Photoreduction of Benzophenone by Amines, Alcohols, and Hydrocarbons. Medium Effects. Photochemical Oxidative Deamination[1,2]

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Abstract: Benzophenone undergoes photoreduction by primary amines, RR′CHNH$_2$, and by secondary amines, RR′CHNHR″, leading to high yields of benzpinacol and the imines, RR′CH=NCHRR′ and RR′C=NR″, respectively. The reactions proceed rapidly in dilute solution without excess amine, leading to effective synthesis of imines, to oxidative deamination of primary amines, and to degradation of secondary amines. Photoreduction by primary amines is similar or faster in rate than by 2-propanol; photoreduction by secondary amines is about half as fast. Photoreduction by neat tertiary amines is slower, but the rate is markedly increased by dilution with hydrocarbons. The rate of photoreduction of benzophenone by 2-propanol may also be faster in hydrocarbon solution than in neat 2-propanol. Light-absorbing transients may cause decreased rates in neat amines and alcohols. Benzophenone is photoreduced slowly in aliphatic hydrocarbons in reactions which are inhibited by mesityl disulfide.

The photoreduction of benzophenone by alcohols has been long and widely studied,[3–7] and may lead in high yields to the aldehyde or ketone derived from the alcohol and to benzpinacol, or, in alkaline medium, to benzhydrol.[8] Ketones may also undergo photoreduction by ethers[9–11] and by hydrocarbons,[2,12–16] reactions which may lead to the expected mixtures of products. Amines have been little studied as reducing agents in these photochemical reactions, and it seemed that such studies might prove interesting and useful.[2,16] Amines might show the high reactivity of alcohols, and primary and secondary amines might be converted to imines (eq 1, 2, and 3) corresponding to the carbonyl compounds obtained from alcohols, conversions which are not readily effected by common oxidizing agents. The imines might then be hydrolyzed to aldehydes and ketones, providing photochemical procedures for oxidative deamination and for degradation of secondary amines. These and other results have been obtained,

$$\mathrm{RCH_2NH_2} \longrightarrow \mathrm{RCH{=}NH} \longrightarrow \mathrm{RCH{=}O} \qquad (1)$$

$$\mathrm{R_2CHNH_2} \longrightarrow \mathrm{R_2C{=}NH} \longrightarrow \mathrm{R_2C{=}O} \qquad (2)$$

$$\mathrm{RR'CHNHCHRR'} \longrightarrow \mathrm{RR'C{=}NCHRR'} \longrightarrow \mathrm{RR'C{=}O} + \mathrm{H_2NCHRR'} \qquad (3)$$

and will be described in this and in later reports.

Results

Irradiation of 0.20 *M* benzophenone in 2-butylamine for 2.5 hr, followed by concentration under vacuum, led to an essentially quantitative yield of benzpinacol. The amine and other volatile products should be removed fairly soon after the irradiation, since the pinacol is decomposed slowly to benzophenone and benzhydrol by the amine with a half-life of about 45 hr at room temperature. Irradiation of 0.8 *M* benzophenone and 0.8 *M* 2-butylamine in benzene led to a 91% yield of benzpinacol and to an essentially quantitative yield of N-2-butylidene-2-butylamine, $CH_3CH_2C(CH_3){=}NCH(CH_3)CH_2CH_3$. The benzene solution was assayed for the imine by quantitative infrared measurement, in comparison with an authentic sample prepared from reaction of 2-butanone with 2-butylamine. Similar results were obtained by vapor phase chromatographic analysis of the benzene solution. The imine was isolated by distillation, and treatment of it with 2,4-dinitrophenylhydrazine led to the 2,4-dinitrophenylhydrazone of 2-butanone.

Photoreduction of benzophenone in isobutylamine was quite similar. Irradiation of a 0.3 *M* solution of benzophenone in the amine for 2.3 hr led to 85% yield of benzpinacol. Analysis of the distillate by vapor phase chromatography indicated 85% yield of N-isobutylideneisobutylamine, $(CH_3)_2CHCH{=}NCH_2CH(CH_3)_2$; comparison was made with a sample prepared from reaction of isobutyraldehyde with isobutylamine. Treatment of the distillate with 2,4-dinitrophenylhydrazine led to the 2,4-dinitrophenylhydrazone of isobutyraldehyde. The same imine was also prepared in high yield by irradiation of benzophenone with a dilute solution of isobutylamine in benzene. A third primary amine, cyclohexylamine, 1.0 *M* in benzene, was photooxidized by 1.0 *M* benzophenone, leading in high conversion to benzpinacol and to N-cyclohexylidenecyclohexylamine. Treatment of the reaction mixture with aqueous hydrochloric acid led to hydrolysis and to recovery of cyclohexanone, characterized as its 2,4-dinitrophenylhydrazone, 43% conversion of the initial amine, 85% yield.

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(2) For a preliminary report on part of this work see S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965).

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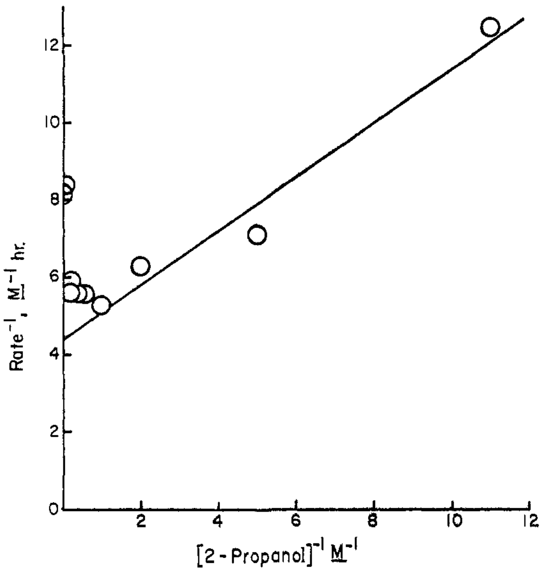


Figure 1. Photoreduction of 0.2 *M* benzophenone by 2-propanol in benzene; effect of concentration of 2-propanol.

Secondary amines were also readily photooxidized. A solution of 1.0 *M* benzophenone and 0.50 *M* diisopropylamine in benzene led to benzpinacol and to N-isopropylideneisopropylamine, $(CH_3)_2C{=}NCH(CH_3)_2$, with infrared spectrum identical with that of a sample synthesized from acetone and isopropylamine. A solution of 1.0 *M* benzophenone and 0.50 *M* di-2-butylamine in benzene led to 90% yields of benzpinacol and N-2-butylidene-2-butylamine, $CH_3CH_2C(CH_3){=}NCH(CH_3)CH_2CH_3$.

The rates of photoreduction of 0.2 *M* solutions of benzophenone in amines and in solutions of amines in benzene were measured and compared with the rates of photoreduction of 0.2 *M* benzophenone in 2-propanol. Some rates and relative rates are listed in Table I.

Table I. Rates of Photoreduction of 0.2 *M* Benzophenone in Amines and Hydrocarbons

Reducing medium	Rate, *M* hr^{-1} ± 10%	Rel rate
2-Propanol	0.12	1.0
2-Butylamine	0.16	1.3
Cyclohexylamine	0.13	1.1
1 *M* cyclohexylamine in benzene	0.13	1.1
n-Butylamine	0.12	1.0
1 *M* *n*-butylamine in benzene	0.12	1.0
n-Hexylamine	0.11	0.9
Isobutylamine	0.15	1.3
t-Butylamine	0.020	0.17
Di-*n*-propylamine	0.055	0.46
Di-*n*-butylamine	0.064	0.53
Diisopropylamine	0.042	0.35
1:4 Diisopropylamine–benzene	0.066	0.55
Triethylamine	0.023	0.19
0.5 *M* triethylamine in benzene	0.070	0.58
Tributylamine	0.047	0.39
Diisopropylethylamine	0.058	0.48
0.5 *M* diisopropylethylamine in benzene	0.096	0.80
2,2,4-Trimethylpentane	0.040	0.33
n-Hexane	0.030	0.25
Cyclohexane	0.028	0.23
Cyclohexene	0.025	0.21
n-Butyl chloride	0.017	0.14

The relative rates are somewhat greater than those for which values had been reported in the preliminary report.[2] This discrepancy arose because the rates had previously been compared inadvertently with that of 0.44 *M* benzophenone in 2-propanol, which, under the conditions of the experiments, was greater than the rate for the less concentrated solution.

The solutions were irradiated in Pyrex under argon with a GE H-85-A3 lamp, and the standard rate, that of 0.2 *M* benzophenone in 2-propanol, was 0.12 *M* hr^{-1}. Photoreduction in 2-butylamine and in isobutylamine was more rapid, 0.16 *M* hr^{-1} and 0.15 *M* hr^{-1}, respectively. Photoreduction in cyclohexylamine, *n*-butylamine, and *n*-hexylamine showed rates similar to that in 2-propanol. Dilution of the primary amines, cyclohexylamine and *n*-butylamine, from neat amine to 1 *M* in benzene led to no decrease in these rapid rates. The primary amine *t*-butylamine, lacking the α-C–H and containing only methyl and amino hydrogen, showed a very low rate, 0.020 *M* hr^{-1}, relative rate 0.17.

Photoreduction of 0.2 *M* benzophenone in secondary amines was somewhat less rapid than in the primary amines. The rates in the unbranched secondary amines, di-*n*-propylamine and di-*n*-butylamine, were substantial, 0.46 and 0.53 as great as that in 2-propanol, respectively, 0.35 and 0.41 as great as that in 2-butylamine. The rate in the branched secondary amine, diisopropylamine, was somewhat less, 0.35 as great as that in 2-propanol. It was found that this amine became more effective when it was diluted with benzene; a 1:4 solution in benzene led to photoreduction at a rate 0.55 as great as that in the standard, about 60% greater than that in the undiluted amine.

This effect was even more pronounced in photoreduction by tertiary amines. Photoreduction in unbranched triethylamine was slow, 0.19 as great as the standard. However, the reaction proceeded three times faster in 0.5 *M* triethylamine in benzene, 0.58 as great as in 2-propanol. The rates were greater in tributylamine and in diisopropylethylamine than in triethylamine, 0.39 and 0.48 as great as the standard, respectively. The effectiveness of diisopropylethylamine was also increased by dilution, a solution of 0.5 *M* amine in benzene leading to protoreduction of 0.2 *M* benzophenone at 1.7 times the rate in the undiluted amine, 0.8 of the rate in undiluted 2-propanol.

The accelerating effect of dilution with hydrocarbon in photoreduction by secondary and tertiary amines indicated that this effect should be explored in photoreduction in 2-propanol. Some results are summarized in Table II and Figure 1.

Photoreduction in 4:1 2-propanol–benzene, 10.5 *M* 2-propanol, was 40% faster than that in undiluted 2-propanol, and the rate continued to increase with dilution down to about 1.0 *M* 2-propanol. The initial rate decreased at concentrations less than 1.0 *M* 2-propanol but remained faster than that in the undiluted alcohol down to 0.2 *M* 2-propanol. It appeared that benzene was not required for the increase; dilution with isooctane also led to increased rate. However, dilution with *t*-butyl alcohol, which is itself relatively unreactive, did not lead to increased rate.

The high reactivity in comparatively dilute solutions of alcohols, as with the amines, may be of use in synthesis. Benzene solutions, 0.2 *M* in benzophenone and

Table II. Photoreduction of 0.2 M Benzophenone by 2-Propanol. Effect of Diluent

2-Propanol, M	Diluent	Rate, M hr^{-1} ± 10%	Rel rate
13.1	...	0.12	1.0
12.5	Benzene	0.12	1.0
10.5	Benzene	0.17	1.4
6.5	Benzene	0.17	1.4
5.2	Benzene	0.18	1.5
2.6	Benzene	0.18	1.5
1.6	Benzene	0.18	1.5
1.0	Benzene	0.19	1.6
0.5	Benzene	0.16	1.3
0.2	Benzene	0.14	1.2
0.1	Benzene	0.08	0.7
2.6	Isooctane	0.16	1.3
2.6	*t*-Butyl alcohol	0.12	1.0

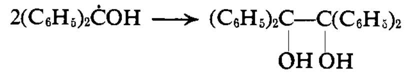
(a) 0.5 M in isoborneol and (b) 0.5 M in *l*-borneol, showed photoreduction at rates essentially the same as that in 0.5 M 2-propanol, 1.3 times greater than in undiluted 2-propanol. Irradiation of a solution of 2.0 M benzophenone and 1.0 M *l*-borneol in benzene led to precipitation of benzpinacol and to 90% yield of camphor.

Discussion

Photoreduction of benzophenone in primary or secondary amines containing the group RR'CHNHR'' leads to high yields of benzpinacol and of the imine derived from two molecules of primary amine or from one molecule of the secondary amine. It seems likely that one hydrogen is transferred from the amine to the photoexcited ketone, and that a second hydrogen is transferred from the amine-derived radical to a second molecule of benzophenone. The ketyl radicals form benzpinacol; the imine from a primary amine reacts with a second molecule of amine. Reactions analogous to those written for photoreduction in alcohols may be written

$$(C_6H_5)_2C{=}O^* + RR'CHNH_2 \longrightarrow (C_6H_5)_2\dot{C}OH + RR'\dot{C}NH_2 \quad (4)$$

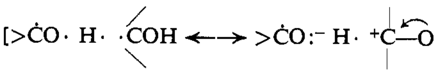
$$(C_6H_5)_2C{=}O + RR'\dot{C}NH_2 \longrightarrow (C_6H_5)_2\dot{C}OH + RR'C{=}NH \quad (5)$$



$$2(C_6H_5)_2\dot{C}OH \longrightarrow (C_6H_5)_2\underset{\displaystyle OH}{\underset{|}{C}}{-}\underset{\displaystyle OH}{\underset{|}{C}}(C_6H_5)_2 \quad (6)$$

$$RR'C{=}NH + RR'CHNH_2 \longrightarrow RR'C{=}NCHRR' + NH_3 \quad (7)$$

In the alcohol the carbinol C–H is weaker than the O–H bond, and polar factors may contribute to stabilization of the transition state for abstraction of this hydrogen by the triplet ketone. Evidence from racemization[11,17,18] and from deuterium exchange[11,18] in inhibition of the reactions by mercaptans supports initial abstraction of this hydrogen. The low reactivity of *t*-butylamine, which lacks the α-C–H, indicates that this is necessary for rapid reaction but does not require that the α-C–H be abstracted first. Relevant evidence has been obtained in study of deuterium isotope effects[19] and will be reported later.



The formation of the imine from two molecules of the primary amine may have practical synthetic value, since the reactions can be carried out in dilute solution, essentially stoichiometrically, and in the absence of excess amine. The imine may, of course, be prepared directly when the amine and corresponding carbonyl compound are both available. Hydrogenation of the imine may lead from the primary amine to the secondary amine. Hydrolysis of the imine leads to the carbonyl compound, aldehyde or ketone, and to recovered amine. This oxidative deamination of primary amines is not readily effected by other procedures. Argentic picolinate[20] and a number of other oxidizing agents have been used with varying degrees of success. Other oxidation products of the primary amines, including oximes, are formed from most of these reagents.[21]

Photoreduction in the secondary amine, $R_2CHNHCHR_2$, converts it to the imine, $R_2C{=}NCHR_2$, probably by reactions analogous to those of eq 4 and 5. This dehydrogenation may also be carried out catalytically,[22] by treatment with argentic picolinate,[20] and by other chemical oxidizing agents; chemical oxidations generally lead to a mixture of products, including hydroxylamines, reaction occurring first at the nitrogen. The imine, formed in high yield in the photochemical process, may be hydrolyzed to the carbonyl compound and primary amine, affording an effective degradation procedure. Photoreduction in a tertiary amine leads to an amine-derived radical which may enter into combination reactions, complicating the products. Simplification of this situation has been achieved and will be reported later.[19]

Study of the rates of the photoreductions was informative. Primary amines which contained α-C–H were generally more reactive than the common photoreducing agent, 2-propanol. The high reactivity of the primary amines was not affected by dilution down to low concentration (1 M in benzene), allowing ready photoreduction in such solutions for synthetic purposes. In the preparative experiments, which were done before the rate measurements, irradiations were undoubtedly carried out for unnecessarily long periods. The secondary amines retained substantial, if diminished, reactivity. The tertiary amines showed varied and diminished reactivity, but, unexpectedly, their reactivity was markedly increased on dilution with benzene. It should be noted that, since half of the photoreduction of the ketone in 2-propanol and in primary and secondary amines may arise from a thermal hydrogen atom transfer which may not be important in tertiary amines, the increased rates in dilute tertiary amines may correspond to more effective abstraction of hydrogen by the excited ketone than from the alcohol and the other amines. Enhanced reactivity with dilution by hydrocarbon has also been observed in photoreduction of *p*-aminobenzophenones,[16] and in that case it was attributed to the effect of solvent on the relative

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stabilities of the chemically reactive n $\rightarrow$ π^* triplet and the unreactive charge-transfer (or $\pi \rightarrow \pi^*$) triplet. Such an explanation does not appear possible in the photoreduction of benzophenone by amines. It seems likely that the change of medium from amine to hydrocarbon leads to less light-absorbing transient, and thus to more efficient absorption of light by the ketone.[19]

The acceleration of photoreduction of benzophenone by 2-propanol, observed when the alcohol is diluted with benzene or with the aliphatic hydrocarbon, also appears to result from a diminished presence of a light-absorbing transient.[23] This intermediate may be a charge-transfer complex[24] which persists to higher concentration in the more polar, hydroxylic medium. This may account for the absence of acceleration when the dilution is carried out with *t*-butyl alcohol. Although the stoichiometry of the photoreduction of benzophenone in alcohols and in primary and secondary amines may be simple, leading to high yields of pinacol and carbonyl compound or imine, the processes involved appear to be complex.

Detailed studies of quantum yields of these reactions, effected by monochromatic light, will be described later. They confirm that the acceleration of photoreduction with dilution corresponds to an increase in quantum yield and is not an artifact.[19,23] It may be noted that the quantum yield for the standard reaction in Tables I and II, photoreduction of 0.2 *M* benzophenone in 2-propanol, is about 1 under the conditions of these experiments.[23] Quantum yields of the other reactions listed in the tables may be estimated from this. The scanty data for photoreduction at low concentrations of 2-propanol, Table II, Figure 1, may be extrapolated to $1/C = 0$, indicating a limiting quantum yield of 2. This has physical significance only when the system behaves at high concentration of alcohol in the same way as it does at low concentration of alcohol. In fact it does not under the present conditions of irradiation and concentration of benzphenone, and the observed quantum yield in undiluted 2-propanol is little more than half the extrapolated value. This is the common situation in photoreduction of benzophenone in 2-propanol, and it is not unique to this system. A curve similar to that in Figure 1 had previously been obtained and reported for the acetophenone–α-methylbenzyl alcohol–benzene system.[18]

During the course of this work a few experiments were carried out on photoreduction of benzophenone in some hydrocarbons and in an alkyl halide (Table I), and on inhibition of these reactions by a disulfide. *n*-Hexane, cyclohexane, and cyclohexene showed similar comparatively low reactivities, 0.25–0.21 as great as 2-propanol. Isooctane appeared to be a little more reactive. *n*-Butyl chloride appeared to be the least effective of the compounds examined. Heteroatom activation of the adjacent C–H, seen in alcohols and in amines, does not appear to be afforded by chlorine. Abstraction by the electrophilic triplet ketone oxygen[15] of hydrogen from a carbon attached to oxygen or nitrogen may be facilitated by electron donation from the heteroatom. In the alkyl halide the inductive effect of the halogen may dominate, reducing reactivity.

Irradiation for several hours of 0.2 *M* benzophenone in isooctane and in *n*-butyl chloride in the presence of 0.015–0.020 *M* mesityl disulfide led to essentially no photoreduction. Inhibition by sulfur compounds, previously reported in alcohols[17,18] and in ethers,[11] is thus found also in saturated hydrocarbons. It probably occurs through similar hydrogen atom transfer reactions. It is likely that the initial hydrogen abstraction occurs and that the ketyl is oxidized by thiyl radical, and the alkyl radical is reduced by mercaptan. The system is returned to its initial state, and the sulfur compounds are regenerated in their alternate valence states and used repeatedly.

$$(C_6H_5)_2C{=}O^* + RH \longrightarrow (C_6H_5)_2\dot{C}OH + R\cdot \tag{8}$$

$$(C_6H_5)_2\dot{C}OH + AS\cdot \longrightarrow (C_6H_5)_2C{=}O + ASH \tag{9}$$

$$R\cdot + ASH \longrightarrow RH + AS\cdot \tag{10}$$

Finally, benzophenone reacts, on irradiation in cyclohexene, no more rapidly than in cyclohexane, the unsaturation apparently not leading to more rapid abstraction of the allylic hydrogen. The reaction was not inhibited by 0.03 *M* mesityl disulfide although it is a photoreduction and not formation of oxetane.[25] Perhaps the irradiation results in rapid addition of thiyl radicals to the olefin, leading to thioethers which are ineffective in transfer of hydrogen.

Experimental Section

Benzophenone was Fisher Certified Reagent grade, mp 47–48°. Recrystallization did not affect the rates. The hydrogen donor solvents were reagent or spectro grade. Amines were freshly distilled before use. Benzophenone (0.910 g, 5.00 mmoles, 0.20 *M*) was dissolved in the solvent in a 25-ml volumetric flask, and four 5-ml aliquots were transferred to Thunberg tubes. The solutions were degassed three times with argon flushing and irradiated under argon on an air-cooled turntable with a GE H-85-A3 lamp, along with a sample of 0.44 *M* or 0.20 *M* benzophenone in 2-propanol which was irradiated for 2 hr as a reference standard. In rate studies tubes were removed at half-hour intervals; 0.60-ml samples were diluted to 25 ml with 2-propanol and analyzed for remaining 2-benzophenone by measurement of absorption at 333 mμ for irradiations carried out in alcohols, primary and secondary amines, isooctane, and cyclohexene. For irradiations carried out in tertiary amines, *n*-hexane, cyclohexane, and *n*-butyl chloride analyses for remaining benzophenone were made by measurement of absorption at 6.02 μ. Dilutions and analyses were carried out within 1 hr after irradiation, to reduce error caused by decomposition of benzpinacol by amines. Ultraviolet spectra were obtained on a Cary 14 spectrophotometer. Ultraviolet analyses at fixed wavelength were obtained on a Beckman DU spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer. Melting points are uncorrected.

Preparation of Aldimines and Ketimines. (i) N-Isobutylideneisobutylamine. Isobutyraldehyde (18.0 g, 0.247 mole) was added over a period of 2 hr with stirring at 0° to 18.3 g (0.247 mole) of isobutylamine in the presence of 3 g of molecular sieves. Stirring was continued for 15 min, KOH flakes were added, and the organic layer was separated and stored over crushed KOH in the refrigerator overnight. The product was decanted and distilled from KOH pellets, bp 125–127°, lit.[26] bp 130–131°.

(ii) N-Isopropylideneisopropylamine. Concentrated HCl (five drops) was added to a mixture of 17.1 g (0.294 mole) of acetone and 18.1 g (0.307 mole) of isopropylamine. The temperature quickly rose to 50° and slowly dropped. The solution stood over molecular sieves for 3 days, was dried over KOH, and distilled, leading to starting materials and to the product, bp 92–93°, lit.[27] bp 93.5°.

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(iii) **N-2-Butylidene-2-butylamine** was prepared in the same way, bp 130–132°, lit.[27] bp 134.5°; absorption bands at 3.45 (vs), 6.02 (s), 6.95 (s), 7.33 (s), and 7.45 μ sh.

Product Studies. (i) **In 2-Butylamine.** A solution (5 ml, 0.20 *M*) of benzophenone in 2-butylamine was degassed and irradiated for 2.5 hr. A 3-ml aliquot was concentrated immediately under vacuum at room temperature, and the residue was washed with hexane, leading to benzpinacol, 0.103 g (0.283 mmole), 96% yield, mp and mmp 182–184° dec. Infrared spectra and thin layer chromatography confirmed the identity.

(ii) **In 2-Butylamine–Benzene.** Solutions of 0.292 g (3.99 mmoles, 0.8 *M*) of 2-butylamine and 0.730 g (4.01 mmoles, 0.8 *M*) of benzophenone made up to 5 ml with benzene were degassed and irradiated for 24 hr. The ultraviolet spectrum indicated essentially complete consumption of the benzophenone. A sample was diluted fourfold, and its infrared spectrum was compared with that of a 0.2 *M* solution of synthesized N-2-butylidene-2-butylamine; the comparison indicated ~95–100% conversion of the amine to the imine. The imine was obtained by distillation, bp 130–132°, and its infrared spectrum was identical with that of the authentic sample, with an additional band at 5.81 μ, probably due to some 2-butanone. The solution was analyzed by vapor phase chromatography on an Aerograph A-90-P instrument, retention time 13 min, 20% silicone GE SF-96 on 60–80 Chromosorb, column temperature 147°, injector 183°, 30 psi of helium. The retention time and peak shape were identical with that of an authentic sample, and the peak area indicated 95–100% yield of the imine. Added synthesized imine did not alter the shape of the peak.

A few drops of distillate from an irradiated solution were added to 1 ml of a solution of dinitrophenylhydrazine, leading to the 2,4-dinitrophenylhydrazone of 2-butanone, mp 108–111°, mixture melting point with the derivative from 2-butanone and with that prepared from N-2-butylidene-2-butylamine, 109–111°.

An irradiated solution, 5 ml, was lyophilized and the residue was washed with hexane, leaving benzpinacol, 0.665 g (3.66 mmoles), 91% yield, mp and mmp 182–184° dec.

(iii) **In Isobutylamine.** A 5.9-ml solution of 0.322 g (1.76 mmoles, 0.3 *M*) of benzophenone in isobutylamine was irradiated for 2.3 hr and lyophilized. The residue was washed with hexane, leading to benzpinacol, 0.271 g (0.74 mmole), 85% yield. A small part of the distillate was treated with dinitrophenylhydrazine solution, leading to the dinitrophenylhydrazone, identical with that obtained from isobutyraldehyde and with that from N-isobutylideneisobutylamine, mp 182–184°, mmp 182–184°. Analysis by vapor phase chromatography of an aliquot of the distillate and comparison of the peak area with that of a known concentration of the synthesized imine indicated 85% yield of the imine, retention time 16 min, 20% silicone GE SF-96 on 60–80 Chromosorb, column 148°, injector 280°, 48 psi of helium.

(iv) **In Isobutylamine–Benzene.** A 5-ml solution of 0.546 g (3.00 mmoles, 0.60 *M*) of benzophenone and 0.120 g (1.64 mmoles, 0.33 *M*) of isobutylamine in benzene was degassed and irradiated for 24 hr. Analysis of the distillate by vapor phase chromatography, as described above, indicated 90–100% conversion to N-isobutylideneisobutylamine. The infrared spectrum was identical with that of the synthesized sample.

(v) **In Diisopropylamine.** A solution (0.2 *M*) of benzophenone in diisopropylamine was irradiated and lyophilized as described for 2-butylamine, leading to benzpinacol, 85% yield. Treatment of the distillate with 2,4-dinitrophenylhydrazine led to the 2,4-dinitrophenylhydrazone of acetone, mp and mmp 122–124°.

(vi) **In Diisopropylamine–Benzene.** A solution of 1.83 g (0.010 mole, 1.0 *M*) of benzophenone and 0.505 g (5.05 mmoles, 0.50 *M*) of diisopropylamine in benzene was irradiated for 35 hr. The ultraviolet spectrum indicated absence of benzophenone. The infrared spectrum indicated the presence of a 90–100% yield of N-isopropylideneisopropylamine. The liquid was decanted from benzpinacol and lyophilized and the combined residues were washed with hexane, leading to 1.68 g (4.65 mmoles), 92% yield, of benzpinacol, mp and mmp 184–186°. An infrared spectrum of the distillate was identical with that of a synthesized sample of the imine.

(vii) **In Di-2-butylamine–Benzene.** A solution of 1.00 *M* benzophenone and 0.50 *M* di-2-butylamine in benzene was irradiated for 40 hr and worked up as described in vi, leading to a 90% yield of benzpinacol and 90–100% N-2-butylidene-2-butylamine, as indicated by vapor phase chromatography.

(viii) **In Cyclohexylamine–Benzene.** Aliquots of a solution of 2.48 g (0.025 mole, 1.0 *M*) of cyclohexylamine and 4.55 g (0.025 mole, 1.0 *M*) of benzophenone in 25 ml of spectro grade benzene were degassed and irradiated for 24 hr. Ultraviolet and infrared spectra indicated that the benzophenone had reacted and that benzpinacol and N-cyclohexylidenecyclohexylamine were major products. One aliquot was decanted and evaporated, and the residues were washed with hexane, leading to benzpinacol, 85% yield. A second aliquot, 10 ml, was stirred with 15 ml of 0.1 *N* HCl for 24 hr and treated with ten drops of concentrated HCl. The aqueous layer was saturated with NaCl and the benzene layer was separated, washed with salt solution, and distilled. The distillate was dried over potassium carbonate. Quantitative infrared and vapor phase chromatographic analyses indicated 85% yield of cyclohexanone based on the imine, 43% conversion of the initial cyclohexylamine. The chromatogram showed a single peak, retention time 10.5 min, identical with that of authentic cyclohexane, 2% SF 30 on Chromosorb W, injector 130°, column 115°, 38 psi of helium. The 2,4-dinitrophenylhydrazone of cyclohexanone was obtained, mp and mmp 158–160°.

(ix) **In Borneol–Benzene.** A solution of 1.54 g (0.010 mole, 1.0 *M* *l*-borneol) and 3.64 g of benzophenone (0.020 mole, 2.0 *M*) in 10 ml of benzene was degassed and irradiated for 24 hr. The solution was decanted, and the residue was washed with hexane, leading to benzpinacol, 2.74 g (0.0075 mole), 75% yield, mp 182–184°. Analysis of the decanted solution by infrared absorption and vapor phase chromatography indicated 90% yield of camphor, retention time 9 min, 2% SF 30 on Chromosorb W, injector 200°, column 150°, 58 psi of helium, peak unaffected by addition of authentic camphor. The solution was evaporated, leading to camphor, mp 175–177° from ethanol, 2,4-dinitrophenylhydrazone mp 172–175°, lit.[28] mp 175°.

Disproportionation of Benzpinacol by Amines. (i) A solution (0.10 *M*) of benzpinacol in *n*-butylamine was allowed to stand at room temperature for 4 days. The ultraviolet spectrum indicated formation of 0.11 *M* benzophenone. The infrared spectrum indicated presence of benzhydrol, a sample of which was isolated, mp 60–64°.

(ii) A sample of the initial solution above was boiled under reflux for 1 hr (~78°). The ultraviolet and infrared spectra indicated complete disproportionation to benzophenone and benzohydrol.

(iii) Formation of benzophenone in a 0.10-*M* solution of benzpinacol in 2-butylamine was followed, by absorption measurements at 334 mm, for 3 days at 25°. The reaction showed first-order kinetics, with 50% decomposition in 45 hr.

(iv) Benzpinacol, corresponding to a 0.10-*M* solution, was suspended in diisopropylamine. After 2 days at room temperature essentially no disproportionation was detected. The suspension was heated under reflux (~83°) for 2.5 hr; a solution resulted and the ultraviolet spectrum indicated complete disproportionation.

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(28) J. L. Brady, *J. Chem. Soc.*, 756 (1931).