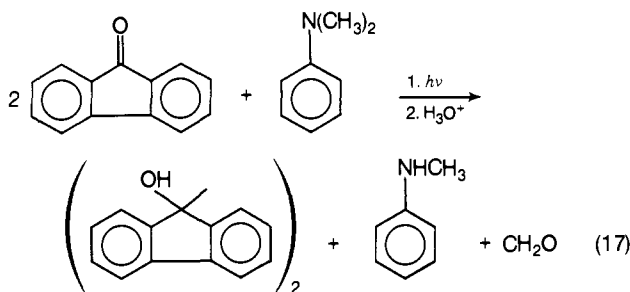
(81) N. J. Turro and T. Lee, *Mol. Photochem.*, **2**, 185 (1970).

groups, perhaps as steric and inductive effects counteract. Quantum yields for the methylanilines rise as the other alkyl group is enlarged; diethylaniline shows a maximum quantum yield in this set. Further increase in size decreases quantum yield, and the diisopropyl compound is the poorest photoreducing agent. This is opposite to what is observed in ethyldiisopropylamine, $\varphi = 1.2$

3. Products and Stoichiometry of Photoreduction by *N,N*-Dialkylanilines⁷⁹

Quantum yields for these reactions are less than 1 and give no evidence as to transfer of two reducing groups per amine molecule. However, irradiation of 0.10 *M* fluorenone in 0.064 *M* solutions in benzene of dimethylaniline, methylethylaniline, and methylisopropylaniline led to >92% reduction of ketone, supporting reduction of two ketone molecules by each molecule of amine.

Reduction of fluorenone by dimethylaniline in benzene, followed by hydrolysis, led to 98% pinacol, 90% *N*-methylaniline as the benzenesulfonamide, and 66% formaldehyde as the dimedone derivative, based on the stoichiometry shown in eq 17. A similar reduction with diethylaniline led to 99% pinacol and 100% acetaldehyde by chromatography, based on the stoichiometry of eq 17. This indicates either transfer of two reducing groups or quantitative disproportionation of amine-derived radicals. The latter is exceedingly unlikely for the ethyl compound and probably impossible for dimethylaniline.



Examination⁷⁹ by ir and nmr indicated that photoreduction by diethylaniline in benzene led to pinacol and *N*-ethyl-*N*-vinylaniline, amine-derived radical presumably reducing ground state ketone (eq 18).

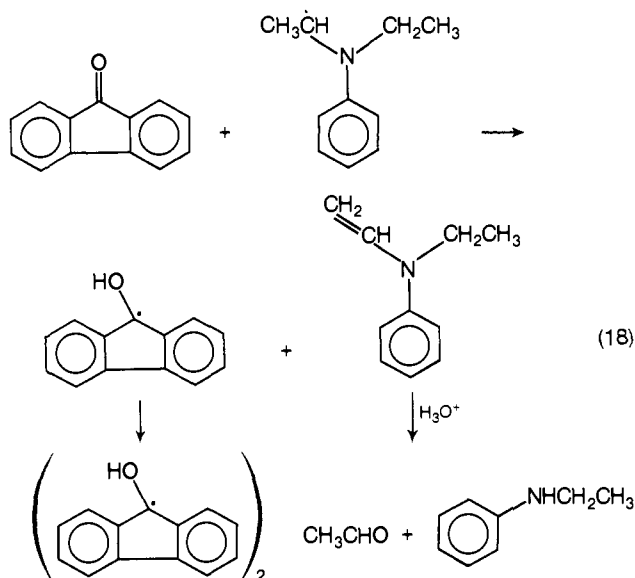
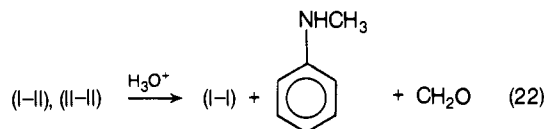
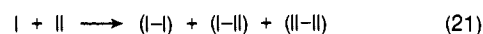
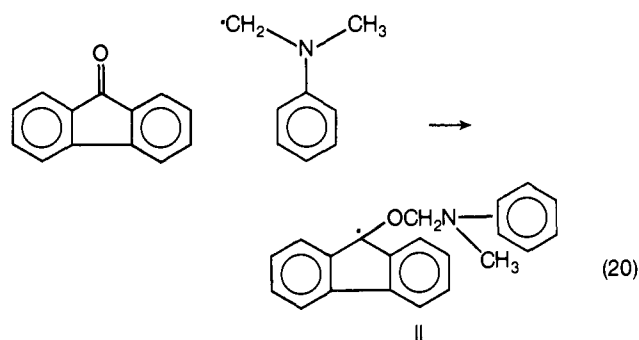
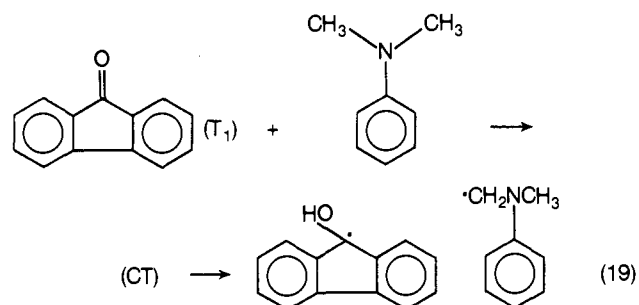


TABLE IV. Photoreduction of 0.003 *M* Fluorenone by 0.01 *M* C₆H₅NRR' in Benzene

R	R'	$k_{\text{Ir}}, M^{-1} \text{sec}^{-1}$	Quantum yield
CH ₃	CH ₃	4.7×10^8	0.58
CH ₃	C ₂ H ₅	2.8×10^8	0.62
CH ₃	<i>i</i> -C ₃ H ₇	4.8×10^8	0.68
C ₂ H ₅	C ₂ H ₅	4.4×10^8	0.79
<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	2.6×10^8	0.44
C ₂ H ₅	<i>i</i> -C ₃ H ₇		0.30
<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	2.3×10^8	0.09

Examination by ir and nmr indicated that in photoreduction by dimethylaniline in benzene a substantial part of the pinacol and all the *N*-methylaniline were formed in the hydrolysis step (eq 22). The spectral data were consistent with hydrogen abstraction, reduction of a second fluorenone by addition of amine derived radical, and combination and cross combination of radicals (eq 19–21). Similar results have been obtained in photoreduction of fluorenone by *p*-methyl- and *p*-methoxydimethylanilines.⁷⁹



Analysis by nmr of the photolysis of fluorenone and methylethylaniline in benzene indicated that abstraction occurs largely from the methyl group. After hydrolysis no acetaldehyde was detected. A similar result was obtained in photoreduction by methylethylaniline of benzophenone, *p*-aminobenzophenone, acetophenone, and 2-naphthaldehyde.⁷⁹ Demethylation appears to be the strongly preferred reaction course.

Analysis of a photolysate of fluorenone and methylisopropylaniline indicated ~20% attack on the isopropyl group, leading after hydrolysis to acetone, and major abstraction of hydrogen from the methyl group. Photoreduction by diisopropylaniline led to quantitative yield of acetone.⁷⁹

4. Quenching of Fluorenone by Anilines and *N*-Alkylanilines

Anilines which lack transferable α -hydrogen, as expected, are quenchers of fluorenone excited state and retard its photoreduction by triethylamine⁸² and by *N,N*-dimethylaniline.⁷⁹ In a series of para-substituted anilines, p -XC₆H₄NH₂, quenching of fluorenone triplet and retardation of photoreduction are enhanced by electron-donating substituents (X = C₂H₅O, CH₃) and slightly by Br, and retarded by electron-withdrawing substituents, X = CH₃CO, C₂H₅OCO, CN. Values of k_q were in the range 1×10^8 – $1 \times 10^{10} M^{-1} \text{ sec}^{-1}$. The data may be fitted to a linear plot of $\log k_{IR}$ vs. σ^\pm , $\rho = -0.9$,⁷⁹ supporting a CT mechanism. Yet, aniline-*N,N*-*d*₂ is a less efficient quencher than the protio compound, $k_H/k_D = 1.3$, indicating partial electron-partial hydrogen involvement in the quenching.⁷⁹

These compounds are also very efficient quenchers for the singlet of fluorenone, with rate constants approaching diffusion-controlled values, $\sim 2 \times 10^{10} M^{-1} \text{ sec}^{-1}$, and thus the rates were little affected by the substituents.⁸²

Diphenylamine,⁸² $k_q \sim 8 \times 10^9 M^{-1} \text{ sec}^{-1}$, is a more efficient quencher than aniline; DABCO,⁸² $k_q \sim 2 \times 10^9 M^{-1} \text{ sec}^{-1}$, is similar to aniline, while triphenylamine⁸³ is less efficient. That DABCO is a quencher and not a photoreducing agent may indicate that it forms a very stable CT complex with excited fluorenone.

Despite the presence of potentially transferable α -hydrogen, mono-*N*-alkylanilines resemble the anilines rather than the *N,N*-dialkylanilines and are not photoreducing agents, but efficient quenchers for fluorenone. Some interaction rate constants have been measured by using them as quenchers for photoreduction of fluorenone by *N,N*-dimethylaniline.⁷⁹ Values of the rate constants for a set of compounds, C₆H₅NHR, are (R = CH₃) $7.1 \times 10^9 M^{-1} \text{ sec}^{-1}$, (R = C₂H₅) $4.2 \times 10^9 M^{-1} \text{ sec}^{-1}$, (R = *i*-C₃H₇) 3.7×10^9 , (R = *c*-C₆H₁₁) $3.9 \times 10^9 M^{-1} \text{ sec}^{-1}$, and (R = H) $2.2 \times 10^9 M^{-1} \text{ sec}^{-1}$.

D. Physical Observations

Photolysis of fluorenone in a solution of triethylamine in ethanol led to the radical anion of the ketone, which was characterized by esr.²¹ It was not clear whether this was formed by electron abstraction from the amine via the CT complex (eq 3) or by dissociation of the 9-hydroxy-9-fluorenyl radical in the basic alcoholic medium. In addition to the pinacol and the mixed product formed in neat triethylamine and in its solution in benzene,⁶⁶ 9-fluorenol was formed in the photoreduction by the amine in alcoholic media.²¹ This could be due to reactions of the radical anion.^{12,84}

Irradiation of fluorenone in ethanol, ethers, and hydrocarbon did not lead to esr spectra.¹⁹ Irradiation of fluorenone in neat triethylamine or in solutions of triethylamine or *N,N*-dimethylaniline in tetrahydrofuran, dimethoxyethane, or toluene led to esr spectra which were interpreted in terms of the 9-hydroxy-9-fluorenyl radical. Spectra of the amine derived radicals were not characterized. Spectra of the 9-hydroxy-9-fluorenyl radical, and to a lesser extent of the benzophenone ketyl radical, are perturbed by triethylamine, presumably by hydrogen bonding with this basic amine.¹⁹ The effect may be great-

er with the hydroxy fluorenyl radical, which may be expected to be more acidic.

VII. Photoreduction of Naphthyl Carbonyl Compounds

A. Properties of Excited Naphthyl Carbonyl Compounds

Naphthyl carbonyl compounds have low-lying π - π^* triplet states⁸⁵ which show little if any reactivity in photoreduction by alcohols⁸⁶ and in oxetane formation,⁸⁸ while they may be photoreduced by tri-*n*-butylstannane.⁸⁷ It was reported that 2-acetonaphthone was photoreduced by triethylamine,^{66,21} leading to the pinacol.²¹ 2-Naphthaldehyde and 2-acetonaphthone showed triplet yields, as indicated by dimerization of 1,3-cyclohexadiene, which were high and unaffected by change of solvent from cyclohexane to acetonitrile.²⁶ Emission spectra and lifetimes indicated that the solvent did not affect the configuration of the triplet at least at 77°K.²⁶ Lower yields of triplet were observed in *tert*-butyl alcohol. Fluorenone⁷³ and *p*-aminobenzophenone²⁹ show diminished triplet yields in polar solvents and possible change in the configuration of triplets.³³ These naphthyl carbonyl compounds allow study of the effects of polarity of solvent on the photoreduction process itself, presumably independently of effects on triplet yields and configurations.²⁶

B. Photoreduction of 2-Naphthaldehyde²⁶

2-Naphthaldehyde was photoreduced rapidly by triethylamine in acetonitrile, about 0.15 as fast by di-*n*-propylamine and little if at all by primary amines. This order of activity is the same as that of other carbonyl compounds with π - π^* triplets.^{29,73} Photoreduction by triethylamine in benzene, *tert*-butyl alcohol, acetonitrile, or acetone led to the meso and *dl* pinacols. Quantum yields for photoreduction by 0.1 *M* triethylamine are high in dipolar solvents, acetonitrile and acetone, $\phi = 1.2$ and 1.0, respectively, less in *tert*-butyl alcohol, 0.6, possibly corresponding to lower triplet yield, but lower in benzene, cyclohexane, and isooctane, 0.4, <0.05 and ~ 0.0 , respectively, despite high triplet yields. Polarity of solvent was important for reactivity, possibly by assisting in formation of the initial CT complex (eq 3) since the naphthyl carbonyl compounds lack both high triplet energy and radical anion stability. The photoreductions do not appear to show evidence of singlet quenching at higher concentrations of amine. Quenching of the photoreduction by piperylene is 15-fold more effective in benzene than in acetonitrile, indicating a higher value to this extent of k_{IR} in the dipolar solvent. This is also seen in a lower dependence of quantum yield on concentration of amine in acetonitrile than in benzene. The bicyclic amine DABCO and the aromatic amine aniline, both with low ionization potentials, were unexpectedly poor quenchers for the photoreduction by triethylamine, while DABCO did retard the less efficient photoreduction by di-*n*-propylamine. 2-Naphthaldehyde is photoreduced little if at all by DABCO, while *p*-aminobenzophenone and fluorenone show moderate and low reactivity to this amine.

Uncertainty in the value of k_q for quenching by piperylene leads to doubt about the values of k_{IR} for interac-

(82) G. A. Davis and S. G. Cohen, *Chem. Commun.*, 622 (1970).

(83) S. G. Cohen and G. A. Davis, unpublished results, supported by the National Science Foundation.

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(85) V. Ermolaev and A. Terenin, *Sov. Phys. Usp.*, **3**, 423 (1960).

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

(87) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962).

tion of 2-naphthaldehyde triplet with triethylamine. Based on $k_q \sim 6 \times 10^8 M^{-1} \text{sec}^{-1}$, estimated values of k_{1T} are reported:²⁶ $8 \times 10^6 M^{-1} \text{sec}^{-1}$, in acetonitrile; $5 \times 10^5 M^{-1} \text{sec}^{-1}$ in benzene.

C. Photoreduction of 2-Acetonaphthone²⁶

Photoreduction of 2-acetonaphthone by amines resembles that of 2-naphthaldehyde, but with diminished reactivity. 2-Acetonaphthone was photoreduced efficiently by triethylamine in acetonitrile, about 0.05 as rapidly by di-*n*-propylamine, and very little by primary amines. Photoreduction by triethylamine in acetonitrile led to the meso and *d,l* pinacols in similar yields, and to some cross-coupling products. Quantum yields for photoreduction by 0.1 *M* triethylamine were lower than for 2-naphthaldehyde but showed a similar dependence on solvent: $\phi = 0.7$, acetonitrile; 0.1, *tert*-butyl alcohol; 0.04, benzene; and ~ 0.0 , in cyclohexane. The reactions do not appear to show quenching of singlet by amines. Reduction in the dipolar acetonitrile shows a lower dependence on concentration and lower sensitivity to quenching by piperylene, and thus a higher value of k_{1T} than in benzene. Aniline was a weak retarder for the photoreduction in acetonitrile and appeared to interact with triplet acetonaphthone about as rapidly as triethylamine. Estimated values of k_{1T} for interaction of 2-acetonaphthone triplet with triethylamine are $6 \times 10^5 M^{-1} \text{sec}^{-1}$ in acetonitrile and $1 \times 10^5 M^{-1} \text{sec}^{-1}$ in benzene.²⁶ The two values might be somewhat higher if the value of k_q for piperylene on which these were based was underestimated.

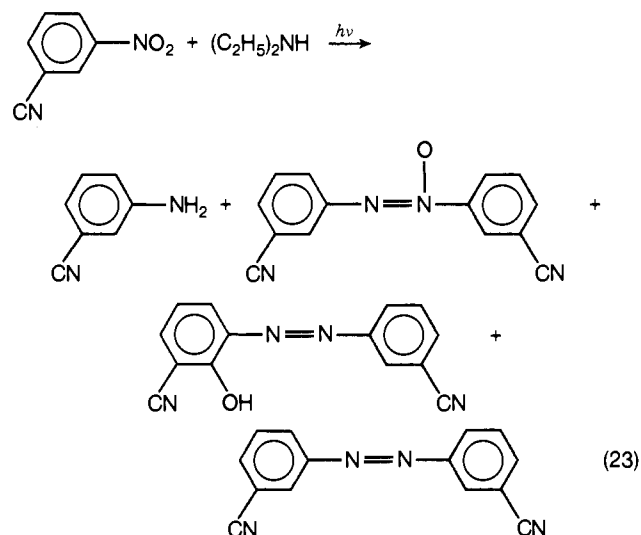
VIII. Some Related Photoreductions

A. Anthraquinone-2-sulfonic Acid

The photoreduction of anthraquinone-2-sulfonic acid by methylamine in H₂O and methylamine-*N,N*-d₂ in D₂O showed an inverse isotope effect, $k_H/k_D = 0.58$. This effect was greater than could be accounted for by a solvent isotope effect and was taken to indicate that the reaction proceeded by an initial electron transfer rather than by direct abstraction of hydrogen.⁸⁸ A similar observation was made in photoreduction of benzophenone by *N*-deuterated primary amines.⁷

B. Aromatic Nitro Compounds

Photoreduction of nitrobenzene by diethylamine led to aniline and 2-hydroxyazobenzene.⁸⁹ In a more detailed study⁹⁰ photoreduction by diethylamine of nitrobenzene, *m*-nitroanisole, and *p*-nitroanisole in quartz, $\lambda > 215 \text{ nm}$, led predominantly to the anilines. Photoreduction in Pyrex, $\lambda > 290 \text{ nm}$, led predominantly to the azo compounds and to the 2-hydroxyazo compound or to the azoxy compound. Photoreduction of *m*-nitrobenzotrile by diethylamine in Pyrex led to all four products (eq 23); similar photoreduction of *p*-nitrobiphenyl led largely to the azoxy compound, while 1-nitronaphthalene led to the amino compound. Photoreductions by triethylamine in Pyrex led from nitrobenzene to aniline and azo compound, from *o*-nitrotoluene to the four products, predominantly the aniline, and from 2,6-dimethylnitrobenzene and *o*-nitroaniline to the amino compounds. It was proposed that photoreduction of the nitro compounds proceeds *via*

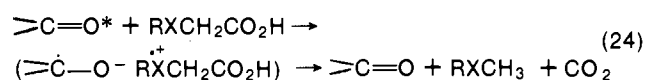


the $\pi-\pi^*$ triplet state, on the basis of sensitization by benzophenone and quenching by biacetyl and by octafluoronaphthalene. Hydrogen abstraction, rather than electron transfer, was favored as the initial step on energetic grounds, but it appears that a charge-transfer mechanism remains feasible. A sequence of reactions was proposed in which nitroso intermediates lead in thermal free radical reactions to hydroxylamines, and the latter are photoreduced to anilines.⁹⁰

Irradiation of the sterically hindered 1,4-di-*tert*-butyl-2-nitrobenzene in diethylamine and triethylamine led to the hydroxylamine, and to a small extent to the amine, and to intramolecular cyclization to an indolone.⁹¹ The latter is the sole product when irradiation is carried out in various solvents in the absence of amines.

C. Decarboxylation by Ketones, Quinones, and Nitro Compounds

Benzophenone, biacetyl, benzoquinone, tetrachlorobenzoquinone, anthraquinone, and phenanthroquinone have been found to photosensitize the decarboxylation of acids of the type $\text{RXCH}_2\text{CO}_2\text{H}$ ($\text{X} = \text{O}, \text{S}, \text{NH}$), phenoxyacetic acid, phenylthioacetic acid, *n*-butylthioacetic acid, and *N*-*o*-chlorophenylglycine. Reduction products of the carbonyl compounds were found.⁹² Xanthone, fluorenone, 2-acetonaphthone, and acetophenone were also found to photosensitize the decarboxylation of these acids.⁹³ Quenching by naphthalene of the benzophenone-sensitized decarboxylations in benzene led to values of k_{1T} , 1.7×10^7 , 1.0×10^8 , 1.6×10^8 , and $2.1 \times 10^9 M^{-1} \text{sec}^{-1}$, respectively, for the acids listed above.⁹⁴ The rate constants for the S and N compounds were similar to those found for quenching of benzophenone triplet by thioethers⁹⁵ and by *N,N*-dimethylaniline,¹⁵ respectively. It was proposed^{93,94} that the reactions occur *via* charge-transfer interaction between the excited carbonyl compound and the heteroatom X (eq 24).



(91) D. Döpp, *Chem. Ber.*, **104**, 1058 (1971).

(92) R. S. Davidson and P. R. Steiner, *J. Chem. Soc. C*, 1682 (1971).

(93) R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc. C*, 3482 (1971).

(94) R. S. Davidson and P. R. Steiner, *Chem. Commun.*, 1115 (1971).

(95) J. B. Guttenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969).

(88) G. Eigenman, *Helv. Chim. Acta*, **46**, 864 (1963).

(89) J. A. Barltrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc. C*, 1142 (1967).

(90) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc. C*, 1467 (1968).

1-Nitronaphthalene, 4-nitrobiphenyl, 1,3-dinitrobenzene, 4-methylnitrobenzene, and nitrobenzene photosensitized the decarboxylation of *N*-*o*-chlorophenylglycine and phenylthioacetic acid.⁹⁶ It was proposed that these reactions proceeded *via* charge-transfer interaction between the excited nitro compound and the heteroatom.⁹⁶

D. Photosensitized Oxidation of Amines

1. Sensitized by Benzophenone

Benzophenone-sensitized reactions of amines with oxygen in benzene have led to mixtures of products in low to moderate yields.⁹⁷ Reactions of dialkylanilines led to aniline, monoalkylanilines, acylanilines, and aldehydes. Similar treatment of primary, secondary and tertiary aliphatic amines led to aldehydes and ketones and imines. The reaction of DABCO led to the cross-coupling product of benzophenone ketyl radical and the radical derived by abstraction of hydrogen from the amine. Quantum yields were >1 for tertiary amines and <1 for secondary and primary amines. It was proposed that the reactions proceeded by photoreduction and by abstraction of hydrogen from the amine by the excited triplet ketone.⁹⁷ The amine-derived radicals were oxidized by oxygen, and the benzophenone ketyl radical was oxidized back to benzophenone, which was recovered in high yield. This course was favored⁹⁷ over reaction of the sensitizer with oxygen because of (i) the high values of rate constants k_{1T} for reaction of benzophenone triplet with amines,¹⁵ coupled with relatively high amine to oxygen concentration ratio, and (ii) quenching of singlet oxygen by certain of the amines without their undergoing chemical change.⁹⁸

2. Sensitized by Xanthone, Fluorenone, *p*-Aminobenzophenone, and 2-Acetonaphthone⁶³

Xanthone, fluorenone, *p*-aminobenzophenone, and 2-acetonaphthone have been reported to photosensitize the oxidation by oxygen of triethylamine, di-*n*-propylamine, and *n*-propylamine. The reactions led in low yields to aldehydes and imines, and to diethylamine from triethylamine. All the reactions were much less efficient than with benzophenone as sensitizer, consistent with lower rates of interaction of these excited ketones with amines^{6,26,66} and increased importance of quenching of the excited states by oxygen. Reversible hydrogen abstraction from primary and secondary amines was also suggested.⁶³

E. Reduction by Phenylenediamines and Dihydropyridines

1. *N,N'*-Diphenyl-*p*-phenylenediamine and Its Diimine⁹⁹

Flash irradiation of this diamine in acidified EPA below -140° led to spectra attributed to the triplet and to the semiquinone positive ion, formed in small amount. Similar irradiation of a mixture of it and the diimine led to strong development of the spectrum of the semiquinone positive ion, as that of the triplet decayed. An electron was transferred from triplet diamine to the diimine, and protonation occurred from the solvent.

2. Reduction of Halomethanes by Phenylenediamines and Dihydropyridines

Irradiation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine led to little if any photoionization and formation of Wurster's Blue in solvents of widely varying dielectric constant. The ionization was sensitized by halogenated solvents, more strongly by bromine- than chlorine-containing methanes. A charge-transfer complex and dissociative reduction of the organic halide by the amine were proposed.¹⁰⁰

Solution-phase photochemistry of *N,N'*-diphenyl-*p*-phenylenediamine, *N,N'*-dimethyl *N,N'*-diphenyl-*p*-phenylenediamine, *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine, and *p*-hydroxydiphenylamine has been studied.¹⁰¹ Ultraviolet irradiation in nonhalogenated solvents yielded fluorescence only. Irradiation in chloroform or carbon tetrachloride led to the radical cations of the amines, which may also be formed by electrochemical or chemical oxidation. Dissociative electron attachment to the halomethane was proposed, leading to halomethyl radical and halide ion. No evidence for charge-transfer complexes was found. The decrease in fluorescence quantum yield, the increase in quantum yield for oxidation of amine as chloroform was added to ethanol, and the absence of quenching by oxygen supported the first excited singlet as the reacting state.¹⁰¹

Reduction of bromotrichloromethane to chloroform and bromide ion by 1,2,6-trimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine and by 2,6-dimethyl-3,5-dicarbomethoxy-1,4-dihydropyridine has been studied. The reaction may be initiated by light or thermally, and proceeds by a free radical mechanism, with quantum yield of 10–100. Transfer of hydrogen from C-4 to trichloromethyl radical and dissociative transfer of an electron from the amine-derived radical to bromotrichloromethane were proposed as chain-propagating steps. The photochemical reaction was initiated by excitation of the dihydropyridine.¹⁰²

IX. Photoreduction of Heterocyclic Compounds

A. Methylene Blue, Eosin, and Rose Bengal

1. Photoreduction of Methylene Blue by Methyl Amines¹⁰³

Methylene Blue was reduced *via* a metastable intermediate to the leuco dye by irradiation in evacuated aqueous solutions of methylamines. The order of reactivity was trimethylamine \gg dimethylamine $>$ methylamine, and quantum yields were quite low. It was proposed that trimethylamine was converted to the *N*-oxide, and the redox process involved the dissociation of water.

2. Photoreduction of Methylene Blue by *N*-Phenylglycines

The photoreduction of Methylene Blue by ring-substituted *N*-phenylglycines has been studied in aqueous solution under nitrogen.¹⁰⁴ The reactions may be analogous to the decarboxylations photosensitized by carbonyl compounds^{92–94} and nitro compounds,⁹⁶ but product studies

(96) R. S. Davidson, S. Korkut, and P. R. Steiner, *Chem. Commun.*, 1052 (1971).

(97) (a) R. F. Bartholomew and R. S. Davidson, *Chem. Commun.*, 1174 (1971); (b) *J. Chem. Soc. C*, 2342 (1971).

(98) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

(99) H. Linschitz, M. Ottolenghi, and R. Bensasson, *J. Amer. Chem. Soc.*, **89**, 4592 (1967).

(100) W. C. Meyer, *J. Phys. Chem.*, **74**, 2118, 2122, 2127 (1970).

(101) E. A. Fitzgerald, Jr., P. Wuelfing, Jr., and H. H. Richtol, *J. Phys. Chem.*, **75**, 2737 (1971).

(102) J. L. Kurz, R. Hutton, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **83**, 584 (1961).

(103) H. Ohata and M. Koizuniv, *Bull. Chem. Soc. Jap.*, **30**, 136, 142 (1957).

(104) S. Matsumoto, *Bull. Chem. Soc. Jap.*, **35**, 1860, 1866 (1962); **37**, 491, 499 (1964).

were not reported. Substitution of methyl for amino and methylene hydrogens increased quantum yields somewhat, while acylation of the amino group decreased reactivity.

Limiting quantum yield for photoreduction of Methylene Blue by *N*-phenylglycine was 0.27, and the value was decreased by both electron-donating substituents, $\varphi \sim 0.0$ for *p*-CH₃O, and by electron-withdrawing substituents, $\varphi \sim 0.05$ for *p*-NO₂. Bromo substituents were particularly effective in decreasing quantum yields. A similar effect of electron-withdrawing and -donating substituents in decreasing quantum yields was observed in the photoreduction of fluorenone by dimethylanilines.⁸⁰

By use of *p*-phenylenediamine as a diffusion-controlled quencher, the lifetime of Methylene Blue triplet was calculated,¹⁰⁴ 4.2×10^{-5} sec. This, combined with data from plots of inverse quantum yields vs. inverse concentrations of phenylglycines, led to values of k_{ir} for interaction of excited triplet Methylene Blue with the amino compounds. Values increased with electron donation, from $5.8 \times 10^4 M^{-1} \text{ sec}^{-1}$ for *p*-CN, to $2 \times 10^8 M^{-1} \text{ sec}^{-1}$ for the *p*-CH₃O compound, which was studied as a quencher. A Hammett plot of $\log k/k_0$ against σ^- was presented.¹⁰⁴ A somewhat better fit was obtained⁷⁹ in a plot of $\log k_{ir}$ against σ^\pm , $\rho = -2.23$, with *p*-CN leading to an abnormally low value. Again the reaction shows similarity to that of fluorenone-dimethylaniline system.⁸⁰ The photoreduction of Methylene Blue is noteworthy because of its very low triplet energy, ~ 34 kcal/mol,¹⁰⁵ apparently compensated by its very favorable reduction potential,¹⁰⁶ 19 kcal/mol. The very marked dependence of k_{ir} on electron donation by substituents is consistent with this.

3. Dye-Photosensitized Oxidation of Amines

Photoreduction, abstraction of hydrogen by excited dye from amine, was proposed as the initial process in the oxidation by oxygen of tertiary aliphatic amines, sensitized by Methylene Blue, Eosin, and Rose Bengal.⁹⁷ Products similar to those of the benzophenone-sensitized reactions were obtained, and oxidation was sensitized only in systems in which anaerobic photoreduction of the dyes was efficient.^{97,107} In the dye-sensitized oxidations in methanol, tertiary aliphatic amines reacted efficiently, leading to carbonyl compounds, imines, and some *N*-oxide. Secondary and primary aliphatic amines showed low reactivity; aniline, dialkylanilines, and DABCO were unreactive. Some of the oxidations were more efficient at lower oxygen pressure, when triplet dye was less efficiently quenched by oxygen and more available for abstraction of hydrogen from the amine. Flash photolysis of solutions of the dyes and tertiary amines in methanol led to spectra of transients which were attributed to the radical anions of the dyes. It was proposed that radicals were formed by transfer of hydrogen from the amine radical cation to the radical anion. The amine-derived radical was then oxidized further by oxygen, and the dye-derived radical was reoxidized to the dye by oxygen.¹⁰⁷

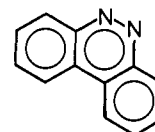
B. Phthalocyanine and Porphyrins

Copper phthalocyanine has been photoreduced by amines, amides, and ureas in deaerated aqueous solu-

tion. The fully *N*-alkylated compounds were the most reactive in each set.¹⁰⁸ The reductions proceed by electron transfer, and the nitrogen compounds act as both reducing agents and quenchers. Products of oxidation of the nitrogen compounds were not characterized.

Photoreduction of chlorophylls and of the magnesium free compounds, the pheophytins, by benzylamine and phenylhydrazine in benzene has been described.¹⁰⁹ Chlorophyll a was photoreduced to the 5,6-dihydro compound. Chlorophyll b led to a mixture which included the product of reduction of the 3-formyl to the 3-methylol group. This product was further reduced reversibly at the 5,6 position. The pheophytins were photoreduced to the β,δ -dihydro compounds.

C. Benzo[*c*]cinnoline (9,10-Diazaphenanthrene)

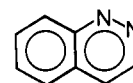


9,10-Diazaphenanthrene has been photoreduced by triethylamine in benzene, leading to the 9,10-dihydro-9,10-diazaphenanthrene, which was characterized as the 9,10-diacetyl derivative, and reoxidized to the starting compound.¹¹⁰ The inverse plot of quantum yield of photoreduction against concentration of amine led to a limiting quantum yield of 0.8. Values of k_{ir} appeared similar in photoreduction and in quenching of fluorescence by triethylamine. Photoreduction appeared to occur substantially from the $n-\pi^*$ excited singlet, $k_r \simeq 6 \times 10^9 M^{-1} \text{ sec}^{-1}$.¹¹⁰

D. Cinnoline (1,2-Diazanaphthalene) and Pyridazine (1,2-Diazene)

Preliminary experiments have been carried out on photoreduction of two other 1,2-diaza heterocycles.¹¹¹

1. Cinnoline



Photoreduction of cinnoline by triethylamine in benzene appeared to lead to a dimeric reduction product, possibly the 4,4' coupling product. This, on heating, led to a mixture, apparently of cinnoline and 1,2-dihydrocinnoline. Low-temperature phosphorescence was long lived, indicating the presence of triplet, π,π^* configuration. However, photoreduction by triethylamine was not quenched by piperylene, indicating that a singlet, probably $n-\pi^*$, was the reactive excited state. Consideration of theoretical radiative lifetime and absence of fluorescence, and the effect of concentration of triethylamine on the quantum yield of photoreduction, $k_d/k_{ir} \sim 0.1$, led to an estimated value of $k_{ir} \sim 3 \times 10^{10} M^{-1} \text{ sec}^{-1}$.¹¹¹

2. Pyridazine



(105) D. R. Kearns, R. A. Hollins, A. U. Khan, N. W. Chambers, and P. Radlick, *J. Amer. Chem. Soc.*, **89**, 5455 (1967).

(106) M. von Stackelberg, "Polarigraphische Arbeitsmethoden," Walther De Gruyter and Co., Berlin, 1950, p 309.

(107) R. F. Bartholomew and R. S. Davidson, *J. Chem. Soc. C*, 2347 (1971).

(108) G. Eigenman, *Helv. Chim. Acta*, **46**, 855 (1963).

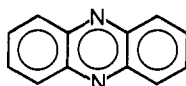
(109) W. Hendrich, *Acta Biochim. Pol.*, **16**, 111 (1969); *Biochim. Biophys. Acta*, **162**, 265 (1968).

(110) G. A. Davis and S. G. Cohen, *Chem. Commun.*, 675 (1971).

(111) G. A. Davis and S. G. Cohen, unpublished results. Work supported by the National Science Foundation.

Photoreduction of pyridazine by triethylamine in benzene appeared to lead to a dimeric reduction product, which could be converted to a diacetyl derivative. Pyridazine showed weak fluorescence, which, like that of benzo[*c*]cinnoline was quenched by triethylamine. Photoreduction appeared to occur largely from the $n-\pi^*$ excited singlet state.¹¹¹

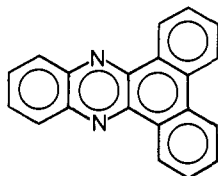
E. Phenazine (5,10-Diazaanthracene)



Phenazine has been photoreduced by triethylamine in benzene.¹¹² The product was largely the 5,10-dihydro compound, which was readily reoxidized by air to phenazine. The $\pi-\pi^*$ singlet and triplet states were ruled out as significant contributors to the reactivity, the singlet on the basis of its low lifetime, the low-energy $\pi-\pi^*$ triplet on the basis of its long lifetime, and the low sensitivity of the photoreduction to diffusion-controlled quencher. This left the $n-\pi^*$ singlet as the major reactive state, as it was for the preceding three compounds. The rate constant for interaction of the excited state with triethylamine was $\geq 10^9 M^{-1} \text{ sec}^{-1}$. Photoreduction by tri-*n*-butylstannane showed similar properties to that by triethylamine. Photoreduction by 2-propanol was less efficient, $k_T \sim 10^6 M^{-1} \text{ sec}^{-1}$.¹¹²

F. Dibenzo[*a,c*]phenazine, 1,2:3,4:6,7-Tribenzophenazine, Quinoxaline (1,4-Diazanaphthalene), and 5,6:7,8-Dibenzoquinoxaline

1. Dibenzo[*a,c*]phenazine

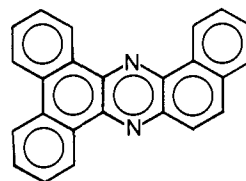


This compound was photoreduced at 366 nm by triethylamine in benzene as indicated by decrease in absorption at 345–405 nm, increase >405 nm, and formation of isosbestic points. The reduction product was oxidized rapidly by air back to the starting material, but attempts to prepare derivatives of it by acetylation and methylation failed. The product may be the *N,N'*-dihydro compound. The quantum yield was 0.7 at 0.25 *M* amine and was lower at both higher and lower concentrations of amine. Extrapolation of the low concentration data led to a limiting quantum yield of ~ 0.85 . The reduction was quenched efficiently by 1,3,5-hexatriene and by 1,4-cyclohexadiene. Fluorescence was quenched, but rather inefficiently, by triethylamine. Fluorescence was quenched very little by cyclohexadiene. The reduction was due almost entirely to reaction of the excited triplet state. This has π,π^* configuration, triplet energy ~ 53 kcal/mol.¹¹³ The decrease in quantum yield at high amine concentrations may be due to quenching of the singlet π,π^* state.

(112) G. A. Davis, J. D. Gresser, and P. A. Carapellucci, *J. Amer. Chem. Soc.*, **93**, 2179 (1971).

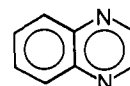
(113) F. Dörr and H. Gropper, *Ber. Bunsenges. Phys. Chem.*, **67**, 193 (1963).

2. 1,2:3,4:6,7-Tribenzophenazine



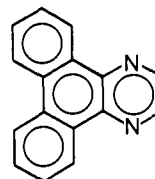
This compound was photoreduced at 405 nm by triethylamine in benzene,¹¹¹ presumably leading to the *N,N'*-dihydro compound. The reduction product was oxidized rapidly by air back to the starting material. The quantum yield was 0.2 at 0.12 *M* amine and was lower at both higher and lower concentrations of amine. The extrapolated limiting quantum yield was 0.3. The reduction was quenched by 1,3,5-hexatriene. Fluorescence emission was quenched efficiently by triethylamine, and the decrease in reduction at higher amine concentration may be attributed to quenching of the singlet π,π^* state. The photoreduction was due largely to reaction of the excited triplet state. This has π,π^* configuration, triplet energy ~ 54 kcal/mol.¹¹³

3. Quinoxaline



Quinoxaline was photoreduced by triethylamine in benzene, apparently initially to a dihydro compound which was reoxidized by oxygen to quinoxaline.¹¹¹ The reaction was quenched effectively by small concentrations of piperylene indicating that the reactive excited state was a triplet. This has $\pi-\pi^*$ configuration.¹¹⁴

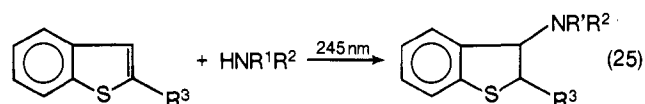
4. 5,6:7,8-Dibenzoquinoxaline



This compound was photoreduced by triethylamine in benzene.¹¹¹ The quantum yield was ~ 0.1 at ca. 0.01–0.05 *M* amine, and decreased slowly with decrease in concentration and rapidly with increase in concentration. This negative effect of high concentration of amine on quantum yield was accompanied by quenching of fluorescence and indicated quenching of singlet by amine. The low concentration data indicated a limiting quantum yield of ~ 0.2 . The reactive excited state was a triplet, of $\pi-\pi^*$ configuration.¹¹³

G. Benzo[*b*]thiophene

This compound has been reported to undergo reductive amination when irradiated with propylamine or piperidine¹¹⁵ (eq 25).



(114) F. Dörr, H. Gropper, and N. Mika, *Ber. Bunsenges. Phys. Chem.*, **67**, 202 (1963).

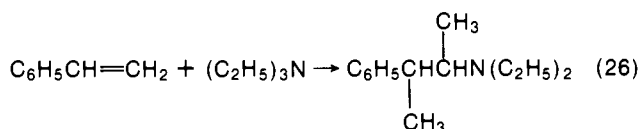
(115) A. LaBlanche, *J. Chem. Soc. D*, 892 (1971).

X. Photoreduction of Hydrocarbons

A. Styrenes, Diphenylacetylene, and α,β -Unsaturated Carbonyl Compounds

1. Styrene, 1-Phenylcyclohexene, 1-Phenylcyclopentene, and Indene¹¹⁶

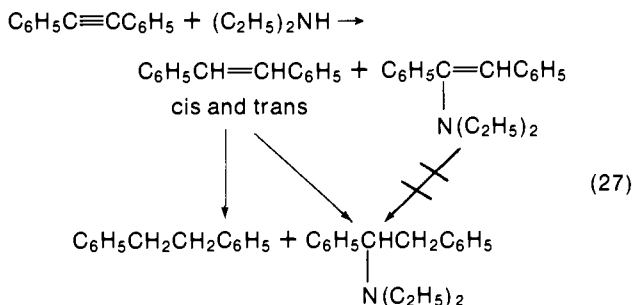
Irradiation of styrene in triethylamine has led to addition of C-1 of the amine to the α -carbon of the double bond (eq 26). The reaction proceeded in the direction of abstraction of α -hydrogen from the amine by the terminal carbon, leading to the more stable α -phenylethyl radical, followed by combination of the two radicals. Photoaddition of triethylamine and trimethylamine to 1-phenylcyclohexene, and of triethylamine to 1-phenylcyclopentene and to indene, led to similar products. Photoaddition of isopropylamine to 1-phenylcyclohexene led to a mixture of products, from addition of C-1 and of N to the α -carbon of the double bond. The adducts were accompanied by the reduction products, the dihydro derivatives of the olefins, and yields of these compounds increased with rising temperature.



The addition of trimethylamine to 3,3-dimethylindene was stereospecifically *cis*, indicating that the reaction did not proceed *via* truly free radicals.¹¹⁶

2. Diphenylacetylene and Stilbene¹¹⁷

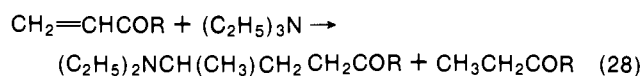
Irradiation of diphenylacetylene with diethylamine has led to 1,2-diphenylethane and 1,2-diphenyl-1-diethylaminoethane, both of which may also be formed from *cis*- and *trans*-stilbene, and to 1,2-diphenyl-1-diethylaminoethylene (eq 27). The reaction was not affected by pyrene as quencher or triphenylene as sensitizer and was thought to involve singlet excited diphenylacetylene and to proceed by an ionic mechanism. Irradiation in triethylamine or *N*-methylmorpholine led to recovery to diphenylacetylene.¹¹⁷



3. α,β -Unsaturated Ketones and Esters

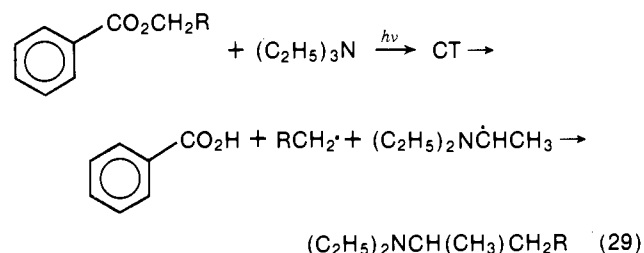
Irradiation of α,β -unsaturated ketones and esters in triethylamine has led to products of addition of C-1 of the amine to the β -carbon and hydrogen to the α -carbon of the unsaturated compound.¹¹⁸ The products may result from 1,4 addition, starting with abstraction of α -hydrogen

by the carbonyl oxygen and ending with ketonization. Reduction of the double bond leading to dihydro compounds was an important competing reaction (eq 28).



4. Allylic Esters

Irradiation of allylic and benzyl benzoates, and to a lesser extent some alkyl benzoates, in triethylamine led to benzoic acid and the α -alkylated amines. It was suggested that the reaction was initiated by electron transfer from amine to the triplet ester.¹¹⁹ Transfer of a proton and cleavage of the ester-derived radical would lead to the alkyl and amine-derived radicals, which may combine (eq 29).



B. Benzene, Naphthalenes, Anthracene, and Acenaphthylene

1. Benzene

Irradiation of piperidine or cyclohexylamine in benzene led to 1:1 adducts, derivatives of 1,4-dihydrobenzene in which N of the amine was bonded to C-1 of the hydrocarbon. Methylamine, *n*-butylamine, and 2-butylamine also seemed to lead to analogous products, and even ammonia led to some 1:1 photoadduct. The reactions were accounted for in terms of an intermediate 1,4-biradical form of benzene, a possible tautomer of triplet benzene.¹²⁰

Irradiation of an equimolar mixture of triethylamine and benzene led to traces of tetrahydrobiphenyl and 1,4-cyclohexadiene and to a small amount of the 1,4-adduct of triethylamine to benzene in which C-1 of the amine is bonded to C-1 of the hydrocarbon.¹²¹ In the presence of 10 mol % of methanol, rates were increased markedly and the adduct comprised 80% of the products. Water and trimethylammonium ion also acted as efficient proton donors. Similar effects of proton donors were found in the 1,4-photoadditions of trimethylamine and tri-*n*-butylamine to benzene. Protonation of the radical anion of the hydrocarbon, in the ion pair or charge-transfer complex, may be effected by the hydroxylic or acidic additive.

Irradiation of pyrrole in benzene led to 1:1 adducts of which the predominant component was the derivative of 1,4-dihydrobenzene in which C-2 of pyrrole was bonded to C-1 of the hydrocarbon. The triplet diradical was suggested as the reactive intermediate. *N*-Methylpyrrole failed to undergo this reaction.¹²²

(116) R. C. Cookson, S. M. de B. Costa, and J. Hudec, *Chem. Commun.*, 753 (1969).

(117) M. Kawanisi and K. Matasunaga, *Chem. Commun.*, 313 (1922).

(118) R. C. Cookson, J. Hudec, and N. A. Mirza, *Chem. Commun.*, 180 (1968).

(119) R. C. Cookson, J. Hudec, and N. A. Mirza, *Chem. Commun.*, 824 (1967).

(120) M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Commun.*, 862 (1967).

(121) D. Bryce-Smith, M. T. Clarke, and A. Gilbert, *Chem. Commun.*, 916 (1971).

(122) M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Commun.*, 263 (1967).

2. Naphthalene¹²³

Irradiation of naphthalene and triethylamine in acetonitrile led to 1,4-dihydronaphthalene as major product, 1,1'-(1,1',4,4'-tetrahydro)binaphthyl, and the 1,4 addition product of triethylamine to naphthalene, in which C-1 of the amine has added to C-1 of the hydrocarbon. Photoreduction products were also obtained from irradiation of 1- and 2-methoxynaphthalenes with triethylamine. An electron transfer mechanism was suggested on the basis of the similarity of the products to those of the Birch reduction, introduction of deuterium when the reduction was carried out in the presence of D₂O, and the reported singlet charge-transfer complex between naphthalene and triethylamine;¹²⁴ 1:1 photoadducts between naphthalene and primary and secondary amines have been mentioned.¹²⁰

Irradiation of naphthalene and pyrrole in ethanol or acetonitrile led to 1,4- and 1,2-dihydronaphthalenes in which C-2 of pyrrole has added C-1 or C-2, respectively, of the hydrocarbon.¹²⁵ The excited singlet of naphthalene was proposed as the reactive state, since the reaction was not sensitized by benzophenone or acetophenone, and the fluorescence of naphthalene was quenched by pyrrole with high efficiency, $k_T \sim 3 \times 10^9 M^{-1} \text{ sec}^{-1}$. Reduction by *N*-deuteriopyrrole led to deuterium in the reduction product. Fast exciplex or radical ion pair formation was proposed, and similarity in some respects to photoreduction of benzophenone by amines was suggested.¹²⁵

3. Anthracene

Irradiation of anthracene and dimethylaniline in acetonitrile led to small quantities of photodimer, 9,10-dihydroanthracene, and tetrahydrobianthryl, and to a good yield 9-(*p*-dimethylaminophenyl)-9,10-dihydroanthracene. In the presence of D₂O, deuterium was introduced into the three reduction products. Essentially only photodimer was formed in benzene as solvent.¹²⁶

In toluene, quenching of anthracene fluorescence by dimethylaniline was accompanied by charge-transfer formation, characterized by its emission. In acetonitrile, fluorescence was quenched, CT emission was not observed, and radical ions were formed. Charge-transfer formation competed with dimerization via the excited singlet, and reduction products were formed from the ion radicals and charge-transfer complex.¹²⁷

The 1:1 adducts were also obtained from aniline and *N,N*-dimethyl-*m*-toluidine with anthracene. With *N,N*-dimethyl-*o*-toluidine little adduct was obtained and photodimer was the major product. With *N,N*-dimethyl-*p*-toluidine, 9,10-dihydroanthracene and tetrahydrobianthryl were the major products.¹²⁶

In another study, irradiation of anthracene with *N,N*-dimethylaniline or triethylamine in acetonitrile led similarly to 9,10-dihydroanthracene, tetrahydrobianthryl, and aminated anthracenes. Irradiation with *n*-butylamine in benzene or acetonitrile, and with dimethylaniline in benzene, led to photodimer, and with triethylamine in benzene to photodimer and tetrahydrobianthryl.¹²⁸

(123) J. A. Barltrop and R. J. Owers, *Chem. Commun.*, 1462 (1970).

(124) M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Lett.*, **3**, 71 (1969).

(125) J. J. McCullough, C. W. Huang, and W. S. Wu, *Chem. Commun.*, 1368 (1970).

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(128) R. S. Davidson, *Chem. Commun.*, 1450 (1969).

4. Acenaphthylene

Irradiation of acenaphthylene with *N,N*-dimethylaniline or triethylamine in benzene, or with neat triethylamine, led to *cis* and *trans* photodimers. Irradiation with the amines in acetonitrile led to reduction product, acenaphthene, and the *cis* photodimer. It was suggested that reduction in acetonitrile proceeded via the radical ions, and the *trans* photodimer formed from triplet acenaphthylene.¹²⁸

C. Photosensitized Oxidation of Amines¹²⁹

Analogously to the sensitization of photooxidation of amines by carbonyl compounds and dyes (sections VIII.D, IX.A) by initial transfer of hydrogen from amine to sensitizer, the photooxidation of tertiary amines may be sensitized by aromatic hydrocarbons. Anthracene, naphthalene, perylene, and phenanthrene photosensitized the oxidation by oxygen of triethylamine, tri-*n*-propylamine, and *N,N*-diethylaniline in acetonitrile. Primary and secondary aliphatic amines were unreactive. This sensitization of oxidation of tertiary amines did not occur in benzene, just as the aromatic hydrocarbons are not photoreduced in benzene. It was proposed that radical ions were formed in acetonitrile, and these led to the observed oxidation products of the tertiary amines: carbonyl compounds, imines, and secondary amines. The aromatic hydrocarbons were generally recovered in high yields, as their radicals and radical anions were reoxidized by oxygen. Amine radical cations were converted to radicals by proton transfer to the radical anions or to O₂⁻, and the amine-derived radicals reacted with oxygen. Quantum yields for photoreduction of the hydrocarbons by the amines in the absence of oxygen were reported: ~ 1 by *N,N*-dimethylaniline, < 0.2 by triethylamine.¹²⁹

D. Physical Observations

An electron transfer mechanism for quenching of fluorescence was proposed early.^{130,131} Support for this was found in quenching of fluorescence of acridine and perylene by amines.^{78,132} The amine was more efficient the lower its ionization potential,¹³³ and quenching by univalent reduction of the excited molecules was proposed. The perylene monoanion radical was characterized by its absorption, which was very strong in polar solvents. This absorption was not seen in hydrocarbon solvent, where triplet-triplet absorption was enhanced. An excited CT complex was proposed as an intermediate which could lead to (a) the radical ions, (b) excited triplet, and (c) ground state molecules.¹³²

Such interactions are common and occur readily because electronically excited molecules have a lower ionization potential and higher electron affinity than molecules in the ground state.⁷⁸ The differences are equal to the excitation energies. Either the electron donor or the electron acceptor may be excited, and their interaction in polar solvents may occur at a distance of 7 Å and lead to electron transfer and formation of radical anion and cation without direct contact and without intermediate for-

(129) R. F. Bartholomew, D. R. G. Brimage, and R. S. Davidson, *J. Chem. Soc. C*, 3482 (1971).

(130) E. Baur, *Z. Phys. Chem., Abt. B*, **16**, 465 (1932).

(131) J. Weiss and H. Fischgold, *Z. Phys. Chem., Abt. B*, **32**, 135 (1936).

(132) H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallmann and G. M. Spruch, Ed., Wiley, New York, N. Y., 1962, p 74.

(133) A. Weller, *Prog. React. Kinet.*, **1**, 187 (1961).

mation of a CT complex. Quenching of fluorescence of perylene by diethylaniline in polar solvents proceeded at diffusion-controlled rates.⁷⁸

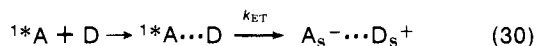
A structureless long-wavelength fluorescence band occurred when the fluorescence of aromatic hydrocarbons was quenched by arylamines and was attributed to the excited charge-transfer complex.⁷⁸ There was a red shift and a decrease in intensity of this emission with increasing solvent polarity. At $\epsilon > 30$ no such emission was detected despite strong quenching of the normal fluorescence of anthracene, perylene, tetracene, and coronene. In acetonitrile transient absorption spectra were observed which were due to the hydrocarbon triplet and to the radical anion and cation.^{134, 135}

A detailed kinetic study supported the preceding conclusions.¹³⁶ Quenching of fluorescence of perylene by aniline and dimethylaniline was studied in solvents of varying dielectric constant. No CT emission was observed in solvents of $\epsilon > 12$, while CT emission was observed in solvents of low dielectric constant. In solvents of $\epsilon = 12-38$, quenching of fluorescence appeared nearly diffusion controlled. The dissociation energy of the CT complex between excited perylene and dimethylaniline in benzene was calculated to be 8.1 kcal.

XI. Effects of Ionization Potentials of Donors, Reduction Potentials of Acceptors, and Excited State Energies

A. Excited Ion Pair and Excited Charge-Transfer Complex

The free energy change for formation of solvated ion pairs from excited singlet hydrocarbon acceptor and diethylaniline donor (eq 30) has been calculated in accor-

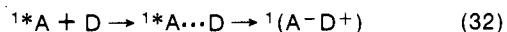


dance with eq 31, from the oxidation potential of the donor $E(D/D^+)$, the reduction potential of the acceptor,

$$\Delta G_{ET} = E(D/D^+) - E(A^-/A) - \Delta E_{0,0}(A) - (e_0^2/\epsilon a) \quad (31)$$

$E(A^-/A)$, the energy of the zero-zero transition of the hydrocarbon; $\Delta E_{0,0}(A)$, and the free energy gained when the radical ions are brought to encounter distance, a , in the solvent dielectric constant, ϵ . The values of ΔG in acetonitrile are favorable, -14 and -11 kcal/mol, for anthracene and perylene, respectively, and remain negative for essentially all aromatic hydrocarbons.¹³⁴

Rate constants for quenching of fluorescence of anthracene by diethylaniline were essentially diffusion controlled over a range of dielectric constant from n -hexane to acetonitrile.¹²⁷ With decreasing dielectric constant of solvent, ΔG for formation of ions will eventually become positive and rate of ion formation will decrease. However, the rate of complex formation (eq 32) was virtually sol-



vent independent, and the probability of formation of complex increased with decreasing polarity of solvent. The diffusion-controlled quenching of fluorescence in nonpolar solvents was due to complex and in polar solvents to radical ions.¹²⁷ The charge-transfer complex,

like the excimer, "is one excited singlet state species in which the electrons of the partners are mutually coupled by exchange."¹³⁷ Binding energies of such complexes in hexane may be calculated from the excited singlet energy, emission energy, and ground state repulsion, 8.5 and 6.5 kcal/mol for anthracene and pyrene with diethylaniline, respectively.¹³⁷

In these systems the ion pair and the CT complex lie between the excited singlet and triplet, and charge recombination may lead to the triplet.¹³⁸ The hydrocarbon triplet may not then be quenched rapidly by an electron transfer mechanism similar to that for quenching fluorescence. Triplet yields, studied by nanosecond flash, were high and similar after quenching of fluorescence of anthracene by diethylaniline in both toluene and acetonitrile, via CT complex and ion pair intermediates, respectively.¹³⁹

A large number of excited singlet charge-transfer complexes between aromatic hydrocarbons and their derivatives substituted with electron-donating and electron-withdrawing substituents have been studied and their fluorescence emissions characterized. When virtually pure CT complexes were formed, maximum emission frequencies observed in hexane were directly related to the differences in the polarographic oxidation and reduction potentials measured in polar solvents (eq 33). A similar re-

$$\nu^{\max}(\text{CT}) = E(D/D^+) - E(A^-/A) - \Delta \quad (33)$$

lationship was proposed for phosphorescence emission from triplet states. Linear correlations were observed between emission maxima and reduction potentials for a series of complexes with a common donor, and between emission maxima and oxidation potential for complexes with a common acceptor.¹⁴⁰

Excited triplet charge-transfer complexes have been studied in rigid glass, and eq 33 has been applied to their phosphorescence emission maxima.¹³⁸

B. Rates of Donor-Acceptor Interaction

Rate constants for quenching by typical electron donors of singlet fluorescence of aromatic compounds have been measured in acetonitrile and shown to be related to ΔG_{ET} for the electron transfer process.¹⁴¹ The latter could be calculated from spectroscopic data and polarographic redox potentials (eq 31). The rate constant reached a diffusion-controlled limit for $\Delta G_{ET} < -10$ kcal/mol, decreased with increasing ΔG_{ET} , and became proportional to $\exp(\Delta G_{ET}/RT)$ when $\Delta G_{ET} > 5$ kcal/mol. The acceptors, 3,4-benzacridine, anthracene, 1,2-benzanthracene, and 1,12-benzperylene, showed diffusion-controlled fluorescence quenching with donors of low oxidation potential, i.e., tetramethyl-*p*-phenylenediamine, methoxydimethylanilines, etc., and rates decreasing as much as four orders of magnitude with donors of higher oxidation potential, i.e., dimethoxybenzenes. The observed rate constants agreed satisfactorily with those calculated from the spectroscopic and thermodynamic data. The possible extension of this treatment to triplet interaction was indicated.

(137) A. Weller, *Fast React. Primary Processes Chem. Kinet., Proc. Nobel Symp.*, 5, 413 (1967).

(138) H. Beens and A. Weller, in "Molecular Luminescence," E. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 203.

(139) C. R. Goldschmidt, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, 75, 1025 (1971).

(140) H. Beens and A. Weller, *Acta Physiol. Pol.*, 34, 593 (1968).

(141) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 73, 834 (1969).

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(135) H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, 47, 1183 (1967).

(136) W. R. Ware and H. P. Richter, *J. Chem. Phys.*, 48, 1595 (1968).

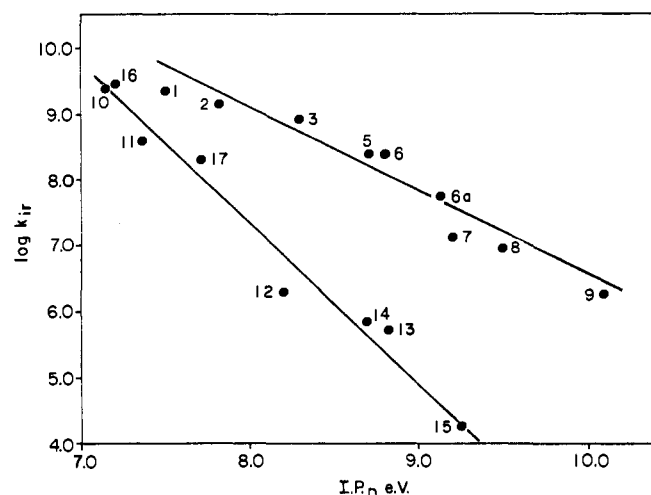


Figure 1. Relation of rate constant for quenching of benzophenone triplet, k_{IR} , to ionization potential of donor, IP_D . Donors: 1, triethylamine; 2, *N*-methyl-2-butylamine; 3, di-*n*-butyl sulfide; 5, 2-butylamine; 6, 3-methyl-2-pentene; 6a, *cis*-2-butene; 7, *n*-propylmercaptan; 8, di-*n*-propyl ether; 9, 2-propanol; 10, *N,N*-dimethylaniline; 11, triphenylphosphine; 12, anisole; 13, toluene; 14, diphenyl ether; 15, benzene; 16, 1,4-diaza[2.2.2]bicyclooctane (DABCO); 17, 1-aza[2.2.2]bicyclooctane (ABCO).

The interaction between typical excited aromatic hydrocarbon acceptors and tertiary aromatic and aliphatic amine donors, leading to CT complexes, was examined spectroscopically over a temperature range in hydrocarbon solvents. Energies of the complexes were determined and agreed well with values calculated in accord with eq 31. Entropies of formation of the complexes were rather constant, -18 ± 1 eu, and enthalpies varied from -2.7 to -10.2 kcal/mol.¹⁴² From the published relations, ΔG_c for charge-transfer formation in the excited singlet state may be represented by eq 34.

$$\Delta G_c = E(D/D^+) - E(A^-/A) - {}^1\Delta E_{0,0} - T\Delta S_c + 3 \text{ kcal/mol} \quad (34)$$

From these relations it has been proposed that excited triplet CT complex formation between carbonyl compounds and amine and other donors might be described in accordance with eq 35.¹⁴³ In this expression ionization

$$\Delta G_c \sim IP_D - E(A^-/A) - {}^3\Delta E_{0,0} + C \quad (35)$$

potential was used in place of oxidation potential since more values were available, and the difference was included in the constant term. The entropy term was also included in the constant. In the examples to which this was applied, ΔG_c was generally >5 kcal/mol and considered to be equal to the free energy of activation for formation of the complex, ΔG_c^\ddagger . A linear relation was sought between $\log k_{IR}$ for interaction of triplet carbonyl compounds and ΔG_c . For a series of donors with a constant acceptor this would relate $\log k_{IR}$ with IP_D , and for a series of acceptors with a constant donor, $\log k_{IR}$ with $[-{}^3\Delta E_{0,0} - E(A^-/A)]$.

Linear relationships were reported between $\log k_{IR}$ and IP_D for interaction n,π^* triplet benzophenone with 17 donors of widely varied structure drawn from the classes of aliphatic primary, secondary, and tertiary amines, tertiary aromatic amine, thioether, aliphatic mercaptan, aliphatic and aromatic ether, phosphine, alcohol, olefins, and aromatic hydrocarbons.

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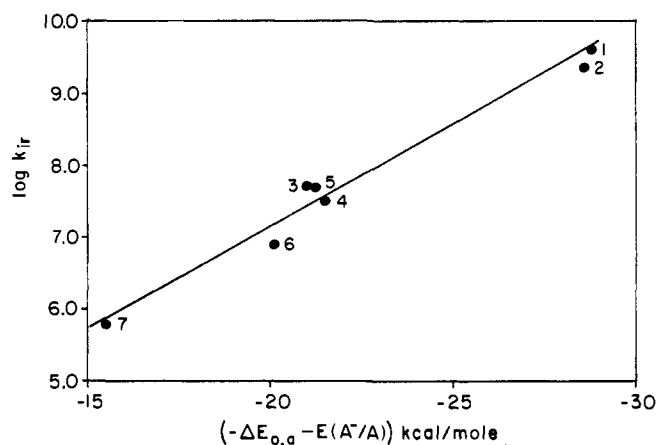


Figure 2. Relation of rate constant for quenching by triethylamine of acceptor triplets, k_{IR} , to triplet energy and reduction potential $[-\Delta E_{0,0} - E(A^-/A)]$, of acceptors: 1, valerophenone; 2, benzophenone; 3, *p*-aminobenzophenone; 4, fluorenone; 5, biacetyl; 6, 2-naphthaldehyde; 7, 2-acetonaphthone.

Primary and secondary anilines, phenols, and thiophenols, which may quench largely by transfer of H from the heteroatom, did not fit the relationship. The data lay largely on two lines, one for aliphatic the other predominantly for aromatic donors (Figure 1). The values of slope were much lower than that observed when complete electron transfer occurred,¹⁴¹ while rate constants spanned the same range, 10^6 – 10^{10} M^{-1} sec^{-1} . The small slope, the small effects of polarity of solvent, and the high rates despite unfavorable ΔG_c indicated that these interactions of excited benzophenone with electron donors involve only partial transfer of charge and may be rapid because of mixing of electronic and chemical, *i.e.*, hydrogen transfer, processes. Thus the two processes which have been described for abstraction of H by triplet ketones,^{6,7} polar contribution to stabilization of the transition state for abstraction of H from alcohols (eq 2) and abstraction of H from amines *via* CT complexes (eq 3), might differ as the processes start and become more similar at the transition state. Variation in extent of H and electron transfer in the transition state may be the norm, the extent depending upon the relative values of the terms of eq 35.

A linear relationship between $\log k_{IR}$ and IP_D was also reported for interaction of $\pi-\pi^*$ triplet fluorenone with a more limited series of compounds: primary, secondary, and tertiary aliphatic amines, tertiary aromatic amines, and a thioether.¹⁴⁴ The slope was greater than in the benzophenone system, indicating a greater sensitivity to IP_D , and increasing polarity of solvent led to larger increases in k_{IR} . Both effects indicated that, with lower triplet energy and more favorable reduction potential, fluorenone reacted largely by electron transfer.

Finally a linear relationship between $\log k_{IR}$ and $[-{}^3\Delta E_{0,0} - E(A^-/A)]$ was found for interaction of a single donor, triethylamine, with a series of carbonyl acceptors of widely varying reduction potential, triplet energy, and triplet configuration (Figure 2). The combination of triplet energy and reduction potential may be a more useful and sensitive guide to carbonyl reactivity and values of k_{IR} than the triplet energies alone and the triplet types.¹⁴⁴

Acknowledgment. We are pleased to acknowledge support of the National Science Foundation in the preparation of this manuscript.

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