Kinetics of Photoreduction of Benzophenones by Amines, Deamination and Dealkylation of Amines[1]

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Abstract: Kinetics of photoreduction of aromatic ketones by aliphatic amines are consistent with a mechanism involving rapid charge-transfer interaction between the ketone triplet and amine, k_{ir}, followed by hydrogen transfer and formation of radicals, k_h, or by charge destruction and quenching, k_e. The quenching property is demonstrated by retardation by *tert*-butylamine of photoreduction of benzophenone by 2-butylamine. Photoreduction by aqueous amines is not complicated by light-absorbing by-products, and values of k_{ir} for the photoreduction of 4-benzoylbenzoic acid by amines in aqueous pyridine were determined. They are 6×10^8, 1×10^8, and 6×10^7 M^{-1} sec^{-1} for reduction by tertiary amines, a secondary amine, and a primary amine, respectively. Quantum yields depend upon the fraction $f = k_h/(k_h + k_e)$, and have values ~0.73, 0.28, 0.55 for tertiary, secondary, and primary amines, respectively. Photoreduction of 4-benzoylbenzoic acid by triethylamine in benzene is complicated by light-absorbing transients, but has an initial quantum yield of ~1.5 for formation of ketyl radicals, similar to that in aqueous solution. Photoreduction of benzophenone by 2-butylamine shows similar quantum yields, ~1.1, in benzene, acetonitrile, and aqueous pyridine. The value of k_{ir} is higher in benzene, 2×10^8 M^{-1} sec^{-1}, than in 1:1 aqueous pyridine, 2×10^7 M^{-1} sec^{-1}, while k_r for reaction with 2-propanol is the same in the two media, 2×10^6 M^{-1} sec^{-1}. The transfer of two reducing groups from amine to excited and ground state ketone is discussed. Depending upon structure, the reactions lead to imines and enamines, and, with *N*-methyl groups, may involve immonium ions or adducts of initially formed radical to ground state ketone. The reactions provide a useful procedure for dealkylation of tertiary to secondary amines, in which methyl and other small groups are preferentially removed, and for quantitative oxidative deamination of primary amines.

The photoreduction of benzophenone by aliphatic amines containing a $>CHN<$ group is an efficient process, and, with primary and secondary amines in dilute solution in hydrocarbons, leads to high yields of benzpinacol and of imines containing the $C{=}N$ group.[2] Photoreduction of benzophenone by neat tertiary aliphatic amines was inefficient.[2a] The efficiency rose remarkably when the tertiary amine was diluted with hydrocarbon, an effect which was attributed to the observed formation of less light-absorbing by-products in the hydrocarbon solution.[2b] However, high yields of pure products were not isolated.

Solutions of tertiary aliphatic amines in hydrocarbons subsequently proved to be effective photoreducing agents for ketones which have π–π^* or charge-transfer triplets. *p*-Aminobenzophenone, which is not photoreduced by alcohols or primary amines, is photoreduced by triethylamine in cyclohexane, $\varphi = 0.6$.[3] Fluorenone is not photoreduced by alcohols, but is photoreduced with low efficiency by primary and secondary amines, and with high efficiency by 0.1 M triethylamine in cyclohexane, $\varphi = 0.9$.[4] High concentration of tertiary amine leads to quenching of fluorenone singlet.[5] Low reactivity of *p*-aminobenzophenone[6] and fluorenone[7] in polar solvents is largely due to decreased intersystem crossing.

Photoreduction of aromatic ketones by alcohols proceeds by abstraction by the ketone triplet[8] of hydrogen from the carbinol carbon.[9] Abstraction of this hydrogen may be facilitated by a polar contribution to the stability of the transition state[2b]

$$\left[Ar_2\dot{C}O\cdot\ H\cdot >\dot{C}{-}XH \longleftrightarrow Ar_2\dot{C}O^-\ H\cdot\ >\overset{+}{\dot{C}}\overset{\curvearrowleft}{-}XH\right]$$

The thought that the N of amines might similarly facilitate abstraction of hydrogen prompted us to study photoreduction by amines.[2] In the photoreduction of *p*-aminobenzophenone by tertiary amines, the bicyclic bridgehead diamine, 1,4-diazobicyclooctane, showed fairly high reactivity, $\varphi = 0.25$.[3] While the stabilization indicated above may not require full planarity of the $>CX-$ grouping, this indicated that activation by adjacent N might arise from an initial charge-transfer interaction, followed by hydrogen transfer, eq 1.[3] This

$$Ar_2C{=}O^* + >NCH< \xrightarrow{k_{ir}} \left[Ar_2\dot{C}{-}O^-\ >\overset{+}{N}\dot{C}H<\right] \longrightarrow$$
$$Ar_2\dot{C}{-}OH + >N\dot{C}< \quad (1)$$

different mode of reaction might account in part for the high reactivity of amines.

The photoreduction of benzophenone by 0.1–10 M 2-butylamine in benzene[10] showed low sensitivity to concentration of amine and of physical quenchers, corresponding to a low, favorable ratio of rate constant for deactivation of excited ketone to that for its reaction with the amine, $k_d/k_{ir} = 0.03$ M, and to a high value of k_{ir}, 2×10^8 M^{-1} sec^{-1}, based on $k_q = 6 \times 10^9$ M^{-1} sec^{-1} for diffusion controlled quenching by naphthalene. However, the limiting quantum yield was only 1.1 as com-

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(1) A preliminary report on part of this work has been published, S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, 91, 3690 (1969).

(2) (a) S. G. Cohen and R. J. Baumgarten, *ibid.*, 87, 2996 (1965); (b) *ibid.*, 89, 3471 (1967).

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

(4) S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968).

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

(6) S. G. Cohen, M. D. Saltzman, and J. B. Guttenplan, *Tetrahedron Lett.*, 4321 (1969).

(7) J. B. Guttenplan and S. G. Cohen, *ibid.*, 2125 (1969).

(8) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 14, 958 (1962)

(9) G. O. Schenck, W. Medev, and M. Pape, *Proc. U. N. Int. Conf. Peaceful Uses At. Energy*, *2nd*, 29, 352 (1958).

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

pared with 2 in photoreduction by 2-propanol[11] for which values of k_d/k_r and k_r are substantially less favorable. Light-absorbing transients were not observed nor were reversible abstraction of hydrogen or disproportionation of the amine-derived radicals detected in experiments with optically active 2-butylamine. To account for the relatively low quantum yield and the other properties of the reaction, it was proposed[10] that the amines acted as both reducing and quenching agents, and that the reaction proceeded by very rapid formation of a charge-transfer complex, k_{ir}, which might be followed by hydrogen transfer and formation of radicals, k_h, or by charge destruction and quenching, k_e, eq 2. Comparison of

$$\begin{tikzcd}
Ar_2C{=}O^* + R_2CHNH_2 \arrow[r, "k_{ir}"] & {[Ar_2\dot{C}{-}O^- \; R_2CH\overset{+}{N}H_2]} \arrow[dl, "k_e"'] \arrow[d, "k_h"] \\
Ar_2C{=}O + R_2CHNH_2 & Ar_2\dot{C}{-}OH + R_2\dot{C}NH_2
\end{tikzcd} \tag{2}$$

photoreduction of benzophenone by cyclohexylamine and cyclohexylamine-*1-d* indicated[10] a small deuterium isotope effect, $k_H/k_D = 1.6$, as compared with 2.7 in photoreduction by alcohols.[12,13] This is consistent with a hydrogen transfer facilitated by prior charge transfer, eq 2.

We were unable to make a kinetic analysis of photoreduction of benzophenone by secondary and tertiary amines because of light-absorbing by-products, which were decreased but not eliminated by dilution of the amines with hydrocrabon. This difficulty did not arise in studies of *p*-aminobenzophenone and fluorenone, where light-absorbing transients are not observed. Because of the proposed polar mechanism of abstraction of hydrogen from amines it appeared reasonable to examine the photoreduction of a benzophenone by amines in aqueous systems. Such media are not suitable for study of ketones like fluorenone or *p*-aminobenzophenone, but are satisfactory for the reactive ketones with n–π* triplets.[14] Although photoreduction by alcohols in hydroxylic and aqueous media is seriously complicated by light-absorbing transients,[15] photoreduction of 4-benzoate in aqueous solutions of primary, secondary, and tertiary amines proceeded efficiently without complication from light-absorbing transients, probably due to the high pH, and led to high yields of the hydrol and to products of oxidative–hydrolytic cleavage of the amines.[16] The systems lend themselves to quantitative study, a detailed description of which we now report.

Experimental Section

Materials. Benzophenone was Fisher Certified Reagent, mp 47.5–48.5°. 4-Benzoylbenzoic acid was from Aldrich, mp 202–202.5°. 2-Butylamine, bp 63–64°, *tert*-butylamine, bp 44–46°, diisopropylamine, bp 83–84°, diisopropylethylamine, bp 127°, *N,N*-dimethylbenzylamine, bp 39–40° (17 mm), and triethylamine, bp 88–89°, were obtained from Eastman Kodak Co. and redistilled. *N*-Methyl-2-butylamine (K and K Laboratories) was redistilled, bp 80°, and showed a single band on glc. 2-Propanol, pyridine, and naphthalene were Fisher Certified Reagent grade. 4-Cyanobenzyl chloride was from K and K Laboratories.

N,N-Dimethyl-2-butylamine was prepared[17] from 25 g (0.34 mol) of 2-butylamine, 88 g (1.7 mol) of 90% formic acid, and 65 g (0.75 mol) of 35% formaldehyde: 12 g (0.12 mol); 35% yield; bp 92–93°; lit.[17] bp 94°.

Methyl diisopropylamine was prepared similarly from 50 g (0.50 mol) of diisopropylamine, 64 g (1.25 mol) of 90% formic acid, and 47 g (0.55 mol) of formaldehyde: 32 g (0.28 mol); 56% yield; bp 109–111°; lit.[18] bp 109–112°.

N,N-Dimethyl-*p*-cyanobenzylamine was prepared from 10 g (0.22 mol) of dimethylamine and 10 g (0.073 mol) of *p*-cyanobenzyl chloride: 5.7 g (0.36 mol); 50% yield; bp 140–141° (20 mm); lit.[19] bp 130–132° (15 mm). The product had an appropriate nmr spectrum.

2,5-Dichloro-3,6-dimethoxybenzoquinone was prepared from 7.2 g (0.050 mol) of methyl iodide and 5 g (0.012 mol) of the disilver salt of 2,5-dichloro-3,6-dihydroxybenzoquinone (Eastman Kodak Co.): dark red crystals; 0.42 g (1.8 mmol); 15% yield; mp 142.5–144.5°; lit.[20] mp 141–142°. The nmr spectrum in $CDCl_3$ showed one band at τ 5.75.

Irradiation. Extinction coefficients of the n–π* bands and concentrations of 4-benzoylbenozic acid and of benzophenone were determined by measurement of absorbances against solvent in 1-cm cells on a Beckman DU spectrophotometer, or against air on a Cary 14 spectrophotometer. Irradiation tubes, degassing procedure, and irradiation equipment have been described.[3b] Pyrex tubes 10 mm i.d., or 10 mm × 10 mm, fitted with Fisher-Porter Teflon closures were calibrated by simultaneous photoreduction of 0.060 *M* benzophenone in 2-butylamine on the irradiation wheel, 8 cm from a GE H85-A3-UV lamp. Analysis for benzophenone was made from the absorbance at 342 nm, ε 142, in a 1-mm cell. Irradiation tubes, sealed to a 1-mm quartz absorption cell, were used for detection of light-absorbing transients. In kinetic studies irradiations were carried out on a wheel, with tubes located at 8 or 4 cm from the central lamp. The lamp was either the GE lamp or an Osram Spektrallampe, Hg–I, which was about half as intense as the GE lamp. Rates of photoreduction were determined from the decrease in ketone absorbance of suitably diluted aliquots with time of irradiation. Solutions of 4-benzoylbenzoic acid which were irradiated at alkaline pH were diluted, 1 ml to 25 ml, with 2-propanol containing 0.3 *N* HCl to neutralize all base and convert the ketone to the free acid; the absorbance was measured at 336 nm, ε 187. Standard solutions of 0.1 *M* benzophenone in 2-butylamine were irradiated on the wheel at the same time to monitor light intensity. These solutions were diluted 1 ml to 25 ml with 2-propanol and absorbance was measured at 334 nm, ε 150. In the photoreduction of benzophenone in pyridine–water solutions, dilutions were 1 to 25 with 0.3 *N* HCl in 2-propanol, ϵ_{334} 150.

Photoreduction of 0.1 *M* 4-benzoylbenzoic acid by 2.0 *M* triethylamine in benzene was followed by decrease in infrared absorbance. Solutions were diluted 1 to 5 with benzene and transmittance was measured at 1660 cm^{-1} against benzene on a Perkin-Elmer Model 257 spectrophotometer. Transmittance was converted to absorbance and ketone concentrations were determined from a calibration curve.

Quantum yields were determined on a Bausch and Lomb 38-86-01 monochromator at 334 nm, with a Corning 7-54 filter. Light intensity was monitored with a potassium ferrioxalate actinometer,[21] $\varphi = 1.25$. Solutions were stirred magnetically during irradiation.

Reduction Products of 4-Benzoylbenzoic Acid. Portions, 5 ml, of a solution of 0.1 *M* 4-benzoylbenzoic acid in 85:15 2-propanol–water were irradiated on the wheel for 1.5 hr, 8 cm distant from the Osram lamp. A 1-ml aliquot of unirradiated solution, diluted 1:25 with 1:1 2-propanol–water had absorbance 0.784 at 332.5 nm, ε 214; a 1-ml aliquot of irradiated solution, similarly analyzed had absorbance 0.270; a 1-ml aliquot of irradiated solution, treated with 1 ml of 1 *N* NaOH for 22 hr, and then acidified and diluted had absorbance 0.55. This indicated 66% photoreduction, leading entirely to the pinacol.

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[11] A. Beckett and G. Porter, *Trans. Faraday Soc.*, 2038 (1963).

[12] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

[13] W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

[14] S. G. Cohen, R. Thomas, and M. N. Siddiqui, *J. Amer. Chem. Soc.*, **89**, 5845 (1967).

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

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

[17] H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *ibid.*, **55**, 4571 (1933).

[18] F. Klages, G. Nobler, F. Kircher, and M. Block, *Justus Liebigs Ann. Chem.*, **547**, 1 (1941).

[19] W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **26**, 371 (1961).

[20] F. Kehrmann, *J. Prakt. Chem.*, 40, 370 (1889).

[21] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

Three 5-ml portions of 0.095 *M* 4-benzoylbenozic acid in 85% 2-propanol–water were irradiated similarly for 8 hr and concentrated. The residue was washed with water, ethanol, and petroleum ether, leading to the pinacol: 0.30 g (93% yield); mp 184–195° dec. The infrared spectrum in KBr showed broad bands at 3560–3400 and 3100–2800, strong absorption at 1690–1670, and a peak at 1605 cm^{-1}. *Anal.* Calcd for $C_{28}H_{22}O_6$: C, 74.00; H, 4.90. Found: C, 74.0; H, 4.8 (Dr. C. Fitz).

A solution (25 ml) of 0.55 g of 4-benzoylbenzoic acid in 1:1 2-propanol–water, brought to pH 12.1 with NaOH, was irradiated with the Osram lamp for 46 hr. The absorbance at 337.5 nm of an acidified 1-ml aliquot indicated complete reduction. The remainder was acidified with 5 ml of 1 *N* HCl and concentrated. The residue was washed with water and petroleum ether and dried: 4-carboxybenzhydrol; 0.50 g; 95% yield; mp 167–168°, lit.[22] mp 164–165°. A sample of 4-carboxybenzhydrol was prepared by treament of 1.00 g of 4-benzoylbenzoic acid in 15 ml of 0.33 *N* NaOH with 0.10 g of sodium borohydride at room temperature for 24 hr. The solution was then heated, cooled, and acidified leading to the hydrol: 0.76 g; mp 167–168°; mixture mp with the product from the photoreduction, 167–168°. The infrared spectrum in KBr showed broad absorption, 3300–2500, with maxima at 3260, 2900–2800, and 2640, and a shoulder at 2530, strong absorption at 1710–1690, and a peak at 1610 cm^{-1}. This infrared spectrum was identical with that of the sample prepared by the photoreduction.

A 24-ml solution of 0.10 *M* 4-benzoylbenzoic acid and 1.74 *M* *N*,*N*-dimethyl-2-butylamine in water was irradiated with the Osram lamp for 26 hr and the absorbance at 332.5 nm indicated complete photoreduction. A 10-ml portion was acidified with HCl, and the precipitate was collected, washed with water, and dried: 4-carboxybenzhydrol; 0.184 g; 82% yield; mp and mixture mp with an authentic sample 167–169°. A similar photoreduction of 0.10 *M* 4-benzoylbenzoic acid by 0.5 *M* triethylamine in water led to the hydrol in 84% yield.

Solutions of 0.040 *M* benzophenone and 2.0–0.05 *M* 2-butylamine in 1:1 pyridine–water containing 0.02 *N* NaOH were irradiated 8 cm from the GE lamp for 17–19 min. In a typical run the absorbance at 334 nm of an appropriately diluted aliquot fell from 0.72 initially to 0.54 after irradiation, 25% reaction. Addition of 0.04 ml of 5 *N* NaOH led to an increase in absorbance of 0.57 indicating that 30% of the reduction product was pinacol, the remainder, hydrol.

Oxidation Products of Triethylamine. Portions, 5 ml, of a solution of 0.1 *M* 4-benzoylbenzoic acid and 0.5 *M* triethylamine in water were irradiated on the wheel 4 cm from the GE lamp. Aliquots were diluted 1 ml to 25 with 0.028 *N* HCl in 2-propanol, the absorbance was measured at 338.5 nm, ϵ 185, and the per cent photoreduction was calculated. Tubes were irradiated about 15 min, leading to 30–40% reduction. Analysis for acetaldehyde was made by glc on a Varian Aerograph 200 gas chromatograph 3-μl injection, 6.5-ft column 15% UCON polar on Chromosorb W 60–80, column, detector, and injector temperatures 54, 160, and 190°, respectively. Concentrations and yields of acetaldehyde were determined from peak areas using 2-propanol as an internal standard. Yield of acetaldehyde was 90% based on the amount of ketone reduced. Peak areas due to diethylamine were also determined and converted to concentrations by comparison with areas from standard solutions of acetaldehyde and diethylamine in water. Column, detector, and injector temperatures were 51, 98, and 115°, respectively. Yield of diethylamine was 85% after 70 and 85% reduction of the ketone. A portion of irradiated solution was cooled, acidified, and filtered and the filtrate was treated with 2,4-dinitrophenylhydrazine solution. This led to the dinitrophenylhydrazone of acetaldehyde, with correct infrared spectrum, 77% yield, based on reduced ketone. A 5-ml portion of an irradiated solution, after 50% reduction, was treated with 0.2 g of *p*-toluenesulfonyl chloride and 2.5 ml of 10% NaOH, leading to the *N*,*N*-diethyl-*p*-toluenesulfonamide: mp 59.5–60° from ethanol–water; mp, with an authentic sample, 59.8–60°.

Oxidation Products of *N*,*N*-Dimethyl-2-butylamine. Portions, 5 ml, of a solution of 0.10 *M* 4-benzoylbenzoic acid and 0.50 *M* *N*,*N*-dimethyl-2-butylamine in water were irradiated, diluted, and examined at 338.5 nm as described above. A 4-ml aliquot was brought to pH 4.5 with HCl and sodium acetate, cooled, and filtered. The filtrate was treated with 0.26 g of dimedone in 100 ml of water, leading to the derivative of formaldehyde: 0.052 g; mp 185–192°; lit.[23] 190°. After 57% reduction of the ketone, the yield of formaldehyde was 77%. A similar solution of the ketone and amine in 1:2 pyridine–water led to dimedone derivative, 0.034 g, mp 192–193.5°, corresponding to 83% conversion to formaldehyde after 44% reduction.

For the reaction in water, analysis for 2-butanone was made by glc on the column described above. Column, detector, and injector temperatures were 54, 185, and 130°, respectively. Peak area to concentration ratios due to 2-butanone were determined by comparison with a standard solution of 2-butanone in water. Yield of 2-butanone, based on amount of ketone reduced, was 6.2%.

A solution, 24 ml, of 0.10 *M* 4-benzoylbenzoic acid and 1.74 *M* *N*,*N*-dimethyl-2-butylamine in water was irradiated with the Osram lamp for 26 hr and absorbance measurement indicated complete photoreduction. A 10-ml portion was treated with 0.1 ml of phenyl isothiocyanate, leading to *N*-phenyl-*N*′,*N*′-methyl-2-butylthiourea: 0.018 g; mp 91–98° from 95% ethanol; mp 91–98° with an authentic sample of mp 96–98°. The infrared spectrum was identical with that of the authentic sample. *Anal.* Calcd for $C_{12}H_{18}N_2S$: C, 64.79; H, 8.15; N, 12.59. Found: C, 64.8; H, 8.1; N, 12.7 (Dr. C. Fitz).

A second 10-ml portion was acidified and filtered, and the filtrate was treated with 2,4-dinitrophenylhydrazine solution, leading to the 2,4-dinitrophenylhydrazone of formaldehyde: 0.022 g; mp 165–167° from ethanol; lit.[24] mp 166°; mixture mp 165–168°.

Oxidation Products of Other Amines. Portions of solutions of 0.10 *M* 4-benzoylbenzoic acid and 0.50 *M* *N*,*N*-dimethylbenzylamine and 0.10 *M* 4-benzoylbenzoic acid and 0.50 *M* *N*,*N*-dimethyl-*p*-cyanobenzylamine in 2:1 *tert*-butyl alcohol–water were irradiated to 61–73% reduction and analyzed by glc as described for acetaldehyde, but with column, detector, and injector temperatures 145, 186, and 180°, respectively, for benzaldehyde, and 145, 250, and 180° for *p*-cyanobenzaldehyde. Neither aromatic aldehyde was detected. A 3-ml portion of the *N*,*N*-dimethylbenzylamine solution was irradiated for 30 min; 73% reduction of the 4-benzoylbenzoic acid. This solution was treated with *p*-toluenesulfonyl chloride and alkali, concentrated, and cooled, leading to 0.0076 g, 20% yield, of *N*,*N*-methylbenzyl-*p*-toluenesulfonamide: mp 93–95°; lit.[25] 94.4–94.8°.

Portions of a solution of 0.10 *M* 4-benzoylbenzoic acid and 2.1 *M* 2-butylamine in water were irradiated to 60% reduction. Analysis for 2-butanone was made with 2-butanol as an internal standard on an Aerograph 1200 chromatograph, flame ionization detector, 8-ft column, 15% UCON on Chromosorb W 60–80, column, detector, and injector temperature 50, 142, and 243°, respectively.

Portions of a solution of 0.10 *M* 4-benzoylbenzoic acid and 0.50 *M* diisopropylamine in water were irradiated. Analysis for acetone was made with 2-butanol as an internal standard on the Aerograph 1200 chromatograph, column, detector, and injector temperatures 30, 256, and 190°, respectively.

Photooxidation Products of Amines in Benzene. Eight 6-ml portions of a solution of 0.1 *M* 4-benzoylbenzoic acid and 0.5 *M* triethylamine in dried benzene were irradiated for 16 min 4 cm from the GE lamp. A portion, 0.6 ml, of a solution of 0.16 g of 2,5-dichloro-3,6-dimethoxybenzoquinone in 5 ml of dried benzene, was added to the contents of each irradiation tube, which became deep blue. The solutions were filtered, and the filtrates were combined, concentrated to 10 ml, and placed on a column of neutralized aluminum oxide, which had been deactivated with water. Elution with benzene led to a yellow eluate which was discarded, and a blue one. This was concentrated and the residue was crystallized from 60–110° petroleum ether: blue needles; 2,5-dichloro-3-methoxy-6-(2-diethylaminovinyl)quinone (I); 0.038 g; mp 104–105°; lit.[26] mp 109–110°. The spectrum in benzene showed absorption at 640, 378, and 310 nm, ϵ 8.8×10^3, 6.0×10^3, and 2.3×10^4, respectively. The nmr spectrum in $CDCl_3$ showed a triplet at τ 8.7, CH_3, a quartet at 6.6, CH_2, a singlet at 5.8, CH_3O, and doublets at 4.3 and 1.7, vinyl H. *Anal.* Calcd for $C_{13}H_{15}O_3NCl_2$: C, 51.31; H, 4.97; N, 4.60. Found: C, 51.60; H, 5.17; N, 4.64 (Schwarkopf Laboratories).

A solution of 0.39 g (1.66 mmol) of 2,5-dichloro-3,6-dimethoxybenzoquinone, 0.40 g (1.66 mmol) of benzoyl peroxide, and 0.81 g (8.0 mmol) of freshly distilled triethylamine in 25 ml of benzene

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[22] T. Zincke, *Justus Liebigs Ann. Chem.*, 161, 102 (1872).

[23] M. V. Ionescu and V. N. Georgescu, *Bull. Soc. Chim. Fr.*, 49, 2913 (1927).

[24] N. R. Campbell, *Analyst*, 61, 391 (1936).

[25] H. Carothers, C. F. Bickford, and G. J. Hurwitz, *J. Amer. Chem. Soc.*, 49, 2913 (1927).

[26] D. Buckley, S. Dunstan, and H. B. Henbest, *J. Chem. Soc.*, 4880, 4901 (1957).

Table I. Photoreduction of 0.1 *M* 4-Benzoylbenzoic Acid by 0.5 *M* Aqueous Amines. Cleavage Products of the Amines

Amine	Solvent	Products: Compound	Products: % yield
Et_3N	H_2O	$CH_3CH{=}O$	90
		Et_2NH	85
2-$BuNMe_2$	H_2O	$CH_2{=}O$	77
	1:2 C_5H_5N-H_2O	$CH_2{=}O$	83
	H_2O	$CH_3CH_2COCH_3$	6
i-Pr_2NEt	2:1 *tert*-BuOH-H_2O	$CH_3CH{=}O$	49
		CH_3COCH_3	22
	2:1 C_5H_5N-H_2O	CH_3COCH_3	24
$C_6H_5CH_2NMe_2$	2:1 *tert*-$BuOH_2$-H_2O	C_5H_5CHO	~0
		$C_6H_5CH_2NHMe$	>20
p-$CNC_6H_4CH_2NMe_2$	2:1 *tert*-BuOH-H_2O	*p*-CNC_6H_4CHO	~0
i-Pr_2NH	H_2O	CH_3COCH_3	100
2-$BuNH_2$[a]	H_2O	$CH_3CH_2COCH_3$	100

[a] 2.1 *M*.

was allowed to stand in the dark for 1.75 hr. The mixture was filtered, chromatographed, and worked up as described above leading to the same blue product: 0.175 g (0.58 mmol); 35% yield. The infrared and ultraviolet spectra of the compound prepared in the two ways were identical.

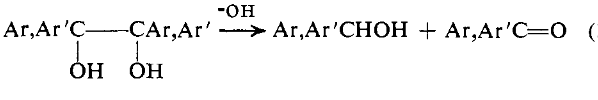
Portions, 6 ml, of 0.1 *M* 4-benzoylbenzoic acid and 0.50 *M* triethylamine in dried benzene were irradiated for 16 min, 4 cm from the GE lamp. A portion was shaken with 1 *N* HCl and the aqueous layer was treated with dinitrophenylhydrazine solution, leading to dinitrophenylhydrazone of acetaldehyde, mp 141–147° from ethanol, with infrared spectrum identical with that of an authentic sample. Another portion of irradiated benzene solution was extracted with 1 *N* HCl, and the extract was made alkaline and treated with *p*-toluenesulfonyl chloride, leading to *N*,*N*-diethyl-*p*-toluenesulfonamide: mp 56–59.5° from ethanol–water; mixture mp with an authentic sample, 58–60°.

A solution of 0.10 *M* 4-benzoylbenzoic acid and 0.50 *M* *N*,*N*-dimethyl-2-butylamine in benzene was irradiated and hydrolyzed as described above. Treatment of the aqueous extracts with 2,4-dinitrophenylhydrazine led to the dinitrophenylhydrazone of formaldehyde, mp 161–165°, and treatment with phenyl isothiocyanate led to *N*-phenyl-*N*′,*N*′-methyl-2-butylthiourea, mp 90–96°.

Portions, 3 ml, of a solution of 0.10 *M* benzophenone and 0.50 *M* triethylamine in dried benzene were irradiated for 10 min 4 cm from the GE lamp. Analysis at 1660 cm^{-1} on samples diluted 1:5 with benzene indicated 14% reduction. Treatment with 2,5-dichloro-3,6-dimethoxy-*p*-benzoquinone and analysis at 640 nm indicated formation of 0.0038 *M* diethylvinylamine, 54% yield of enamine based on 1 mol of enamine/2 mol of benzophenone reduced.

Results

A. Products. 4-Benzoylbenzoic acid was chosen for study since it would be soluble as the carboxylate ion in dilute aqueous solutions of the amines. The free acid itself is photoreduced readily by aqueous 2-propanol to the pinacol, shown by isolation in 93% yield and by base decomposition of a photolysate to regenerate half the photoreduced ketone, eq 3. Photoreduction of this ketone by aqueous 2-propanol at pH 12 leads directly to the benzhydrol, by disproportionation of the ketyl radical ions or of ketyl radical and radical ion,[27] eq 4. The 4-carboxybenzhydrol was isolated in 95% yield and was identical with the product of reduction of this ketone by sodium borohydride.



$$\underset{\text{OH}}{\text{Ar,Ar}'\text{C}}\text{---}\underset{\text{OH}}{\text{CAr,Ar}'} \xrightarrow{^-\text{OH}} \text{Ar,Ar}'\text{CHOH} + \text{Ar,Ar}'\text{C}{=}\text{O} \quad (3)$$

$$\text{Ar,Ar}'\dot{\text{C}}\text{—OH} + \text{Ar,Ar}'\dot{\text{C}}\text{—O}^- \xrightarrow{H_2O} \text{Ar,Ar}'\text{CHOH} + \text{Ar,Ar}'\text{C}{=}\text{O} + {}^-\text{OH} \quad (4)$$

Photoreduction of 4-benzoylbenzoic acid by aqueous amines at pH 12 also leads to the benzhydrol in high yield, and no evidence of pinacol was found. On the other hand, photoreduction of benzophenone by 2-butylamine at pH 12 led to a photolysate, treatment of which with additional alkali led to regeneration of a fraction of the theoretical amount of ketone, indicating that both pinacol and hydrol were formed even at pH 12. Study of both benzophenone and 4-benzoylbenzoic acid was continued, but the latter was preferred for studies in the aqueous media since it is converted quantitatively to hydrol. Formation of pinacol, unstable in the alkaline reaction solutions, is an undesired complication.

Photoreduction of the ketone is accompanied by oxidation of the amine, and in aqueous solutions, by hydrolytic cleavage of the oxidized amine. Some products resulting from the photooxidation by 4-benzoylbenzoic acid of several amines in aqueous solution are summarized in Table I.

In analyses for acetaldehyde, Table I, reactions were carried out with higher light intensity for short periods, to low conversions, since the acetaldehyde was not stable in the aqueous alkali. However, the secondary amines formed from the tertiary amines are stable and analyses for them may be made at high conversions. The yields of acetaldehyde and diethylamine from triethylamine were determined by glc. The products were also characterized as the dinitrophenylhydrazone of acetaldehyde and as *N*,*N*-diethyl-*p*-toluenesulfonamide. The high yields of formaldehyde from *N*,*N*-dimethyl-2-butylamine are those of the isolated dimedone derivative, and are probably minimum values. The analysis for 2-butanone was made by glc against a standard and the low yield is fairly accurate. The major amine cleavage product, *N*-methyl-2-butylamine, was characterized as *N*-phenyl-*N*′,*N*′-methyl-2-butylthiourea. Preference for attack on a methyl group appears greater than statistical.

Photoreductions by diisopropylethylamine were carried to 50–65% conversion of the ketone and yields of acetone and acetaldehyde were determined by glc. Abstraction of hydrogen from isopropyl and ethyl have equal statistical probability, and again attack on the least substituted center was favored. Photoreduction by the *N*,*N*-dimethylbenzylamines led to no benzaldehyde or *p*-cyanobenzaldehyde which we could detect by glc. The yield of *N*-methylbenzylamine is that of the isolated *p*-toluenesulfonamide and is a minimum value.

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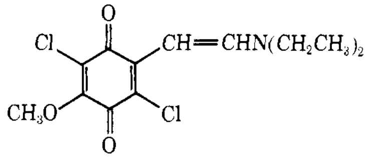
(27) N. M. Stein and S. G. Cohen, unpublished results.

Analysis of prepared solutions indicated that 10% yield of benzaldehyde from dimethylbenzylamine would have been detected, and that hydrogen is abstracted preferentially from methyl.

The yields in Table I are based on 1 mol of carbonyl compound from oxidative cleavage of amine for each mole of ketone reduced. This cleavage of the amine requires that two reducing groups be transferred from amine to oxidizing species. The first group is an α-H, transferred to the excited ketone, eq 2. For primary and secondary amines the second group may, but need not be the NH, leading to an imine, RCH=NR′, in which R′ is H or alkyl. For tertiary amines the second reducing group may be a β-H, leading to an enamine, vinyldiethylamine, $CH_2{=}CHN(CH_2CH_3)_2$, from triethylamine, or an electron from N leading to an immonium ion, $CH_2{=}N^+R_2$, when the initial abstraction has been from methyl. Hydrolysis *in situ* of the imine, enamine, or immonium ion would lead to the observed cleavage products.

Formation of imines in photoreduction by primary and secondary amines in hydrocarbon solutions was reported previously.[2] Formation of an enamine in photoreduction by a tertiary amine has now been demonstrated. Treatment of a photolyzed solution of 0.1 *M* 4-benzoylbenzoic acid and 0.5 *M* triethylamine in benzene with 2,5-dichloro-3,6-dimethoxybenzoquinone led to the product of displacement of a methoxy group by diethylvinylamine



I

This was identical with the product prepared by treatment of the quinone and triethylamine in benzene with benzoyl peroxide in the dark.[26] Treatment of the photolysate in benzene with aqueous acid led to acetaldehyde and diethylamine, presumably by hydrolysis of the enamine. The products were characterized as the dinitrophenylhydrazone and toluenesulfonamide, respectively. The derivative I is intensely blue, ϵ_{640} 8800, and spectrophotometric analysis for it in a photolysate of benzophenone and triethylamine in benzene indicated that the enamine had been formed in 54% yield. The reduction products in benzene are those of a one electron reduction and the yield is based on 1 mol of enamine per 2 mol of ketone reduced. The calculated yield would be higher if cross coupling product and dimer of amine-derived radicals are formed and could be measured. A photolysate of benzophenone and *N*,*N*-dimethyl-2-butylamine in benzene showed no blue color on treatment with the quinone reagent, indicating either formation of an unreactive enamine or predominant abstraction of hydrogen from a methyl group. Hydrolysis with acid of a photolysate of 0.10 *M* 4-benzoylbenzoic acid and 0.50 *M* *N*,*N*-dimethyl-2-butylamine in benzene led to the products of abstraction of hydrogen from methyl, the same products as in photolysis in aqueous amine, formaldehyde, and *N*-methyl-2-butylamine, characterized as their derivatives with 2,4-dinitrophenylhydrazine and phenyl isothiocyanate, respectively. Experiments to demonstrate presence of the enamine were carried out in carefully dried benzene, since benzene which had been distilled but allowed to stand and come in contact with air absorbed sufficient water to hydrolyze the enamine. In such solutions some acetaldehyde was observed and measured by glc without intentional hydrolysis after irradiation. Formation of *N*-methylaniline in photoreduction of benzophenone by dimethylaniline in benzene[28] may also have been facilitated by the presence of water.

B. Kinetics. Irradiation of 0.1 *M* 4-benzoylbenzoic acid in 2 *M* triethylamine in benzene led to a decrease in absorbance at λ_{max} 344 nm, but the absorbance decreased still further when the irradiated solution was allowed to stand in the dark, indicating presence of a light-absorbing transient. Further experiments indicated that a new relatively stable product was formed, λ_{max} 325 nm, which persisted after 5 days' standing. This product was decomposed by irradiation, but was not studied further. Formation of these by-products leads to non-zero-order rates of photoreduction, as they build up, absorb part of the incident light, and possibly act as quenchers.[15] Their presence also complicates measurement of the rate of photoreduction of the ketone, but this can be estimated from the decrease in the carbonyl absorbance at 1600 cm^{-1}. The rate of photoreduction in this system was measured relative to that of photoreduction of 0.1 *M* benzophenone by neat 2-butylamine,[10] $\varphi = 1.1$. The relative rate fell from 0.72 at 15% reduction to 0.53 at 25% reduction and 0.38 at 43% reduction. A plot of inverse relative rate against per cent reaction was linear and extrapolated back to an initial relative rate of 1.4, $\varphi \sim 1.55$.

Photoreduction by tertiary amines in aqueous solutions led to no light-absorbing transients. Irradiation of 2×10^{-3} *M* 4-benzoylbenzoic acid in 0.26 *M* triethylamine in water led to decrease in absorbance at 332 nm from start of the irradiation, and to no further change when the irradiated solution was allowed to stand in the dark. At this low initial concentration of ketone, formation of light-absorbing transients or products would be detected very readily. In more concentrated solutions, opaque at the wavelength of irradiation, the photoreduction shows zero-order kinetics.

Quantum yields were determined by ferrioxalate actinometry for photoreduction at 334 nm of 0.1 *M* sodium 4-benzoylbenzoate by amines and by 2-propanol in 1:1 pyridine–water containing 0.02 *M* NaOH over that required to neutralize the benzoylbenzoic acid. Results are summarized in Table II. These quantum yields are for reduction to the hydrol, which involves two ketyl radicals per molecule of ketone reduced, eq 4. The quantum yields for formation of ketyl radicals or for transfer of reducing groups from amine to ketone are two times the values listed in Table II.

In order to determine kinetic constants for these reactions, rates of photoreduction by light filtered through Pyrex were determined as a function of concentration of amine, and of added quencher, naphthalene, at 1 *M* amine. Results are summarized in Tables III and IV. Linear inverse plots of rate against concentration of reducing agent lead to limiting rates for high concentration of reducing agent. Comparison of the limiting rate with the rate and quantum yield at 1.0 *M* reducing agent leads to limiting quantum yields which are included in

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[28] R. S. Davidson, *Chem. Commun.*, 2, 575 (1966).

Table II. Quantum Yields for Photoreduction at 334 nm of 0.10 *M* 4-Benzoylbenzoic Acid in 0.12 *N* NaOH in 1:1 Pyridine–Water

Reducing agent, compd, 1.0 *M*	φ	$\varphi_{\lim}$
2-$BuNH_2$	0.50	0.55
2-BuNHMe	0.27	0.28
2-$BuNMe_2$	0.75	0.76
Et_3N	0.68	0.70
2-PrOH	0.42	1.0

Table III. Effects of Concentration of Reducing Agent on Photoreduction of 0.10 *M* 4-Benzoylbenzoic Acid in 0.12 *N* NaOH in 1:1 Pyridine–Water

Reducing agent		$10^2 \times$ rate,	Slope/
Compound	*M*	$M\ hr^{-1}$	intercept[a]
2-$BuNH_2$	1.00	3.41	0.10
	0.50	3.02	
	0.10	1.82	
	0.05	1.21	
2-BuNHMe	1.00	2.28	0.030
	0.20	1.90	
	0.10	1.83	
	0.05	1.59	
	0.03	1.13	
2-$BuNMe_2$	1.00	5.74	0.011
	0.50	5.72	
	0.10	5.02	
	0.05	4.82	
Et_3N	1.00	5.78	0.021
	0.40	5.87	
	0.20	5.44	
	0.10	4.94	
	0.06	4.53	
	0.05	4.16	
2-PrOH	2.00	3.70	1.65
	1.40	3.43	
	1.00	2.48	
	0.40	1.14	
	0.20	0.553	
	0.10	0.271	
	0.05	0.166	

[a] k_d/k_{ir}, *M*, eq 9.

Table IV. Effects of Naphthalene on Rate of Photoreduction of 0.10 *M* 4-Benzoylbenzoic Acid by 1.0 *M* Reducing Agent in 0.12 *N* NaOH in 1:1 Pyridine–Water

Reducing agent	Naphthalene, $M \times 10^3$	$10^2 \times$ rate, $M\ hr^{-1}$	Slope/ intercept[a]
2-$BuNH_2$	0	3.51	40
	4.59	2.61	
	10.6	2.22	
	19.9	1.94	
	38.4	1.28	
2-BuNHMe	0	2.67	16
	10.2	1.99	
	22.6	1.85	
	25.4	1.89	
	57.5	1.31	
2-$BuNMe_2$	0	4.93	2.7
	16.6	4.56	
	27.2	4.66	
	42.4	4.43	
	89.9	3.94	
Et_3N	0	3.92	3.4
(1.21 *M*)	26.9	3.79	
	34.0	3.69	
	43.7	3.60	
	58.5	3.66	
	80.5	3.14	
2-PrOH	0	2.40	650
	1.09	1.67	
	1.51	1.48	
	2.66	1.16	
	4.08	0.78	

[a] $k_q/(k_d + k_{ir}(RH))$, M^{-1}, eq 10.

Table V. Effects of Solvent on Quantum Yields for Photoreduction at 344 nm of 0.10 *M* Benzophenone by 1.00 *M* 2-Butylamine

Solvent	φ (1.0 *M*)	$\varphi_{\lim}$
Benzene	1.04	1.12[a]
Acetonitrile	0.98	1.04
0.02 *N* NaOH in 1:1 pyridine–H_2O	0.74 (1.13)	0.77 (1.18)

[a] Reference 10.

Table II. Rates of photoreduction by amines, as compared with photoreduction by the alcohol, show low sensitivity to presence of quencher and low dependence on concentration of amine. The quantum yields at 1 *M* amine are little less than the limiting quantum yields. Nevertheless the quantum yields for photoreduction by amines remain well below the maximum value of 1 for these alkaline solutions, while that for photoreduction by the alcohol attains the maximum value in the limit.

An examination was made of effects of solvent on photoreduction by an amine. Quantum yields were determined by ferrioxalate actinometry for photoreduction at 344 nm of benzophenone by 2-butylamine in several solvents. Some results are given in Table V. Examination by base decomposition of the photolysate formed in the aqueous alkaline medium indicated 30% content of pinacol in the reduced product, the remainder hydrol. The latter is derived from two ketyl radicals and a correction for this may be applied to place the quantum yield on the same basis as that for photoreduction in benzene and acetonitrile, in which the pinacol alone is formed. This leads to a quantum yield of 1.13 for formation of ketyl radical in aqueous alkali from 1 *M* amine.

Effects of concentration of reducing agent and of added quencher, naphthalene, on photoreduction of benzophenone in these solvents were examined. Results are summarized in Tables VI and VII. Linear inverse plots of rates against concentration of reducing agents lead to limiting rates, and these may be converted to limiting quantum yields, which are included in Table V. Sodium hydroxide was added to the aqueous 2-butylamine solutions so that alkalinity and relative yields of pinacol and hydrol would remain constant with changing concentration of amine. Some related data for photoreduction by 2-propanol are included.

While the rate of photoreduction of benzophenone by the primary amine, 2-butylamine, is little affected by change in polarity of solvent from benzene to acetonitrile and aqueous pyridine, it was markedly decreased in *tert*-butylamine as solvent. In a set of photoreductions carried out simultaneously on the wheel, rates of photoreduction of 0.10 *M* benzophenone by neat 2-butylamine and by 1.0 *M* 2-butylamine in cyclohexane were the same, 0.066 ± 0.001 $M\ hr^{-1}$, while in 1 *M* 2-butylamine in *tert*-butylamine the rate was 0.021 $M\ hr^{-1}$. This demonstrates quenching of excited benzophenone

Table VI. Effect of Concentration of Reducing Agent on Photoreduction of 0.10 *M* Benzophenone

Solvent	Reducing agent Compd	*M*	$10^2 \times$ rate, *M* hr^{-1}	Slope/ intercept[a]
0.02 *N* NaOH in 1:1 pyridine–H_2O	2-$BuNH_2$	1.00	6.34	0.031
		0.40	6.30	
		0.20	5.75	
		0.10	4.94	
		0.05	4.12	
Acetonitrile	2-$BuNH_2$	1.00	8.20	0.054
		0.52	7.46	
		0.10	5.73	
		0.05	4.04	
Benzene[b]	2-$BuNH_2$			0.03
1:1 pyridine–H_2O	2-PrOH	1.00	8.10	0.10
		0.20	5.46	
		0.10	3.46	
		0.06	2.31	
		0.03	1.82	
Benzene[c]	2-PrOH			0.16

[a] k_d/k_{ir}, *M*, eq 9. [b] Reference 10. [c] Reference 15.

Table VII. Effect of Naphthalene on Photoreduction of 0.10 *M* Benzophenone by 1.0 *M* 2-Butylamine and by 1.0 *M* Propanol in Several Solvents

Solvent	Reducing agent	Naphthalene, $M \times 10^3$	$10^2 \times$ rate, *M* hr^{-1}	Slope/ intercept[a]
0.02 *N* NaOH in 1:1 pyridine–H_2O	2-$BuNH_2$	0.00	5.95	160
		7.33	3.92	
		17.0	2.84	
		24.6	2.33	
		40.0	1.42	
		56.8	0.88	
1:1 pyridine–H_2O	2-$BuNH_2$	0.00	7.07	170
		9.06	4.49	
		17.2	2.94	
		28.3	2.02	
		36.7	1.61	
		53.4	1.02	
Acetonitrile	2-$BuNH_2$	0.00	6.85	28
		46.1	2.89	
		60.2	2.57	
Benzene	2-$BuNH_2$	0.00	8.86	27
		5.56	6.85	
		9.30	6.55	
		20.6	5.43	
		31.0	4.55	
		42.4	3.84	
1:1 pyridine–H_2O	2-PrOH	0.00	8.95	1800
		3.29	2.56	
		5.96	1.58	
		10.0	0.96	
		12.3	0.71	
Benzene	2-PrOH	0.00	11.8	3300
		5.92	7.45	
		8.75	5.09	
		18.1	2.56	
		25.0	1.74	
		31.3	1.14	

[a] $k_q/(k_d + k_{ir}(\mathrm{RH}))$, M^{-1}, eq 10.

by the amino group of an aliphatic amine which lacks α-hydrogen, *tert*-butylamine.

Discussion

Photoreduction of 4-benzoylbenzoic acid by amines in aqueous media is an efficient process which reduces the ketone to the hydrol and oxidizes and cleaves amines in reactions which proceed in high yields. The reactions are particularly useful in study of tertiary amines, since their light-induced reactions with benzophenone in nonpolar media are less well defined. In the aqueous amine solutions light-absorbing by-products are not formed; alkali also minimizes formation of absorbing transients in photoreduction of ketones by alcohols. In tertiary amines which contain different alkyl groups, *N*,*N*-dimethyl-2-butylamine, ethyldiisopropylamine, and *N*,*N*-dimethylbenzylamines, hydrogen is abstracted preferentially from the least substituted carbon, from methyl and ethyl groups, Table I. This occurs despite the lower C–H bond strength of the substituted alkyl and benzyl groups, which might be important if the process involved a direct abstraction of hydrogen, and despite the greater acidity of the benzyl hydrogen, which might influence transfer of a proton in a charge-transfer complex, k_h, eq 2. Steric factors appear to dominate in directing the transfer of hydrogen and formation of the radicals, presumably in the charge-transfer complex, eq 2. This results in oxidative cleavage of the less hindered group. The selectivity appears to be substantially greater than in oxidative cleavage of amines by aqueous bromine.[29]

Quantitative oxidative deamination of the primary amine, 2-butylamine, to 2-butanone, Table I, is also of interest. The intermediate imine $CH_3CH_2C({=}NH)CH_3$, is hydrolyzed in the aqueous medium, while, when the photoreduction was studied in hydrocarbon,[2] the imine reacted with a second mole of amine to form a secondary imine, $CH_3CH_2C(CH_3){=}NC(CH_3)CH_2CH_3$. Hydrolysis of this leads to 50% deamination of the original amine. The secondary amine, diisopropylamine, appeared to undergo quantitative oxidation to imine, and cleavage to carbonyl compound and amine, a reaction which also proceeds quite well *via* photoreduction in hydrocarbon solution.[2] Transfer of the second reducing group from primary and secondary amines to ground state ketone may be that of H from N, eq 5.

$$\mathrm{Ar,Ar'C{=}O} + \mathrm{R\dot{C}HNHR'} \longrightarrow \mathrm{Ar,Ar'\dot{C}{-}OH} + \mathrm{RCH{=}NR'} \qquad (5)$$

$$\mathrm{R'} = \mathrm{H \text{ or alkyl}}$$

Excess of amine over ketone was used in these studies, but this is not required. Excess ketone may be used and the efficiency of interaction of excited ketone with amine is so high that equivalent quantities might be used even in dilute solution and lead to useful procedures for oxidative deamination of primary amines, for dealkylation of secondary and tertiary amines to primary and secondary amines, respectively, and in particular for demethylation of secondary and tertiary amines.

Accurate study of kinetics and products of photoreduction of benzophenone by tertiary amines in hydrocarbon has not been feasible because of light-absorbing products[2,10] which cause rates to decrease with extent of reaction. In the present work extrapolation of inverse rate against per cent reaction back to zero reaction indicated an initial quantum yield of 1.55 for photoreduction of 4-benzoylbenzoic acid by triethylamine in benzene. This high quantum yield indicates that two reducing groups may be transferred from triethylamine in benzene, one to excited and one to ground state ketone, eq 6, and that enamine, $CH_2{=}CHN(CH_2CH_3)_2$, and pinacol are formed in substantial yields.

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(29) N. C. Deno and R. E. Fruit, Jr., *J. Amer. Chem. Soc.*, 90, 3502 (1968).

$$\mathrm{Ar,Ar'C{=}O + CH_3\dot{C}HNR_2 \longrightarrow Ar,Ar'\dot{C}OH + CH_2{=}CHNR_2} \tag{6}$$

The enamine was characterized as compound I by hydrolysis to acetaldehyde and diethylamine. Pinacols from 4-benzoylbenzoic acid and from benzophenone were detected by tlc.

The quantum yield for formation of ketyl radical in photoreduction of 4-benzoylbenzoic acid by triethylamine in the aqueous medium is 1.4, Table II, and the enamine may also be formed in this system as a reactive intermediate. The high quantum yield, 1.5, Table II, for formation of ketyl radical in photoreduction of 4-benzoic acid by *N*,*N*-dimethyl-2-butylamine, and predominant cleavage of the methyl group indicate that transfer of the second reducing group to ground state ketone need not lead to an enamine, and may involve an immonium ion

$$\mathrm{Ar,Ar'C{=}O + \cdot CH_2NR_2 \longrightarrow Ar,Ar\dot{C}{-}O^- + CH_2{=}\overset{+}{N}R_2} \tag{7}$$

or an addition product

$$\mathrm{Ar,Ar'C{=}O + \cdot CH_2NR_2 \longrightarrow Ar,ArC{-}O\ {-}CH_2NR_2} \tag{8}$$

An immonium ion may be favored in aqueous systems. Such ionic intermediates have been proposed for oxidation of tertiary amines by benzoyl peroxide,[30] chlorine dioxide,[31] *N*-bromosuccinimide,[32] and quinones.[26] Radical cations such as those proposed as part of the charge-transfer complex, eq 1, have been characterized by esr spectra.[33,34] The addition product, eq 8, is also the product of combination of the two ions of eq 7. It may be favored in nonpolar media and also be formed in reactions of primary and secondary amines. The enamines, immonium ion, and radical addition compound may all hydrolyze to the observed oxidative cleavage products.

The effect of concentration of amine on quantum yield, in a process proceeding *via* eq 2 and 5, 6, 7, or 8 may be indicated by eq 9.

$$1/\varphi = 1/af + k_d/afk_{ir}(\mathrm{Am}) \tag{9}$$

The ratios of slope to intercept of the inverse plots of the data of Table III lead to the values k_d/k_{ir}, Table III. Equation 9 differs from the equation which applies to the usual photoreduction by an alcohol[12] by the factor f, which is the fraction of the reaction of triplet with amine which leads to hydrogen abstraction, the remainder leading to quenching. From eq 2, $f = k_h/(k_h + k_e)$ and has a maximum value of 1. To the extent that it is less than 1, it leads to limiting quantum yields less than the maximum value. The factor a includes the fractional yield of triplet and the contribution of the second reducing step, eq 5, 6, 7, or 8, and of disproportionations. It has a maximum value of 2 for reduction to pinacol, 1 for reduction to hydrol. The quantum yield for photoreduction of 4-benzoylbenzoic acid by 2-propanol in the aqueous alkaline system reaches the theoretical limiting value, Table II. We find no evidence that the amines lead to singlet quenching in these experiments, and the triplet yield may be essentially quantitative. The high yields of pinacol[2] and hydrol in reduction by amines in hydrocarbon and aqueous systems, respectively, the correspondingly high yields of imines[2] and cleavage products, and the lack of evidence for disproportionation of amine-derived radicals and for reversible hydrogen abstraction from amines[10] indicate that the second reducing step has high efficiency in these photoreductions by amines, as it has in reduction by alcohols. Thus the factor a may have its maximum value in these systems and limiting quantum yields less than the maximum may be due to the factor f. To this extent f may be calculated from the intercepts of inverse plots of quantum yield against concentration of amine obtained from the data of Table III. In these experiments the values of f may be equal to the limiting quantum yields, Table II. Transfer of the hydrogen from α-C in the charge-transfer complex, eq 2, appears to be most efficient for the tertiary amines, $f = 0.7$, has intermediate efficiency for the primary amine, $f = 0.55$, and lowest efficiency for the secondary amine, $f = 0.28$. The reason for this is not clear, but a similar order has been reported for the rates of photoreduction of all-3-copper phthalocyaninsulfonic acid by aliphatic amines, tertiary > primary > secondary.[35]

The data of Table IV, the effects of naphthalene on the photoreduction of 4-benzoylbenzoic acid by amines in aqueous alkali, may be fitted to eq 10.

$$1/\varphi = 1/af + k_d/afk_{ir}(\mathrm{Am}) + k_q(\mathrm{Q})/afk_{ir}(\mathrm{Am}) \tag{10}$$

The plots of inverse quantum yield against concentration of quencher have slopes, $k_q/afk_{ir}(\mathrm{Am})$, and intercepts, $(k_d + k_{ir}\cdot(\mathrm{Am}))/afk_{ir}(\mathrm{Am})$; ratios of slope to intercept, $k_q/(k_d + k_{ir}(\mathrm{Am}))$, are given in Table IV. Values of k_{ir} may be calculated on the basis of diffusion controlled values of k_q and the determined values of k_d/k_{ir}, without reference to the values of a and f. Values of k_q in these media were calculated from the Debye equation, $k = 8RT/3 \times 10^3\ \eta$, and measured viscosities, η, and were 2.5-3 $\times$ $10^9\ M^{-1}\ \mathrm{sec}^{-1}$. Results are summarized in Table VIII.

Table VIII. Kinetic Constants, Photoreduction of 0.10 *M* 4-Benzoylbenzoate Anion by Amines and 2-Propanol in 0.12 *N* NaOH in 1:1 Pyridine–Water

Reducing agent	k_q/k_{ir}	k_{ir}, $M^{-1}\ \mathrm{sec}^{-1}$	k_d, sec^{-1}
2-BuNH$_2$	44	6.3×10^7	6.3×10^6
2-BuNHMe	16	1.6×10^8	4.8×10^6
2-BuNMe$_2$	2.7	9.3×10^8	1.0×10^7
Et$_3$N	4.2	6.0×10^8	1.3×10^7
2-PrOH	1700	1.7×10^6	2.8×10^6

The insensitivity of photoreduction by amines to physical quenching is seen in the low values of k_q/k_{ir}. The value of 1700 for photoreduction of 4-benzoylbenzoate by 2-propanol is similar to that for benzophenone in 2-propanol[11,36] and in 2-propanol in *tert*-butyl alcohol,[15] indicating that this ratio is little affected by the change in ketone and solvent in this study. The low values of k_q/k_{ir} correspond to values of k_{ir} for interaction of excited ketone with amines which are much higher than the values of k_r for abstraction of hydrogen from 2-pro-

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(30) L. Horner and W. Kirmse, *Justus Liebigs Ann. Chem.*, 597, 48 (1955).

(31) D. H. Rosenblatt, L. A. Hull, D. C. DeLuca, G. T. Davis, R. C. Weglein, and H. K. R. Williams, *J. Amer. Chem. Soc.*, 89, 1163 (1967).

(32) H. J. Dauben, Jr., and L. L. McCoy, *ibid.*, 81, 4863 (1959).

(33) T. M. McKinney and D. H. Geske, *ibid.*, 87, 3013 (1965).

(34) A. J. Tench, *J. Chem. Phys.*, 38, 593 (1963).

(35) G. Eigenmann, *Helv. Chim. Acta*, **46**, 855 (1963).

(36) S. G. Cohen and W. V. Sherman, *J. Amer. Chem. Soc.*, **85**, 1642 (1963).

panol, 37 times greater in the case of the primary amine, 94 times greater for the secondary amine, and 350 and 550 times greater for the tertiary amines. The latter values are little less than k_q for quenching and approach diffusion control. This order of reactivity parallels decrease in ionization potential[37] and is consistent with abstraction of hydrogen proceeding *via* an initial charge-transfer interaction. The values of k_d for self- and solvent-induced quenching are higher in solutions containing amine than in that containing alcohol, and are highest in the presence of tertiary amines. The reasons for this are not clear, and may indicate association of ketone and amine which affects triplet stability.

Efficient use of this reaction as a synthetic or degradative dealkylation procedure requires that a tertiary amine react predominantly in the presence of the secondary amine product, and that a secondary react predominantly in the presence of the primary amine product. Preferential reaction depends on both interaction rate and quantum yield, and may be indicated by the relative values of the product, $f \times k_{ir}$. The tertiary amines triethylamine and *N,N*-dimethyl-2-butylamine have values of this function of 4×10^8 and 7×10^8, respectively, the secondary amine *N*-methyl-2-butylamine, 4.5×10^7, and the primary amine, 3.5×10^7. It appears that these reactions may be useful for dealkylation of tertiary to secondary amines.

Polarity of solvent might be expected to have effects on a process which is thought to be initiated by a charge-transfer interaction and then to undergo either quenching or formation of radicals. In the system that was studied, photoreduction of benzophenone by 2-butylamine, the quantum yield was remarkably unaffected as the solvent was changed from benzene to acetonitrile to alkaline aqueous pyridine, $\varphi \sim 1.1$, Table V. Benzophenone undergoes efficient intersystem crossing, independent of solvent, unlike fluorenone and *p*-aminobenzophenone. Values of k_d/k_{ir} are low, and the quantum yields depend largely on the values of f, $k_h/(k_h + k_e)$. This may be relatively independent of solvent since the two competing processes have similar charge characteristics, conversion of the dipolar charge-transfer complex to neutral radical or to neutral ground state molecules.

Effects of solvent on the initial interaction, k_{ir}, and on k_d may be calculated from the data of Tables VI and VII on effects of concentration of reducing agent and of quencher, naphthalene, in the benzophenone-2-butylamine system. An experimental value for k_q in benzene,[38] 6.3×10^9 M^{-1} sec^{-1}, was used, 1.1×10^{10} M^{-1} sec^{-1} was used in acetonitrile, and values calculated from the Debye equation, $\sim 3 \times 10^9$ M^{-1} sec^{-1} were used for the aqueous solutions. Values for the rate constants are summarized in Table IX.

Because of uncertainties in the values of k_q on which the other constants are based, small differences may not be commented on. Abstraction of hydrogen from 2-propanol is unaffected by solvent change, values for k_{ir} being the same in benzene and in aqueous pyridine, and k_d is also little affected. However, k_{ir} for interaction of excited ketone with the amine is lower by an order of magnitude in the aqueous system than in the organic solvents. This may arise from hydrogen bonding of the n electrons of the amine with water, decreasing reactivity in the aqueous system. Acetonitrile may facilitate slightly formation of the charge-transfer complex. Possible stabilization of the complex by the dipolar solvent may be countered partly by greater solvation of the amine by acetonitrile than by benzene. The value of k_{ir} in benzene, determined here by naphthalene quenching of photoreduction by 2-butylamine, 2.3×10^8 M^{-1} sec^{-1}, is essentially identical with that determined from quenching by 2-butylamine of the phosphorescence of benzophenone,[39] 2.5×10^8 M^{-1} sec^{-1}. As with 4-benzoylbenzoic acid, values of k_d for benzophenone triplet appear greater in the presence of amine, and the effect is greater in the organic solvents in which association of ketone and amine may be more important.

Table IX. Kinetic Constants, Photoreduction of 0.10 *M* Benzophenone by 2-Butylamine and 2-Propanol in Several Solvents

Solvent	Reducing agent	k_q/k_{ir}	k_{ir}, M^{-1} sec^{-1}	k_d, sec^{-1}
Benzene	2-BuNH$_2$	28	2.3×10^8	7.0×10^6
Acetonitrile	2-BuNH$_2$	29	3.8×10^8	2.0×10^7
0.02 *N* NaOH in 1:1 pyridine–H$_2$O	2-BuNH$_2$	170	1.7×10^7	5.3×10^5
Benzene	2-PrOH	3800	1.7×10^6	2.7×10^5
1:1 pyridine–H$_2$O	2-PrOH	2000	1.5×10^6	1.5×10^5

The proposed mechanism, eq 2, requires that aliphatic amines be both quenchers and reducing agents for aromatic ketones. Triethylamine quenches the singlet of aromatic hydrocarbons,[40] diethylamine may quench the singlet and triplet state of naphthalene,[41] triphenylamine quenches the triplet of benzophenone,[42] and tertiary amines quench the singlet of fluorenone.[6] It is desirable to demonstrate independently quenching of the n-π* triplet of an aromatic ketone by an aliphatic amine. Such quenching by *tert*-butylamine is observed in the photoreduction of benzophenone by 1.0 *M* 2-butylamine in *tert*-butylamine. The reaction is 0.32 as fast as the photoreduction in neat 2-butylamine or in 1 *M* 2-butylamine in cyclohexane. This decrease in rate cannot be due to a medium effect, to high concentration of amino group, since the concentration is the same in neat 2-butylamine. It cannot be due to low concentration of reactive amine, since it is the same in 1 *M* 2-butylamine in cyclohexane. The decrease in rate is due to competition by the amino group of *tert*-butylamine with that of 2-butylamine for the excited ketone, forming a charge-transfer complex, eq 1, which in the absence of an α-hydrogen leads to quenching k_e, eq 2. The concentration of *tert*-butylamine is $\sim$8.4 times that of 2-butylamine, indicating that k_{ir} for *tert*-butylamine is about 0.25 as great as that for 2-butylamine, $\sim 6 \times 10^7$ M^{-1} sec^{-1}. This is an approximate value since some photoreduction occurs in neat *tert*-butylamine.[2b] Nevertheless, it is quite similar to that determined by

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(37) R. Kiser, "Tables of Ionization Potentials," Atomic Energy Commission TID-6142, Manhattan, Kan., June 1960.

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

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

(40) H. Leonhardt and A. Weller, *Z. Phys. Chem.*, 29, 277 (1961).

(41) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 4, 745 (1968).

(42) R. S. Davidson, *Mol. Photochem.*, 1, 71 (1969).

quenching by *tert*-butylamine of phosphorescence of benzophenone,[39] $7.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. That the value is lower than that for 2-butylamine may be due to a less favorable steric factor for interaction of the benzophenone triplet with the nonbonding electrons of N.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. II. Self-Reactions of *N*-Alkyl Nitroxides and *N*-Phenyl Nitroxide[1,2]

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Abstract: The self-reactions of methyl, isopropyl, *tert*-butyl, and phenyl nitroxides in solution have been examined by epr spectroscopy. The reaction is a disproportionation to yield a hydroxylamine and a nitroso compound: $2\text{RNHO}\cdot \rightarrow \text{RNHOH} + \text{RNO}$. Rate constants for this reaction have been measured in several solvents. In benzene at 25° the rate constants are in the range 4×10^7 to $3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. For R = phenyl and R = *tert*-butyl the reaction was shown to be reversible and the equilibrium constants were measured over a range of temperature. The measured enthalpy change for the reaction with R = *tert*-butyl is in good agreement with that calculated (for $\text{R} = \text{CH}_3$) from the heats of formation of the various species involved. Evidence is presented for hydrogen bonding of methyl nitroxide in methanol. The rate constant for the slow conversion of phenyl nitroxide to azoxybenzene has also been measured over a range of temperature in benzene.

It has been known for some time from qualitative observations made during the recording of the electron paramagnetic resonance spectra of nitroxide radicals that *N*-alkyl and *N*-aryl nitroxides are much less stable than the majority of *N,N*-dialkyl or *N,N*-diaryl nitroxides. The epr spectra of phenyl nitroxide[5-10] and several alkyl nitroxides (*e.g.*, $\text{MeNHO}\cdot$,[11,12] *i*-$\text{PrNHO}\cdot$,[13] *tert*-$\text{BuNHO}\cdot$,[13,14] $\text{PhCH}_2\text{NHO}\cdot$[15]) have been reported but there have been no quantitative studies of the stabilities or of the decay of any of these radicals. In Part I[2] we described an epr study of the kinetics and mechansim of the self-reaction of *N,N*-diethyl nitroxide in solution. The present paper describes a similar study of the self-reactions of methyl, isopropyl, *tert*-butyl, and phenyl nitroxides.

Experimental Section

The general experimental procedure has been described previously.[2] Nitroxide radicals were produced from the appropriate hydroxylamine in the cavity of a Varian E3 epr spectrometer. The hydroxylamine was oxidized to nitroxide by *tert*-butoxy radicals formed by the photolysis of di-*tert*-butyl peroxide (0.05–0.5 *M* generally)

$$\textit{tert}\text{-BuOOBu-}\textit{tert} \xrightarrow{h\nu} 2\textit{tert}\text{-BuO}\cdot$$

$$\textit{tert}\text{-BuO}\cdot + \text{RNHOH} \longrightarrow \textit{tert}\text{-BuOH} + \text{RNHO}\cdot$$

When the light was cut off the decay of the signal due to $\text{RNHO}\cdot$ was rapid. The general procedure of Weiner and Hammond[16] was used to monitor the radical decays. That is, the light beam was chopped by a rotating sectored disc and a large number of identical decays were collected by a Fabri-Tek 1072 signal averager. In most cases the reactant solution flowed slowly through the cavity during an experiment. This prevented the build-up of nitroxide radicals which were more stable than the nitroxide under study, but did not interfere with the measurement of radical decays or of radical concentrations.

N-Methylhydroxylamine hydrochloride was obtained from Aldrich and was recrystallized from ethanol–ether. Neutralization of the dried salt with sodium glycolate yielded the free base which was distilled at reduced pressure under helium into receivers cooled in liquid nitrogen. This material was used immediately in the epr experiments without exposure to air.

N-Isopropylhydroxylamine and *N*-*tert*-butylhydroxylamine were prepared by reduction of the corresponding nitro compounds using the method described by Meisenheimer and Chou.[17] The hydroxylamine hydrochlorides were treated in the same way as for the methyl compound. *N*-Phenylhydroxylamine was prepared by the method of Vogel.[18]

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(1) Issued as NRCC No. 12239.

(2) Part I: K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 93, 902 (1971).

(3) NRCC Fellow, 1967–1969.

(4) NRCC Fellow, 1969–1970.

(5) A. L. Buchachenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1120 (1963).

(6) C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, 230 (1964).

(7) E. J. Geels, R. Konaka, and G. A. Russell, *Chem. Commun.*, 13 (1965).

(8) G. C. Letourneux, H. Lemaire, A. Rassat, and J. P. Ravet, *Bull. Soc. Chim. Fr.*, 1975 (1965).

(9) T. A. J. W. Wajer, A. Mackor, T. J. deBoer, and J. D. W. van Voorst, *Tetrahedron Lett.*, 1941 (1967).

(10) G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, **89**, 3821 (1967).

(11) C. J. W. Gutch and W. A. Waters, *J. Chem. Soc.*, 751 (1965).

(12) J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

(13) T. A. J. W. Wajer, A. Mackor, and T. J. deBoer, *Tetrahedron*, **25**, 175 (1969).

(14) M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. B*, 395 (1970).

(15) D. F. Minor, W. A. Waters, and J. V. Ramsbottom, *ibid.*, *B*, 180 (1967).

(16) S. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 1659 (1968).

(17) J. Meisenheimer and L.-H. Chou, *Justus Liebigs Ann. Chem.*, **539**, 78 (1939).

(18) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, p 629.

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