in a 100-ml three-necked flask equipped with a magnetic stirrer, addition funnel, reflux condenser, and drying tube. The ketone (0.02 mol) was added dropwise to the stirring benzene solution and the mixture was heated under reflux for 4 hr. The cooled benzene solution was then poured into 100 ml of ice water and extracted with ether.

The ether extracts were dried over magnesium sulfate and most of the ether was removed under reduced pressure at approximately 20 Torr. Pumping (0.1 Torr) on the residue with a Dry Ice trap in the line separated the benzene and cyclopropyl hydrocarbons from a mixture of solid carboxamides. This mixture was washed with hexane, dried, and analyzed by nmr spectroscopy (Table I). The pure amides were isolated from the mixture by sublimation or by recrystallization from water or a combination of methylene chloride and pentane. The cyclopropyl hydrocarbons were identified by their infrared and nmr spectra (Table I).

The aqueous phase remaining after ether extraction was neutralized and was concentrated until salt precipitation occurred. The solution was then extracted with ether and the ether solution was treated as described.

Products and Kinetics of Photoreduction of Acetophenone by Amines and Alcohols[1]

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Abstract: Photoreduction of acetophenone by 2-butylamine leads to acetophenone pinacol and to N-2-butylidene-2-butylamine. Photoreduction of acetophenone and of *p*-methylacetophenone by α-methylbenzylamine leads to the three products of coupling of the radicals formed by the initial abstraction of hydrogen, pinacols, amino alcohols, and diamines. The radicals derived from the purely aliphatic alcohols and amines reduce a second molecule of ketone. The aryl alkyl ketone- and amine-derived radicals are of similar stability and both survive and couple. Acetophenone is not photoreduced by α-methylbenzyl acetate, and is photoreduced with low efficiency by N-acetyl-α-methylbenzylamine. Quantum yield for photoreduction of acetophenone by 1 *M* α-methylbenzyl alcohol in benzene is 0.37, by 0.5 *M* α-methylbenzylamine is 0.49, and by 0.5 *M* 2-propanol is 0.75. Light absorbing transients are formed to a greater extent and photoreduction is less efficient at high concentrations of each of these reducing agents. Efficiency of photoreduction first increases with dilution with benzene, and then decreases at high dilution. Extrapolation of the dilute solution values leads to hypothetical limiting quantum yields for photoreduction of acetophenone by α-methylbenzyl alcohol in benzene, φ 0.54; by 2-propanol in benzene, φ 1.2, with $k_d/k_r = 0.28\ M$; by α-methylbenzylamine in benzene, φ 0.61, with $k_d/k_{ir} = 0.049\ M$. For photoreduction by this amine a Stern–Volmer treatment of quenching by naphthalene leads to $k_q/k_{ir} = 84$, $k_{ir} = 7.1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, and $k_d = 3.5 \times 10^6\ \text{sec}^{-1}$. Photoreduction of acetophenone by 1 *M* 2-butylamine in benzene, $\varphi \sim 1.1$, is 1.40 as efficient as in neat 2-butylamine. A light-absorbing transient is not formed in this amine, and the lower efficiency in this neat amine may be due to π,π^* character in ketone triplet in this medium, or to deactivating solvation of ketone and triplet by the amine.

Acetophenone is photoreduced when irradiated in solution with aliphatic alcohols and with α-methylbenzyl alcohol,[2] and the reactions lead to the *meso*- and *dl*-acetophenone pinacols. In photoreduction of aromatic ketones, the triplet state is the reactive species,[3,4] the n,π^* triplet is the most reactive of the triplets, and the π,π^* and charge-transfer triplets have low or no reactivity.[5,6] Acetophenone has low-lying n,π^* and π,π^* triplet states of similar energy,[7] and reported quantum yields for photoreduction by 2-propanol are 0.5[7] and 0.68.[8] The photoreduction proceeds by formation of the ketyl radical,[9] eq 1. Acetone (1 mole) is

$$C_6H_5\overset{*}{C}OCH_3 + (CH_3)_2CHOH \longrightarrow C_6H_5\dot{C}(OH)CH_3 + (CH_3)_2\dot{C}OH \quad (1)$$

formed for every 2 moles of acetophenone reduced,[10] and the alcohol-derived radical may reduce a second molecule of acetophenone in a dark reaction, eq 2. The

$$C_6H_5COCH_3 + (CH_3)_2\dot{C}OH \longrightarrow C_6H_5\dot{C}(OH)CH_3 + (CH_3)_2C{=}O \quad (2)$$

acetophenone ketyl radicals lead to the pinacols, the 2,3-diphenyl-2,3-dihydroxybutanes. The ratio of *dl* and *meso* products,[11] as affected by solvent,[11b] by alkalinity[11b] and by amine[11b] reducing agents, has been investigated. In work related to our study of effects of medium on the photoreduction of benzophenone,[12] of *p*-aminobenzophenone,[13] and of fluorenone,[14] we have

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studied the kinetics of photoreduction of acetophenone by alcohols and the kinetics and products of photoreduction by amines. Photoreduction of each of these ketones shows individual characteristics related to the nature and relative energies of its excited states. We now wish to report some results of the study of the photoreduction of acetophenone.

Experimental Section

Materials. Acetophenone, Fisher Certified Reagent, was distilled bp 48° (0.15 mm). *p*-Methylacetophenone (Eastman Kodak Co.) was used as received. α-Methylbenzylamine (Eastman Kodak Co.) was distilled through a spinning band column, bp 48° (2 mm), and stored under argon. α-Methylbenzyl alcohol (Eastman Kodak Co.) was distilled through a spinning band column, bp 43.5–45° (0.2 mm), and stored under argon. It is autoxidized readily and is generally contaminated with acetophenone. α-Methylbenzyl alcohol was resolved as described in the literature[15] and esterified with acetyl chloride. N,N-Dimethyl-α-methylbenzylamine (K & K) was redistilled, bulb to bulb, at 0.1 mm. α-Methylbenzyl acetate (K & K) was distilled similarly at 0.1 mm pressure. α-Methylbenzyl cyanide (Aldrich) was used as received. 2-Butylamine (Eastman Kodak Co.) was redistilled shortly before being used. Pyridine, cyclohexane, and 2-propanol, Fisher Reagent grade, were used as received. Benzene was from Eastman Kodak Co., Spectrograde. 1,1-Diphenylethane was prepared by treatment of styrene with excess benzene and sulfuric acid,[16] bp 63–64° (0.05 mm). N-α-Methylbenzylacetamide was prepared by treatment of 12.1 g (0.10 mole) of α-methylbenzylamine with 25 g (0.25 mole) of acetic anhydride, 14.3 g, 88% yield, mp 75–77° from benzene–petroleum ether (lit.[17] mp 57°).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.77; H, 7.77; N, 8.37 (Schwarzkopf).

Irradiations. Determination of rates of photoreduction were carried out on 3–5-ml aliquots in 1-cm diameter Pyrex Thunberg tubes. The solutions were degassed by the freeze–thaw procedure and left under argon in ground glass or Teflon joint closed tubes. The tubes were irradiated on a rotating turntable, 8 cm from the center, at which was located a GE H85-A3 lamp. In quantum yield measurements 4-ml aliquots were degassed in 1-cm square Pyrex tubes, kept under argon, and irradiated for 50–100 min at 313 nm with an Osram SP-200 lamp in a Bausch and Lomb 38-86-01 grating monochromator. Concentration of acetophenone was monitored by measurement of the absorbance at 320 nm in 1-mm absorption cells, either sealed to the irradiation tube or separate. When absorbing transients were observed the solutions were shaken with air and allowed to stand for several hours before the absorbance was measured. Absorbances were measured either on a Beckman DU-2 or Cary 14 spectrophotometer. Quantum yields were determined by ferrioxalate actinometry.[18] Solutions of ferrioxalate were irradiated at 313 nm for 2 min before and after irradiation of the acetophenone solutions and the increase in absorbance at 510 nm was measured.

Products of Photoreduction of Acetophenone by α-Methylbenzylamine. Acetophenone (2.47 g, 0.0206 mole) and α-methylbenzyl amine (12.9 g, 0.107 mole) were diluted to 100 ml with benzene and irradiated under argon for 11.5 hr adjacent to the GE lamp. Absorbance at 320 nm indicated ~90% reduction of acetophenone. Excess amine was removed at 0.1 mm, bath temperature, 100°. The residue, a pale yellow glass, 4.61 g, was taken up in 25 ml of methylene chloride, and 75 ml of petroleum ether (bp 20–40°) and treated with HCl gas, leading to an organic solution and to a white precipitate (4.87 g, mp 145–153°, 0.017 mole) calculated as 2,3-diphenyl-3-amino-2-butanol hydrochloride. The organic solution was concentrated leading to a residue, mp 87–93°, with the infrared spectrum identical with that of previously prepared[10] acetophenone pinacol, 0.61 g (~24% yield). A portion of the hydrochloride salt was crystallized from water, mp 122–132° dec.

Anal. Calcd for $C_{16}H_{20}NOCl\cdot H_2O$: C, 65.0; H, 7.5; N, 4.7. Found: C, 64.7; H, 7.4; N, 4.8 (C. Fitz).

Another fraction was obtained from 2-propanol–water, mp 166–170°, which may have been the diamine dihydrochloride.

A portion of the hydrochloride salt was dissolved in water, treated with hydrochloric acid and sodium nitrite, and extracted with methylene chloride. This was concentrated and led to an oil, 3,3-diphenyl-2-butanone, with infrared spectrum, glpc retention time, and oxime, mp 151–153°, identical with those of an authentic sample. A sample of 3,3-diphenyl-2-butanone was prepared from 5.5 g (0.023 mole) of acetophenone pinacol, boiled for 2 hr in 50 ml of 1:1 H_2O–H_2SO_4, 4.8 g (0.021 mole), bp 93–99° (0.03 mm). A sample was converted to the oxime mp 153–156°, from ethanol (lit.[19] mp 151°), mixture melting point with that obtained *via* the hydrochloride salt, 152–156°.

A portion of the hydrochloride salt was treated with aqueous alkali and extracted with methylene chloride, and the extract was concentrated. A portion of the oil residue was distilled leading to an oil which gradually solidified, 2,3-diphenyl-3-amino-2-butanol.

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.81. Found: C, 79.45; H, 8.15 (Schwarzkopf); N, 5.5 (C. Fitz).

Products of Photoreduction of *p*-Methylacetophenone by α-Methylbenzylamine. (i) A 100-ml benzene solution of 3.96 g (0.0296 mole) of *p*-methylacetophenone and 7.73 g (0.064 mole) of α-methylbenzylamine was degassed and irradiated under argon for 69 hr with the GE lamp. Benzene was removed and the residue, 11.2 g, was dissolved in methylene chloride and extracted with hydrochloric acid. The organic layer was concentrated and the residue was distilled, bp 145–150° (0.1 mm), crude pinacol of *p*-methylacetophenone, 1.5 g, 38% yield. It was characterized by its infrared spectrum and tlc behavior which was identical with that of the pinacol obtained below. The hydrochloric acid extract was made alkaline and extracted with methylene chloride, leading to a residue, which, on treatment with petroleum ether led to 2,3-diamino-2,3-diphenylbutane, 0.57 g, 14% yield, mp 122–124° from ethanol–water. The nmr spectrum in $CDCl_3$ showed no tolyl methyl groups; it showed aromatic protons, τ 2.79, and methyl and amine protons, τ 8.45 and 8.30, in a ratio of 10:10; on addition of D_2O the ratio of aromatic to methyl protons became 10:6.

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.18; H, 8.41; N, 11.85 (Schwarzkopf).

(ii) A 100-ml benzene solution of 4.08 g (0.0304 mole) of *p*-methylacetophenone and 6.09 g (0.051 mole) of α-methylbenzylamine was irradiated for 64 hr. Solvent and excess amine were removed under vacuum leaving a residue, 8.67 g. A portion, 2.32 g, was chromatographed on alumina. The pinacol of *p*-methylacetophenone was eluted with benzene, 0.34 g, 31% yield from the ketone-derived radicals, mp 128–134° from petroleum ether–benzene.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.20; H, 8.32 (Schwarzkopf).

Benzene–ether (1:1) eluted an intermediate fraction, 0.50 g, rich in the amino alcohol, and ether and ether–ethanol eluted the amino alcohol, 2-*p*-tolyl-3-phenyl-3-amino-2-butanol, 0.68 g, 31% yield, mp 121–125° from benzene–cyclohexane, mixture melting point with the pinacol depressed to 100–115°.

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.53; H, 8.29; N, 6.16 (Schwarzkopf).

Ethanol eluted an intermediate mixture, 0.30 g, and then 2,3-diamino-2,3-diphenylbutane, 0.263 g, 24% yield from the amine-derived radicals, with ir spectrum identical with that of the compound obtained in the preceding run.

Photoreduction of Acetophenone by 2-Butylamine. (i) Acetophenone (3.72 g, 0.031 mole) and 2-butylamine (13.8 g, 0.19 mole) were diluted to 100 ml with benzene. The solution was degassed and irradiated in Pyrex under argon next to a GE H-85-A3 lamp for 42 hr. The absorbance at 320 nm indicated essentially complete disappearance of acetophenone. The solution was concentrated under vacuum, and the residue was stirred with petroleum ether (bp 20–40°) and filtered, leading to a solid, 3.16 g, mp 86–97°, with infrared spectrum in methylene chloride identical with that of acetophenone pinacol. The mother liquor led to two further crops of acetophenone pinacol, 0.26 and 0.28 g, essentially quantitative yield of the pinacol.

(ii) Acetophenone (4.23 g, 0.0353 mole) and 2-butylamine (2.07 g, 0.0284 mole) were diluted to 25 ml with benzene. Aliquots totaling 19 ml were degassed and irradiated under argon for 64 hr. The absorbance at 320 mμ indicated 80% reduction of acetophe-

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none, 100% based on the amount of amine available. The infrared spectrum of the solution, diluted with benzene and taken against benzene, was essentially identical with that obtained previously for N-2-butylidene-2-butylamine.[20] Benzene was distilled at atmospheric pressure, and the imine was distilled from the residue under vacuum, 0.6 g, 30% yield, with infrared spectrum identical with that obtained previously. A portion was added to a solution of 2,4-dinitrophenylhydrazine leading to the 2,4-dinitrophenylhydrazone of 2-butanone, mp 108–110°.

(iii) Solutions of 0.10 *M* acetophenone in neat (9.57 *M*) 2-butylamine, and in 1.0 *M* 2-butylamine in benzene were degassed and irradiated for 100 min under argon 8 cm from the GE lamp. Absorbances were measured at 320 nm in 1-mm cells. The reaction in 2-butylamine showed no evidence of an absorbing intermediate. The rates of photoreduction were, in neat amine, 5.7×10^{-4} *M* min^{-1}, and in 1.0 *M* amine in benzene, 7.9×10^{-4} *M* min^{-1}.

Results

In preliminary experiments rates of photoreduction of 0.1 *M* acetophenone by a set of potential reducing agents of related structure, $C_6H_5CH(X)CH_3$, 1.0 *M* in benzene, were compared on a turntable. Some results are summarized in Table I.

Table I. Photoreduction of 0.10 *M* Acetophenone by 1.0 *M* $C_6H_5\underset{\substack{|\\X}}{C}HCH_3$ in Benzene

-X	Irr, hr	Reductn, %	Rel rate
-OH	1.7	33	1.0
$-NH_2$	1.7	49	1.5
$-OCOCH_3$	16.5	0	0
$-NHCOCH_3$	6.3	12	0.1
$-C_6H_5$	2.5	14	0.3
-H	19.5	56	0.15
2-Propanol[a]	1.7	59	1.8
2-Butylamine[b]	1.7	79	2.4
2-Butylamine[c]	1.7	57	1.7

[a] 1 *M* 2-propanol in C_6H_6. [b] 1 *M* 2-butylamine in benzene. [c] Neat amine.

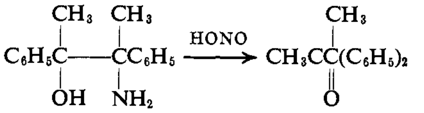
The data in Table I may be compared, with the rate of photoreduction by α-methylbenzyl alcohol as standard. α-Methylbenzylamine leads to 50% greater rate than the corresponding alcohol. The acetate ester of the alcohol did not photoreduce acetophenone, and irradiation of acetophenone with optically active α-methylbenzyl acetate led to no decrease in optical rotation. Conversion of the amine to the amide reduces photoreduction activity by an order of magnitude. Irradiation of acetophenone in a 1.0 *M* benzene solution of the tertiary amine, $X = N(CH_3)_2$, led to a light-absorbing product which did not permit ready evaluation of the rate of photoreduction, a result previously encountered in the photoreduction of benzophenone by tertiary amines.[20] Ethylbenzene, X = H, shows low reactivity, similar to that of the benzophenone–aliphatic hydrocarbon system.[21] The second phenyl group in 1,1-diphenylethane, $X = C_6H_5$, appears to lead to increased reactivity, possibly due to the diphenylmethyl hydrogen.

2-Propanol led to 80% faster photoreduction than did α-methylbenzyl alcohol. 2-Butylamine led to 35% faster photoreduction than did 2-propanol, 60% faster than did α-methylbenzylamine. The amines show intrinsically greater reactivity than the corresponding alcohols, while the purely aliphatic compounds, 2-propanol and 2-butylamine, may be more reactive than the aralkyl alcohol and -amine merely because of reduction of a second molecule of ketone by the initially formed aliphatic radicals, eq 2 and 3.[21]

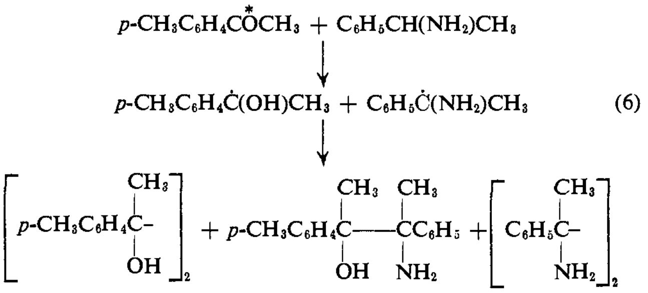
$$C_6H_5COCH_3 + C_2H_5\dot{C}(NH_2)CH_3 \longrightarrow C_6H_5\dot{C}(OH)CH_3 + C_2H_5C(CH_3){=}NH \quad (3)$$

The products of photoreduction by the amines are relevant to this consideration. Photoreduction of 0.2 *M* acetophenone by 1 *M* α-methylbenzylamine led to 24% yield of the pinacol and a mixture of nitrogen-containing products. From this the amino alcohol, 2,3-diphenyl-3-amino-2-butanol, formed by coupling of the initially formed radicals, eq 4, was isolated. This was obtained as the hydrochloride, which, on treatment with alkali, was converted to the free base. On treatment with nitrous acid it was converted to 3,3-diphenyl-2-butanone, eq 5. Photoreduction of 0.3 *M* *p*-methylacetophenone by α-methylbenzylamine proceded similarly and allowed isolation of the three products of combination of the initially formed radicals in comparable yields.

$$C_6H_5\overset{*}{C}OCH_3 + C_6H_5CH(NH_2)CH_3 \longrightarrow C_6H_5\dot{C}(OH)CH_3 + C_6H_5\dot{C}(NH_2)CH_3 \quad (4)$$



$$C_6H_5\underset{OH}{\overset{CH_3}{C}}\text{——}\underset{NH_2}{\overset{CH_3}{C}}C_6H_5 \xrightarrow{HONO} CH_3\underset{\| \atop O}{C}\overset{CH_3}{C}(C_6H_5)_2 \quad (5)$$



$$\begin{gathered} p\text{-}CH_3C_6H_4\overset{*}{C}OCH_3 + C_6H_5CH(NH_2)CH_3 \\ \downarrow \\ p\text{-}CH_3C_6H_4\dot{C}(OH)CH_3 + C_6H_5\dot{C}(NH_2)CH_3 \quad (6) \\ \downarrow \\ \left[p\text{-}CH_3C_6H_4\underset{OH}{\overset{CH_3}{C}}\text{–}\right]_2 + p\text{-}CH_3C_6H_4\underset{OH}{\overset{CH_3}{C}}\text{——}\underset{NH_2}{\overset{CH_3}{C}}C_6H_5 + \left[C_6H_5\underset{NH_2}{\overset{CH_3}{C}}\text{–}\right]_2 \end{gathered}$$

On the other hand photoreduction of 0.3 *M* acetophenone by the aliphatic amine 2-butylamine (2 *M* in benzene) leads to a quantitative yield of the pinacol, as the reaction of eq 3 leaves the acetophenone-derived radical as the sole radical in solution. The imine reacts further with amine, leading to N-2-butylidene-2-butylamine, as reported previously.[21] Photoreduction of acetophenone by neat 2-butylamine proceded only 0.7 as rapidly as by 1.0 2-butylamine in benzene, and a light-absorbing transient was not observed.

Quantum yields were determined by ferrioxalate actinometry for photoreduction of acetophenone by three of the compounds of Table I. Photoreduction in the benzene solutions showed zero-order kinetics and little or no evidence of a light-absorbing intermediate, while in neat 2-propanol a substantial amount of light-absorbing transient was observed. Results are summarized in Table II.

In some rate studies irradiation of acetophenone at 313 nm was carried out (a) in neat 2-propanol, (b) in 1:1 2-propanol–benzene (6.4 *M*), and (c) in 1.6 *M* 2-propanol in benzene. In neat 2-propanol the optical den-

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Table II. Quantum Yields for Photoreduction of Acetophenone at 313 nm

$C_6H_5COCH_3$, *M*	Reducing agent: Compound	Reducing agent: *M*	Solvent	Quantum yield, φ
0.103	$C_6H_5CH(NH_2)CH_3$	0.51	C_6H_6	0.49
0.126	$C_6H_5CH(OH)CH_3$	0.96	C_6H_6	0.37[a]
0.103	$(CH_3)_2CHOH$	0.51	C_6H_6	0.75
0.106	$(CH_3)_2CHOH$	12.8		0.30

[a] This quantum yield is lower than that reported in our earlier paper, ref 10. The present results, obtained with monochromatic light and under better controlled conditions, are more reliable. On the basis of this new value, and comparative rate data of the earlier work, the extrapolated limiting quantum yield for photoreduction of acetophenone by α-methylbenzyl alcohol in benzene is 0.54.

sity rose initially over the range 300–380 nm. The absorbance at 320 nm rose from 0.351 to 0.391 after 27 min irradiation and then began to fall; it was 0.309 after 65 min irradiation and this fell after admission of air and standing in the dark to 0.230, corresponding to 35% photoreduction, and a rate of 0.019 *M* hr.$^{-1}$ The difference in the spectra, between that after irradiation and that after standing, indicated that the transient had λ_{max} at 332 nm and a small minimum at 322 nm. In 1:1 2-propanol–benzene the absorbance at 320 nm rose during 8 min irradiation and then began to fall. In 1.6 *M* 2-propanol the absorbance at 320 nm remained constant for a few minutes and then fell, and the rate of photoreduction was 0.031 *M* hr^{-1}.

Photoreduction of acetophenone by 2-propanol was examined as a function of concentration of the alcohol in benzene. Solutions were irradiated for 65–75 min 8 cm from an Osram Spektrallampe type Hg/I. Results are summarized in Table III. Rates of photoreduction increased by 50% as concentration of 2-propaol decreased from 12.8 *M* (heat) to *ca.* 1 *M*, and then decreased with further dilution.

Table III. Effect of Concentration of Alcohol on the Rate of Photoreduction of 0.1 *M* Acetophenone by 2-Propanol in Benzene

2-Propanol, *M*	Rate, $10^4 \times M$ min^{-1}	Quantum yield, φ
12.84 (neat)	3.81	0.55[a]
3.02	4.99	0.72
1.31	5.48	0.79
1.22	5.55	0.80
1.10	5.74	0.83
0.684	5.61	0.81
0.341	4.45	0.64
0.174	3.05	0.44

[a] The rates were converted to quantum yields, based on the determination φ = 0.75 at 0.51 *M* 2-propanol.

Photoreduction of acetophenone by α-methylbenzylamine was examined as a function of concentration of the amine in benzene. Solutions were irradiated simultaneously for 60 to 100 min on a turntable 8 cm from the GE lamp. Results are summarized in Table IV. The rate of photoreduction increased 2.5-fold as the concentration of amine was decreased from neat (7.7 *M*) amine down to 0.2 *M* in benzene. In neat amine the absorbance increased with irradiation, indicating a great deal of absorbing intermediate. At 2.65 *M* amine a substantial amount of absorbing transient was formed, and some was detected at 1.0 *M* amine. At lower concentration none was observed, and below 0.22 *M* amine the rate of photoreduction decreases.

Table IV. Effect of Concentration of Amine on Photoreduction of 0.1 *M* Acetophenone by α-Methylbenzylamine in Benzene

Amine, *M*	Rate, $10^4 \times M$ min^{-1}	Quantum yield, φ
7.73 (neat)	2.08	0.20[a]
2.65	3.80	0.36
1.00	4.84	0.46
0.506	5.11	0.49
0.223	5.28	0.51
0.214	5.15	0.49
0.110	4.06	0.39
0.050	3.33	0.32
0.029	2.44	0.23
0.016	1.57	0.15

[a] The rates were converted to quantum yields based on the determination, φ 0.49, at 0.506 *M* amine.

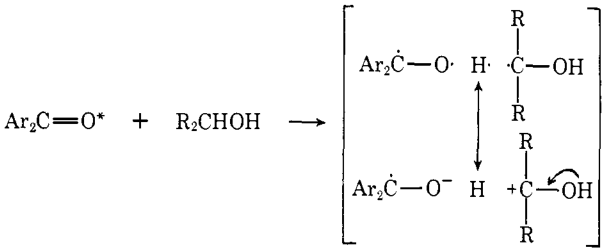
A study was made of the effect of naphthalene on the photoreduction of 0.13 *M* acetophenone by 1.0 *M* α-methylbenzylamine in benzene. Solutions were irradiated simultaneously for 3 hr on the turntable. Rates were determined from the absorbance at 320 nm, and absorbances at the two higher concentrations of naphthalene were corrected for absorption by naphthalene. Results are given in Table V.

Table V. Effects of Naphthalene on Photoreduction of 0.13 *M* Acetophenone by 1.00 *M* α-Methylbenzylamine

Naphthalene, *M*	Rate, $10^4 \times M$ min^{-1}
0	4.10
0.0051	3.10
0.0102	2.45
0.0204	1.73
0.0408	0.98

Discussion

The triplet of acetophenone has the reactivity of an electrophilic radical, and the photoreduction proceeds with high efficiency when abstraction of hydrogen may occur from carbon atoms which have potential electron-donating substituents, as from the alcohols and amines of Table I. The effect has been attributed, in the case of alcohols,[20] to a polar contribution to the transition state for the abstraction of hydrogen, eq 7, and in the case of amines, to a rapid initial interaction of the triplet with the electrons of nitrogen, eq 8.[13,20] These mecha-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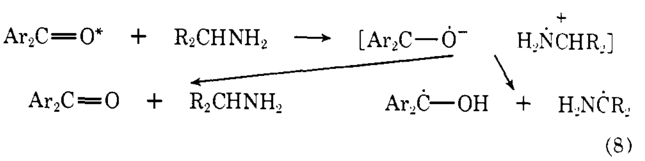
(8)

nisms may, under appropriate availability of electron and hydrogen, coalesce into one, intermediate between the two. Acylation of the hydroxyl and amino groups reduces the electron-donating power of the α-heteroatoms and the photoreducing activity of the compounds. The ester appeared totally unreactive; the maintenance of optical activity during irradiation of acetophenone with optically active α-methylbenzyl acetate indicates that possible reversal of the hydrogen abstraction process did not account for absence of observed photoreduction. The inefficient photoreduction by the amide appeared complex, and it slowed down markedly with extent of reaction. An electron-attracting substituent, the cyano group in α-methylbenzylcyanide, deactivated, and extended irradiation of acetophenone with a solution of this compound in benzene led to no photoreduction.

The aliphatic compounds, 2-propanol and 2-butylamine, cause more rapid reduction than α-methylbenzyl alcohol and α-methylbenzylamine, respectively, because of the thermal reduction of second molecules of acetophenone by the 2-hydroxy-2-propyl and 2-amino-2-butyl radicals, eq 2 and 3. The corresponding reaction is possible with the α-hydroxy-α-methylbenzyl radical but it would merely change the identity of the radical and not increase the rate. Experiments with optically active α-methylbenzyl alcohol indicate that it does not occur.[2,10] The corresponding reaction is possible with the α-amino-α-methylbenzyl radical and it would increase the rate of disappearance of acetophenone, eq 9.

$$C_6H_5COCH_3 + C_6H_5\dot{C}(NH_2)CH_3 \longrightarrow C_6H_5\dot{C}(OH)CH_3 + C_6H_5C(CH_3){=}NH \quad (9)$$

If it did occur rapidly the sole radical in solution would be the α-hydroxy-α-methylbenzyl radical and the acetophenone would be converted essentially completely to its pinacol. This reaction does not occur rapidly, the amine derived radical persists, and the mixture of products, pinacol, amino alcohol, and diamine, expected from coupling of two different radicals, is found in the photoreduction of acetophenone and of p-methylacetophenone by α-methylbenzylamine, eq 4–6. These redox reactions do not occur more rapidly than the coupling reactions because that of the radical from α-methylbenzyl alcohol is thermoneutral, and the reaction of the radical from α-methylbenzylamine, eq 9, may be slightly endothermic. The redox reactions of the radicals from the purely aliphatic alcohols and amines with acetophenone, eq 2 and 3, lead to the more stabilized aralkyl radicals, and are exothermic, and rapid. These reactions lead to aliphatic ketone and imine, respectively,[21] and cause the pinacols to be the sole products of reduction of the ketone.

The quantum yields, Table II, for the photoreductions in benzene are consistent with the relative rates in Table I, and the rate data may be converted to approximate quantum yields based on φ 0.37 for the standard reaction in the table, the photoreduction of acetophenone by 1.0 M α-methylbenzyl alcohol. The quantum yields are substantially lower than those observed in corresponding reactions of benzophenone, 0.30 in neat 2-propanol as compared with[12] 1.2, 0.75 in 0.5 M 2-propanol as compared with[12] 1.4, and 0.37 by 1 M α-methylbenzyl alcohol as compared with[22] 0.6–0.7 for photoreduction of benzophenone by 1 M benzhydrol. However, the photoreduction of benzophenone by benzhydrylamine, which corresponds formally to the acetophenone-α-methylbenzylamine reaction, does not appear to occur.[23] In this case the amine-derived radical may persist. The tetraphenylaminoethanol, which is not known, may not be stable, but may undergo an intramolecular base-catalyzed decomposition to the starting materials; or the amino- and hydroxydiphenylmethyl radicals may disproportionate.

The higher quantum yield in photoreduction by 0.5 M 2-propanol in benzene than by undiluted 2-propanol is noteworthy; it is analogous to the effect observed in the photoreduction of benzophenone in these media,[12] and in the photoreduction of acetophenone in neat α-methylbenzyl alcohol and in solutions of this alcohol in benzene.[10] In all these cases substantial development of a light-absorbing intermediate is observed in solutions high in concentration of alcohol, and less or none is observed in dilute solutions of the alcohol in benzene. A substantial part of the increase in rate resulting from dilution with benzene may result from decrease in the light-absorbing intermediates, which may act as an inner filter.[12] With acetophenone, the more polar solutions, high in alcohol content, may also lead to triplets which have more π,π^* character[7] and are less reactive. It would appear that such an effect on triplet character may not account for the similar medium effect observed with benzophenone.[12] With both ketones the alcoholic solvent may decrease reactivity of whichever triplet is formed by solvation or hydrogen bonding with the triplet.[12]

An inverse plot of the data for the photoreduction of acetophenone at the lowest concentrations of 2-propanol in benzene, Table II, is linear. On the basis that the quantum yield at 0.51 M 2-propanol is 0.75, the limiting quantum yield for photoreduction of acetophenone by 2-propanol, obtained by extrapolation, is 1.2, for conditions under which the system would behave in neat 2-propanol as it does in dilute solutions of 2-propanol in benzene. This is not observed under the conditions of our experiments. This value is lower than the corresponding value for benzophenone,[12] 1.9. The low limiting quantum yield may indicate a lower yield of n,π^* triplet or formation of a less reactive triplet with π,π^* character in benzene also. This plot also leads to a higher value of the ratio of rate constant for decay of the triplet to abstraction of hydrogen from 2-propanol in benzene, $k_d/k_r = 0.28$ M for acetophenone, as compared with 0.16 M for benzophenone. This probably arises from a higher value of k_d for acetophenone.[24]

The quantum yield for photoreduction of acetophenone by α-methylbenzylamine also increased as the amine was diluted with benzene down to about 0.2 M amine, Table IV. More light-absorbing intermediate was observed at the higher concentration of amine. An inverse plot of the data below 0.22 M amine, Figure 1, is linear, and extrapolation leads to a hypothetical limiting quantum yield of 0.61 if the system could behave in neat amine as it does in dilute solutions of the amine in benzene. The ratio of slope to intercept leads to the ratio of rate constant for deactivation to that for inter-

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(23) R. J. Baumgarten and S. G. Cohen, unpublished results.

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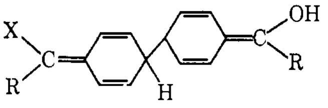
action of the triplet with the amine, $k_d/k_{ir} = 0.049\ M$. A Stern–Volmer plot of the data of the naphthalene-quenching experiments, Table V, is linear, with ratio of slope to intercept = 80 M^{-1}, and ratio of rate constant for quenching by naphthalene to that for interaction of the triplet with the amine, $k_q/k_{ir} = 84$; $k_{ir} = 7.1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, based on $k_q = 6.0 \times 10^9\ M^{-1}\ \text{sec}^{-1}$; this leads to $k_d = 3.5 \times 10^6\ \text{sec}^{-1}$. The value of k_{ir} is more than an order of magnitude greater than that for abstraction of hydrogen from α-methylbenzyl alcohol by the acetophenone triplet,[10] $k_r = 3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, based on the same value for k_q; the value of k_d in the amine system is slightly higher than that in the α-methylbenzyl alcohol reaction, in which $k_d = 1 \times 10^6\ \text{sec}^{-1}$. The high value of k_{ir} in reaction with the amine, accompanied by only fairly high quantum yields, is generally observed with amines[13,14,20,25] and is consistent with the proposed mechanism involving a rapid initial electron or charge-transfer interaction,[13,21] which may be followed either by reduction or by quenching, eq 8.

In the photoreduction of acetophenone by 2-butylamine a light-absorbing transient was *not* observed, but the reduction was more rapid in 1 *M* 2-butylamine in benzene than in neat 2-butylamine. The absence of an intermediate is not unexpected, since in the photoreduction of benzophenone by 2-butylamine none was observed; but in that case the rates decreased in a normal way with decreasing concentration of amine.[20] The conditions leading to or preventing formation absorbing of intermediates are not clear.[26,27] They may have a structure of the isopinacol type, I, and they may undergo thermal and base-catalyzed decompositions. They may be formed more readily in hydroxylic, solvating, solvents, which may decrease α–α coupling as compared with *para–para* coupling.[12] They are formed less readily or are more rapidly decomposed in strongly alkaline media which greatly facilitates study of photoreduction by all classes of amines in aqueous systems.[25,28] 2-Butylamine and other low molecular weight aliphatic amines may be sufficiently alkaline and polar to prevent buildup of the transients.



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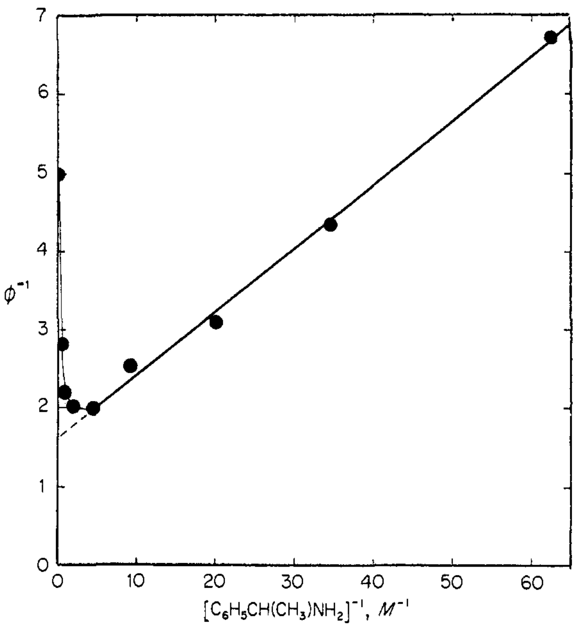

Figure 1. Effect of concentration of amine on quantum yield for photoreduction of 0.1 *M* acetophenone by α-methylbenzylamine in benzene.

While observed effect on light-absorbing transients may account in large part for increased rates of photoreduction of acetophenone and benzophenone[10,12] by alcohols and some amines on dilution with hydrocarbon, this cannot apply to the acetophenone–2-butylamine system and a different effect of medium must be sought. We have reported that photoreduction of fluorenone by triethylamine is made more efficient by dilution with a hydrocarbon and is prevented by dilution with an alcohol.[14] In undiluted amine quenching of excited singlet of fluorenone occurs,[29] while in alcohol, intersystem crossing is diminished.[30] Such possible effects of the aliphatic amine on efficiency of intersystem crossing of acetophenone may be examined in the future. However, we do not observe fluorescence of acetophenone, and this makes study of singlet quenching difficult; and the high rates of interaction of excited triplets with amines complicate study of effects of concentration of amines on intersystem crossing efficiency. The n,π* and π,π* triplets of acetophenone are of similar energy,[7] the multiplicity of the lower lying excited state may vary with solvent,[31] and dilution with hydrocarbon may favor the n,π* triplet or n,π* character in the triplet and thus increase reactivity. Also, the carbonyl group may be solvated at high concentration of primary amine by interaction of carbon and oxygen with electrons and hydrogen of nitrogen, respectively. This may carry over to solvation and stabilization of the triplet and lower its reactivity, whatever its multiplicity. Reaction then requires desolvation and interaction of the triplet oxygen with the electron of nitrogen, the initial interaction being counterproductive.

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