much more readily than *cis* material with *p*-nitrobenzoyl chloride, and a modified procedure was used to selectively form the chloro-*p*-nitrobenzoate. The epoxide mixture (~40% *trans*), 144.7 g (0.86 mol) was taken up in 1 l. of pyridine, and 112 g (0.60 mol) of *p*-nitrobenzoyl chloride was added. After stirring for 3 days a small amount of water was added to decompose any excess acid chloride, and the product was taken up in ether, washed with water and dilute acid, dried, and evaporated to give 20% of brown oil. This material was mulled with pentane at low temperature and filtered. The solid residue (85 g) was recrystallized three times from methanol to give 6.3 g (5.2% based on *trans*-epoxide), mp 120–121.5°, of the chloro-*p*-nitrobenzoate.

Evaporation of the pentane wash gave 128 g of yellow oil; retreatment with *p*-nitrobenzoyl chloride (61.5 g, 0.33 mol) in pyridine as described above gave 155 g of yellow semisolid. After washing with pentane and recrystallization from methanol, an additional 22.3 g of *trans*-epoxide derivative was obtained: mp 120–121.7°, combined yield 23.6%. The pure *trans*-epoxide was regenerated as described previously.[32]

The pentane solution from this second washing was evaporated to give 103 g of liquid residue. This product was distilled through a spinning-band column, bp 82–84° (3.5 mm), to give 41.5 g of nearly pure (97%) *cis*-epoxide (48% based on available *cis* material). Analysis was accomplished by LAH reduction and vpc examination of the alcohol products.

2-Methyl-Δ^2-octalin Oxide. The Diels–Alder adduct of isoprene and *p*-benzoquinone was reduced with zinc in acetic acid[33] to give 6-methyl-2,3,4a,5,8,8a-hexahydro-1,4-napthoquinone (84%), mp 84.0–84.5°[34] (recrystallized twice from ether). To 44 g of this material in 300 ml of ethylene glycol was added 65 ml of 85% hydrazine hydrate. After refluxing for 1 hr, 55 g of potassium hydroxide was added in portions; further heating caused the olefinic product to steam distill. The organic phase was dried and distilled to give 33.5 g (90%) of 2-methyl-Δ^2-octalin, bp 87° (10 mm).[34] The olefin was a mixture of *trans*-(69.2%) and *cis*-ring-fused (30.8%) material which was not further separated.

Treatment with *m*-chloroperbenzoic acid in ether gave a mixture of four epoxides which were tentatively identified on the basis of olefin composition and product distribution anticipated by comparison with other systems (*e.g.*, *cis*-4,5-dimethylcyclohexene[5]). In order of increasing vpc retention time (Carbowax 4M) these are: *cis,cis*[22] (1.6%); *trans,cis* (**21**, 35.7%); *cis,trans* (35.7%); *trans,trans* (26.0%).

This mixture (33 g, 0.2 mol) was subjected to the selective derivitization procedure described earlier, using 24 g (0.14 mol) of *p*-nitrobenzoyl chloride. A pasty yellow solid (44 g) was obtained. Four recrystallizations from methanol gave 7 g (0.02 mol) of pale yellow solid (mp 146.8–148°). Basic hydrolysis gave pure *trans,cis*-2-methyl-Δ^2-octalin oxide, bp 78° (4 mm).

Reduction Procedure. Reductions were in general carried in refluxing ether using a sevenfold molar excess of reducing agent. Potassium hydroxide solution was used to quench the excess hydride. The organic phase was dried and concentrated by evaporation through a Vigreux column prior to vpc analysis.

Product Identification. The tertiary alcohol products were prepared by methylation of the appropriate ketones. Samples of pure *trans*- (the major isomer from equilibration) and mixed *cis*- and *trans*-2,5-dimethylcyclohexanones were reduced by LAH to identify the 2,5-dimethylcyclohexanols. LeBel and Ecke's[17] results served to characterize the products from the 1-methyl-4-*t*-butylcyclohexene oxides. Grignard methylation of *trans*-2-decalone (69% axial alcohol), hydroboration of 2-methyl-Δ^2-octalin, and analogy with the 1-methyl-4-*t*-butylcyclohexene oxide were used to deduce the structures of the products from **21**.

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On the Mechanism of the Photoreduction of Aryl N-Alkylimines

Albert Padwa,[1] William Bergmark, and Deran Pashayan

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received November 23, 1968*

Abstract: The mechanism and scope of the photoreduction of some aryl N-alkylimines is described. Irradiation of a series of benzaldehyde N-alkylimines in 95% ethanol affords dihydro photodimers, whereas irradiation of several benzophenone N-alkylimines gives the reduced benzhydrylalkylamines. The excited states of the imines were shown not to be reactive intermediates but instead ketyl radicals were clearly implicated as the active reducing agent. These ketyl radicals were derived from carbonyl compounds present in the reaction mixture as an impurity, an added sensitizer, or as a photogenerated species. Comment is made regarding the relevance of these results to previous reports of imine photoreduction and photoalkylation.

One of the most active areas of organic photochemistry has been the study of systems which possess a carbonyl group.[2–5] As a result of these studies the photochemical transformations of organic molecules containing this functional group have been categorized into a number of primary photochemical processes.[6] This state of affairs contrasts sharply with the present status of the structurally related imine system, the photochemistry of which is mainly qualitative with relatively little available in the way of quantum yield data and kinetic studies. Even though the photochemistry of the C–N double bond has not been the subject of mechanistic studies, a considerable number of diverse reports have accumulated in the literature without critical review. Irradiation may lead to isomerization,[7,8] prototropy,[9] rearrangement,[10–12] addi-

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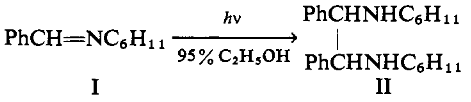
tion,[13,14] oxidation,[15] hydrolysis,[16] cyclization,[17-19] photoreduction,[20-26] and photoalkylation.[27-30] Of these processes, photoreduction is the most widely observed but, in many respects, the least fully investigated. A comparison of the photoreduction of the imine group with the extensively studied aryl ketone system could be of practical and theoretical interest. The elegant studies of Hammond,[31] Cohen,[32] Pitts[33] and others have indicated that intra- and intermolecular hydrogen abstraction processes in carbonyl photochemistry can be a most useful probe into the nature and reactivity of the excited state. This comparison and our interest in the chemical consequences of electronic excitation of aryl N-alkylimines prompted this study.

The feasibility of a formal comparison of the photochemistry of these two functional groups requires first a consideration of the spectroscopic properties of the imine system. The ultraviolet absorption spectra of nonconjugated imines generally show a band of modest intensity ($\varepsilon \sim 100$) in the 235-mμ region which is considered to be due to an $n-\pi^*$ transition.[34] Its carbonyl counterpart is found at longer wavelength with a lower band intensity.[35] With aryl alkyl ketones the carbonyl $n-\pi^*$ band is bathochromically shifted with enhancement of band intensity. On the other hand, aryl N-alkylimines do not generally show a distinct band that can be attributed to an $n-\pi^*$ transition, since this band is often obscured by the intense $\pi-\pi^*$ absorption. However, the long-wavelength tail of a conjugated imine such as benzalaniline has been interpreted to be partially due to an $n-\pi^*$ transition.[35] From the above considerations we conlude that in a number of imine systems the long-wavelength absorption is derived from population of a state of $n-\pi^*$ configuration. Irradiation at this long-wavelength tail assures that at least the lowest energy singlet (and possibly the lowest triplet) of aryl N-alkylimines possesses an $n-\pi^*$ configuration. The interest in $n-\pi^*$ states stems from the fact that in carbonyl photochemistry they have been designated as the reactive state in hydrogen abstraction,[36] although some exceptions have begun to appear in the literature.[37] Extending this reasoning, some workers[22,24] have suggested that the $n-\pi^*$ excited state of the imine is the reactive state in photoreduction. Our preliminary studies[21] on the photoreduction of benzaldehyde N-alkylimines disclosed a number of disquieting features which altered this conception of the reaction. In this paper we present evidence that these photoreductions do not involve the excited states of the imines at all, but are the result of a most interesting set of circumstances which serve to illustrate the hazards and complicating features in photochemistry.

Results and Discussion

Irradiation of a dilute solution ($10^{-4}\ M$) of benzaldehyde N-cyclohexylimine (I) in 95% ethanol with Pyrex-filtered light from a 450-W medium-pressure lamp (Hanovia, Type L) for 24 hr gave a 95% yield of the *meso* and *dl* modifications of N,N′-dicyclohexyl-1,2-diphenyl-1,2-diaminoethane (II). Fractional crystallization of the mixture from ethanol afforded the *meso* dihydro dimer, mp 143–144°, in 90% yield.[38] The structure of the *meso* isomer is inferred from its composition ($C_{26}H_{36}N_2$) and spectral data which include infrared absorption bands for NH and a monosubstituted phenyl ring (see Experimental Section). The nmr spectrum showed signals for ten aromatic protons (τ 2.88, m), two methine protons (τ 6.29, s) as well as a signal for the cyclohexyl and amino protons (τ 7.92–9.40, 24 H, m). The mass spectrum shows an intense peak (base) at m/e 188 (M/2). This fragmentation is characteristic of the α cleavage of amines[39] and is especially appealing for dihydro dimer II. A second intense peak also appears at m/e 106 and can be attributed to loss of cyclohexene from the M/2 fragment. This is substantiated by the appearance of a metastable peak at m/e 59.8. Structure II was further established by the undepressed mixture melting point and the identity of its spectral properties with those of a sample obtained by the high yield reductive dimerization of I with aluminum amalgam.[40]



$$\mathrm{PhCH{=}NC_6H_{11}} \xrightarrow[95\%\ \mathrm{C_2H_5OH}]{h\nu} \begin{array}{c}\mathrm{PhCHNHC_6H_{11}}\\ |\\ \mathrm{PhCHNHC_6H_{11}}\end{array}$$

I II

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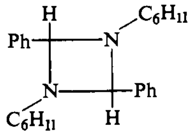

i

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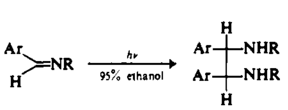
Table I. Photoreduction of Benzaldehyde N-Alkylimines



III IV

IV	Ar	R	% yield of IV	IV mp, °C
a	Ph	CH_2Ph	95	151–152
b	Ph	*t*-Bu	80	129–130
c	Ph	CH_3	65	133–134
d	*p*-C_6H_4Cl	C_6H_{11}	88	184–185
e	*p*-$C_6H_4CH_3$	CH_2Ph	92	143–144
f	*o*-$C_6H_4CH_3$	CH_2Ph	95	120–122
g	*p*-$C_6H_4OCH_3$	CH_2Ph	90	172–173
h	*p*-$C_6H_4N(CH_3)_2$	CH_2Ph	25	178–180

In an effort to gain insight into the mechanism and scope of the photoreduction, we investigated the photolytic behavior of a series of related benzaldehyde N-alkylimines. Such an investigation was of concern since it is well known that substituents can markedly influence the behavior of aryl ketones. Substitution on the aromatic ring of an aryl ketone often tends to perturb energy levels which are closely spaced and which vary considerably in chemical reactivity.[33] Photoreduction of aryl ketones can also be diverted by trival processes such as photoenolization when *o*-hydroxy or *o*-methyl substituents are present.[41,42] In marked contrast to the substituent effects noted in the aryl ketone system, our findings were that imine photoreductions proceeded smoothly in 95% ethanol without apparent effect by substituents. In each case, dihydro dimers IVa–h were isolated in good yield from the irradiation of imines IIIa–h (see Table I). Details are given in the Experimental Section.

While direct irradiation of a number of benzaldehyde N-alkylimines in 95% ethanol leads to very efficient photoreduction, the imines are not photoreduced in 2-propanol, a solvent which is very effective in photoreducing benzophenone.[43] Photoreduction proceeded readily, however, when 2-propanol was diluted with water and led to the dihydro photodimers and acetone. We attribute this behavior to partial hydrolysis of the imine in the aqueous solvent followed by sensitization by small amounts of benzaldehyde which can compete favorably with imine as a light-absorbing component at wavelengths greater than 290 mμ. Excitation with 254-mμ light does not result in photoreduction since almost all of the light is absorbed by the imine under these conditions. The N-alkylimines are readily photoreduced when irradiated in 2-propanol (λ >290 mμ) in the presence of low concentrations of triplet photosensitizers such as benzaldehyde and benzophenone. For the case of *p*-dimethylaminobenzaldehyde N-benzylimine (IIIh), no photoreduction occurred upon irradiation with Pyrex-filtered uv light. Sensitization by benzophenone (achieved by irradiation at 254 mμ, a region where benzophenone absorbs strongly and the imine IIIh to a much lesser extent) does result in photoreduction.[44] This behavior is in marked contrast to *p*-dimethylaminobenzophenone which does not readily undergo photoreduction.[45]

It would thus appear that, unlike aryl ketones, arylimines do not have high intersystem-crossing efficiencies and that photoreaction seemingly takes place from the triplet manifold achieved only by energy transfer from a ketone triplet. That the triplet state of the imine is not the active hydrogen-abstracting species is shown by the fact that benzophenone's phosphorescence is not quenched (EPA glass at 77°K) by the imine.[46] Also noteworthy is the fact that the imine itself shows no detectable emission and does not quench the small amount of benzaldehyde emission. The conclusion that triplet energy transfer from benzophenone to the imine is not involved in the photoreduction is further supported by examination of the rate processes involved. A triplet–triplet energy transfer from benzophenone to the imine that is diffusion controlled can be expressed in the following fashion where

$$\frac{-d[S^{*3}]}{dt} = k_q[\text{imine}][S^{*3}]$$
$$= 3.2 \times 10^9[10^{-4}][S^{*3}]\ M\ \text{sec}^{-1}$$
$$= 3.2 \times 10^5[S^{*3}]\ M\ \text{sec}^{-1}$$

$[S^{*3}]$ is the concentration of the triplet sensitizer and k_q is the rate constant for bimolecular quenching in 2-propanol. The value of k_q can be calculated from Debye's relation for 2-propanol at 25°.[47] The other competitive process involves abstraction of a hydrogen from the solvent by the triplet state of the sensitizer. The rate constant of this reaction in 2-propanol has already been determined by Porter[43] as

$$\frac{-d[S^{*3}]}{dt} = k_r[i\text{-PrOH}][S^{*3}]$$
$$= 1.28 \times 10^6[13.1][S^{*3}]\ M\ \text{sec}^{-1}$$
$$= 1.68 \times 10^7[S^{*3}]\ M\ \text{sec}^{-1}$$

From these two expressions it is quite apparent, that at low concentrations of imine (10^{-4} *M*), the formation of the ketyl radical is 50 times faster than triplet–triplet energy transfer.

These observations when taken together suggest that the photoreduction does not involve an excited state of the imine but rather is brought about by one or more of the intermediates of the ketone photoreduction.[48] The photoreaction may be represented by the sequence of reactions 1–4, starting with abstraction of hydrogen from the carbinol carbon by the lowest excited triplet state of the sensitizer. Additional support for this mechanism

$$Ph_2CO^* + (CH_3)_2CHOH \rightarrow (Ph)_2\dot{C}OH + (CH_3)_2\dot{C}OH \quad (1)$$

$$(Ph)_2\dot{C}OH + ArCH{=}NR \rightarrow Ph_2CO + ArCHNHR \quad (2)$$

$$(CH_3)_2\dot{C}OH + ArCH{=}NR \rightarrow CH_3COCH_3 + Ar\dot{C}HNHR \quad (3)$$

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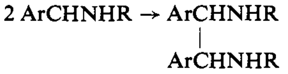


$$2\,\mathrm{ArCHNHR} \rightarrow \begin{array}{c}\mathrm{ArCHNHR}\\ |\\ \mathrm{ArCHNHR}\end{array} \qquad (4)$$

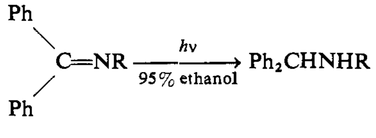
comes from the examination of the efficiency of a number of triplet sensitizers in effecting imine photoreduction. Thus, benzophenone, benzaldehyde, acetophenone, and xanthone sensitize in that order of efficiency and are themselves not consumed. High-energy sensitizers, such as dibenzothiophene and triphenylamine, that do not themselves photoreduce in alcohol are ineffective as sensitizers. These data are summarized in Table II.

Table II. Efficiency of the Sensitizer in Effecting the Photoreduction of Benzaldehyde N-Benzylimine[a]

Sensitizer[b]	E_t,[c] kcal	Φ[d]
None[e]		<0.006
Benzophenone	68.5	0.70
Benzaldehyde	71.9	0.69
Acetophenone	73.6	0.18
Xanthone	74.2	0.12
Diphenylamine	72	<0.015
Dibenzothiophene	69.7	0.004
Triphenylamine	70.1	<0.015
Benzonitrile	77	<0.015

[a] Quantum yields were measured in degassed 2-propanol solutions, 0.028 M in imine at 300 mμ. [b] Present in sufficient concentration to absorb virtually all the light. [c] Triplet excitation energies (E_t) were obtained from ref 4. [d] Quantum yields for the disappearance of imine. [e] Irradiation at 254 mμ.

Our curiosity about imine photoreductions was further intensified by the appearance of a report that benzophenone N-benzylimine was photoreduced to the corresponding amine as opposed to a dihydro photodimer.[22] We have subsequently found that imines Va–d do indeed undergo facile photoreduction to amines VIa–d.



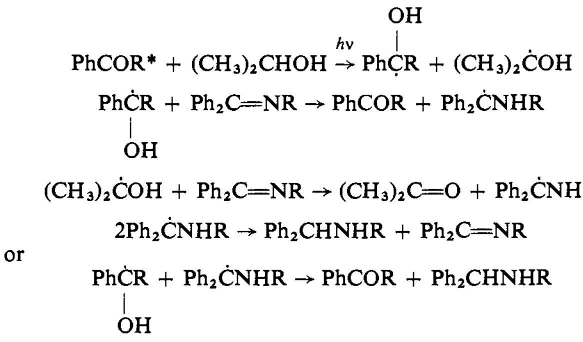
Va, R = CH_3 VI
b, R = CH_2Ph
c, R = C_6H_{11}
d, R = COC_6H_5

Table III. Quantum Efficiency of Benzophenone N-Methylimine Photoreduction *vs.* Different Sensitizers[a]

Sensitizer	Concn, M	Φ_{AM}[b]	Φ_{IM}[c]	Φ_{AC}[d]	Φ'_{AC}[e]
None		<0.003	<0.003		
Benzophenone	0.017	0.66	0.72	0.90	0.82
Benzaldehyde	0.025	0.60	0.67	0.91	0.90
Acetophenone	0.021	0.16	0.30	0.36	0.74
Xanthone	0.015	0.09	0.30	0.13	0.45
Dibenzothiophene	0.033	<0.003	<0.002		
Triphenylamine	0.009	<0.003	<0.004		
Hexachlorobenzene	0.011	<0.002			

[a] Photoreductions carried out in degassed 2-propanol with 300-mμ light. [b] Quantum yield for appearance of amine VIa. [c] Quantum yield for disappearance of imine Va. [d] Quantum yield for appearance of acetone in the photoreduction of imine Va. [e] Quantum yield for appearance of acetone using pure 2-propanol as solvent.

Scheme I



$$\mathrm{PhCOR^{*}} + \mathrm{(CH_3)_2CHOH} \xrightarrow{h\nu} \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\dot{\mathrm{C}}}}\mathrm{R} + \mathrm{(CH_3)_2\dot{C}OH}$$

$$\mathrm{Ph}\underset{\mathrm{OH}}{\underset{|}{\dot{\mathrm{C}}}}\mathrm{R} + \mathrm{Ph_2C{=}NR} \rightarrow \mathrm{PhCOR} + \mathrm{Ph_2\dot{C}NHR}$$

$$\mathrm{(CH_3)_2\dot{C}OH} + \mathrm{Ph_2C{=}NR} \rightarrow \mathrm{(CH_3)_2C{=}O} + \mathrm{Ph_2\dot{C}NHR}$$

$$2\mathrm{Ph_2\dot{C}NHR} \rightarrow \mathrm{Ph_2CHNHR} + \mathrm{Ph_2C{=}NR}$$

or

$$\mathrm{Ph}\underset{\mathrm{OH}}{\underset{|}{\dot{\mathrm{C}}}}\mathrm{R} + \mathrm{Ph_2\dot{C}NHR} \rightarrow \mathrm{PhCOR} + \mathrm{Ph_2CHNHR}$$

The data listed in Table III reflect the quantum efficiency of photoreduction of benzophenone N-methylimine as a function of various sensitizers. Once again the efficiency of sensitization is paralleled by the ability of the sensitizer to be photoreduced in an alcoholic medium. Thus benzophenone, benzaldehyde, acetophenone, and xanthone are sensitizers that can abstract hydrogen from a solvent molecule, whereas dibenzothiophene, triphenylamine, and hexachlorobenzene cannot. It is interesting to note that the efficiencies of the four ketones to sensitize the photoreduction of imines IIIa and Va are considerably different (Tables II and III). With the thought of obtaining a quantitative correlation, the rates of photoreduction of the four ketone sensitizers were compared to the efficiencies of these same ketones as sensitizers[49] in the photoreduction of imine Va. Considering the analytical problems and the number of variables such as concentration and intensity, the method of comparison that was judged most nearly parallel was an analysis for acetone formation. Such an assay gives directly the net amount of hydrogen abstracted from solvent. The data in Table III was obtained for such a correlation and this information is plotted in Figure 1. The points for benzophenone and benzaldehyde fall on a line whose slope is equal to unity, indicating that these ketones were abstracting hydrogen from solvent at an undiminished rate. From the yields of amine and disappearance of starting imine, it is also apparent that the imine serves as an effective hydrogen atom scavenger, regenerating the aryl ketone and suppressing the formation of the usual pinacols (Scheme I). The location of acetophenone and xanthone below the line implies an inefficiency in sensitization other than normally experienced with benzaldehyde or benzophenone. We attribute this difference, in part, to the reduced efficiency of hydrogen abstraction by acetophenone and xanthone in 2-propanol and, in part, to the partial quenching of these higher energy triplets by the imine.[51] The contribution of the former is evident from

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[49] The term "sensitizer" does not necessarily imply a mechanism, but simply describes the effect "of making a substrate more sensitive to irradiation."[50]

[50] G. O. Schenck, Conference of the 13th Conference of Chemistry at the University of Brussels, Brussels, Oct 1965, Interscience Publishers, Inc., New York, N. Y., 1967, p 142.

[51] The less efficient sensitization by acetophenone was also noted by Fischer[22] who attributed this effect to the ability of acetophenones triplet to preferentially abstract hydrogen from the benzhydrylalkylamine rather than the solvent. This selectivity phenomenon, which in effect lowers the quantum yield, was observed with acetophenone but not with benzophenone. Such a selectivity would be remarkable considering the minute amount of amine present. The marked "on–off" contrast between acetophenone and benzophenone is even more remarkable and unprecedented.

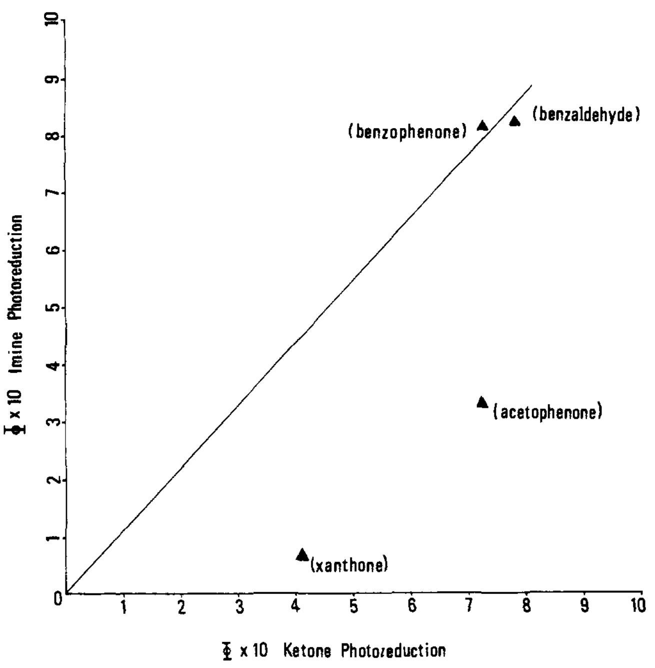
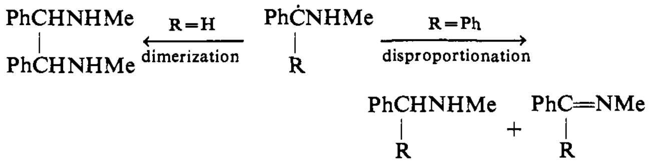


Figure 1. Quantum yields of ketone photoreduction *vs.* ketone-sensitized imine reaction.

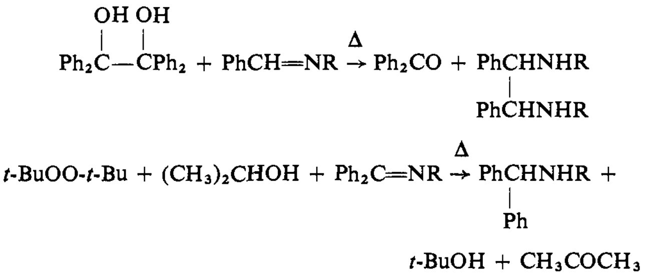
Table III. What is also obvious from Figure 1 is that this effect alone does not fully explain acetophenone and xanthone's reduced efficiency in imine sensitization. Our earlier observations of nonemission of the imines and the inability of these compounds to quench benzaldehyde's phosphorescence suggests that the triplet energy levels to arylimines are located between 72 and 85 kcal. If the value of this level is close to 72 kcal, then partial quenching of xanthone (E_t = 74.2) and acetophenone (E_t = 73.6) could be expected. With this possibility in mind, we examined the quenching of benzonitrile (E_t = 77 kcal) phosphorescence by imine Va in an EPA glass at 77°K. The results obtained are in full accord with this interpretation. Thus, benzonitrile phosphorescence decreased in intensity as the imine concentration was increased. At an imine concentration of 10^{-3} *M* and with benzonitrile absorbing virtually all the light, less than 1% of its former light intensity was obtained.

The results of the photolyses of the benzophenone N-alkylimines can be readily accommodated in the proposed mechanistic framework. It is noteworthy that the tendency of the imino radicals to either dimerize or to disproportionate is reflected not only in the photoreduction sequence, but also in the reduction of the imines by reaction with ketyl radicals generated by chemical means.



$$\begin{array}{c}\mathrm{PhCHNHMe}\\ |\\ \mathrm{PhCHNHMe}\end{array} \xleftarrow[\text{dimerization}]{\mathrm{R=H}} \begin{array}{c}\mathrm{Ph\dot{C}NHMe}\\ |\\ \mathrm{R}\end{array} \xrightarrow[\text{disproportionation}]{\mathrm{R=Ph}} \begin{array}{c}\mathrm{PhCHNHMe}\\ |\\ \mathrm{R}\end{array} + \begin{array}{c}\mathrm{PhC{=}NMe}\\ |\\ \mathrm{R}\end{array}$$

When an experiment was run using benzophenone ketyl radicals generated from the thermal decomposition of benzpinacol,[52] the same tendency of the imino radical to dimerize or to disproportionate was noted. When the thermal decomposition of di-*t*-butyl perioxide was carried out in 2-propanol, it was noted that dihydro dimers were obtained from benzaldehyde N-alkylimines, whereas amines were isolated with benzophenone N-alkylimines.

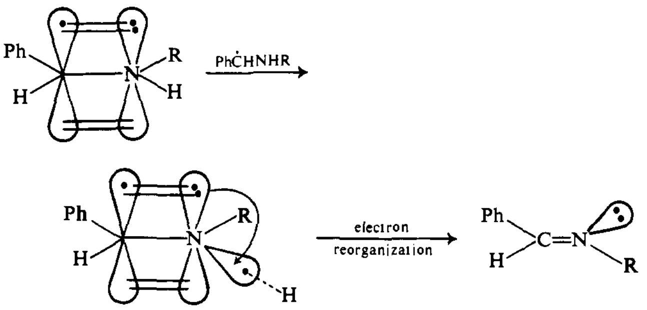


$$\mathrm{Ph_2\overset{OH}{\overset{|}{C}}{-}\overset{OH}{\overset{|}{C}}Ph_2} + \mathrm{PhCH{=}NR} \xrightarrow{\Delta} \mathrm{Ph_2CO} + \begin{array}{c}\mathrm{PhCHNHR}\\ |\\ \mathrm{PhCHNHR}\end{array}$$

$$t\text{-BuOO-}t\text{-Bu} + \mathrm{(CH_3)_2CHOH} + \mathrm{Ph_2C{=}NR} \xrightarrow{\Delta} \begin{array}{c}\mathrm{PhCHNHR}\\ |\\ \mathrm{Ph}\end{array} + t\text{-BuOH} + \mathrm{CH_3COCH_3}$$

Similarly, the type of product obtained from the aluminum–amalgam reduction was dependent on the structure of the starting imine. Table IV summarizes the results of such experiments with the imines investigated.

The effects noted parallel the well-documented increase in disproportionation to coupling ratios of free radicals as they change from primary to tertiary.[53] The rate constant for combination should become smaller as the radical becomes more hindered since the F strain (strain from the front due to compression necessary to form a bond) increases with substitution. In this respect, it is interesting to note that irradiation of acetophenone N-benzylimine in 95% ethanol affords a mixture of products (dihydro dimer–amine, 90:10). This behavior is in marked contrast to the other types of imines investigated which give rise to a single component. The preference for the relatively unhindered phenylaminomethyl radical to couple may be related to the higher activation energy required for disproportionation. The planar benzyl radical is undoubtedly stabilized to a degree by orbital overlap with the lone pair of electrons on nitrogen. As the amino hydrogen is transferred in the disproportionation reaction, extensive electron reorganization must occur in the transition state before the C–N double bond can be formed. This reorganization raises the activation energy for the over-all disproportionation and, consequently, coupling becomes the preferred route. For the case of the more hindered diphenylaminomethyl radical, disproportionation becomes the preferred route since radical coupling is retarded by F strain.



It should be pointed out that the proposed mechanistic scheme for imine photoreduction involves intermediates similar to those proposed by Cohen in the photoreduction of aromatic ketones using amines as hydrogen sources.[54]

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(52) D. C. Neckers, A. P. Schaap, and J. Hardy, *J. Am. Chem. Soc.*, **88**, 1265 (1966).

(53) S. W. Benson and W. B. Demore, *Ann. Rev. Phys. Soc.*, **16**, 412 (1965).

(54) S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **89**, 3471 (1967).

Table IV. Chemical Reduction of Imines by Means of Ketyl Radicals in 2-Propanol at 130°

Imine	Concn, *M*	Cosubstrate	Concn, *M*	Redn product	% yield	Reaction time, hr
IIIa	0.013	*t*-Butyl peroxide	0.090	Dimer IVa	32	12
IIIa	0.13	Benzpinacol	0.072	Dimer IVa	46	144
IIIb	0.15	Aluminum–amalgam		Dimer IVb	80	10
Va	0.041	*t*-Butyl peroxide	0.032	Amine VIa	51	30
Va	0.041	Benzpinacol	0.025	Amine VIa	70	144
Vc	0.15	Aluminum–amalgam		Amine VIc	98	15

For that case the reverse of reaction 2 has been suggested as an important step. A direct comparison of the data is not possible since those studies employed aliphatic amines

$$Ph_2CO + Ph\dot{C}HNHR \rightleftarrows Ph_2\dot{C}OH + PhCH{=}NR$$

as hydrogen donors. In an attempt to determine the importance of the reverse reaction in our systems, we examined the photoreduction of benzophenone using dibenzylamine as the hydrogen source. The observation

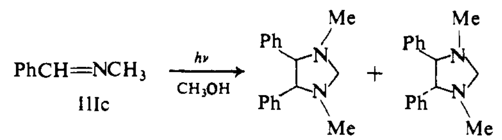
$$Ph_2CO + PhCH_2NHCH_2Ph \xrightarrow{h\nu} Ph_2\dot{C}OH + Ph\dot{C}HNHCH_2Ph$$

$$Ph\dot{C}HNHCH_2Ph + Ph_2CO \rightarrow Ph_2\dot{C}OH + PhCH{=}NCH_2Ph$$

of a significant amount of benzaldehyde N-benzylimine implies that this reverse reaction may be occuring under the reaction conditions. It would appear that the direction of the equilibrium is controlled by the ratio of concentrations of the imine and aryl ketone used as sensitizer.

Some comment is in order concerning the nature of the unsensitized irradiation. Although imine photoreduction occurs readily if the imine and the solvent are impure or contain water, reduction will still occur even if the solvent and imine are rigorously purified. We attribute the photoreactivity to a prior photooxidative generation of a carbonyl compound followed by subsequent sensitization.[49] Such complex photoprocesses which result in the formation of carbonyl compounds from imines have been described by Kan and Furey.[15] The lack of reactivity of the excited state of the imines themselves prompts us to suggest that the excited states undergo very efficient nonradiative decay to ground state thereby precluding hydrogen abstraction.

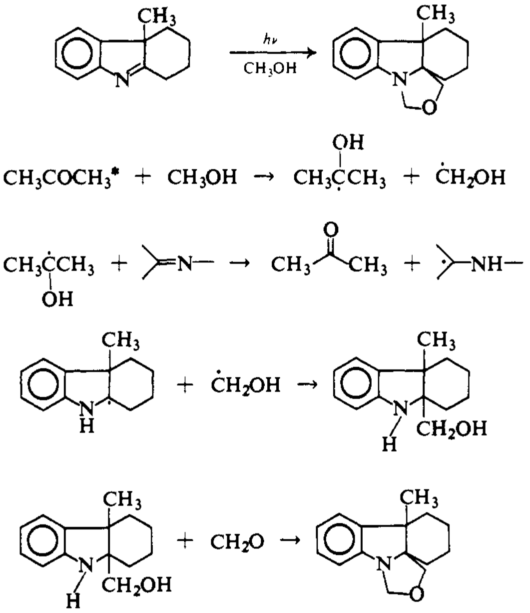
A recent report by Cerutti and Schmid on the photoreaction of benzaldehyde N-methylimine (IIIc)[26] prompts us to describe the details of our results in this system. These authors claimed that the irradiation of IIIc in methanol gave a mixture of *dl*- and *meso*-1,3-dimethyl-4,5-diphenylimidazolidine (VII, VIII) as primary photoproducts. Our results indicate that the best mechanistic interpretation for this transformation is the initial formation of the dihydro dimer IVc followed by condensation with the formaldehyde formed from methanol. In fact, we observed that VII was obtained in high yield when dihydro dimer IVc was treated with formaldehyde in the dark. The claim by the authors that IVc could not be an intermediate was supported only by the fact that the irradiation of IVc in methanol did not give the observed products. However, the necessary coreagent (*i.e.*, formaldehyde) was not present.



VII VIII

Likewise, other examples of imine photoalkylations reported in the literature may be best described by a scheme similar to that outlined above. For example, the photoalkylation of indolenes[26] in a methanol–acetone solvent may be rationalized in the fashion shown in Scheme II.

Scheme II



We are thus suggesting that for certain imine systems the observed photochemistry may be readily rationalized by a ground-state reaction of the imine with a ketyl radical. These ketyl radicals are derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species.

Experimental Section[55]

Synthesis of Substituted Benzaldehyde N-Alkylimines. A solution of the aldehyde and amine in toluene was refluxed for several hours

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[55] All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associate high-resolution spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were determined with an Hitachi Perkin-Elmer RMU 6-E instrument.

using a separator to remove the water formed. The solution was then evaporated and distilled *in vacuo*. In this manner the following imines were prepared and their properties were compared to those described in the literature.

Benzaldehyde N-Cyclohexylimine (I). A yield of 80% of I was formed after 6 hr of reflux, bp 117–120° (2.0 mm) (lit.[56] 135° (12 mm)).

Benzaldehyde N-Benzylimine (IIIa). A yield of 58% of IIIa was formed after 8 hr of reflux, bp 113–115° (0.09 mm) (lit.[57] 115–116° (0.1 mm)).

***p*-Chlorobenzaldehyde N-Cyclohexylimine (IIId).** A yield of 75% of IIId was formed after 12 hr of reflux, mp 57–58° (lit.[58] 58°).

***p*-Tolualdehyde N-Benzylimine (IIIe).** A yield of 70% of IIIe was formed after 8 hr of reflux, bp 140–143° (3.0 mm) (lit.[59] 207–208° (27 mm)).

***p*-Methoxybenzaldehyde N-Benzylimine (IIIg).** A yield of 69% of IIIg was formed after 10 hr of reflux, mp 37–38° (lit.[59] 39–40°).

***p*-Dimethylaminobenzaldehyde N-Benzylimine (IIIh).** A yield of 51% of IIIh was formed after 18 hr of reflux, mp 75–77° (lit.[59] 76–77°).

***o*-Tolualdehyde N-Benzylimine (IIIf).** A yield of 71% of IIIf was formed after 15 hr of reflux: bp 150–152 (1.0 mm); λ_{max}^{EtOH} 250 mμ (ε 18,000); nmr ($CDCl_3$), τ 7.60 (3 H, s), 5.33 (2 H, s), 2.82 (9 H, m), 2.20 (1 H, s). *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.80; H, 7.22; N, 6.69. Found: C, 86.25; H, 7.34; N, 6.84.

Benzaldehyde N-*t*-Butylimine (IIIb). A yield of 60% of IIIb was obtained by heating equivalent amounts of benzaldehyde and *t*-butylamine over potassium hydroxide pellets; bp 47–48° (0.6 mm); λ_{max}^{EtOH} 244 mμ (ε 16,000); nmr ($CDCl_3$), τ 8.74 (9 H, s), 2.60 (5 H, m), 1.80 (1 H, s).

Benzaldehyde N-methylimine (IIIc) was prepared by passing a stream of methylamine through a refluxing solution of benzaldehyde in toluene for 7 hr. Distillation of the residue on a 2-ft spinning-band column gave an 81% yield, bp 74° (5 mm) (lit.[60] 99–103° (42 mm)).

Benzophenone N-methylimine (Va) was prepared by passing a stream of methylamine through a refluxing solution of benzophenone in xylene for 7 hr. Distillation of the residue on a 2-ft spinning-band column gave a 66% yield, bp 98–99° (0.5 mm) (lit.[61] 93–95° (0.4 mm)).

Benzophenone N-benzylimine (Vb) was prepared according to the procedure of Reddelien[62] in 75% yield, mp 59–60° (lit.[62] 60–61°).

Benzophenone N-cyclohexylimine (Vc) was prepared by heating 5.0 g of dichlorodiphenylmethane with 11 g of cyclohexylamine at 100° for 20 min. Distillation of the residue gave a 78% yield, mp 45–46° (lit.[63] 47–49°).

N-Diphenylmethylenebenzamide (Vd), mp 116–117°, was prepared by the procedure of Exner.[64]

Acetophenone N-benzylimine was prepared from acetophenone and benzylamine using toluene as the solvent in 53% yield, mp 39–41° (lit.[65] 44°).

General Irradiation Procedure. Irradiations were conducted in an immersion reactor using a Hanovia 450-W medium-pressure lamp with a Pyrex filter. The photolyses were terminated when starting material could not be detected by infrared or ultraviolet spectroscopy. The photolysis mixtures were usually worked up by evaporation of the solvent at reduced pressure followed by recrystallization from 95% ethanol.

General Procedure for the Aluminum-Amalgam Reduction of Aryl N-Alkylimines. To a solution of 3.0 g of the imine in 200 ml of moist ether was added 3 molar equiv of aluminum-amalgam.[66] The mixture was allowed to stand at room temperature for 16 hr. At the end of this time the reaction mixture was filtered and the filtrate was concentrated at room temperature. Recrystallization of the crude solid from 95% ethanol afforded a material that was identical in all respects with that formed from the photolysis of the corresponding imine.

Irradiation of Benzaldehyde N-Cyclohexylimine (I). A solution of 2.0 g of I in 500 ml of 95% ethanol was photolyzed for 22 hr. Removal of the solvent gave 1.8 g (90%) of *meso*-N,N′-dicyclohexyl-1,2-diaminoethane (II),[40] mp 143–144°. *Anal.* Calcd for $C_{26}H_{36}N_2$: C, 82.92; H, 9.64; N, 7.44. Found: C, 82.99; H, 9.68; N, 7.43. The infrared spectrum ($CHCl_3$) is characterized by bands at 3.10, 3.40, 6.90, and 13.74 μ. The ultraviolet spectrum in 95% ethanol has λ_{max} 242 mμ (ε 610). The nmr spectrum shows a broad band for the cyclohexyl hydrogens between τ 7.92 and 9.40, a singlet at τ 6.29 (2 H), and the aromatic protons appear at 2.88 (10 H).

Irradiation of Benzaldehyde N-Benzylimine (IIIa). Photolysis of a solution containing 1.0 g of IIIa in 1 l. of 95% ethanol for 18 hr gave 0.95 g (95%) of N,N′-dibenzyl-1,2-diphenyl-1,2-diaminoethane (IVa), mp 151–152°. Structure IVa was established by the identity of its infrared spectrum and undepressed mixture melting point with an authentic sample prepared by the procedure of Japp and Moir.[67]

Irradiation of Benzaldehyde N-*t*-Butylimine (IIIb). A solution of 1.5 g of IIIb in 500 ml of 95% ethanol was irradiated for 24 hr. Evaporation of the solvent and recrystallization gave 1.2 g (80%) of dihydro photodimer IVb, mp 129–130°. *Anal.* Calcd for $C_{22}H_{32}N_2$: C, 81.43; H, 9.94; N, 8.63. Found: C, 81.57; H, 9.97; N, 8.60. The infrared spectrum (KBr) is characterized by bands at 3.03, 3.30, 6.22, 6.90, and 13.12 μ. The ultraviolet spectrum (95% ethanol) has λ_{max} 249 mμ (ε 600). The nmr ($CDCl_3$) shows singlets at τ 9.34 (18 H) and 6.46 (2 H) and 2.80 (10 H). The mass spectrum of IIIb included peaks with *m/e* at 163, 162 (base peak), 106, 91, and 79.

Irradiation of Benzaldehyde N-Methylimine (IIIc). Photolysis of a solution containing 1.0 g of IIIc in 500 ml of 95% ethanol for 28 hr gave 0.65 g (65%) of dihydro dimer IVc, mp 131–133° (lit.[68] 135°). *Anal.* Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.21; H, 8.43; N, 11.56. The infrared spectrum (KBr) has bands at 3.08, 6.90, and 13.20 μ. The ultraviolet spectrum has λ_{max} (95% ethanol) 247 mμ (ε 425). The nmr spectrum is characterized by bands at τ 8.00 (6 H, s), 6.57 (2 H, s), and 2.82 (10 H, s). The mass spectrum included peaks with *m/e* at 121, 120 (base), and 42.

Irradiation of *p*-Chlorobenzaldehyde N-Cyclohexylimine (IIId). A solution of 1.0 g of IIId in 500 ml of 95% ethanol was irradiated for 20 hr. Evaporation of the solvent and recrystallization of the residue from ethanol gave 88% yield of dihydro dimer IVd, mp 184–185°. The spectroscopic properties of IVd were entirely analogous to those of dihydro photodimer II.

Irradiation of *p*-Tolualdehyde N-Benzylimine (IIIe). A solution of 1.0 g of IIIe in 500 ml of 95% ethanol was photolyzed for 16 hr. Removal of the solvent gave 0.91 g (92%) of dihydro dimer IVe, mp 143–144°. *Anal.* Calcd for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66. Found: C, 85.78; H, 7.77; N, 6.70. The infrared spectrum (KBr) is characterized by bands at 3.10, 3.40, 6.23, 6.90, and 13.55 μ. The ultraviolet spectrum has λ_{max} (95% ethanol) 248 mμ (ε 150). The nmr spectrum ($CDCl_3$) shows singlets at τ 8.33 (2 H, NH) and 7.71 (6 H, methyl H), an AB doublet at 6.50 and 6.71 (total 4 H, benzylic protons with $J_{AB} = 14$ cps), a singlet at 6.32 (2 H, methine protons), and a multiplet for the aromatic protons at 2.89 (18 H).

Irradiation of *o*-Tolualdehyde N-Benzylimine (IIIf). Photolysis of a solution containing 1.0 g of IIIf in 500 ml of 95% ethanol for 16 hr gave 0.95 g (95%) of dihydro dimer IVf, mp 120–122°. *Anal.* Calcd for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66. Found: C, 85.49; H, 7.70; N, 6.54. The infrared spectrum (KBr) has peaks at 3.10, 3.40, 6.24, 6.90, and 13.62 μ. The ultraviolet spectrum in 95% ethanol has λ_{max} 255 mμ (ε 120). The nmr spectrum ($CDCl_3$) shows singlets at τ 8.27 (6 H, methyl) and 7.53 (2 H, NH), an AB doublet at 6.38 and 6.53 (total 4 H, benzylic protons with $J_{AB} = 14$ cps), a singlet at 5.94 (2 H, methine protons), and a multiplet for the aromatic protons at 2.80 (18 H).

Irradiation of *p*-Methoxybenzaldehyde N-Benzylimine (IIIg). A solution of 1.0 g of IIIg in 500 ml of 95% ethanol was photolyzed for 12 hr. Removal of the solvent gave 0.9 g (90%) of IVg, mp 172–173°. *Anal.* Calcd for $C_{30}H_{32}N_2O_2$: C, 79.61; H, 7.13; N, 6.19. Found: C, 79.54; H, 7.54; N, 6.26. The infrared spectrum (KBr) has bands at 3.10, 3.40, 6.20, 6.85, and 13.45 μ.

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The ultraviolet spectrum has λ_{max} 230, 274, 282 mμ (ε 18,000, 2400, 1800). The nmr spectrum ($CDCl_3$) shows a singlet at τ 8.32 (2 H, NH), AB pattern at 6.46 and 6.68 (4 H, benzylic protons, $J = 14$ cps), a singlet at 6.31 (2 H, methine protons), singlet at 6.17 (6 H, OCH_3), and a multiplet at 2.88 (18 H).

Irradiation of *p*-Dimethylaminobenzaldehyde N-Benzylimine (IIIh). A solution of 1.0 g of IIIh and 0.1 g of benzophenone in 1 l. of 95% ethanol was photolyzed with a 2537-Å lamp for 8 hr. Removal of the solvent and recrystallization of the residue from 95% ethanol gave dihydro dimer IVh, mp 178–180°. *Anal.* Calcd for $C_{32}H_{38}N_4$: C, 80.29; H, 8.00; N, 11.71. Found: C, 80.00; H, 8.17; N, 11.43. The infrared spectrum was characterized by bands at 6.20, 6.61, 7.43, 10.50, and 14.41 μ. The nmr spectrum ($CDCl_3$) shows singlets at τ 8.03 (2 H, NH), 6.98 (12 H, $N(CH_3)_2$), and 6.30 (2 H, methine protons), an AB pattern at 6.41 and 6.60 ($J_{AB} = 14$ cps), and a multiplet at 2.92 (18 H).

Irradiation of Acetophenone N-Benzylimine. Photolysis of a solution containing 1.0 g of acetophenone N-benzylimine in 500 ml of 95% ethanol for 12 hr gave 0.85 g of the dihydro photodimer N,N′-dibenzyl-1,2-diphenyl-1,2-dimethyldiaminoethane, mp 148–149°. *Anal.* Calcd for $C_{30}H_{32}N_2$: C, 85.67; H, 7.67; N, 6.66. Found: C, 85.54; H, 7.81; N, 6.65. The ultraviolet spectrum (95% ethanol) has λ_{max} 242 mμ (ε 750). The nmr spectrum ($CDCl_3$) has a singlet at τ 8.35 (6 H, CH_3), a singlet at 7.92 (2 H, NH), an AB quartet at 6.50 and 6.68 (4 H, $J = 14$ cps), and a doublet for the aromatic protons at 2.83 (20 H). This material was identical in all respects with the dimer prepared from the aluminum-amalgam reduction of starting material. Examination of the mother liquors obtained from recrystallization of the dimer by glpc indicated the presence of 0.11 g (10%) of α-phenylethyl-N-methylamine.

Photolysis of Benzophenone N-Alkylimines. In a typical example a solution of 2.0 g of benzophenone N-methylimine and 0.1 g of benzophenone in 500 ml of anhydrous 2-propanol was irradiated for 7 hr. Evaporation of the solvent left an oil which on distillation gave 1.8 g (90%) of a solid material. Recrystallization from hexane gave a crystalline material, mp 38–39°, that was identified as benzhydrylmethylamine as judged by the identity of its infrared spectrum with that of an authentic sample.[69] In an analogous fashion the related N-substituted benzophenone imines Vb–d were photoreduced to the corresponding amines in high yield. In all cases authentic samples of the amines were prepared by catalytic hydrogenation or aluminum amalgam reduction of the starting imine.

Thermal Decomposition of Benzpinacol in the Presence of Benzophenone N-Methylimine. Benzpinacol (37 mg) and benzophenone N-methylimine (Va) (40 mg) were dissolved in 4 ml of anhydrous 2-propanol and the solution was heated in a sealed tube at 130° for 6 days. Analysis of the resulting residue by glpc on a 5 ft × 0.25 in. 10% Versamid on Chromosorb W (60–80 mesh) column at 150° revealed the presence of benzhydrylmethylamine (70%) and benzophenone (64%).

Pyrolysis of Benzpinacol in the Presence of Benzaldehyde N-Benzylimine. A solution of benzpinacol (420 mg) and benzaldehyde N-benzylimine (406 mg) in 16 ml of 2-propanol was heated in a sealed tube at 130° for 6 days. Cooling and opening of the tube resulted in a spontaneous precipitation. The collected precipitate mp 148–149°, was identified as the *meso* dihydro dimer IVa (46%). Evaporation of the solution and sublimation of the residue gave 304 mg of benzophenone, mp 47–48°, identified by its infrared spectrum.

Thermal Decomposition of Di-*t*-butyl Peroxide in the Presence of Aryl-N-alkylimines. A solution of imine Va (40 mg) and di-*t*-butyl peroxide (18 mg) in 4 ml of 2-propanol was heated in a sealed tube at 130° for 30 hr. Evaporation of the solvent and analysis of the residue by glpc using a 5 ft × 0.25 in. 10% Versamid on Chromosorb W (60–80 mesh) column at 150° revealed the presence of benzyhydrylmethylamine (51%). In a similar manner a solution of imine IIIa (122 mg) and di-*t*-butyl peroxide in 5 ml of 2-propanol was heated in a sealed tube at 130° for 12 hr. Removal of the solvent and crystallization of the residue gave dihydro dimer IVa, mp 148–149°.

Preparation of *meso*-1,3-Dimethyl-4,5-diphenylimidazolidine (VIII). A solution of dihydro dimer IVc (100 mg) and 1 ml of a 37% aqueous formaldehyde solution in 30 ml of absolute methanol was allowed to stand at room temperature for 48 hr. Evaporation of the solvent afforded a thick oil which was purified by thick layer chromatography to give a white crystalline material, mp 47–48° (lit.[26] 49°), identified as *meso*-1,3-dimethyl-4,5-diphenylimidazolidine. The nmr spectrum (CCl_4) shows a singlet at τ 7.21 (6 H), a doublet at 6.94 (1 H, $J = 3.0$ cps), a singlet at 6.25 (2 H), a doublet at 5.74 (1 H, $J = 3.0$ cps), and a singlet at 3.11 (10 H).

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with either a central light source (internal water-cooled mercury arc lamp Hanovia, Type L450-W) or with a GE "Sunlight" phosphor source with peak energy at 300 mμ. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer quantum yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 *M*.[31] After the irradiation the tubes were opened and an internal standard (biphenyl) was added. The solutions were analyzed by glpc using a F & M 5750 instrument with either a 11 ft × 0.25 in. 10% Versamid or 10% Apiezon J column on 60–80 mesh Chromosorb W treated with DMCS. The conversions were run to 15% or less and the mass balance were generally better than 95%.

Luminescence Spectra. The emission spectra were made on a Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. Emitting species were identified by the identity of the spectral emission distribution, lifetimes, and excitation spectra with authentic samples. Highly purified imines produced only weak emission from the corresponding ketone or aldehyde. Benzophenone's phosphorescence emission was not quenched by added imine. In the benzonitrile quenching experiments, a 0.15 *M* EPA glass exhibited an emission which could be reduced by a factor of 100 by the addition of 0.001 *M* benzophenone N-methylimine. Additional emission was observed from benzophenone ($<10^{-5}$ *M*) with an intensity one-third that of benzonitrile. The two emissions overlapped but could easily be separated by the 100-fold difference in lifetime. Further increases in imine concentration resulted in complete suppression of benzonitrile's emission.

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