Table VII. Solvolysis of *p*-Nitrophenyl Palmitate Catalyzed by Imidazole and/or Phenol-Containing Compounds in 30% (v/v) 1-Propanol–Water at 26°, Ionic Strength 0.02

| | $k_{cat}$, l./mol min, at pH | | | |
|---|---|---|---|---|
| Catalyst | 7.08 | 7.90 | 8.98 | 9.97 |
| HPNI | 7.20 | 9.61 | 10.86 | 12.56 |
| MPNI | | | | 14.58 |
| *p*-Cresol | | | | 1.10 |
| Imidazole | 2.15 | 2.74 | 2.08 | 2.43 |

The results in Table VII indicate that imidazole and *p*-cresol are less efficient in catalyzing the solvolysis of a long-chain substrate than a short-chain substrate (Table VI). The decrease in catalyst efficiency can be attributed to steric hindrance caused by the long aliphatic chain located at the acyl portion of the substrate. The imidazole-catalyzed hydrolysis of esters of *p*-nitrophenol have been reported to be subject to steric hindrance.[26] The steric hindrance should be even larger if the long-chain compounds HPNI and MPNI are used as the catalyst.

In spite of more severe steric crowding, the MPNI- or HPNI-catalyzed solvolysis of *p*-nitrophenyl palmitate (PNPP) was more efficient (relative to imidazole) than the solvolysis of *p*-nitrophenyl acetate (PNPA) as previously expected. Polyoxyethylene (23) lauryl alcohol was reported[27] not to form micelles in aqueous solutions which contain 25% (by volume) or more of an additive, such as ethanol or 1,4-dioxane. The small observed rate enhancement during the solvolysis of PNPP catalyzed by long-chain compounds can, therefore, be attributed to a hydrophobic attraction between the substrate and the catalyst.

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# Electron Transfer in the Type II Photoelimination of α-Aminoacetophenones

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**Abstract:** The type II photoelimination reaction of a series of α-aminoacetophenones has been studied. Quantum yields and rate constants for product formation were determined in several solvents. These ketones were found to undergo photoelimination with extraordinarily high rates but with modest quantum efficiency. Photoelimination of α-amino ketones with low-lying π–π* triplet states also occurs with enhanced reaction rates. Attachment of an electron-withdrawing benzoyl group to the nitrogen atom decreases the rate of photoelimination. The results can best be rationalized by an electron-transfer route for which the rate constant may exceed diffusion control.

Studies of the photochemistry of ketones that possess a hydrogen-bearing γ carbon have shown that two major reaction pathways are available.[2–21] The first involves a photoelimination reaction, commonly called the Norrish type II cleavage,[22] to yield olefins and smaller carbonyl compounds, and the second involves the formation of cyclobutanols.[23] Both reactions appear to be intramolecular with little or no detectable side reactions and have been visualized as arising from a common biradical intermediate. In the case of aryl alkyl ketones, both reactions proceed by way of a triplet which leads to a 1,4-biradical intermediate which may either cyclize, undergo cleavage, or revert to starting ketone by reabstraction of hydrogen. The lines of evidence implicating the reversibility of the hydrogen transfer step are based on kinetic data[4,24] and are reinforced by stereochemical[25,26] and deuterium isotope effects.[21,27,28]

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The correlation of photochemical reactions of aryl ketones with the nature of their excited states is a subject of current interest.[29–33] The photoreactivity of these systems depends on the nature of the lowest triplet, with $^3(n-\pi^*)$ states being generally reactive and $^3(\pi-\pi^*)$ states nonreactive. An illustration of this concept is that butyrophenone, with a low-lying[3] $(n-\pi^*)$ state, undergoes the Norrish type II reaction with ease, while *p*-phenylbutyrophenone, with a low-lying $^3(\pi-\pi^*)$ state, is unreactive.[9] Introduction of substituent groups into the aromatic ring of aryl alkyl ketones can drastically alter the intramolecular hydrogen atom abstracting ability of the carbonyl group. Electron-releasing substituents increase the lifetime of the triplet state[34,35] and also decrease the rate constant and/or quantum yield for type II photoelimination.[5,8]

Previous investigations have established that $^3(n-\pi^*)$ and $^3(\pi-\pi^*)$ states of aryl alkyl ketones lie close together and mix vibronically.[13,35–38] The relative energy levels of the two states are sensitive to both substituent and solvent changes. Polar solvents increase the $\pi-\pi^*$ character of the triplet by stabilizing the $\pi-\pi^*$ state relative to the $n-\pi^*$ state. Yang, McClure, and coworkers recently proposed that the hydrogen atom abstraction reactions of methyl- and methoxy-substituted aryl ketones occur from the lowest triplet state which is mostly $\pi-\pi^*$ in character but which is also vibronically coupled with the closely spaced $n-\pi^*$ triplet.[39,40] At a later date Wagner formulated an alternate proposal.[41] He suggested that the photoelimination of *p*-methoxyphenyl alkyl ketones actually occurs from the upper $n-\pi^*$ triplet state, which lies approximately 3 kcal above the lowest vibrational level of the $\pi-\pi^*$ state, and that both states equilibrate thermally before the reaction occurs.

We previously reported that aliphatic amines are efficient photoreducing agents for biphenyl-substituted ketones.[42] These biphenyl-substituted ketones possess a low-lying $\pi-\pi^*$ configuration and have a triplet energy of approximately 61 kcal.[43] We have also found that *p*-phenylphenacylamines undergo smooth photoelimination even though the lowest lying triplet state is a $\pi-\pi^*$ triplet.[42] In nonpolar media, the $n-\pi^*$ triplet of biphenyl-substituted ketones lies at least 10 kcal above the lowest $\pi-\pi^*$ triplet. Such a large energy separation will minimize vibronic interactions of the two states. It is also difficult to imagine thermal equilibration of the two states with an energy gap of *ca.* 10 kcal. Consequently, photoreaction of biphenyl-substituted ketones should occur exclusively from the lowest lying $\pi-\pi^*$ state in contrast to the situation encountered by Yang[40] and Wagner[41] with *p*-methoxy-substituted aryl ketones. In order to account for the photoreactivity of the $\pi-\pi^*$ triplet state of *p*-phenylphenacylamines we suggested that the low-lying $\pi-\pi^*$ state interacts with an electron on nitrogen to form an ion pair or a charge-transfer complex. This paper amplifies the earlier report and presents a more detailed analysis of the photochemistry of α-aminoacetophenones.

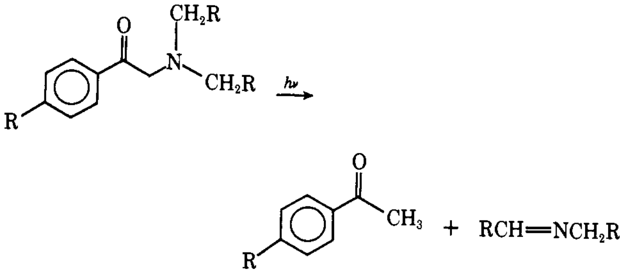
## Results

**Products and Quantum Yields.** α-(*N*,*N*-Dialkylamino) aryl ketones (**1–4**) were prepared by the reaction of a secondary amine with the appropriate α-bromo ketone. The spectral data and elemental analyses were consistent with these structures and are summarized in the Experimental Section. There is no evidence in the uv, ir, or nmr spectra of these ketones for interaction between the amino and carbonyl functions as had been found with certain cyclic amino ketones.[44] The major fragments in the mass spectrum of these ketones correspond to α and/or β cleavage (McLafferty rearrangement) in agreement with the assigned structures.

$$\underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{ArC}}}\mathrm{CH_2Br} + \mathrm{RCH_2NHCH_2R} \longrightarrow \underset{\displaystyle \mathrm{O}}{\underset{\|}{\mathrm{ArC}}}\mathrm{CH_2}\underset{\displaystyle \mathrm{CH_2R}}{\underset{|}{\mathrm{N}}}\mathrm{CH_2R}$$

**1**, Ar = Ph; R = H
**2**, Ar = R = Ph
**3**, Ar = Biph; R = Ph
**4**, Ar = 2-naphthyl; R = Ph

α-(*N*,*N*-Dialkylamino) aryl ketones (**1–4**) were irradiated in degassed benzene, ethanol, or *tert*-butyl alcohol solution (0.02–0.08 *M*) using a 450-W medium-pressure mercury arc. All quantum yields were determined at 3130 Å on degassed solutions irradiated in parallel with benzophenone–benzhydrol actinometer solutions.[45] Quantum yields were determined at 25° and product formation was analyzed by glpc after 5–15% conversion. The major products of the solution-phase photolysis of α-(*N*,*N*-dialkylamino) aryl ketones (**1–4**) are those resulting from the photocycloelimination reaction. The quantum yield was independent of per cent reaction from 2 to 15%. No products other than the Norrish type II reaction products were observed. All attempts to isolate or detect (nmr spectroscopy) N-substituted 3-



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azetidinols have failed. Although Claisen and Searles[46] have claimed to isolate 1-methyl-3-phenylazetidin-3-ol (9% yield) from the irradiation of **1**, their results could not be repeated.

In an attempt to determine the rate constants for photocycloelimination of the excited states of ketones **1**–**4**, we have studied the variation of quantum yield *vs.* quencher concentration. Surprisingly, the photoelimination of these ketones could not be quenched by modderate concentrations (0.05 mol) of 1,3-cyclohexadiene or high concentrations of piperylene (1.0 *M*). The failure to quench the reaction implies that the reaction of these ketones is too rapid for diffusion of the excited state to quencher molecule. The results are given in Table I.

**Table I** Quantum Yields for Ketone Formation from α-(*N*,*N*-Dialkylamino) Aryl Ketones[a]

| Compd no. | Solvent | Quencher | Φ |
|---|---|---|---|
| **1**[b] | Benzene | | 0.052 |
| | Benzene | Piperylene[d] | 0.045 |
| | *tert*-Butyl alcohol | | 0.046 |
| | Ethanol | Piperylene[d] | 0.050 |
| **2**[b] | Benzene | | 0.13 |
| | Benzene | Piperylene[d] | 0.13 |
| | *tert*-Butyl alcohol | | 0.14 |
| | Ethanol | Piperylene[d] | 0.14 |
| **3**[c] | Benzene | | 0.14 |
| | Benzene | 1,3-Cyclohexadiene[e] | 0.14 |
| | *tert*-Butyl alcohol | | 0.14 |
| | Ethanol | 1,3-Cyclohexadiene[e] | 0.14 |
| **4**[c] | Benzene | | 0.16 |
| | Benzene | 1,3-Cyclohexadiene[e] | 0.14 |
| | *tert*-Butyl alcohol | | 0.15 |
| | Ethanol | 1,3-Cyclohexadiene[e] | 0.15 |

[a] Average of three or more determinations at 3130 Å. [b] 0.08 *M*. [c] 0.033 *M*. [d] 1.0 *M* quencher. [e] 0.05 *M* quencher.

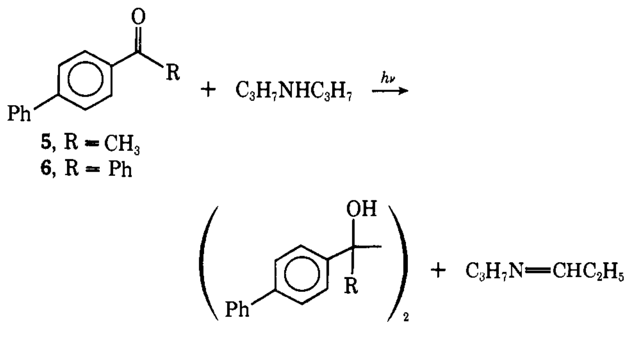
The quantum yield at 3130 Å for the production of acetophenone from ketone **1** is 0.13 in benzene and is invariant with solvent polarity. The quantum yields for acetophenone formation from ketones **1** and **2** (Table I) are smaller than those for simple phenyl alkyl ketones (*i.e.*, valerophenone Φ = 0.33 in benzene). On the other hand the quantum yields for ketone formation from **3** and **4** are significantly larger than those of the related biphenyl and naphthyl alkyl ketones. For example, Pitts and coworkers reported that *p*-phenylbutyrophenone does not undergo photocycloelimination.[9] The unusual absence of a cyclization product with the amino ketones also deserves comment. Whereas elimination is the predominant reaction (>80%) for aryl alkyl ketones, cyclobutanol formation is the major route with α-alkoxyacetophenones.[18] With α-(*N*-tosyl-*N*-methylamino)acetophenone, 3-azetidinol formation is the only path followed.[47] Factors which determine cyclization to elimination ratios are not well understood and the situation with amino ketones **1**–**4** is evidently more complex than for aryl alkyl ketone derived biradicals.

For ketones **1**–**4**, the quantum yield is independent of solvent polarity. This observation differs markedly from Wagner's results in the simple phenyl alkyl ketone system.[4] Wagner found that polar solvents increase the quantum yield for product formation. The lower quantum yields in nonpolar solvents were attributed to reversal of the hydrogen abstraction process which is retarded by hydrogen bonding of the biradical hydrogen in polar solvents. Reverse γ-hydrogen transfer of the biradical intermediate does not satisfactorily explain the low quantum yield in the amino ketone system. Unless the amino nitrogen plays an unusual role in binding the solvent, an alternate rationale to account for the low quantum yield in the amino ketone system must be sought. It should be pointed out that Turro and Lewis found that polar solvents decrease the quantum yields with α-alkoxyacetophenones.[18] Evidently the situation is more complex with α-amino- and α-alkoxyacetophenones when compared with simple phenyl alkyl ketones, undoubtedly due to the presence of the neighboring heteroatom in these systems.

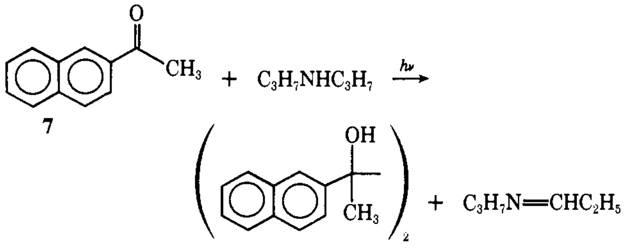
The lowest lying triplet state of ketone **2** was demonstrated to be n–π* as evidenced from its phosphorescence emission spectrum in a methanol–ethanol glass (4:1) at 77°K. The 0–0 band of **2** corresponds to a triplet energy of 73 kcal and the vibrational spacing between the 0–0 and 0–1 band is 1870 cm$^{-1}$. The 77°K lifetime was determined as *ca.* 20 msec, also consonant with an n–π* assignment. In sharp contrast, the triplet energies of **3** and **4** were determined to be 61 and 58 kcal, respectively. The radiative lifetime was 0.6 sec for **3** and 1.4 sec for **4**. These observations verify that the low-lying triplet states of **3** and **4** are π–π* in nature.[43]

Although α-amino ketones **3** and **4** have low-lying ${}^3(\pi-\pi^*)$ states they still exhibit photoreactivity comparable to that of **1** and **2**. This observation is quite unusual since the ability of an aryl alkyl ketone to undergo photoelimination is dependent on the nature of the lowest lying triplet state, with ${}^3(n-\pi^*)$ states being reactive and ${}^3(\pi-\pi^*)$ states being generally unreactive.

A related situation was encountered during the photolysis of biphenyl-substituted ketones with secondary amines. Irradiation of 0.02 *M* 4-acetylbiphenyl (**5**) and 0.1 *M* di-*n*-propylamine in benzene led to a high yield of pinacol and the corresponding imine. Similarly, photoreduction of 4-phenylbenzophenone (**6**) and 2-acetonaphthone (**7**) in di-*n*-propylamine proceeded



**5**, R = CH$_3$
**6**, R = Ph



**7**

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smoothly, and afforded good yields of pinacol. The pinacols were identified by comparison with authentic samples prepared by the reaction of aluminum amalgam with the parent ketone. All three of these ketones possess low-lying $^3(\pi-\pi^*)$ states. The quantum efficiencies of photoreduction are given in Table II. The photoreduction of ketones **5**–**7** could be quenched with 1,3-cyclohexadiene ($E_t$ = 54 kcal),[48] indicating that the reaction proceeds through a quenchable excited triplet. While these ketones undergo appreciable photoreduction with alkylamines, they are not photoreduced by alcohols or hydrocarbons. Cohen[49] and Davidson[50] have also reported that amines are effective in reducing ketones, in which the excited state of lowest energy is of the $\pi-\pi^*$ type (*e.g.*, fluorenone and *p*-aminobenzophenone).

**Table II.** Quantum Yields for Photoreduction of Aryl Ketones **5**–**7**

| Ketone[a] | Hydrogen donor | Quencher[c] | $\Phi^d$ |
|---|---|---|---|
| **5** | 2-Propanol | | 0 |
| | Di-*n*-propylamine[b] | | 0.20 |
| | Di-*n*-propylamine[b] | 1,3-Cyclohexadiene | 0.09 |
| **6** | 2-Propanol | | 0 |
| | Di-*n*-propylamine[b] | | 0.20 |
| | Di-*n*-propylamine[b] | 1,3-Cyclohexadiene | 0.04 |
| **7** | 2-Propanol | | 0 |
| | Di-*n*-propylamine[b] | | 0.17 |
| | Di-*n*-propylamine[b] | 1,3-Cyclohexadiene | 0.01 |

[a] 0.2 *M* ketone. [b] 3.3 *M* di-*n*-propylamine in benzene. [c] 5 × $10^{-2}$ mol of quencher. [d] Quantum yield for disappearance of starting ketone.

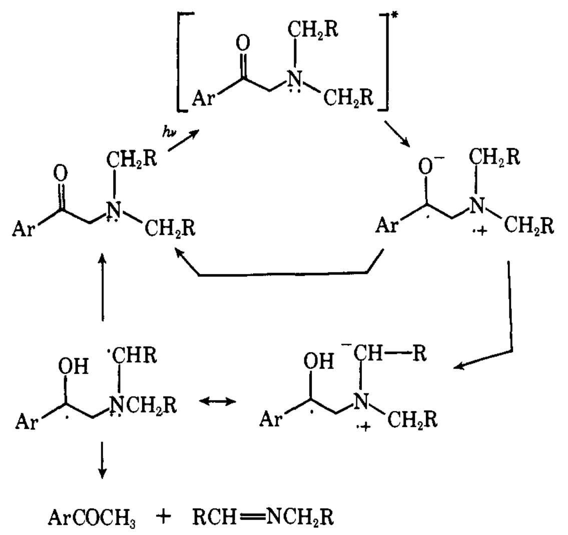
## Discussion

There have been several recent reports on the photoreduction of aromatic ketones by aliphatic and *N*-alkylarylamines.[51,52] Cohen originally suggested that photoreduction of ketones by amines proceeds *via* rapid charge-transfer interaction of the ketone triplet with the amine followed either by charge destruction and quenching or by hydrogen transfer and formation of radicals.[49]

$$\begin{tikzcd} Ar_2CO^* + RCH_2\ddot{N}R_2' \arrow[r] & {[Ar_2\dot{C}—O^- \; RCH_2\overset{\cdot +}{N}R_2']} \arrow[dl] \arrow[d] \\ Ar_2CO + RCH_2NR_2' & Ar_2\dot{C}OH + R\dot{C}H\ddot{N}R_2' \end{tikzcd}$$

Evidence in favor of this mechanism includes (a) moderately high quantum yields and low sensitivity to concentration of amines; (b) the quenching of benzophenone triplets by amines which do not contain abstractable hydrogens; (c) the ineffectiveness of known triplet quenchers upon the reduction by amines; (d) the lack of specificity of attack of the excited carbonyl group upon the C–H bonds of alkylated amines; and (e) the relatively small kinetic deuterium isotope effect shown in reduction by amines.

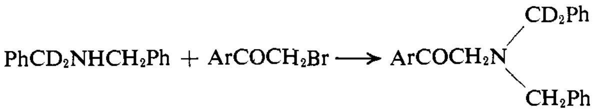
The results encountered in the photoelimination reactions of α-amino ketones **1**–**4** are unusual in several respects: (a) remarkably rapid reaction rates; (b) moderate quantum yields; (c) quantum efficiency appears to be independent of solvent polarity; (d) negligible yields of cyclization product; (e) high reactivity of $\pi-\pi^*$ triplet states. Such marked differences in behavior of α-amino ketones **1**–**4** relative to simple phenyl alkyl ketones imply different mechanisms for photoelimination. We suggest that the sum of the available evidence is most consistent with an intramolecular electron-transfer mechanism as shown below.



The low quantum efficiency of the photoelimination coupled with the failure to quench the triplet suggests that the excited state interacts with an electron on nitrogen to form an ion pair or charge-transfer complex. The lack of quenching implies that this process proceeds at a rate exceeding diffusion control. Back transfer of an electron in the complex would regenerate starting ketone and account for the less than maximum quantum yield. Transfer of a proton from the benzylic carbon to the ketyl radical and electron reorganization will produce the same 1,4 biradical as would be obtained by simple hydrogen abstraction. It appears that attack at an electron of nitrogen can occur for both n–$\pi^*$ and $\pi-\pi^*$ triplet states. The sequence of steps outlined above is closely related to the scheme proposed by Cohen to account for the photoreduction of aromatic ketones by amines.[49,51] The electron-transfer hypothesis is also appealing as an explanation for the reactivity of ketones **5**–**7** which possess low-lying $\pi-\pi^*$ triplet states.

Additional evidence for this mechanism was gleaned from experiments with deuterated α-amino ketones **8** and **9**. The preparation of these ketones was readily accomplished by the reaction scheme shown below. The

$$PhCN \xrightarrow{LiAlD_4} PhCD_2NH_2 \xrightarrow{PhCH_2Br} PhCD_2NHCH_2Ph$$



$$PhCD_2NHCH_2Ph + ArCOCH_2Br \longrightarrow ArCOCH_2N\begin{matrix} CD_2Ph \\ CH_2Ph \end{matrix}$$

**8**, Ar = Ph
**9**, Ar = BiPh

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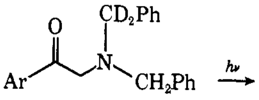
relative ratio of *N*-benzylbenzalimine-*3,3-d*$_2$ (**10**) to *N*-benzylbenzalimine-*1-d*$_1$ (**11**) resulting from irradiation of ketones **8** and **9** was determined by mass spectrometry (see Experimental Section). The deuterium isotope effect on the $\gamma$-abstraction reaction is $k_H/k_D = 1.28 \pm 0.05$ for both ketones. This value is substantially smaller than that reported by Yang and Coulson in the 2-hexanone series, in which deuteration at the $\gamma$-hydrogen leads to kinetic isotope effects of $k_H/k_D = 2.7$ for singlet abstraction and $k_H/k_D = 5.7$ for triplet abstraction.[27] In photoreduction of ketones by alcohols, differences in rates between deuterated and nondeuterated hydrogen donors are in the order of $k_H/k_D \sim 2.7$.[53,54] Whereas a small but positive isotope effect is observed for the $\gamma$-abstraction reaction of **8** and **9**, there is no measurable isotope effect on the quantum yield of product formation. The deuterium isotope effects observed for ketones **8** and **9** are comparable to the relatively small kinetic deuterium isotope effects reported by Cohen and Chao in the photoreduction of benzophenone by alkylamines.[51] Although the transfer of hydrogen from $C_\alpha$ to N appears to be involved at least partially in the rate-determining portion of the reaction profile, the low value of the isotope effect can be considered as further support for the electron-transfer mechanism.

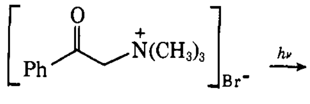


$ArCOCH_3 + PhCH{=}NCD_2Ph + PhCD{=}NCH_2Ph$

**10** **11**

It might be anticipated that increasing the polarity of the medium would favor the electron-transfer route since a significant amount of charge develops with the transfer of an electron from nitrogen to the excited carbonyl group. This is to be expected since it is known that ground-state reactions which proceed by electron transfer show large rate enhancements in acetonitrile relative to benzene.[55] In a related study Wagner found that the intramolecular rate constant for type II photoelimination of $\gamma$-dimethylaminobutyrophenone in methanol was one-tenth that in benzene.[56] Wagner suggested that the solvent effects on the rate were inconsistent with an actual electron-transfer process and instead concluded that formation of a charge-transfer complex occurs. He points out that the charge-transfer process creates a large dipole rather than a formal free charge and that the complex might be subject to different polar solvent effects than a complete electron-transfer process, especially if the electrons on the amine are less available because of hydrogen bonding. Cohen also reports a higher rate constant for interaction of amines with triplets in benzene than in an aqueous medium.[57] Cohen suggests that hydrogen bonding of water with the electron pair on nitrogen renders more difficult attack of the ketone triplet on the N electrons. It appears that the role of solvent in the electron-transfer route of the amino ketone system is complex and difficult to interpret. In view of these difficulties we will not attempt to rationalize the absence of a solvent effect on the quantum yields of $\alpha$-amino ketones **1**–**4**.

The electron-transfer scheme outlined above would predict a decrease in the quantum efficiency of reaction as the pair of electrons on nitrogen become less available. Our experiments show that the quantum yield of the photoreaction decreases substantially ($\Phi < 0.01$) when the substituted phenacylamines are converted to their "onium" derivatives by protonation. The quantum yield of $\alpha$-(*N,N*-dibenzylamino)acetophenone hydrochloride disappearance in ethanol is ten times greater than that of acetophenone formation. This implies that photoreduction by solvent is the major reaction path for this system. Irradiation of $\alpha$-(*N,N,N*-trimethylammonium)acetophenone bromide (**12**) in ethanol gave trimethylamine hydrobromide (90%) and dibenzoylethane (10%), together with small quantities of acetophenone (<5%). The isolation of trimethylamine hydrobromide and dibenzoylethane suggests that photoelimination is at best a minor path. Instead it appears as though the quaternary ammonium salt undergoes homolytic (or heterolytic) $\alpha$-carbon–nitrogen cleavage. An excited state solvolysis of the ammonium salt to form phenacyl bromide cannot be discarded especially since phenacyl bromide rapidly photolyzed in ethanol to form acetophenone.[58] Berchtold and Maycock recently reported that photolysis of the analogous phenacylsulfonium salts affords products resulting from homolytic cleavage of the phenacyl carbon–sulfur bond.[59]



**12**

$(CH_3)_3N{\cdot}HBr + PhCOCH_2CH_2COPh + PhCOCH_3$

It has previously been suggested that the efficiency of electron transfer is related to the ionization potential of the amine used.[60] Electron-donating substituents in the para position of arylamines are known to substantially increase the charge-transfer interaction with ketone triplets, while electron-withdrawing substituents decrease the interaction. In order to determine whether electron-attracting substituents attached to the nitrogen atom of $\alpha$-amino ketones will decrease the rate of photoelimination, we have investigated the photochemistry of $\alpha$-(*N*-benzyl-*N*-benzoylamino)acetophenone (**13**). Irradiation of **13** in benzene with a 450-W Hanovia lamp resulted in a facile Norrish type II photoelimination with formation of acetophenone and 1-benzoyl-2-phenylazetidin-3-ol (**14**). Although *N*-benzoylbenzalimine (**15**) was not isolated, its presence was suggested by the isolation of benzaldehyde and benzamide. This imine is known to be quite unstable and has been reported to hydrolyze readily and give benzaldehyde and

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(56) P. Wagner and A. E. Kemppainen, *ibid.*, 91, 3085 (1969).

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(58) Irradiation of phenacyl chloride in ethanol affords only acetophenone (53%): J. C. Anderson and C. B. Reese, *Tetrahedron Lett.*, 1 (1962).

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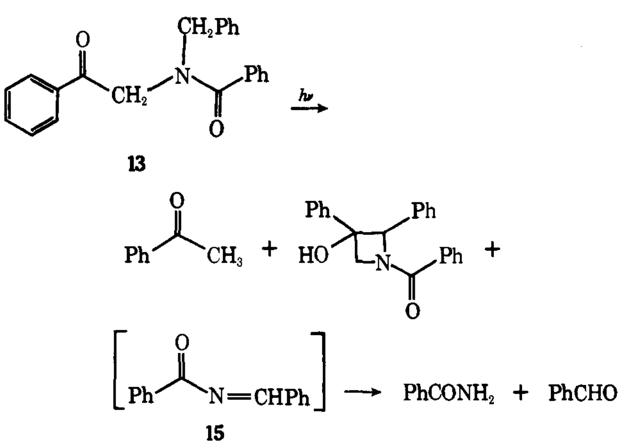

benzamide.[61] Products were identified by preparative glpc and nmr analysis (see Experimental Section).

Photolysis of **13** in degassed benzene solution in the presence of varying amounts of piperylene resulted in the linear Stern–Volmer plot ($\Phi_0/\Phi$ *vs.* quencher) shown in Figure 1. The slope of the Stern–Volmer plot equals $k_q\tau(0.6)$ where $k_q$ is the rate constant for quenching of the ketone triplet by piperylene and $\tau$ is the ketone triplet lifetime. Assuming a value of $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for $k_q$ allows calculation of $1/\tau$. The intramolecular rate constant for **13** ($8 \times 10^9\ \text{sec}^{-1}$) is much faster than that for γ-phenylbutyrophenone ($4 \times 10^8\ \text{sec}^{-1}$).[5] The presence of an amino nitrogen lowers the bond dissociation for C–H homolysis relative to a methylene group. It should be pointed out, however, that by attaching the electron-withdrawing benzoyl group to the nitrogen atom the photoelimination can now be quenched. We were unable to quench the Norrish type II reaction of the related α-(*N*,*N*-dibenzylamino)acetophenone (**2**) system. By decreasing the availability of the electron pair on nitrogen it becomes possible to quench the reaction. The reaction rate is still remarkably large. This result is consistent with the interpretation that α-amino ketones undergo photoelimination by facile electron transfer.

In summary, solvent, substituent, and deuterium isotope effects on the photochemistry of α-aminoacetophenones have been investigated. These ketones were found to undergo photoelimination with extraordinarily high rates but modest quantum efficiency. Photoelimination of α-amino ketones with low-lying π–π* triplet states also occurs with enhanced reaction rates. Attachment of an electron-withdrawing benzoyl group to the nitrogen atom decreases the rate of photoelimination. The results can be rationalized by an electron-transfer route for which the rate constant may exceed diffusion control, although rapid γ-hydrogen abstraction by the n–π* state is not necessarily eliminated from the available data. The deuterium isotope effects observed with ketones **8** and **9** would be expected to be smaller than 2-hexanone since the energy barrier for γ-H abstraction is much lower with benzylic type hydrogens. Decreasing the availability of the nitrogen nonbonding electrons should also decrease the rate of γ-H abstraction as well as electron transfer since the nitrogen electron pair would no longer be able to stabilize the adjacent radical center. The possibility also exists that γ-H abstraction can occur from a n–π* singlet with the biphenyl- and naphthyl-substituted ketones since rate constants for intersystem crossing in β-acetonaphthone and biphenyl are less than $10^{10}\ \text{sec}^{-1}$.[61a] It is also conceivable that the quenching observed for ketone **13** could be singlet rather than triplet quenching in view of the high piperylene concentrations used.[62] It is possible that both explanations can account for the observed characteristics of type II photoelimination of α-aminoacetophenones. The factors which control bond scission and coupling of the amino biradical remains undetermined at this point.

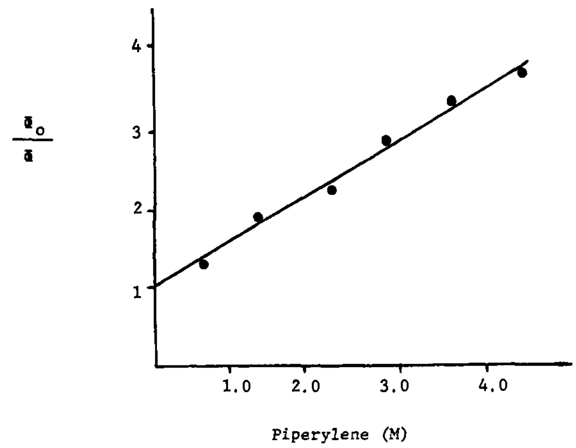

Figure 1. Stern–Volmer plot for quenching of acetophenone formation from α-(*N*-benzyl-*N*-benzoylamino)acetophenone in benzene.

## Experimental Section[63]

**α-(*N*,*N*-Dimethylamino)acetophenone (1).** A mixture of 7.0 g (0.035 mol) of α-bromoacetophenone and 3.16 g (0.070 mol) of dimethylamine in 100 ml of benzene was allowed to stir at 0° for 6 hr. The hydrobromide salt formed was filtered and the filtrate was evaporated to give an oil. Distillation of the residue gave 4.2 g (73%) of **1**, bp 90–94° (1.4 mm) (lit.[64] 126–128° (18 mm)). The nmr spectrum (CDCl$_3$) showed singlets at τ 7.59 (6 H) and 6.18 (2 H) and a multiplet centered at 2.43 (5 H).

**α-(*N*,*N*-Dibenzylamino)acetophenone (2).** A mixture of 20.0 g (0.1 mol) of α-bromoacetophenone and 40.0 g (0.2 mol) of dibenzylamine in 700 ml of benzene was allowed to reflux for 16 hr. The hydrobromide salt formed was filtered and the filtrate was concentrated. Recrystallization of the residue from 95% ethanol afforded 10 g (32%) of **2**, mp 79–81° (lit.[65] 81°). The nmr spectrum (CDCl$_3$) showed singlets at τ 6.25 (4 H) and 6.19 (2 H) and a multiplet centered at 2.73 (15 H). The corresponding hydrochloride salt, mp 190-191°, was prepared by bubbling hydrogen chloride gas through an ethereal solution of **2**.

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(61) S. W. Breuer, T. Bernath, and D. Ben-Ishai, *Tetrahedron Lett.*, 4569 (1966).

(61a) Note Added in Proof. It is generally assumed that simple phenyl ketones undergo intersystem crossing with 100% efficiency. Recent results by Professor P. Wagner (private communication) have shown, however, that the intersystem crossing yield of dialkylaminophenyl alkyl ketones decreases substantially as the amino group approaches the carbonyl group. These new data suggest that the type II photoeliminations reported above may actually be derived by electron transfer from the n–π* excited singlet state.

(62) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).

(63) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer. Tetramethylsilane was used as an internal standard.

(64) H. Braun and A. Weissbach, *Chem. Ber.*, **62**, 2425 (1929).

(65) S. Busch and R. Hefele, *J. Prakt. Chem.*, **83**, 449 (1911).

**$\alpha$-(*N*,*N*-Dibenzylamino)-4-acetylbiphenyl (3).** A mixture of 24.9 g (0.09 mol) of $\alpha$-bromo-4-acetylbiphenyl[66] and 35.7 g (0.18 mol) of dibenzylamine in 700 ml of benzene was allowed to reflux for 16 hr. Removal of the hydrobromide salts followed by recrystallization from 95% ethanol gave 12 g (34%) of **3**, mp 123–124°.

*Anal.* Calcd for $C_{28}H_{25}NO$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.52; H, 6.43; N, 3.46.

The infrared spectrum (KBr) was characterized by bands at 5.93 6.23, 8.20, 10.38, 13.35, and 14.32 $\mu$. The nmr spectrum ($CDCl_3$) showed singlets at $\tau$ 6.25 (4 H) and 6.22 (2 H) and a multiplet centered at 2.70 (19 H). The ultraviolet spectrum (95% ethanol) had a maximum at 250 m$\mu$ ($\epsilon$ 18,000). The mass spectrum showed prominent peaks at *m*/*e* (relative intensity) 210 (45), 196 (5), 181 (10), 153 (10), 152 (10), 91 (100). The corresponding hydrochloride salt was obtained in 90% yield, mp 213–215° dec.

**$\alpha$-(*N*,*N*-Dibenzylamino)-2-acetonaphthone (4).** A solution containing 51 g (0.3 mol) of 2-acetonaphthone in 400 ml of anhydrous ether was treated with 47.9 g (0.3 mol) of bromine. Recrystallization of the crude solid from ethanol afforded 64 g (86%) of $\alpha$-bromo-2-acetonaphthone, mp 80–81°. A mixture of the above $\alpha$-bromo-2-acetonaphthone (34 g) and 53.8 g of dibenzylamine in 700 ml of benzene was allowed to reflux for 24 hr. Recrystallization of the crude solid from 95% ethanol afforded 40 g (81%) of **4**, mp 109–110°.

*Anal.* Calcd for $C_{26}H_{23}NO$: C, 85.45; H, 6.34; N, 3.83. Found: C, 85.46; H, 6.31; N, 3.70.

The infrared spectrum (KBr) was characterized by bands at 5.98, 7.30, 8.40, 10.31, 12.16, 13.56, and 14.38 $\mu$. The ultraviolet spectrum (95% ethanol) exhibited maxima at 346 m$\mu$ ($\epsilon$ 44,500), 282 m$\mu$ ($\epsilon$ 9000), and 340 m$\mu$ ($\epsilon$ 1500). The nmr spectrum ($CDCl_3$) showed singlets at $\tau$ 6.33 (4 H) and 6.20 (2 H) and a multiplet centered at 2.73 (17 H). The mass spectrum showed prominent peaks at *m*/*e* (relative intensity) 274 (4), 210 (86), 127 (15), 91 (100), and 75 (9). The corresponding hydrochloride salt was isolated in 88% yield, mp 220–222°.

**$\alpha$-(*N*,*N*-Dibenzylamino)acetophenone-$\alpha$,$\alpha$-$d_2$ (8).** A mixture of 2.0 g of $\alpha$-bromoacetophenone, 2.0 g of dibenzylamine-$\alpha$,$\alpha$-$d_2$, and 1.1 g of triethylamine in 100 ml of benzene was allowed to stir at room temperature for 48 hr. The precipitated hydrobromide salts were filtered and the filtrate was concentrated under reduced pressure. Crystallization of the oily residue from 95% ethanol gave 1.9 g (59%) of **8**, mp 77–78°. The nmr spectrum ($CDCl_3$) showed a broad singlet at $\tau$ 6.27 (4 H) and multiplets centered at 2.73 (13 H) and 2.23 (2 H). The mass spectrum showed two peaks of equal intensity at *m*/*e* 93 and 91 (base) and had major peaks at 212, 183, 105, and 77.

**$\alpha$-(*N*,*N*-Dibenzylamino)-4-acetylbiphenyl-$\alpha$,$\alpha$-*benzyl*-$d_2$ (9).** A mixture of 2.5 g of $\alpha$-bromo-4-acetylbiphenyl, 1.8 g of *N*,*N*-dibenzylamine-$\alpha$,$\alpha$-$d_2$, and 1.1 g of triethylamine was allowed to reflux for 3 hr. At the end of this time the hydrobromide salts were filtered and the filtrate was concentrated under reduced pressure. Crystallization of the oily residue from 95% ethanol gave 1.3 g (34%) of **9**, mp 121–123°. The nmr spectrum ($CDCl_3$) showed singlets at $\tau$ 6.23 (2 H) and 6.17 (2 H) and a multiplet centered at 2.68 (19 H). The mass spectrum showed two peaks of equal intensity at *m*/*e* 93 and 91 and had major peaks at 309, 212, 181, and 78.

**$\alpha$-(*N*,*N*,*N*-Trimethylammonium)acetophenone Bromide (12).** To a stirred solution containing 5.0 g of $\alpha$-bromoacetophenone in 50 ml of benzene was added a saturated solution of trimethylamine in 50 ml of benzene. After stirring for 2 hr, the precipitated salt was filtered. Recrystallization from absolute ethanol afforded 4.6 g (71%) of **12**, mp 201–203° dec.

*Anal.* Calcd for $C_{11}H_{16}NOBr$: C, 51.38; H, 6.27; N, 5.45. Found: C, 51.04; H, 6.28; N, 5.28.

The infrared spectrum (KBr) was characterized by bands at 3.45, 5.95, 6.92, 8.20, 10.42, 10.90, 13.08, and 14.55 $\mu$. The ultraviolet spectrum (95% ethanol) exhibited maxima at 247 m$\mu$ ($\epsilon$ 1200) and 286 m$\mu$ ($\epsilon$ 1200).

**$\alpha$-(*N*-Benzyl-*N*-benzoylamino)acetophenone (13).** To a stirred solution containing 10.8 g of benzylamine in 200 ml of benzene was added a solution of 10.2 g of $\alpha$-bromoacetophenone in 100 ml of benzene. After 6 hr the hydrobromide salt was filtered. The filtrate was cooled to 0° and a solution of 7.0 g of benzoyl chloride in 100 ml of benzene was added. After stirring for 1 hr the precipitated salts were filtered and the filtrate was concentrated under reduced pressure. The oily residue was recrystallized from heptane–benzene to give 5.0 g (30%) of **13**, mp 124–125°.

*Anal.* Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.19; H, 5.82; N, 4.23.

The infrared spectrum (KBr) was characterized by bands at 5.90, 6.12, 6.90, 10.40, and 14.35 $\mu$. The ultraviolet spectrum (95%) ethanol showed a maximum at 242 m$\mu$ ($\epsilon$ 11,800). The nmr spectrum ($CDCl_3$) showed two broad singlets at $\tau$ 5.28 (2 H) and 5.12 (2 H) and had multiplets centered at $\tau$ 2.65 (13 H) and 2.10 (2 H). The mass spectrum showed a weak parent ion at *m*/*e* (relative intensity) 329 (1), and had peaks at 224 (46), 210 (45), 105 (100), 91 (6), and 77 (2).

**Irradiation and Identification of Photoproducts.** Benzene solutions containing 0.5 g of ketone were photolyzed for several hours with a 450-W Hanovia medium-pressure lamp through Pyrex. Solutions were analyzed by preparative glpc using either an 11 ft × 0.25 in. column of 10% Versamid on Chromosorb P or a 10 ft × 0.25 in. column of 10% Apiezon J on Chromosorb W. Norrish type II products were identified by comparison with authentic samples. 1-Benzoyl-2-phenylazetidin-3-ol (**14**) was isolated as a crystalline solid, mp 165–167°, from the irradiation of $\alpha$-(*N*-benzyl-*N*-benzoylamino)acetophenone (**13**).

*Anal.* Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.36; H, 6.02; N, 4.48.

The infrared spectrum of **14** showed bands at 3.10 (OH group) and 6.21 $\mu$ (C=O). The mass spectrum showed a weak parent ion at *m*/*e* 329 and had other major peaks at 224, 210, 196, 120, 105 (base), 91, and 77.

**Irradiation of $\alpha$-(*N*,*N*-Dibenzylamino)acetophenone-$\alpha$,$\alpha$-$d_2$ (8).** A solution containing 0.8 g of **8** in 500 ml of benzene was irradiated for 3 hr through a Pyrex filter. Removal of the solvent left an oil which showed two major components by glpc analysis. The two components were separated and collected on a 6 ft × 0.25 in. column packed with 8% FS1265 on Diatoport S. Benzaldehyde *N*-benzylimine was analyzed on a Hitachi Perkin-Elmer mass spectrometer (Model RMU-6E) with an ionization voltage of 15 eV. The molecular ion region and the peaks at *m*/*e* 93 and 91 were scanned several times for several samples and the isotopic composition was calculated as an average value corrected for the natural abundance of $^{13}C$.

**Coirradiation of Aryl Ketones with Di-*n*-propylamine.** A solution containing 10 g of the appropriate aryl ketone and 60 g of di-*n*-propylamine in 200 ml of benzene was irradiated with a 550-W Hanovia lamp using a Pyrex filter. Removal of the solvent left a crystalline residue which was further purified by crystallization from chloroform–acetone. In all cases authentic samples of the pinacols were prepared by aluminum amalgam reduction of the starting ketone and were identical with the pinacols isolated from the irradiation.

**Quantum Yield Determinations.** All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450-W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of a solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate per 100 ml of water[3] through the inner jacket. This solution permitted the following wavelength distribution to pass through: 6% 2967 Å, 20% 3025 Å, 62% 3130 Å, 10% 3340 Å. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to $5 \times 10^{-3}$ mm in three freeze–thaw cycles and then sealed. Benzophenone–benzyhydrol actinometry was used for quantum yield determinations. An actinometer quantum yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 *M*.[54] Reliably reproducible output rates of $4.86 \times 10^{16}$ quanta sec$^{-1}$ were recorded. After the irradiation the degree of reaction was determined by quantitative ultraviolet spectroscopy and vapor-phase chromatography. Each quantum yield was the average of three or more analyses of two or more solutions. Reproducibility for simultaneously irradiated samples was ±5% and the overall accuracy of the reported values was ±10%. Photolyses were carried to 15% or less conversion.

**Quenching Studies.** Samples were prepared and analyzed as for quantum yield determination except that varying amounts of piperylene or 1,3-cyclohexadiene were added to the solutions. Six concentrations of piperylene in addition to blanks containing no piperylene were used for the Stern–Volmer plot of ketone **13**. Linear least-squares fits had standard deviations of <10% and repeated determinations agreed to within ±10%.

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(66) M. I. Shevchuk and A. V. Dombrovskii, *Zh. Obshch. Khim.*, 33, 1135 (1963).

**Phosphorescence Emission Studies.** The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using a methanol–ethanol mixture (4:1) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on an *xy* plotter. Samples having short radiative lifetimes (<100 msec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gives the mean lifetime ($\tau$).

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# The Intra- and Intermolecular-Sensitized Photolysis of Substituted Benzoyl Peroxides

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*Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306.* *Received March 3, 1971*

**Abstract:** A series of substituted benzoyl peroxides has been prepared in which the substituent is a benzophenone-like sensitizer. In contrast to the related intermolecular system (benzoyl peroxide plus benzophenone), these peroxides photolyze with quantum yields approaching unity. The effectiveness of the sensitizer in various positions relative to the peroxide functional group has been studied by means of Stern–Volmer quenching experiments, emission experiments, and an intramolecular competition experiment with a diperoxide containing a central benzophenone moiety. Direct photolysis of benzoyl *m*-benzoylbenzoyl peroxide in $CCl_4$ gives chlorobenzene with enhanced proton magnetic resonance absorption; thermolysis gives chlorobenzene with enhanced emission. It is suggested that the low quantum yields obtained with benzoyl peroxide plus benzophenone are due to deactivation of an exciplex.

A salient characteristic of the benzophenone-sensitized photolysis of benzoyl peroxide is the low quantum yield. The work of Walling and Gibian[1] and of Smith[2] on the quantum yield at different peroxide concentrations has shown that the low yield is due to two factors: (i) an energy-transfer rate orders of magnitude below a diffusion-controlled value, and (ii) an inherently low efficiency of utilization of the energy even after the donor has been deactivated by the interaction with the peroxide molecule. In contrast, the quantum yields for the direct photolysis of dialkyl peroxides in the gas phase are near unity.[3,4] The quantum yield for the photolysis of dipropionyl peroxide in solution is moderately high, about 0.6.[5]

In the present paper we report some experiments with benzoyl peroxides having benzophenone-like chromophores as substituents.[6] The intramolecular transfer of excitation energy in these keto peroxides is fast and the utilization of the energy efficient, giving quantum yields near unity in most cases.

Although the intramolecular energy transfer is fast, the rate is still measurable by means of quenching experiments. The way in which the energy transfer depends on the intervening molecular structure suggests that the interaction between the ketonic n–$\pi^*$ and peroxidic functional groups is largely of the "through-bonds"[7] variety rather than simply through space.

Other published work on the photolysis of diacyl peroxides has been concerned with the direct photolysis,[8] singlet-sensitized photolysis,[1,8f,9–14] and triplet-sensitized photolysis.[1,2,9,11,15] It has also been shown, by Kaptein, *et al.*,[11] and by Fahrenholtz and Trozzolo,[14] that the thermolysis and direct photolysis of ordinary diacyl peroxides produce singlet radical pairs while the sensitized photolysis gives either singlet or triplet pairs, depending on the sensitizer. A compound with a naphthyl-sensitizing substituent in the molecule, bis(3-($\beta$-naphthyl)propanoyl) peroxide, has been studied by Kardash and Krongauz.[5]

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