Photoreduction of Aromatic Ketones by Amines. Studies of Quantum Yields and Mechanism[1]

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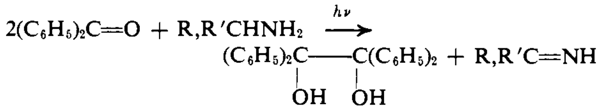
Abstract: Photoreduction of aromatic ketones by aliphatic amines in nonpolar media leads to products, rates, and stoichiometry similar to photoreduction by alcohols and ethers. However, the initial light-induced abstraction of hydrogen appears to show characteristics different from those in the oxygen compounds. Quantum yields for photoreduction at 334 mμ of benzophenone by 2-butylamine, N-methyl-2-butylamine, and N,N-dimethyl-2-butylamine are 1.13, 0.31, and 0.12, respectively. Rates of photoreduction by the primary amine fall very slightly on dilution with benzene, leading to $k_d/k_r = 0.03\ M$, $k_r = 3 \times 10^6\ M^{-1}\ \text{sec}^{-1}$. Rates of photoreduction by the tertiary amine *rise* with dilution with benzene, the quantum yield being 0.40 at 0.26 *M* amine. A light-absorbing transient is formed in the tertiary amine, less so on dilution with benzene, accounting at least in part for the increase in rate with dilution. No light-absorbing transient was observed with the primary amine. Efficiency of transfer of hydrogen from a tertiary amine to an excited ketone compares favorably with that from a primary amine. Photoreduction by the primary amine is insensitive to physical quenchers, $k_q/k_r \cong 40$ for naphthalene, $k_q/k_r \cong 100$ for ferrocene. Photoreduction by optically active 2-butylamine and N,N-dimethyl-2-butylamine leads to no racemization in recovered amine, indicating that reversible hydrogen abstraction from the asymmetric α-C does not occur. Photoreduction in cyclohexylamine-1-*d* shows a small kinetic deuterium isotope effect, $k_H/k_D \cong 1.6$. Photoreduction in primary amines containing $-ND_2$ proceeds slightly more rapidly than in the $-NH_2$ analogs. It is proposed that excited ketone, probably triplet, may abstract an electron or otherwise interact with the lone pair of nitrogen in a rapid process with which physical quenchers compete ineffectively. This is followed by electron return, equivalent to quenching, or by proton transfer from carbon, leading to the initial free radicals. The reaction is effectively inhibited by mercaptan and the later stages are normal free radical reactions.

The photoreduction of aromatic ketones by alcohols, ethers, and hydrocarbons have been known for a long time and have been studied in some detail.[2] Recently the efficient photoreduction of benzophenone by aliphatic amines has been described.[3] The ketone undergoes photoreduction by primary amines, R,R'-$CHNH_2$, and by secondary amines, R,R'CHNHR'', leading to nearly quantitative yields of benzpinacol and the imines, R,R'C=NCHR,R' and R,R'C=NR'', respectively.[3] The reactions proceed rapidly in dilute solution in hydrocarbons without excess amine and lead to ready synthesis of imines (eq 2, 5), to oxidative deamination of primary amines (eq 3), to potential conversion of primary to secondary amines (eq 4), and to degradation of secondary amines to carbonyl compounds and primary amines (eq 6).

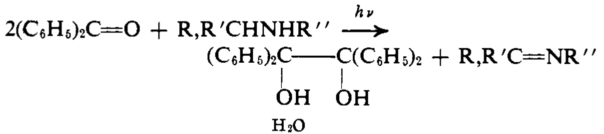

(1)

$$2(C_6H_5)_2C{=}O + R,R'CHNH_2 \xrightarrow{h\nu} (C_6H_5)_2\underset{OH}{\underset{|}{C}}{-}\underset{OH}{\underset{|}{C}}(C_6H_5)_2 + R,R'C{=}NH \tag{1}$$

$$R,R'C{=}NH + R,R'CHNH_2 \longrightarrow R,R'C{=}NCHR,R' + NH_3 \tag{2}$$

$$R,R'C{=}NCHR,R' \xrightarrow{H_2O} R,R'C{=}O + H_2NCHR,R' \tag{3}$$

$$R,R'C{=}NCHR,R' \xrightarrow{H_2} R,R'CHNHCHR,R' \tag{4}$$

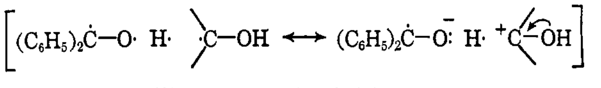

(5)

$$2(C_6H_5)_2C{=}O + R,R'CHNHR'' \xrightarrow{h\nu} (C_6H_5)_2\underset{OH}{\underset{|}{C}}{-}\underset{OH}{\underset{|}{C}}(C_6H_5)_2 + R,R'C{=}NR'' \tag{5}$$

$$R,R'C{=}NR'' \xrightarrow{H_2O} R,R'C{=}O + H_2NR'' \tag{6}$$

Photoreduction in Pyrex of benzophenone by typical primary amines, *n*-butylamine, cyclohexylamine, and 2-butylamine proceeded at rates equal to, and 10 and 30% greater than, the rate of photoreduction in 2-propanol.[3] Typical secondary amines showed substantial, but lower rates, diisopropylamine and di-*n*-butylamine being 0.3 and 0.5 as effective as 2-propanol, respectively. Tertiary amines showed considerable variation in rate, triethylamine, tri-*n*-butylamine, and diisopropylethylamine being 0.2, 0.4, and 0.5 as effective as 2-propanol, respectively. Rates of photoreduction by tertiary amines were increased as much as threefold by dilution to 0.5 *M* in benzene[3] and rates were also increased by dilution with cyclohexane.[4] Reactivity of secondary amines was also increased by dilution with benzene, while photoreduction by primary amines was not enhanced by such dilution.[3]

Hydrogen α to the heteroatom is important for high reactivity in alcohols and amines, and *t*-butyl alcohol[5] and *t*-butylamine[3] both show low reactivity. In alcohols, the C–H bond is weaker than the O–H bond[6] and the oxygen atom may facilitate abstraction of α-C–H by a polar contribution to the transition state.



It has seemed likely that the initial attack by triplet[7] ketone is at the α-C–H. This has been confirmed in inhibition of photoreduction by mercaptans.[8] In amines

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[1] We are pleased to acknowledge generous support of this work by the National Science Foundation under Grants GP-1833 and GP-6366.

[2] A list of references is given in ref 3b.

[3] (a) S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965); (b) S. G. Cohen and R. J. Baumgarten, *ibid.*, **89**, 3471 (1967).

[4] S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967).

[5] S. G. Cohen and S. Aktipis, *Tetrahedron Letters*, **10**, 579 (1965).

[6] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Ltd., London, 1962, pp 127, 135, 141.

[7] (a) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959); (b) H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

[8] S. G. Cohen, S. Orman, and D. A. Laufer, *J. Am. Chem. Soc.*, **84**, 3905 (1962).

Table I. Quantum Yields, 0.2 *M* Benzophenone in 2-Butylamines

λ, mμ	Amine	d(Fe^{2+})/d*t*, *M* hr^{-1}	$-d[(C_6H_5)_2CO]/dt$, *M* hr^{-1}	Quantum yield $-(C_6H_5)_2CO$
334	$CH_3CH_2CH(CH_3)NH_2$	0.053	0.048	1.13
366	$CH_3CH_2CH(CH_3)NH_2$	0.23	0.21	1.10
334	$CH_3CH_2CH(CH_3)NHCH_3$	0.052	0.013	0.31
366	$CH_3CH_2CH(CH_3)NHCH_3$	0.25	0.078	0.38
334	$CH_3CH_2CH(CH_3)N(CH_3)_2$	0.035	0.0034	0.12

the α-C–H bond again is weaker than the N–H bond and the less electronegative nitrogen might make a more important polar contribution to the transition state than adjacent oxygen. The course of the photoreduction in amines might be similar to that in alcohols. However, photoreduction in amines has intrinsic interest; some differences from the reactions in alcohols were noted, and it seemed worthwhile to make a more quantitative study of these reactions.

Results

Photoreduction of benzophenone was examined in a set of three related amines, 2-butylamine, N-methyl-2-butylamine, and N,N-dimethyl-2-butylamine. In the primary and secondary amines λ_{max} was at 342 mμ; in the tertiary amine there was a double absorption peak at 345 and 333 mμ (ϵ_{max} ~132 in the three amines). Quantum yields were determined at 334 and 366 mμ with a ferrioxalate actinometer. Results are summarized in Table I. The quantum yield in the primary amine was 1.1 and quantum yields in these secondary and tertiary amines were $^1/_3$ and $^1/_{10}$, respectively, as great as that in the primary amine.

Rates of photoreduction of 0.2 *M* benzophenone by these three amines were examined in Pyrex with irradiation from a high-pressure mercury lamp as a function of concentration of the amine in benzene. Some results are summarized in Table II. The experiments were carried out at different times with different lamp efficiencies and the rates are not strictly comparable. The data are normalized in the third column by comparison with the rates in 2-butylamine determined concurrently.

Table II. Rates of Photoreduction of 0.2 *M* Benzophenone by the 2-Butylamines in Benzene. Effect of Concentration of Amine

Amine		Rate	
Compd	*M*	*M* hr^{-1}	Rel 2-$BuNH_2$
$CH_3CH_2CHCH_3$	10.0	0.080	1.0
|	1.0	0.074	0.93
NH_3	0.52	0.069	0.86
	0.21	0.056	0.70
	0.10	0.051	0.63
$CH_3CH_2CHCH_3$	8.4	0.024	0.24
|	3.0	0.024	0.24
$NHCH_3$	1.6	0.029	0.36
	0.7	0.028	0.36
$CH_3CH_2CHCH_3$	7.0	0.008	0.08
|	3.2	0.014	0.12
$N(CH_3)_2$	1.0	0.018	0.17
	0.50	0.027	0.21
	0.22	0.024	0.20

The rates decreased slightly as the primary amine was diluted with benzene. In the secondary amine the reaction appeared to be more efficient in dilute rather than concentrated solution. In the tertiary amine the rate increased regularly with decreasing concentration of amine and was at a maximum at 0.5 *M* amine and not significantly less at 0.22 *M*. The quantum yield for photoreduction of 0.2 *M* benzophenone by 0.26 *M* N,N-dimethyl-2-butylamine in benzene was then determined at 334 mμ, 1.48 × 10^{16} quanta sec^{-1}, against a ferrioxalate actinometer. It was found to be 0.40, as compared with 0.12 in the neat tertiary amine.

Experiments were done to ascertain whether formation of a light-absorbing transient occurred and might account in part for these results. The change in absorbancy during irradiation was examined by use of an absorption cell which was sealed to the irradiation tube. Irradiations were carried out at 334 or 336 mμ and absorbancies were measured at about 345 mμ. Irradiation of 0.2 *M* benzophenone in the primary amine, 2-butylamine, and in the secondary amine, N-methyl-2-butyl amine, led to decrease of absorbancy and no change on admission of air. Irradiation of benzophenone in the tertiary amine, N,N-dimethyl-2-butylamine, led to increase in absorbancy throughout the range 340–400 mμ, leaving only a shoulder at 354 mμ; at this wavelength the absorbancy rose from 2.76 to 3.59 during 60 min irradiation.

The effect of dilution with benzene on the increase in absorbancy during the photoreduction by the tertiary amine was then examined. The solutions were irradiated for a period, examined in the spectrophotometer, and returned to the irradiating monochromater (Table III). In the neat tertiary amine the absorbancy rose with irradiation, decreased slightly during the few minutes required for reading the absorbancy, and rose again with further irradiation. The absorbancy levelled off after 80-min irradiation and was steady for the extended period of about 7 hr of the experiment. The decrease due to photoreduction was small compared with the increase due to the transients. At 1.0 *M* amine in benzene the absorbancy rose during 1-hr irradiation and then decreased. At 0.26 *M* amine the initial increase in absorbancy was still less and decrease began earlier. In all cases the absorbancy decreased in the dark to a level which was not further decreased by admission of air. The total final decrease in absorbancy per unit time of irradiation was least for neat amine, larger for 1.0 *M*, and largest for 0.26 *M* amine. This is consistent with the results obtained in the normal measurements in which the solution is irradiated and an aliquot is diluted, shaken with air, and allowed to stand before the absorbancy is measured.

Information about the nature of the excited state of the ketone which is involved in photoreduction may be sought in experiments with physical quenchers.[7] The photoreduction of 0.2 *M* benzophenone by 2-butylamine was studied in neat 2-butylamine and in 1.0 *M*

Table III. Absorbancy during and after Irradiation of 0.2 M Benzophenone in N,N-Dimethyl-2-butylamine Neat and in the Presence of Benzene

9.6 M amine		1.0 M amine		0.26 M amine	
Irradn (dark), min	OD 345 mμ	Irradn (dark), min	OD 344 mμ	Irradn (dark), min	OD 344 mμ
0	2.74	0	2.87	0	2.87
5	2.83	5	2.93	5	2.91
30	3.08	35	2.95	35	2.90
60	3.24	63	2.90	60	2.84
80	3.30	80	2.86	80	2.78
110	3.32	113	2.81	110	2.69
140	3.33	143	2.75	140	2.61
440	3.32	265	2.50	180	2.49
(5)	3.25	(7)	2.46	(6)	2.47
(35)	2.98	(30)	2.37	(30)	2.42
(75)	2.80	(80)	2.36	(80)	2.41
(13 hr)	2.41	(17 hr)	2.34	(17 hr)	2.35
(Air)	2.41	(Air)	2.34	(Air)	2.36

amine in benzene in the presence of varying concentrations of naphthalene and of ferrocene. Solutions were irradiated with the high-pressure mercury lamp for a period (~40 min), an aliquot was taken for analysis, and the remainder was degassed and irradiated again. Two or three points were obtained from each tube; two tubes were irradiated at each concentration of quencher. Average rates, relative to those of similar solutions containing no quencher, irradiated at the same time, are given in Table IV.

Table IV. Effects of Naphthalene and Ferrocene on Rates of Photoreduction of 0.2 M Benzophenone by 2-Butylamine, Neat and 1.0 M in Benzene

Amine, M	Quencher		Rel rate
	Compd	M	
10	. . .		1.00
10	Naphthalene	0.01	0.97
10	Naphthalene	0.02	0.92
10	Naphthalene	0.04	0.87
10	Naphthalene	0.06	0.83
1.0	Naphthalene	0.005	0.85
1.0	Naphthalene	0.01	0.77
1.0	Naphthalene	0.02	0.59
1.0	Naphthalene	0.04	0.45
10	Ferrocene	0.01	0.90
10	Ferrocene	0.02	0.81
10	Ferrocene	0.03	0.75
10	Ferrocene	0.04	0.67
10	Ferrocene	0.06	0.60
1.0	Ferrocene	0.005	0.73
1.0	Ferrocene	0.01	0.63
1.0	Ferrocene	0.02	0.46
1.0	Ferrocene	0.04	0.24
1.0	Ferrocene	0.06	0.19

Naphthalene[9] and ferrocene,[10] effective quenchers for the triplet state of benzophenone, were remarkably ineffective in retarding photoreduction of benzophenone by 2-butylamine. Naphthalene had very little effect in neat 2-butylamine. It was more effective in 1 M 2-butylamine in which ~0.04 M naphthalene halved the rate. Ferrocene appeared slightly more effective than naphthalene in neat amine and was also more effective in 1.0 M 2-butylamine in which about 0.015 M ferrocene halved the rate. Photoreduction in the benzophenone–2-propanol system is far more sensitive to quenching and the rate is halved by about 0.004 M naphthalene[11] or ferrocene.[10]

In order to ascertain whether the α-H is removed reversibly during photoreduction in amines, the reactions were studied in two optically active amines. 2-Butylamine was resolved and active N,N-dimethyl-2-butylamine was prepared by methylation of the active primary amine. Photoreduction of 0.5 M benzophenone in 3.3 M (+)-2-butylamine in benzene was carried to completion. Unreacted amine was isolated by vapor phase chromatography and its rotation was essentially identical with that of the starting amine.

When the rotation of the reaction solution was followed during 4-hr irradiation, it was found to increase from 1.54 to 3.76°. Similar samples made up with inactive amine, irradiated at the same time, and examined in the ultraviolet region for remaining benzophenone showed complete photoreduction in this time. A solution of the optically active amine (3 M) in benzene showed no increase in rotation when (a) benzophenone and (b) benzpinacol were added. When 2-butanone was added the rotation rose from 1.13 to 5.54°, indicating that the rise in rotation during irradiation was due to formation of (+)-N-2-butylidene-2-butylamine (eq 1 and 2). This imine was prepared from (+)-2-butylamine and 2-butanone and found to have a high rotation, $[\alpha]_D$ 66.7°, as compared with that of 2-butylamine, $[\alpha]_D$ 7.35°. A solution of 4.6 mmoles of 0.70 M optically active imine reacted readily with inactive 3.0 M 2-butylamine in benzene. The rotation fell from 4.45 to 1.30° in 1 day and then remained constant. Equilibration of these quantities of active imine and inactive amine would lead to 0.86 mmole of (+)-imine and 3.74 mmole of (+)-amine and a final calculated rotation of 1.35°.

Irradiation of 0.5 M benzophenone in 3.7 M (+)-N,N-dimethylbutylamine also showed increase in rotation during the irradiation, but to a smaller extent than that in the primary amine. The observed rotation rose from 7.72 to 8.53°. Photoreduction was slower; 30% of the ketone was reduced in 24 hr. Benzpinacol was not isolated from the photoreduction in the tertiary amine. However, the unreacted tertiary amine was recovered in high yield and its rotation was essentially identical with that of the starting material.

Other evidence as to mechanism was sought in deuterated systems. 2-Butylamine-N,N-d_2 was prepared by exchange of 2-butylamine with D_2O. The N–H stretching band, double peak with center at 3320 cm^{-1}, was decreased to a trace, the N–H deformation band at 1600 cm^{-1} was absent, and the N–D stretching bands appeared as a triple peak with center at 2450 cm^{-1}. Elementary analysis indicated >99% exchange. Cyclohexylamine-N,N-d_2 was also prepared by exchange with D_2O and elementary analysis indicated 94% exchange. Cyclohexylamine-1-d was prepared by a series of reactions: cyclohexanone was reduced to cyclohexanol-1-d with lithium aluminum deuteride; this was converted into the toluenesulfonate, the tosylate was displaced by azide, and the azide was reduced to the amine. Analysis indicated 99% of one deuterium.

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[9] (a) G. Porter, *Proc. Chem. Soc.*, 291 (1959); (b) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

[10] S. G. Cohen and W. V. Sherman, unpublished results.

[11] S. G. Cohen and W. V. Sherman, *J. Am. Chem. Soc.*, **85**, 1642 (1963).

In one group of experiments the rates of photoreduction were measured for 0.2 *M* benzophenone in 4.9, 0.99, 0.27, 0.078, and 0.038 *M* 2-butylamine and 2-butylamine-N,N-d_2 in benzene. In a second group, rates were measured in 1.0 and 0.21 *M* cyclohexylamine and cyclohexylamine-N,N-d_2 in benzene. In a third group, rates were measured in 1.0 and 0.70 *M* cyclohexylamine and cyclohexylamine-1-*d* in benzene. In most cases, points were taken at several extents of reaction at each concentration of amine and the average rates are reported. The protio and deuterio systems of a single concentration were irradiated at the same time. After a period of irradiation aliquots were taken for analysis and the tubes were degassed and irradiated for another period. Results are summarized in Table V.

Table V. Photoreduction of 0.2 *M* Benzophenone by Deuterium-Labeled Amines in Benzene

Amine		Reduction,	Rate,	
Compd	*M*	%	*M* hr^{-1}	k_H/k_D
2-Butylamine	4.90	17–53	0.101[a]	
2-Butylamine-N,N-d_2	4.90	19–52	0.099[a]	1.02
2-Butylamine	0.99	19–54	0.104[a]	
2-Butylamine-N,N-d_2	0.99	17–66	0.108[a]	0.96
2-Butylamine	0.266	21, 42	0.081	
2-Butylamine-N,N-d_2	0.266	25, 49	0.096	0.84
2-Butylamine	0.0792	18	0.057	
2-Butylamine-N,N-d_2	0.0786	21	0.066	0.86
2-Butylamine	0.0383	11	0.044	
2-Butylamine-N,N-d_2	0.0386	13	0.053	0.83
Cyclohexylamine	1.04	26–67	0.080[a]	
Cyclohexylamine-N,N-d_2	1.04	52, 72	0.089	0.90
Cyclohexylamine	0.216	22–53	0.065[a]	
Cyclohexylamine-N,N-d_2	0.213	24–56	0.070[a]	0.93
Cyclohexylamine	0.99	29,30	0.072	
Cyclohexylamine-1-*d*	0.95	19	0.046	1.55
Cyclohexylamine	0.70	16–73	0.070[b]	
Cyclohexylamine-1-*d*	0.69	15–69	0.44[b]	1.59

[a] Average of three points. [b] Average of four points.

At high concentrations of 2-butylamine, 4.9 *M*, N-deuteration had no effect on the rate. At lower concentrations, the $-NH_2$ and $-ND_2$ compounds appeared to show a difference in rate and at 0.27 to 0.038 *M* amine photoreduction in the deuterioamine appeared to be about 18% faster than that in the protio compound. In the cyclohexylamines the $-ND_2$ also appeared to lead to somewhat (8–10%) more rapid photoreduction than the $-NH_2$ compound. The cyclohexylamines containing C–H and C–D at the $-CNH_2$ group show a deuterium kinetic isotope effect, albeit a small one, with the α-C–H compound undergoing photoreduction about 50% faster than the α-C–D compound.

Information about the free radical nature of the latter stages of the photoreduction may be sought in irradiations carried out in the presence of low concentrations of mercaptan.[5,8] Solutions of 0.20 *M* benzophenone in 1.0 *M* 2-butylamine in benzene, containing none and 0.005–0.05 mole of 2-mesityl mercaptan, were irradiated for periods of time, depending upon the concentration of mercaptan required to lead to similar extents of reduction of the ketone. Each irradiation was carried out in duplicate. Average rates, relative to that of a solution containing no mercaptan, are listed in Table VI.

Table VI. Effect of 2-Mesityl Mercaptan on the Photoreduction of 0.2 *M* Benzophenone by 1.0 *M* 2-Butylamine in Benzene[a]

Mercaptan, *M*	Irradiation, min	Reduction, %	Rel rate
0	40, 80	21, 44	1.00
0.005	100, 191	21, 38	0.37
0.010	180, 378	25, 51	0.25
0.025	360	22	0.12
0.050	900	29	0.06

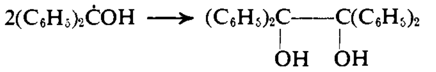
[a] The mercaptan was effective and the rate was halved by 0.0034 *M* sulfur compound.

Discussion

One may write equations for photoreduction of benzophenone by a primary amine analogous to those for photoreduction by 2-propanol[12] and examine their appropriateness in the light of the experimental results. Equations 7–9 and 2 describe the products and stoichiometry of the reaction, formation of equimolar quantities of pinacol and secondary imine. Transfer of a hydrogen from amine-derived radical to benzophenone (eq 8) allows quantum yields to exceed 1.

$$(C_6H_5)_2C{=}O^* + R,R'CHNH_2 \longrightarrow (C_6H_5)_2\dot{C}OH + R,R'\dot{C}NH_2 \quad (7)$$

$$(C_6H_5)_2C{=}O + R,R'\dot{C}NH_2 \longrightarrow (C_6H_5)_2\dot{C}OH + R,R'C{=}NH \quad (8)$$



$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2\underset{OH}{\underset{|}{C}}{-}\underset{OH}{\underset{|}{C}}(C_6H_5)_2 \quad (9)$$

$$R,R'C{=}NH + R,R'CHNH_2 \longrightarrow R,R'C{=}NCHR,R' + NH_3 \quad (2)$$

The quantum yields (Table I) for photoreduction of benzophenone by 2-butylamine at 334 and 366 mμ, 1.13 and 1.10, are similar to that for photoreduction by 2-propanol under the same conditions, 1.16;[13] this is somewhat less, relatively, than might be expected from the measured rates of photoreduction by the amine with unfiltered light, which was about 30% greater than that by the alcohol.[3] This difference may arise in part from variations in formation of light-absorbing transients in the alcohols system under varying conditions of irradiation and will be discussed below. The quantum yield for photoreduction by the tertiary amine, N,N-dimethyl-2-butylamine, was quite low, 0.12, only about 10% as great as that with the primary amine and somewhat less than what might be anticipated from the rates with triethyl- and tributylamine relative to that with 2-butylamine.[3] This indicates that the methyl groups may be less effective hydrogen donors under these conditions than the higher alkyl groups. Quantum yields for photoreduction by the secondary amine, N-methyl-2-butylamine, 0.31 and 0.38 at 334 and 366 mμ, were consistent with the relative rates of secondary and primary amines with unfiltered light and corresponded to the lower part of the range of reactivity of secondary amines.

The rate of photoreduction (Table II) of benzophenone by the primary amine, while decreased slightly by dilution with benzene, was almost as rapid in 1 *M* amine as in neat (10 *M*) amine. The rates down to 0.1 *M* amine may be fitted to a Stern–Volmer plot and a

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(12) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, 81, 1068 (1959).

(13) S. G. Cohen and J. I. Cohen, unpublished results.

value calculated for k_d/k_r, 0.03 M. This value is low, more favorable even than that for benzophenone benzhydrol in benzene,[14] 0.05 M, and indicates insensitivity to concentration of amine. If the small concentrations of carbinol or amine in these benzene solutions do not affect the stability of the triplet, from the measured value[15] of k_d, 1×10^5 sec^{-1}, the value of k_r, the rate constant for abstraction of hydrogen from 2-butylamine by benzophenone triplet, appears to be 3×10^6 M^{-1} sec^{-1}, somewhat higher than that for abstraction from benzhydrol,[14] 1.8×10^6 M^{-1} sec^{-1}.

The rates of photoreduction in the secondary and tertiary amines (Table II) both increased with dilution of the amines with benzene as has been observed previously.[3] The rates did not show a regular increase with decrease in concentration of the secondary amine, but did so with the tertiary amine. The rate was 2.5 times greater at 0.5 and 0.2 M N,N-dimethyl-2-butylamine in benzene than in neat (7.0 M) amine. This effect was even greater when the quantum yields were examined with monochromatic light (334 mμ). The quantum yields were 0.40 and 0.12 in 0.26 M and neat tertiary amine, respectively. Since the primary amine may transfer a second hydrogen in a thermal reaction eq 8, the quantum yield for abstraction of hydrogen from the tertiary amine in dilute solution compares favorably with that in the primary amine. Because of the increase in rate of photoreduction with dilution, a Stern–Volmer plot cannot be drawn and k_r cannot be calculated in this way.

The decrease in rate with dilution of the primary amine and increase in rate with dilution of the tertiary amine may be correlated with the absence and presence, respectively, in these systems of transients which absorb light ineffectively and may act as internal masks. When the absorbancy was followed during monochromatic irradiation in the primary amine, no evidence of such an intermediate was found. The decrease in rate with dilution of amine would be expected from competition between deactivation of the triplet and abstraction of hydrogen. This is in contrast with photoreduction by 2-propanol, a compound which formally appears similar to the primary amine and with which the rate was faster in 1 M alcohol in benzene than in undiluted alcohol.[3] A light-absorbing transient was formed in undiluted 2-propanol and to a much lesser extent when the alcohol was diluted with benzene.[13] Light-absorbing transients are formed to larger extent at high light intensity and have broader absorption than the ketone.[13] They absorb a larger proportion of the light during photoreduction with more intense unfiltered light and this may account for higher relative rates in primary amine *vs.* 2-propanol in irradiation with unfiltered light as compared with monochromatic irradiation.

On the other hand, irradiation in the tertiary amine led to substantial increase in absorbancy (Table III) which slowly decreased on standing in the dark to allow measure of the extent of reduction of the ketone. The increase in absorbancy and formation of the transient were far less in 1.0 and 0.26 M tertiary amine in benzene. In the dilute solutions a larger proportion of the incident light was absorbed by the ketone and this may account at least in part for the higher rates when the amine is diluted with benzene. In the secondary amine, evidence of a light-absorbing intermediate was not found, while an increase in rate on dilution with benzene was observed, although less, proportionately, than that in the tertiary amine. Other factors, in addition to internal masking, appear to affect the rates.

The relative insensitivity of photoreduction of benzophenone in 2-butylamine to the physical quenchers, naphthalene and ferrocene, is noteworthy. These compounds are an order of magnitude less effective in quenching this photoreduction than they are in the benzophenone–2-propanol and benzophenone–benzhyhydrol systems.[9b,10,11] The data for each set of experiments in Table IV may be fitted to a linear plot of $1/\varphi$ against concentration of quencher, and apparent values of k_q/k_r, the ratio of rate constants for quenching to hydrogen abstraction, may be estimated. They have low values: 40 and 33 for naphthalene in neat amine and 1 M amine, respectively; 140 and 70 for ferrocene in neat amine and 1 M amine, respectively, ferrocene being somewhat more effective. If k_q, the rate constant for quenching of benzophenone triplet by naphthalene in benzene, has a diffusion controlled value of $\sim 2 \times 10^9$ M^{-1} sec^{-1}, the value for k_r would appear to be 5×10^7 M^{-1} sec^{-1}, an order of magnitude greater than that calculated from the dependence of rate on concentration of 2-butylamine. The photoreduction might be insensitive to quencher and lead to an apparently high value of k_r (i) if a mechanism other than direct abstraction were involved, (ii) if the excited singlet should be the reactive species, or (iii) if complex formation between ketone and amine occurred and imparted a quasi-unimolecular character to the abstraction process. The absorption spectrum of the ketone in the presence of the amine shows no obvious evidence of complex formation, and the fact that k_q/k_r does not rise with dilution also indicates that association between ketone and amine may not be affecting the reaction.

These results indicate a very high specific rate for reaction of the excited ketone with 2-butylamine. No light-absorbing transient is observed in this system which might lower the efficiency. Yet, the observed quantum yield, $\sim$1.1, is lower than the theoretical maximum, 2, which might be expected from the stoichiometry and which may be observed in the apparently less reactive hydrogen donor, 2-propanol.[12,16]

A reaction which may decrease the efficiency of photoreduction is the thermodynamically favorable reversal of the initial hydrogen abstraction, disproportionation of the photochemically produced free radicals to regenerate starting materials (eq 10). This has not been

$$(C_6H_5)_2\dot{C}OH + R_2\dot{C}X \longrightarrow (C_6H_5)_2C{=}O + R_2CHCX \qquad (10)$$

found to occur in several studies of photoreduction of aromatic ketones in optically active carbinols, the recovered unoxidized alcohols not being significantly racemized.[8,12,17] In photoreduction of benzophenone by an ether evidence for reversal has been found in racemization and deuterium exchange.[18] Photoreduction of benzophenone in excess optically active 2-butylamine and in N,N-dimethyl-2-butylamine led to recovered

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

[15] J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

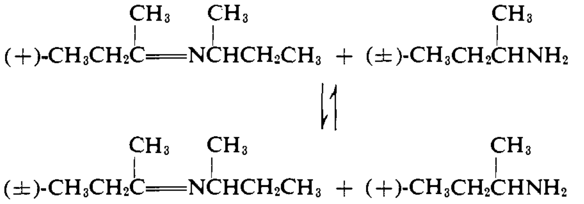
[16] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

[17] C. Weizmann, E. Bergmann, and Y. Hirschberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938).

[18] S. G. Cohen and S. Aktipis, *ibid.*, **88**, 3857 (1966).

amines which had rotations identical with those of the starting materials. The reaction in the primary amine must involve at some stage abstraction of hydrogen from the asymmetric carbon and that in the tertiary amine may well involve this center also. Reversal of such hydrogen abstraction does not occur with these amines and cannot account for low quantum yields.

In photoreduction in the optically active primary amine the observed rotation of the solution actually rose markedly during the irradiation from 1.54 to 3.76°. This effect was due to formation of optically active N-2-butylidene-2-butylamine from reaction of inactive 2-butylimine with active 2-butylamine (eq 2). The active imine is readily prepared from the active amine and 2-butanone and has a high rotation. It retains its activity under the conditions of the experiments and it exchanges readily with inactive 2-butylamine to lead to a mixture of active and inactive amine and imine with the theoretically calculated optical rotation (eq 11).



$$(+)\text{-}CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=\!=}N\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 + (\pm)\text{-}CH_3CH_2\overset{CH_3}{\overset{|}{C}}HNH_2 \rightleftharpoons (\pm)\text{-}CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=\!=}N\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 + (+)\text{-}CH_3CH_2\overset{CH_3}{\overset{|}{C}}HNH_2 \quad (11)$$

That the latter reaction occurs readily supports the rapid occurrence of the reaction of eq 2 during the photoreduction.

Photoreduction in the optically active tertiary amine led to a small increase in observed rotation of the solution. A mixture of products of undetermined composition was formed. Products derived from the radical formed by abstraction of hydrogen from a methyl group of the amine have an unknown and possibly higher rotation than that of the starting amine.

Another reaction consistent with the stoichiometry which might lead to a quantum yield less than 2 is disproportionation of the amine derived radicals (eq 12).

$$R,R'\dot{C}NH_2 + R,R'\dot{C}NH_2 \longrightarrow R,R'CHNH_2 + R,R'C{=}NH \quad (12)$$

This reaction also appears to be ruled out by the absence of racemization in recovered 2-butylamine. Since the amine is not regenerated and the imine is formed in molar equivalent with the pinacol, it appears that reaction 8 does occur, but the maximum quantum yield is not attained.

Evidence as to the nature of the initial abstraction of hydrogen by the excited ketone may be sought in the experiments with deuterated primary amines (Table V). In photoreduction of ketones by alcohols, differences in rates between deuterated and nondeuterated hydrogen donors are very small at high concentrations of the reducing agents but may be observed,[14,19] when present, at low concentrations. At concentrations below 0.27 *M* 2-butylamine-N,N-d_2 photoreduction appeared to show an inverse deuterium kinetic isotope effect, the deuterio compound reacting about 18% more rapidly. Cyclohexylamine-N,N-d_2 also appeared to show a small (~10%) inverse isotope effect. These results indicate that the photoreduction does not proceed by an initial abstraction of hydrogen from nitrogen. Also, an adverse affect[20] on transfer of a second hydrogen (eq 8) is either kinetically unimportant or is outweighed by another factor. Cyclohexylamine-1-*d* led to an isotope effect in the expected direction, $k_H/k_D \sim 1.6$. Abstraction of hydrogen from C α to N appears to be involved in the rate-determining portion of the reaction profile. However, the decrease in rate appears much less than that in the alcohol systems, in which deuterations at the carbinol carbon of benzhydrol[14] and 2-propanol[19] lead to kinetic isotope effect of ~2.7.

A photoexcited aromatic hydrocarbon may abstract an electron from an aromatic amine.[21] It has also been proposed[22] that a chemical oxidizing agent, chlorine dioxide, may initiate its attack on an amine at the nitrogen lone pair in a reversible process. It may be that the photoreduction also is initiated as the excited ketone, with the properties of an electrophilic radical, rapidly interacts with an electron of nitrogen of the amine,[21] perhaps forming an ion pair or a charge-transfer complex (eq 13). This process may be favored somewhat in the $-ND_2$ compounds with their more effective electron release[23] from nitrogen. A substantial part of the barrier to the reaction may be overcome in this part of the process. The reaction may be completed by transfer of a proton from the α-C and electron reorganization (eq 14). This requires only part of the free energy of activation for the over-all process and a small isotope effect may result. Back transfer of an electron in the ions or complex produced in eq 13 would regenerate the starting materials, ketone and amine, without racemization, and account for the less than maximum quantum yield (eq 15). Thus the photoreduction by amines may start by a mechanism which has been proposed for the quenching action of amines and other electron donors[21] and may result, in effect, in partial quenching. But with a proton available for transfer in the electron donor and with an acceptor excited state which can lead to a ketyl radical, partial formation of the free radicals and photoreduction can and does result (eq 14). This mechanism differs in detail from that previously proposed[3b] for heteroatom activation in photoreduction by alcohols, in which the transition state for abstraction of hydrogen is stablized by delocalization of an electron of the heteroatom. While that mechanism is preferred for activation by oxygen, it seemed less well suited to account for ready photoreduction by the bicyclic amine, triethylenediamine.[4] Initial attack at an electron of nitrogen, proposed for the bicyclic amine, may be general for photoreduction by amines.

$$Ar_2C{=}O^* + R_2CHNH_2 \longrightarrow [Ar_2\dot{C}{-}O^-\ \ R_2CH\overset{+}{\dot{N}}H_2] \quad (13)$$

$$[Ar_2\dot{C}{-}O^-\ \ R_2CH\overset{+}{\dot{N}}H_2] \longrightarrow Ar_2\dot{C}{-}OH + R_2\dot{C}NH_2 \quad (14)$$

$$[Ar_2\dot{C}{-}O^-\ \ R_2CH\overset{+}{\dot{N}}H_2] \longrightarrow Ar_2C{=}O + R_2CHNH_2 \quad (15)$$

It might be expected that the cation radical, if formed by electron transfer from the amine, would transfer a proton from nitrogen, rather than from carbon, to the ketyl radical anion (eq 16). This would require that

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

[20] N. C. Yang and S. Murov, *J. Am. Chem. Soc.*, **88**, 2852 (1966).

[21] A. H. Weller and H. Leonhard, *Ber. Bunsenges. Physik. Chem.*, **67**, 791 (1963).

[22] D. H. Rosenblatt, L. A. Hull, D. C. DeLuca, G. T. Davis, R. C. Weglein, and H. K. R. Williams, *J. Am. Chem. Soc.*, **89**, 1158 (1967).

[23] E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 181 (1963).

the second hydrogen be transferred from carbon (eq 17).

$$[\mathrm{Ar_2\dot{C}{-}O^-}\quad \mathrm{R_2CH\overset{+}{\dot{N}}H_2}] \longrightarrow \mathrm{Ar_2\dot{C}{-}OH} + \mathrm{R_2CH\dot{N}H} \qquad (16)$$

$$\mathrm{Ar_2C{=}O} + \mathrm{R_2CH\dot{N}H} \longrightarrow \mathrm{Ar_2\dot{C}{-}OH} + \mathrm{R_2C{=}NH} \qquad (17)$$

Reaction 16 may occur, but the disproportionation of its products may be more rapid than reaction 17. This may regenerate the initial ketone and amine and be the equivalent of back transfer of the electron in lowering quantum yield. Also electron transfer may not be complete in eq 13, ions may not be formed, and the reaction of eq 14 may occur in a charge-transfer complex. Furthermore, the NH group is not required for high reactivity, although its presence does simplify the products. The preliminary experiments[3a] had indicated low reactivity for tertiary amines, but later work[3b] showed increased reactivity with dilution which is now attributed at least in part to less light-absorbing intermediate. In dilute hydrocarbon solution the photochemical transfer of hydrogen from a tertiary amine to benzophenone may be even more efficient than from a primary amine.[3b] In exploratory experiments we have observed that acetophenone is reduced in N,N-dimethyl-2-butylamine at one-half the rate in 2-butylamine. The tertiary amine probably transfers no more than one hydrogen per quantum, while the primary may transfer a second in a dark reaction (eq 8). The rates indicate equal efficiency in transfer of hydrogen from primary and tertiary amines to photoexcited acetophenone. The large difference originally observed is characteristic of the reaction with excited benzophenone at high concentrations of amine.

A related mechanism has been described recently in connection with oxidation of amines by chlorine dioxide in aqueous solution.[24] The observed low isotope effect caused by α-C-deuteration was considered to be a secondary effect on the initial rate-determining abstraction of the electron and the subsequent transfer of H^+ or D^+ was considered fast. We are studying photoreduction of ketones by amines in aqueous solution and some results will be described shortly.

Effective inhibition by 2-mesityl mercaptan of photoreduction of benzophenone by 2-butylamine (Table VI) indicates that the later stages of the reaction proceed by normal free radical processes (eq 8 and 9). Mercaptans, present in low concentration, strongly inhibit the photoreduction of ketone by alcohols and ethers.[5,8,11,18,25] Evidence from racemization and deuterium exchange indicates that in these systems the excited ketone abstracts hydrogen from the donor in the normal way and the inhibition results from rapid hydrogen atom transfer reactions, from mercaptan to a radical intermediate and from a radical to thiyl radical. The photochemically formed radicals are usually reconverted to the starting materials, resulting in inhibition, and the sulfur compounds are regenerated in their alternate valence states and used repeatedly. Inhibition by mercaptan is evidence for the formation and presence of free radicals. The data in Table VI indicate that the efficiency of inhibition by mercaptan of photoreduction of benzophenone by 2-butylamine in benzene was similar to that in the benzophenone–2-propanol systems,[11] 0.0034 *M* mercaptan halving the rate of reduction by the amine while ~0.002 *M* halved the rate in the alcohol. Reactions for the inhibition process may be written analogous to those in the alcohol system (eq 18, 19), but they remain

$$\mathrm{(C_6H_5)_2\dot{C}OH} + \mathrm{AS\cdot} \longrightarrow \mathrm{(C_6H_5)_2C{=}O} + \mathrm{ASH} \qquad (18)$$

$$\mathrm{R\dot{C}HNH_2} + \mathrm{ASH} \longrightarrow \mathrm{RCH_2NH_2} + \mathrm{AS\cdot} \qquad (19)$$

to be confirmed.

Experimental Section

Materials. Benzophenone was Fisher Certified Reagent, mp 47–48°. Acetophenone, Fisher Certified Reagent, was distilled, bp 33° (0.1 mm). Cyclohexanone, Fisher, was distilled, bp 57° (49 mm). Benzene was Eastman Kodak Co. Spectrograde. Lithium aluminum deuteride was from E. Merk AG., 99% D. Sodium deuteroxide was from Metal Hydrides Inc. Deuterium oxide was from Merck Sharpe and Dohme of Canada Ltd., 99.7% minimum isotopic purity. Naphthalene was Baker, AR grade, mp 78–79°. Ferrocene, supplied by Professor M. Rosenblum, was resublimed. 2-Mercaptomesitylene was prepared as described previously,[26] bp 68–69° (0.8 mm). Cyclohexylamine, Eastman Kodak Co., was distilled, bp 57° (49 mm). 2-Butylamine, Eastman Kodak Co., was distilled, bp 73–74°. N-Methyl-2-butylamine, K & K Laboratories Inc., was distilled, bp 76–78°. N,N-Dimethyl-2-butylamine was prepared[27] by treatment of 36.5 g (0.50 mole) of 2-butylamine with 130 g (2.5 moles) of 89% formic acid and 97.5 g (1.2 moles) of 37% formaldehyde; yield, 28 g (0.28 mole, 56%); bp 94°.

(+)-2-Butylamine.[28] A solution of 102 g (1.4 moles) of (±)-2-butylamine in 100 ml of water was treated with 600 ml of 30% (+)-tartaric acid (1.2 moles). The solution was concentrated to half its volume leading to 240 g of salts. The salt was crystallized four times, in each case from half its weight of water. A sample (0.2 g) was treated with 5 ml of 2 *N* NaOH and 0.3 ml of benzoyl chloride, leading to 0.1 g of (+)-N-2-butylbenzamide, $[\alpha]^{20}\mathrm{D}$ +31.0°, 4% in ethanol. The (++)-2-butylammonium hydrogen tartrate (52 g, 0.23 mole) was treated with excess 40% KOH and saturated with solid KOH. The (+)-amine was separated, dried over KOH, and distilled; yield, 14 g (0.19 mole, 27%); bp 63–65°; $\alpha^{24.5}$ (obsd) +5.28° (1 dm); $[\alpha]^{24.5}\mathrm{D}$ +7.35°, neat; lit.[29] $[\alpha]^{20}\mathrm{D}$ +7.48°.

(+)-N,N-Dimethyl-2-butylamine was prepared from 10 g (0.14 mole) of (+)-2-butylamine, 39 g (0.76 mole) of 90% formic acid, 27 g (0.33 mole) of 37% formaldehyde: yield, 7.7 g (0.077 mole, 55%); bp 93–94°; $\alpha^{24.5}$ (obsd) +14.91° (1 dm); $[\alpha]^{24.5}\mathrm{D}$ +20.3° neat.

Anal. Calcd for $C_6H_{15}N$: C, 71.3; H, 14.9; N, 13.8. Found: C, 71.5; H, 14.7; N, 13.7 (Dr. C. Fitz).

(+)-N-2-Butylidene-2-butylamine was prepared from 2.16 g (0.030 mole) of (+)-2-butylamine and 2.40 g (0.033 mole) of 2-butanone, stirred at 0° for 3 hr, and left overnight at room temperature. The product was dried over and distilled from solid KOH; yield, 1.16 g (0.0091 mole, 30%); bp 47–48° (15 mm); α^{24} (obsd) +26.17° (0.5 dm), neat; $[\alpha]^{24}\mathrm{D}$ +68.2°; α^{24}(obsd) +3.62° (1 dm), 5.4% in benzene; $[\alpha]^{24}\mathrm{D}$ +66.7°; bp of inactive compound,[30] 134.5°.

Anal. Calcd for $C_8H_{17}N$: C, 75.5; H, 13.4; N, 11.0. Found: C, 75.6; H, 13.6; N, 11.1 (Dr. C. Fitz).

2-Butylamine-N,N-*d*$_2$. A mixture of 21 g (0.29 mole) of 2-butylamine and 65 g of D_2O was warmed at 50° overnight and distilled. The distillate, bp 64–66°, was treated again with 33 g (1.65 moles) of D_2O for 17 hr and distilled, bp 64–66°. The distillate was dried over 0.5 g of sodium deuteroxide, filtered, and distilled from 0.9 g of sodium deuteroxide; bp 63°; yield, 7 g.

Anal. Calcd for $C_4H_9D_2N$: C, 63.94; HD, 12.64; N, 18.65; D, 5.36. Found: C, 63.8; H, 12.2; N, 18.8; D, 5.4 (C. Fitz). The falling drop method showed 18.15 atom % excess D, 99.9% exchange of 2 D (J. Nemeth).

Cyclohexylamine-N,N-*d*$_2$. A mixture of 42.9 g (0.43 mole) of cyclohexylamine and 86.5 g (4.3 moles) of deuterium oxide was

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(28) A. Fleury-Larsonneau, *Bull. Soc. Chim. France*, **6**, 1576 (1939).

(29) P. Bruck, I. N. Denton, and A. H. Lamberton, *J. Chem. Soc.*, 921 (1956).

(30) D. G. Norton, E. E. Haury, F. C. Davis, L. J. Mitchell, and S. A. Ballard, *J. Org. Chem.*, **19**, 1054 (1954).

stirred overnight. The forerun was removed, 56 g (2.8 moles) of deuterium oxide was added to the residue, and the mixture was stirred at 50° overnight and distilled. The cyclohexylamine-water azeotrope was collected, bp 41° (49 mm), and saturated with sodium chloride and the cyclohexylamine-N,N-d_2 was dried over sodium sulfate and several portions of sodium deuteroxide. The amine was collected, bp 57° (49 mm), and showed a single peak on glpc, 15% UCON, column 100°, detector 145°, injector 130°.

Anal. 14.4% atom excess D, 93.9% exchange of 2 D (J. Nemeth).

Cyclohexylamine-1-*d*. Cyclohexanone (40 g, 0.41 mole) was reduced with 5.8 g (0.12 mole) of lithium aluminum deuteride, leading to cyclohexanol-1-*d*, 35.5 g, with C–D absorption at 2150 cm^{-1}, contaminated with some cyclohexanone, carbonyl absorption at 1700 cm^{-1}. This was treated with 63 g (0.30 mole, Fisher) of *p*-toluenesulfonyl chloride and 56 g (0.71 mole) of pyridine, leading to cyclohexyl-1-*d* *p*-toluenesulfonate: yield, 42 g (0.16 mole, 53%); mp 44.5–45.5° from petroleum ether (bp 30–60°) (lit.[31] mp 44–45° for protio compound). This was boiled under reflux with 18.4 g (0.28 mole) of sodium azide (Fisher) in 400 ml of 3:1 acetone–water for 16 hr.[32] Water was added and the organic layer was extracted with ether and washed with water until the water wash was colorless. Concentration led to cyclohexyl-1-*d* azide: yield 8.3 g (0.066 mole, 41%). This was dissolved in ether and, following a typical procedure,[33] was treated with 8 g (0.21 mole) of lithium aluminum hydride, leading to cyclohexylamine-1-*d*: yield, 1.5 g (0.015 mole, 23%); bp 65° (69 mm).

Anal. Calcd for $C_{12}H_{12}ND$: C, 71.98; HD, 14.07; N, 13.99. Found: C, 71.75; HD, 13.22; N, 13.76.

Deuterium analysis indicated 7.60 atom % excess D, 98.7 % presence of 1 D (J. Nemeth).

Apparatus. Ultraviolet spectra were obtained on a Cary 14 recording spectrophotometer. Ultraviolet absorbances at set wavelength were obtained on a Beckman DU-2 spectrophotometer. Quantitative analyses by infrared spectra were obtained on a Perkin-Elmer IR-21 spectrophotometer. Infrared spectra were obtained on Perkin-Elmer IR-137 and 257 spectrophotometers. Gas–liquid partition chromatography was carried out on an Aerograph A-90-P and an Aerograph Autoprep 700. Optical rotations were obtained on a Zeiss-Winkel circular polarimeter. Melting points are uncorrected.

Extinction coefficients of benzophenone in the amines were determined: in 2-butylamine, λ_{max} 342 mμ (ϵ 132); in N-methyl-2-butylamine, λ_{max} 342 mμ (ϵ 132); in N,N-dimethyl-2-butylamine, λ_{max} 345 mμ (ϵ 130); λ_{max} 333 (ϵ 133) (double peak); in triethylamine, λ_{max} 345 (ϵ 122); λ_{max} 333 (ϵ 124) (double peak).

Irradiations with monochromatic light were carried out with a 200-w high-pressure Osram lamp in a Bausch and Lomb grating monochromater.

Determination of Quantum Yields. Solutions of 0.2 *M* benzophenone in 2-butylamine, N-methyl-2-butylamine, and N,N-dimethyl-2-butylamine were irradiated at 334 and 366 mμ, exit slit 3.0 mm, light intensity 1–6 × 10^{18} quanta min^{-1}. The solutions, 3 ml, in 1-cm square Pyrex Thunberg tubes, were degassed and stirred magnetically. The light intensities were monitored[34] by a ferrioxalate actinometer, 3 ml, φ 1.23 at 334 mμ, 1.21 at 366 mμ.

Rates of Photoreduction. Solutions (3, 4, or 5 ml) in 15-mm ground-glass closed Pyrex Thunberg tubes were degassed by the freeze–thaw method, left under argon, and irradiated for stated periods. The tubes were mounted in a rotating turntable, 4 or 8 cm from a G.E. 85-w A3 lamp, and cooled by an air fan. In photoreduction of benzophenone, aliquots, before and after irradiation, were diluted (a) with benzene and the absorbancies were measured at 344 mμ (ϵ 136) or (b) with 2-propanol and the absorbancies were measured at 334 mμ (ϵ 150).

Photoreduction of acetophenone was studied similarly and the absorbancy was measured at 320 mμ in benzene (ϵ 50.5). In photoreduction of acetophenone by N,N-dimethyl-2-butylamine, aliquots were diluted with benzene; the absorbancy was measured at 5.9 μ and compared with standard solutions.

In study of inhibition by 2-mercaptomesitylene of photoreduction of benzophenone by 2-butylamine in benzene, analyses for residual benzophenone were carried out by dilution with benzene, measurement of absorption at 1660 cm^{-1}, and comparison with a calibration curve.

Absorbancy during Irradiation. Aliquots (3 ml) of benzophenone in each of the 2-butylamines were placed in a square 1-cm Pyrex Thunberg tube to which a 0.106-cm quartz absorption cell was sealed. The samples were degassed and irradiated under argon for stated periods and the absorbancies were measured on a Cary-14 spectrophotometer, with neutral density filters, OD 1.08 or 1.78, in the solvent beam.

i. A solution of 0.2 *M* benzophenone in 2-butylamine was irradiated at 334 mμ and the observed optical densities at λ_{max} 342 mμ, less that of the filter of OD 1.78, were 0, 1.02; 25 min, 0.76; 50 min, 0.51. The rate of disappearance of benzophenone was 0.042 *M* hr^{-1}.

ii. A solution of 0.2 *M* benzophenone in N-methyl-2-butylamine was irradiated at 366 mμ and the observed optical densities at λ_{max} 342 mμ, less that of the filter of OD 1.08, were initially 1.72 and after irradiation for 30 min, 1.16, corresponding to a rate of 0.08 *M* hr^{-1}. There was no change of absorbancy when air was admitted.

iii. A solution of 0.2 *M* benzophenone in N,N-dimethyl-2-butylamine was irradiated for 60 min; the absorbancy at 345 mμ rose from 2.76 to 3.59. The absorbancy fell to 3.18 after the sample stood in the dark for 40 min. Air was admitted and the sample was refrigerated, the absorbancy at 345 mμ falling to 2.66 after 24 hr. The optical densities at 340–400 mμ fell below that of the initial solution. At 300–340 mμ the optical densities remained higher than that of the unirradiated solution.

iv. Solutions of 0.2 *M* benzophenone were irradiated in N,N-dimethyl-2-butylamine, neat and at two concentrations in benzene. Irradiations were at 334 mμ, 1.3 × 10^{16} quanta sec^{-1}. Absorbancies were measured at 344 mμ for benzene solutions and at 345 or 332.5 mμ for undiluted tertiary amine. A 0.100-cm cell containing unirradiated sample was placed in the solvent beam, the difference was measured, and the total optical density was obtained. The readings were made and the tubes were returned for further irradiation. Some results are summarized in Table III.

Photoreduction of Benzophenone by (+)-2-Butylamine in Benzene. A solution of ~0.5 *M* benzophenone and ~3.3 *M* (+)-2-butylamine was prepared from 3 ml of 1 *M* benzophenone in benzene, 2 ml (1.46 g, 0.020 mole) of (+)-2-butylamine, and 1 ml of benzene. It was degassed and irradiated in a Thunberg tube to which was sealed a 1-dm polarimeter tube. The optical rotation was measured initially and after periods of irradiation: 0, +1.54°; 1 hr, 2.18°; 2 hr, 2.80°; 3 hr, 3.50°; 4 hr, 3.76°; 4.5 hr, 3.63°. The volatile products were removed under vacuum at room temperature and collected at −80°. The distillate was extracted with three 5-ml portions of 10% HCl. The extract was neutralized with 20% KOH and saturated with solid KOH. The organic layer was separated and dried over solid KOH, leading to crude 2-butylamine: $\alpha^{24.5}$ (obsd) +7.16° (1 dm), neat. This was purified on an Aerograph Autoprep 700, 20% Carbowax 20M on 60–80 Chromosorb W (column 80°, detector 100°, collector 75°, injector 90°), leading to (+)-2-butylamine, $\alpha^{23.2}$ (obsd) +5.47° (1 dm); starting amine, $\alpha^{23.7}$ (obsd) +5.37° (1 dm), neat.

A solution of 0.447 g (6.13 mmoles, 3.06 *M*) of (+)-2-butylamine made up to 2 ml with benzene had rotation $\alpha^{19.8}$ (obsd) +1.37° (1 dm). Addition of 0.245 g (1.35 mmoles, ~0.7 *M*) of benzophenone led to $\alpha^{19.8}$ (obsd) +1.19°. Further addition of 0.12 g (0.33 mmoles ~0.16 *M*) of benzpinacol led to α^{20} (obsd) +1.13°. This solution was used to dilute 0.103 g (1.43 mmoles) of 2-butanone to 1 ml, leading, after standing overnight, to α^{20} (obsd) +5.54°.

A solution of 0.58 g (4.6 mmoles, ~0.70 *M*, $\alpha^{22.4}$ (obsd) +49.1° (1 dm), neat) of (+)-N-2-butylidene-2-butylamine, 2 ml (1.46 g, 20 mmoles, 3.0 *M*) of (±)-2-butylamine, and 4 ml of benzene was prepared and transferred to a polarimeter tube. The rotation was measured at intervals of time: 0, 4.45°, 0.5 hr, 3.78°; 1.0 hr, 3.26°; 1.5 hr, 2.88°; 2.0 hr, 2.65°; 2.5 hr, 2.19°; 3.5 hr, 1.89°; 6.0 hr, 1.61°; 30 hr, 1.30°, 9 days, 1.32°.

Photoreduction of Benzophenone by (+)-N,N-Dimethyl-2-butylamine in Benzene. A solution of ~0.50 *M* benzophenone and ~3.7 *M* (+)-N,N-dimethyl-2-butylamine was prepared from 3 ml of 1 *M* benzophenone in benzene and 3 ml (2.22 g, 0.022 mole) of the amine. It was degassed and irradiated in a Thunberg tube to which was sealed a 1-dm polarimeter tube. The optical rotation was measured initially and after periods of irradiations: 0, +7.72°; 3 hr, 7.76°; 6 hr, 8.08°; 21.3 hr, 8.43°; 24.3 hr, 8.53°. The reaction was interrupted at this time and ultraviolet absorption indicated 70% reduction of the benzophenone. The volatile product

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was distilled out at room temperature and the amine was isolated as described in the photoreduction by (+)-2-butylamine, leading to 1.52 g (77% recovery) of (+)-N,N-dimethyl-2-butylamine, $\alpha^{20.6}$ (obsd) +15.10° (1 dm), neat. Purification on an Aerograph Autoprep 700, 20% Carbowax 20 *M* on 60–80 Chromosorb W (column 90°, detector 180°, collector 120°, injector 20°) led to no significant change in rotation. Rotation of the amine initially was $\alpha^{24.5}$ (obsd) +14.91°.

Photochemical Conversions of 3*H*-Pyrazoles to Cyclopropenes and 1,2-Diazabicyclo[2.1.0]pent-2-enes[1]

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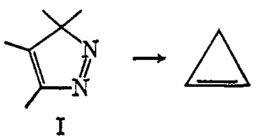
Abstract: A series of six alkyl-substituted 3*H*-pyrazoles has been irradiated with ultraviolet light. In all cases nitrogen elimination occurs and cyclopropenes are formed in variable yields. Using filtered light, ring opening was found to precede nitrogen elimination, and the corresponding diazoalkenes were formed. On irradiation of three fully alkylated 3*H*-pyrazoles isomerization to 1,2-diazabicyclo[2.1.0]pent-2-enes competes with nitrogen elimination. The extent of photoisomerization is solvent and temperature dependent. In all cases the isomerization was found to be fully reversible.

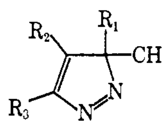
Pyrolysis of pyrazolines has long been known as one of the more versatile syntheses of cyclopropanes.[2–4] More recently it has been observed that nitrogen elimination from the heterocycles can be effected advantageously under photochemical conditions.[3] Several years ago it occurred to us that the reaction might be extended to the 3*H*-pyrazole system (I) which may serve as a convenient precursor of cyclopropenes. In two preliminary communications we have reported that certain 3*H*-pyrazoles can indeed be converted in satisfactory yields to cyclopropenes when illuminated with ultraviolet light.[5,6] Since then other papers have appeared reporting similar reactions.[7,8] It is the purpose of this contribution to give a more detailed account of the scope of the reaction and to report some findings of mechanistic implications. In addition, a novel photoisomerization of 3*H*-pyrazoles to 1,2-diazabicyclo[2.1.0]pent-2-enes and its thermoactivated reversal will be included in the discussion.



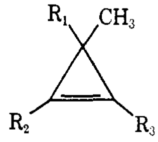
I

Results and Discussion

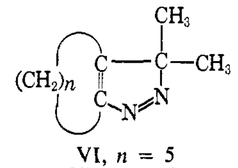
The 3*H*-pyrazole derivatives II–VII used in this study were synthesized by several new methods developed in this laboratory and described elsewhere.[9,10] The photolyses were carried out in Pyrex reaction vessels thus eliminating irradiation with shorter wavelength than 300 mμ. When alkanes or toluene were used as solvents, nitrogen evolution was usually rapid and cyclopropenes VIII–XIII were formed in yields ranging from fair to good. Products were characterized either by direct comparison with samples previously prepared by different methods (VIII and IX) or by elemental analysis, spectral data, and further chemical transformations. The infrared spectra of X–XIII show the characteristic cyclopropene ring vibrations at 1740, 1860, 1840, and 1740 cm^{-1}, respectively.[11] Here, as in previous examples the strong dependence of this frequency on the double bond substitution type is apparent as well as the additional effect caused by a distortion of the "natural" cyclopropene bond angles caused by ring fusion in XII and XIII. The nuclear magnetic resonance spectra show signals for the methyl groups of X–XIII with the expected chemical shifts (listed in Experimental Section). The structure assignment of X is corroborated by the long-



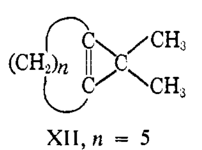
II, $R_1 = R_3 = CH_3$; $R_2 = H$
III, $R_1 = R_2 = R_3 = CH_3$
IV, $R_1 = CH_3$; $R_2 = H$;
$R_3 = C_6H_5$
V, $R_1 = OCH_3$;
$R_2 = R_3 = CH_3$



VIII, $R_1 = R_3 = CH_3$; $R_2 = H$
IX, $R_1 = R_2 = R_3 = CH_3$
X, $R_1 = CH_3$; $R_2 = H$;
$R_3 = C_6H_5$
XI, $R_1 = OCH_3$;
$R_2 = R_3 = CH_3$



VI, $n = 5$
VII, $n = 4$



XII, $n = 5$
XIII, $n = 4$

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(1) Supported by grants from the National Science Foundation, GP-1076 and GP-4212.

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