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Photochemical Reduction in the *N*-Acylketimine System

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Irradiation of a series of *N*-(α-alkylbenzylidene)benzamides in hydrogen-donating solvents results in reduction of the carbon–nitrogen double bond. The photoreduction involves an electronically excited state and does not occur by the chemical sensitization path encountered with simple *N*-alkylimines. Sensitization and emission studies show that the reaction is derived from an n–π^* triplet state. The failure of the imine nitrogen to initiate Norrish type II reactions suggests that the intermolecular hydrogen abstraction by the excited *N*-acylketimine occurs on the oxygen atom of the carbonyl group rather than on the nitrogen atom of the imine chromophore. Stern–Volmer quenching plots show that the rates of hydrogen abstraction of the *N*-acylketimines are low compared with those of aryl ketones. The low quantum efficiency of the photoreduction is attributed to both a low bimolecular hydrogen abstraction rate ($k_r = 1 \times 10^3$ l. mol^{-1} sec^{-1}) and a fast rate of triplet decay.

Aryl imines are known to undergo reduction and reductive dimerization on irradiation in 2-propanol.[1-5] Although the reaction bears analogy to aryl ketone photoreduction, the available data indicate that the reaction is quite different mechanistically in that it appears not to involve the excited state of the imine as an intermediate in the reduction.[1] The reaction has been shown to proceed via an α-amino radical formed by hydrogen atom transfer to the imine from a ketyl radical.[1] The ketyl radical is derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species (see Scheme I).

Scheme I

$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^{*1} \rightsquigarrow Ph_2C{=}O^{*3}$$

$$Ph_2C{=}O^{*3} + (CH_3)_2CHOH \longrightarrow (Ph)_2\dot{C}OH + (CH_3)_2\dot{C}OH$$

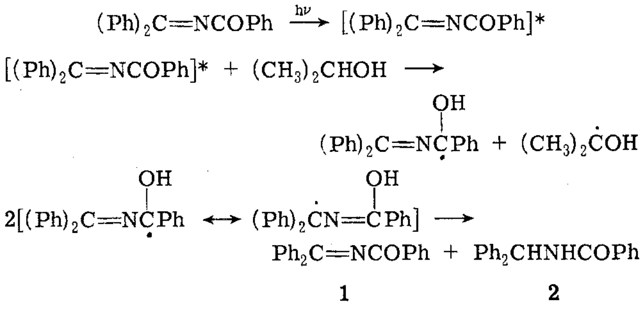
$$(Ph)_2\dot{C}OH + (Ph)_2C{=}NR \longrightarrow Ph_2C{=}O + (Ph)_2\dot{C}NHR$$

$$(CH_3)_2\dot{C}OH + (Ph)_2C{=}NR \longrightarrow (CH_3)_2C{=}O + (Ph)_2\dot{C}NHR$$

$$2(Ph)_2\dot{C}NHR \longrightarrow (Ph)_2C{=}NR + (Ph)_2CHNHR$$

A number of related reports have appeared in the literature showing that reactions apparently involving sensitization by benzophenone in hydrogen-donating solvents proceed, in fact, via formation of ketyl radicals.[6-10] The term "chemical sensitization" was suggested to distinguish between such cases and sensitization involving excitation-energy transfer.[2]

Recently, Okada, Nozaki, Toshima, and coworkers reported that the photoreduction of *N*-(α-phenylbenzylidene)benzamide (1) in 2-propanol proceeds via an electronically excited triplet state (i.e., intramolecular chemical sensitization), in contrast with other diarylketimine photoreductions.[11-14] Similar results were reported by Fraser-Reid and coworkers with related compounds.[15]



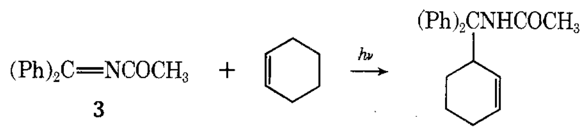
$$(Ph)_2C{=}NCOPh \xrightarrow{h\nu} [(Ph)_2C{=}NCOPh]^*$$

$$[(Ph)_2C{=}NCOPh]^* + (CH_3)_2CHOH \longrightarrow (Ph)_2C{=}N\overset{OH}{\underset{\bullet}{C}}Ph + (CH_3)_2\dot{C}OH$$

$$2[(Ph)_2C{=}N\overset{OH}{\underset{\bullet}{C}}Ph \longleftrightarrow (Ph)_2\dot{C}N{=}\overset{OH}{C}Ph] \longrightarrow \underset{1}{Ph_2C{=}NCOPh} + \underset{2}{Ph_2CHNHCOPh}$$

1 2

The Japanese workers also reported that the excited triplet state of *N*-acyldiphenylmethylenimine (3) can abstract the allylic hydrogens of cyclic and acyclic olefins and produce photochemical addition products (i.e., 4). The photoreduction and addition reactions were completely

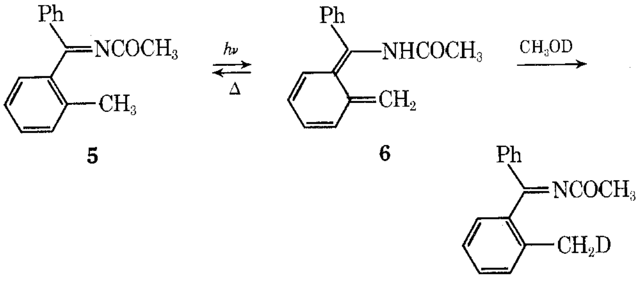


3

4

quenched by piperylene and were markedly retarded by diphenyl sulfide, a good radical scavenger. The yield of photoadduct **4** was enhanced when benzophenone or acetophenone was used as a triplet sensitizer. The mechanism proposed to account for these observations involved excitation of the ketimine followed by intersystem crossing and hydrogen atom abstraction from the solvent by the triplet state.[11-13]

Further support for the involvement of the triplet state in these systems was obtained by studying the photochemistry of several *o*-alkyl aromatic imines (**5**).[14] Irradiation of **5** was reported[14] to result in an isomerization to an enamide derivative (**6**) by a path similar to that observed with the related *o*-alkylbenzophenone system.[16,17]



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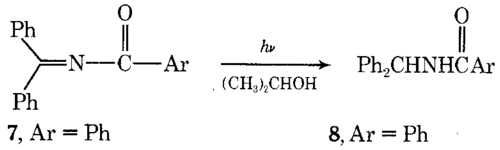
6

On the basis of these observations it would appear as though the mechanism for the reduction of *N*-acylimines is quite different from that followed by *N*-alkylimines. This difference is undoubtedly related to the presence of the carbonyl group in the *N*-acylimine system. These *N*-acylimines are formally aza analogs of α,β-unsaturated ketones. A comparison of the photoreduction of these compounds with the extensively studied α,β-unsaturated ketone system[18] could be of practical and theoretical interest. This comparison and our interest in the chemical consequences of electronic excitation of the C–N double bond prompted us to examine the photoreduction of a number of substituted *N*-acylimines. In this paper we wish to describe results which show that the photoreduction of the *N*-acylimine system can proceed by "chemical sensitization" and by hydrogen abstraction from the triplet state. The specific route followed appears to be a function of the substituent groups present about the 2-azaenone chromophore.

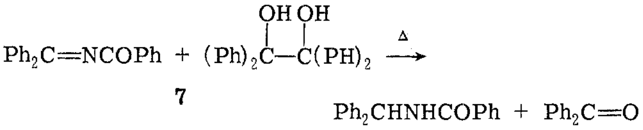
Results and Discussion

Photoreduction in the *N*-Aroyldiphenylketimine System. Irradiation of *N*-diphenylmethylenebenzamide (**7**) in 2-propanol using an internal water-cooled mercury arc lamp equipped with a Pyrex filter for 24 hr afforded *N*-benzhydrylbenzamide (**8**) and acetone in quantitative yield. Similarly, *N*-diphenylmethylene-*p*-anisamide (**9**) in 2-propanol was photoreduced to *N*-benzhydryl-*p*-methoxybenzamide (**10**). In agreement with the Japanese workers,[11] we were unable to detect any dimeric material in the reaction mixture. The quantum yield for the photoreduction of **7** in 2-propanol is extremely low (Φ ca. 10^{-6}) but increases substantially when benzophenone or acetophenone is used as a sensitizer ($\Phi \sim 2 \times 10^{-3}$). The quantum yield is also enhanced when a small amount of water is added to the reaction mixture. High-energy sensitizers such as triphenylene, that do not undergo photoreduction in alcohol, are ineffective as sensitizers. These results suggest that the triplet state of the imine is not the active hydrogen-abstracting species. That the phosphorescence of benzophenone is not appreciably quenched (EPA at 77 K) by the imine is also inconsistent with energy transfer. When an experiment was run using benzophenone ketyl radicals, generated from the thermal decomposition of benzpinacol,[19] reduction of **7** to **8** (also **9** to **10**) occurred. Similarly, thermal decomposition of di-*tert*-butyl peroxide in 2-propanol in the presence of **7** afforded **8** in high yield. These observations when taken together suggest that the photoreduction of **7** in 2-propanol does not involve the excited triplet state of the imine but is brought about by one or more of the intermediates of the ketone photoreduction. The ability of piperylene and diphenyl disulfide to retard the formation of **8** (or **10**) is perfectly consistent with the "chemical sensitization" scheme outlined above (see Scheme I).



7, Ar = Ph
9, Ar = *p*-$OCH_3C_6H_4$

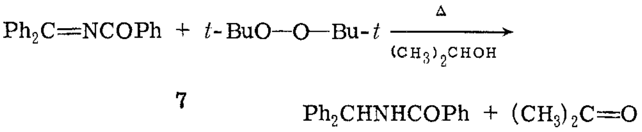
8, Ar = Ph
10, Ar = *p*-$OCH_3C_6H_4$



$$Ph_2C{=}NCOPh + (Ph)_2C(OH){-}C(OH)(PH)_2 \xrightarrow{\Delta} Ph_2CHNHCOPh + Ph_2C{=}O$$

7

8



$$Ph_2C{=}NCOPh + t\text{-}BuO{-}O{-}Bu\text{-}t \xrightarrow[(CH_3)_2CHOH]{\Delta} Ph_2CHNHCOPh + (CH_3)_2C{=}O$$

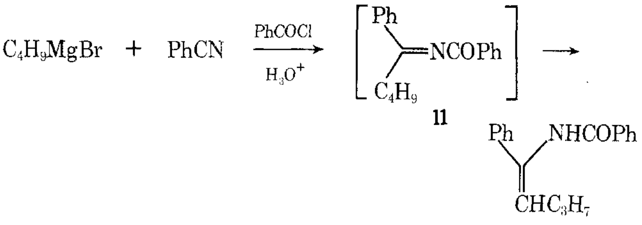
7

8

Some comment is in order concerning the low quantum efficiency of the ketone-sensitized photoreductions in 2-propanol. We have previously suggested that the lack of reactivity of the singlet excited state of the imine can be attributed to rotation about the π bond in the excited state thereby allowing for dissipation of electronic energy.[1] We have recently reported that photoisomerization about the C–N double bond can also be induced by triplet excitation.[20] This would suggest that if triplet energy transfer from benzophenone to **7** (or **9**) occurred, it would be followed by a facile photoisomerization and thereby minimize the bimolecular hydrogen abstraction from the triplet state of the imine. Alternatively, if hydrogen atom transfer from the ketyl radical to the imine were inefficient, a low quantum yield for photoreduction would result.

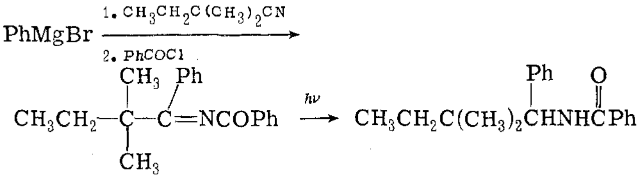
Photoreduction in the *N*-(α-Alkylbenzylidene)benzamide System. The above results clearly indicate that the electronically excited triplet state of *N*-diphenylmethylenebenzamide (**7**) is not involved in the photoreduction in 2-propanol. Instead, photoreduction in this solvent system occurs by "chemical sensitization". This situation does not hold, however, when cyclohexene is used as the solvent. Toshima and coworkers have presented convincing evidence demonstrating the involvement of the electronically excited triplet state of *N*-acyldiphenylmethylenimine in the photochemical addition to cyclic and acyclic olefins.[12] Also, Koch and coworkers have recently shown that the reactions of the related cyclic keto imino ether system proceed through an electronically excited state.[21] In order to probe the excited-state behavior of the *N*-aroylimine system, we have studied the photochemistry of several *N*-(alkylbenzylidene)benzamides which contain a long alkyl side chain. Our expectation was that if hydrogen abstraction occurred on the nitrogen atom of the electronically excited *N*-aroylimine chromophore, then a Norrish type II reaction would occur if the side chain possessed α hydrogens. While Norrish type II photoreactions have been extensively studied for aliphatic,[22] aromatic,[22] and α,β-unsaturated ketones,[23] little is known about the Norrish type II behavior of structurally related imines. Nevertheless, there are several examples reported in the literature where γ-hydrogen transfer to excited imines occurs.[21,24,25]

Our preliminary experiments indicated that a simple straight-chain alkyl group was unsuitable, since attempts to prepare *N*-(α,*n*-butylbenzylidene)benzamide (11) resulted in its rearrangement to the more thermodynamically stable *N*-(1-phenylpentenyl)benzamide (12).[26] This difficulty could be overcome by working with systems which were disubstituted in the α position so as to preclude a 1,3-hydrogen shift. An appropriate model system which was selected for study was *N*-(α-*tert*-pentylbenzylidene)benzamide (13). This *N*-acylimine could be readily prepared by treating phenylmagnesium bromide with 2,2-dimethylbutyronitrile followed by the subsequent addition of benzoyl chloride. The structure of 13 is based on analytical, infrared, ultraviolet, NMR, and mass spectral data (see Experimental Section). Irradiation of 13 in 2-propanol using an internal water-cooled mercury arc equipped with a Vycor filter for 24 hr afforded *N*-(α-*tert*-pentylbenzyl)benzamide (14), mp 123–124°, as the only identifiable photoproduct. The identity of benzamide 14 was established by comparison with an authentic sample prepared from the sodium borohydride reduction of 13. This product was also formed when the irradiation of 13 was carried out using 95% ethanol or cyclohexane as the solvent. Extended irradiation of 13 in benzene, however, resulted in the complete recovery of starting material.



11

12

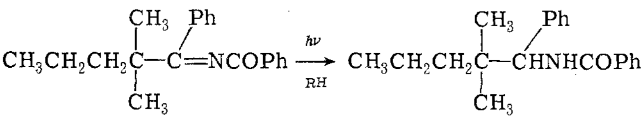


$$\mathrm{CH_3CH_2C(CH_3)_2C(Ph){=}NCOPh} \xrightarrow{h\nu} \mathrm{CH_3CH_2C(CH_3)_2CHNHC(O)Ph}$$

13

14

The failure of 13 to form a type II product on irradiation in benzene prompted us to examine the photochemistry of *N*-[α-(2,2-dimethylbutyl)benzylidene]benzamide (15). In this case, a type II reaction would involve hydrogen transfer from a more reactive secondary position. Wagner and coworkers have previously reported a 15-fold increase in the rate of abstraction of a secondary over a primary hydrogen in the Norrish type II reaction of aromatic ketones.[27] We found, however, that when the irradiation of 15 was carried out in 2-propanol or cyclohexane, the only product formed was the corresponding reduced amine 16.



$$\mathrm{CH_3CH_2CH_2C(CH_3)_2C(Ph){=}NCOPh} \xrightarrow[\mathrm{RH}]{h\nu} \mathrm{CH_3CH_2CH_2C(CH_3)_2CH(Ph)NHCOPh}$$

15

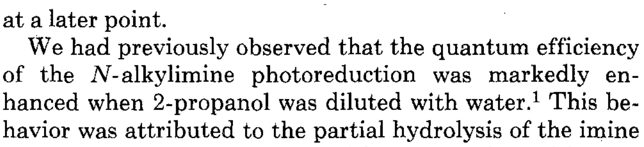
16

Table I
Quantum Yields for the Photoreduction of *N*-(α-Alkylbenzylidene)benzamides[a]

Compd	Solvent	Sensitizer[b]	$\Phi^c \times 10^2$
13	2-Propanol		0.081
13	2-Propanol (95%)		0.068
13	2-Propanol	α,α-Dimethylbutryophenone	0.075
13	2-Propanol	Acetophenone	0.13
13	Cyclohexane		0.23
13	Cyclohexane	*m*-Methoxyacetophenone	0.021
15	2-Propanol		0.053
15	Cyclohexane		0.21
17	2-Propanol		0.062
17	Cyclohexane		0.40
17	Cyclohexane	*m*-Methoxyacetophenone	0.08

[a] Average of three or more determinations. [b] >95% of light being absorbed by the sensitizer. [c] Quantum yield for product formation.

We have also studied the photochemistry of *N*-(α-*tert*-pentylbenzylidene)-*p*-anisamide (17). The effect of placing an electron-donating group on the benzene nucleus of an aryl ketone has been independently studied by Yang[28] and Wagner.[27,29] Electron-releasing substituents were found to increase the lifetime of the triplet state and also decrease the rate constant for type II photoelimination. Wagner suggested that the inefficient hydrogen abstraction which occurs with these *p*-methoxy substituted aryl ketones actually occurs from low equilibrium populations of an upper n–π^* triplet state.[29] On the basis of his observations, we anticipated that a similar situation would exist in the *N*-acylimine system. Irradiation of 17 in cyclohexane or 2-propanol gave *N*-(α-*tert*-pentylbenzyl)-*p*-anisamide (18) as the only identifiable photoproduct (see Experimental Section).



$$\mathrm{CH_3CH_2C(CH_3)_2C(Ph){=}N{-}C(O)C_6H_4{-}\mathit{p}{-}OCH_3} \xrightarrow[\mathrm{RH}]{h\nu} \mathrm{CH_3CH_2C(CH_3)_2CH(Ph)NHC(O)C_6H_4{-}\mathit{p}{-}OCH_3}$$

17

18

Surprisingly, both the quantum yield (see Table I) and the rate constant for the photoreduction of 17 are of the same order of magnitude as those obtained with *N*-benzoylimines 13 and 15. This result will be discussed in some detail at a later point.

We had previously observed that the quantum efficiency of the *N*-alkylimine photoreduction was markedly enhanced when 2-propanol was diluted with water.[1] This behavior was attributed to the partial hydrolysis of the imine in the aqueous solvent followed by chemical sensitization by the small amount of the carbonyl compound formed. If chemical sensitization were to play an important role in the *N*-benzoylimine system, we would expect that the addition of a small amount of water or the deliberate addition of α,α-dimethylbutyrophenone would cause an increase in the quantum efficiency of the photoreduction of 13. As can be seen from Table I, the photoreduction of 13 was actually less efficient in 95% 2-propanol. The fact that the reaction was not enhanced by the addition of water or 2,2-dimethylbutyrophenone provides strong evidence that these photoreductions are not proceeding via a "chemical sensitization" route.

Quantum yields for the triplet-sensitized photoreductions were also determined. Some of the data listed in Table I reflect the quantum efficiency of the photoreduction as a function of the sensitizer used. When acetophenone was employed, the quantum yield for the photoreduction of **13** was enhanced by ca. 60%. The possibility exists that both acetophenone and α,α-dimethylbutyrophenone promote the photoreduction via the chemical sensitization route. In order to avoid this complication, *m*-methyoxyacetophenone was used as a triplet sensitizer. This ketone has a quantum yield of only 0.006 for hydrogen abstraction,[28] a high intersystem crossing efficiency (Φ_{ISC} = 0.96),[27] and a high triplet energy (E_T = 74 kcal/mol).[28] From the results outlined in Table I it can be seen that *m*-methoxyacetophenone was capable of promoting the photoreduction of both **13** and **17.** The quantum efficiencies of the sensitized reactions, however, were significantly reduced. Chapman and coworkers had previously reported that the quantum yield for sensitized photoreactions using *m*-methoxyacetophenone depends on the concentration of the sensitizer.[30] His results showed that high concentrations of sensitizer markedly diminished the quantum efficiency of the photoreaction. This observation was attributed to self-quenching of the sensitizer via excimer formation. Since it was necessary to use high concentrations of *m*-methoxyacetophenone (0.1–0.3 *M*) to assure complete absorption of the incident light (>95%), it would appear as though self-quenching of the sensitizer also occurs with the *N*-acylimine system. This would account for the diminished quantum yields in the sensitized experiments using *m*-methoxyacetophenone. At any rate, the data clearly implicate the involvement of a triplet state in the photoreduction of *N*-acylimines **13, 15,** and **17.**

Further support for an electronically excited triplet state in these photoreductions was obtained from quenching and emission studies. *cis*-Piperylene and naphthalene were employed as photochemical quenchers. Over the concentration range, 0.0001–0.001 *M* *cis*-piperylene, the quantum efficiencies for the photoreduction of **13, 15,** and **17** were significantly diminished. The lowest lying triplet states of *N*-benzoylimines **13** and **15** were demonstrated to be n–π^* as evidenced from their phosphorescence emission spectra in a methanol–ethanol glass (4:1) at 77 K. We note that the 0–0 bands of **13** and **15** correspond to a triplet energy of 68 kcal and the vibrational spacing between the 0–0 and 0–1 band corresponds to 1550 cm^{-1}. The 77 K lifetimes of both imines were determined to be 6 msec, also consonant with an n–π^* assignment. Surprisingly, the triplet excitation energy of *p*-anisamide **17** was found to have a value of 68 kcal, although in this case the vibrational spacing between the 0–0 and 0–1 band was 1100 cm^{-1} and the triplet lifetime was 17 msec. The longer lifetime and smaller vibrational spacing found with **17** would tend to indicate that this imine has some π–π^* character mixed in with the n–π^* state.[31,32] Wagner had previously noted that the intermediate lifetimes and other phosphorescence properties of a number of para-substituted acetophenones can be attributed to strong mixing of n–π^* and π–π^* triplets.[29] He pointed out that mixed triplet states may be close enough energetically to equilibrate before emitting and that, although the major phosphorescence component arises from both states, it occurs principally from the faster emitting n–π^* state. This situation may also obtain for *p*-anisamide **17.**

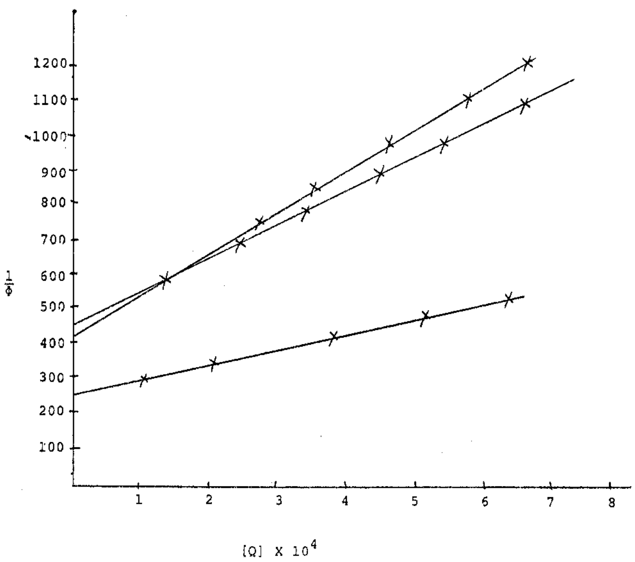


Figure 1. Stern–Volmer plot for the photoreduction of *N*-acylimines **13, 15,** and **17** in cyclohexane.

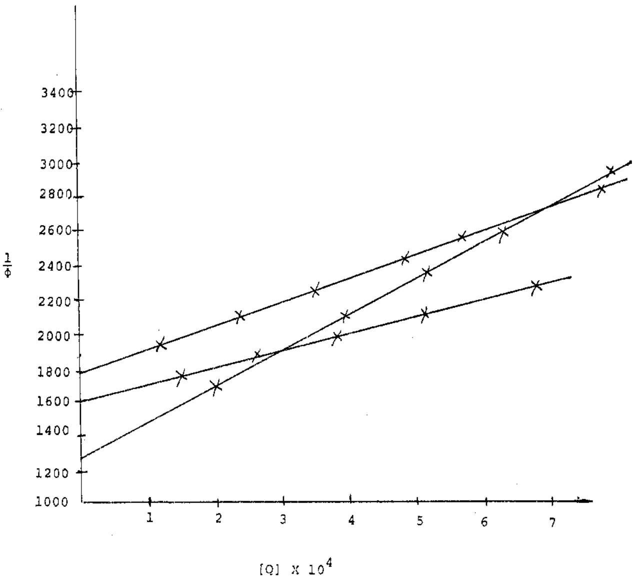


Figure 2. Stern–Volmer plot for the photoreduction of *N*-acylimines **13, 15,** and **17** in 2-propanol.

The quantum yields for the photoreduction of *N*-acylimines **13, 15,** and **17** are considerably smaller than the values obtained for typical aryl ketones.[33] One possibility to account for the low efficiency of the *N*-acylimine system may be related to some molecular feature of the molecule which retards formation of the diradical and allows direct radiationless decay to compete with chemical reaction of the triplet. In order to determine the rates of hydrogen abstraction and radiationless decay we have studied the variation of the quantum yield for photoreduction vs. quencher concentration. Figures 1 and 2 represent plots of the reciprocal of the quantum yield for product formation against piperylene concentration in both cyclohexane and 2-propanol. The Stern–Volmer formulation for quenching a bimolecular hydrogen abstraction of an excited triplet state (rate constant k_r) results in the following expression

$$\frac{1}{\Phi} = \frac{1}{\phi_{ISC}}\left[1 + \frac{k_d}{k_r[RH]} + \frac{k_q[Q]}{k_r[RH]}\right]$$

where ϕ_{ISC} is the intersystem crossing efficiency. The slope of the plot gives $(1/\phi_{ISC})(k_q/k_r[RH])$ and the intercept

Table II
Stern–Volmer Kinetic Data for the Photoreduction of *N*-Acylimines 13, 15, and 17[a]

Compd	Solvent	ϕ_{ISC}	Intercept	Slope × 10^6	$k_r \times 10^3$	$k_d \times 10^6$
13	Cyclohexane[b]	0.21	440	1.17	4.64	4.06
13	2-Propanol	0.23	1260	2.16	0.76	2.62
15	Cyclohexane	0.31	460	0.88	4.23	5.67
15	2-Propanol	0.32	1890	1.27	0.88	6.67
17	Cyclohexane	0.31	250	0.37	9.97	7.40
17	2-Propanol	0.33	1600	0.95	1.16	7.49

[a] 2537-Å light. [b] k_q (cyclohexane) = 1.1×10^{10} l. mol^{-1} sec^{-1}. S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, N.Y., 1973, p 55.

gives $(1/\phi_{ISC})(1 + k_d/k_r[RH])$. The fact that *cis*-piperylene is isomerized to *trans*-piperylene in the presence of excited *N*-acylimine clearly indicates that **13**, **15**, and **17** do in fact intersystem cross. The intersystem crossing efficiency (ϕ_{ISC}) of each of the three *N*-acylimines was independently determined according to the procedure of Lamola and Hammond[34] and is summarized in Table II. Quenching of the triplet state of the *N*-acylimines will be diffusion controlled since the triplet excitation level of all three imines is 68 kcal/mol. From the observed slopes of the Stern–Volmer plots and using $k_q = 5 \times 10^9$ l. mol^{-1} sec^{-1},[35] the values of k_r can be determined (see Table II). Knowing k_r, ϕ_{ISC}, and the intercept we can determine k_d (unimolecular rate of triplet decay to ground state).

The bimolecular rate constant for hydrogen abstraction in 2-propanol by the *N*-acylimine triplet is approximately 1×10^3 l. mol^{-1} sec^{-1}. This bimolecular rate of hydrogen abstraction is quite low compared to the $k_h^{bi} = 4 \times 10^5$ l. mol^{-1} sec^{-1} reported[36] for acetophenone triplet in 2-propanol and the $k_h^{bi} = 6 \times 10^5$ l. mol^{-1} sec^{-1} found[36] for benzophenone triplet in the same solvent. We can see that the rate of hydrogen abstraction is of the order of 100-fold smaller for these *N*-acylimines than for the aromatic ketones. It should be noted, however, that the bimolecular rate constant and quantum efficiency of the photoreduction are comparable to the values reported for α,β-unsaturated ketones (i.e., $\Phi \sim 0.003$ and $k_h^{bi} = 3 \times 10^3$ l. mol^{-1} sec^{-1}).[37,38] Another interesting facet is the rapid rate constant of unimolecular decay of the *N*-acylimine triplet, $k_d \sim (2.6\text{–}7.5) \times 10^6$ sec^{-1}. This is faster than the comparable decay rate constants of acetophenone and benzophenone, which are of the order of 10^5 sec^{-1}.[36,39,40]

Considerable information has now been accumulated about the photochemical reduction of *N*-(α-alkylbenzylidene)benzamides. The more readily derived facts about the photoreduction are the following. (a) The photoreduction of the *N*-acylimine system proceeds from an electronically excited state and does not occur by the chemical sensitization path encountered with simple *N*-alkylimines.[1-4] (b) The quantum efficiencies and rates of hydrogen abstraction are low compared to arylketone photoreductions but are on the same order of magnitude as α,β-unsaturated ketone photoreductions. (c) Sensitization and emission studies show that the photoreduction is derived from an n–π^* triplet state. (d) The absence of Norrish type II products indicates that hydrogen abstraction by the excited *N*-acylimine occurs on the oxygen atom of the carbonyl group rather than on the nitrogen atom of the imine chromophore. (e) The inefficiency of the photoreduction can be attributed to an inherently small bimolecular hydrogen abstraction rate as well as a rapid triplet degradation path. Syn–anti isomerization about the C–N double bond provides an attractive rationale to account for the ease of triplet decay as well as the low intersystem crossing of the excited singlet state.

Two additional points merit some comment. One has to do with the fact that the photoreduction of *N*-diphenylmethylenebenzamide (**7**) in 2-propanol proceeds via the chemical sensitization path. It would appear as though the hydrolytic or photooxidative generation of benzophenone in this solvent system is relatively fast. The lack of reactivity of the excited state of **7** in 2-propanol suggests that the triplet state undergoes an extremely efficient nonradiative decay to ground state, thereby precluding hydrogen abstraction and allowing the benzophenone-induced "chemical sensitization" path to predominate. Another point worth noting is that the rate of hydrogen abstraction of *N*-(α-*tert*-pentylbenzylidene)-*p*-anisamide (**17**) is comparable to the rate observed with the related *N*-benzoylimine system (i.e., **13** or **15**). This observation indicates that any effect the *p*-methoxy group may have in stabilizing the π–π^* character of the excited triplet state of the ketimine is small when compared to the effect it has on arylketone excited states. The reason for this is not at all clear and further work needs to be done before an adequate explanation can be offered.

Experimental Section

All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. 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 100 MHz using a Jeol MH-100 spectrometer.

Attempted Synthesis of *N*-(α-*n*-Butylbenzylidene)benzamide. To a Grignard solution of *n*-butylmagnesium bromide (prepared from 3.6 g of magnesium turnings and 20.5 g of *n*-butyl bromide in 300 ml of ether) was added 15.4 g of benzonitrile in 30 ml of ether. The mixture was heated at reflux for 15 min, cooled to room temperature, and then quenched with 21 g of benzoyl chloride in 30 ml of ether. The resulting mixture was heated at reflux for 15 min and then decomposed with 30 ml of a saturated ammonium chloride solution. The ether layer was separated, washed with 30 ml of water, and dried over sodium sulfate. Evaporation of the solvent under reduced pressure left a solid which was identified as *N*-(1-phenylpentenyl)benzamide (**12**) on the basis of its physical data: ir (KBr) 2.90, 6.01, 6.41, 6.95, 7.15, 7.60, 7.80, 8.51, 8.95, 9.42, 9.80, 10.81, 12.45, and 14.20 μ; NMR (CCl_4) δ 7.1–7.8 (m, 11 H), 5.95 (t, 1 H), 2.15 (m, 2 H), 1.42 (m, 2 H), and 0.90 (t, 3 H).

Preparation of *N*-Diphenylmethylene-*p*-anisamide. A solution containing 39.2 g of bromobenzene in 350 ml of ether was added to a three-neck flask which contained 6.6 g of magnesium turnings in 25 ml of ether. After heating at reflux for 2 hr, a solution containing 23.7 g of benzonitrile in 30 ml of anhydrous ether was added to the above mixture. The mixture was heated at reflux for 30 min, after which time it was quenched with 36 g of *p*-anisoyl chloride in 30 ml of ether. The solution was heated to reflux for an additional 30 min and was then decomposed with 250 ml of a saturated ammonium chloride solution. The ethereal solution was separated and dried over magnesium sulfate. Evaporation of the solvent left an oil which was recrystallized from aqueous methanol to give 22 g of *N*-diphenylmethylene-*p*-anisamide (**9**) as a white solid: mp 157–159°; ir (KBr) 6.01, 7.10, 8.65, 9.25, 9.75, 9.95, 10.40, 10.51, 10.85, 11.70, 12.21, 12.70, 13.15, and 14.35 μ; NMR ($CDCl_3$) δ 7.8 (d, 2 H, *J* = 8.5 Hz), 6.8 (d, 2 H, *J* = 8.5 Hz), 7.40 (m, 5 H), 3.72 (s, 3 H); uv (95% ethanol) 275 nm (ε 22,000); MS *m/e* 285, 180, 135, 105, and 78 (base).

Preparation of *N*-(α-*tert*-Pentylbenzylidene)benzamide (13). A solution containing 5.31 g of bromobenzene in 40 ml of ether was added to a three-neck flask which contained 0.825 g of magnesium turnings in 5 ml of ether. After heating at reflux for 1 hr, a solution containing 3.0 g of 2,2-dimethylbutyronitrile[41] in 20 ml of benzene was added to the solution. The mixture was heated at reflux for 5 hr and stirred at room temperature for an additional 12 hr, after which time it was quenched with 3.66 ml of benzoyl chloride in 30 ml of ether. After heating the mixture at reflux for 4 hr, it was cooled and quenched with 30 ml of a saturated ammonium chloride solution. The aqueous layer was extracted with 50 ml of ether and the combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. Recrystallization of the oil from ether–pentane gave 2.7 g of *N*-(α-*tert*-pentylbenzylidene)benzamide (**13**) as a white solid: mp 51–52°; ir (KBr) 3.40, 6.01, 6.22, 9.75, 9.95, 10.20, 10.65, 13.15, 13.80, 14.25, and 14.50 μ; uv (cyclohexane) 237 nm (ε 12,800), 270 (1280), 300 (360), and 320 (225); NMR ($CDCl_3$) δ 7.4 (m, 10 H), 1.72 (2 H, q, *J* = 8.0 Hz), 1.27 (6 H, s), 1.07 (3 H, t, *J* = 8.0 Hz); *m/e* 279 (M^+), 251, 236, 167, 160, 105 (base), 91, and 77.

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.77; H, 7.66; N, 4.94.

Preparation of *N*-[α-(1,1-Dimethylbutyl)benzylidene]-benzamide (15). A solution containing 2.75 g of bromobenzene in 40 ml of anhydrous ether was added to a three-neck flask which contained 0.425 g of magnesium turnings in 5 ml of ether. After heating at reflux for 2 hr, a solution containing 1.75 g of 2,2-dimethylvaleronitrile[42] in 20 ml of benzene was added to the solution. The above mixture was heated at reflux for 5 hr and stirred at room temperature for an additional 12 hr, and then quenched with 1.8 ml of benzoyl chloride in 15 ml of ether. After heating the mixture at reflux for 4 hr, it was cooled and quenched with 30 ml of a saturated ammonium chloride solution. The aqueous layer was extracted with ether and the combined ethereal extracts were dried over magnesium sulfate and concentrated under reduced pressure to give 3.54 g of an orange oil. This crude oil was subjected to thick layer chromatography using a 20% ether–pentane mixture as the eluent. The major component (R_f 0.43) (60%) was a clear oil whose structure was assigned as *N*-[α-(1,1-dimethylbutyl)benzylidene]-benzamide (**15**) on the basis of its spectral data: ir (neat) 3.25, 5.95, 6.05, 6.22, 9.45, 10.15, 10.45, 10.60, 10.90, 11.91, 12.22, 13.05, 13.80, and 14.40 μ; NMR ($CDCl_3$) δ 6.9–7.8 (m, 10 H), 1.58 (m, 4 H), 1.24 (s, 6 H), and 0.92 (m, 3 H); uv (cyclohexane) 237 nm (ε 14,400), 285, (1130), 295 (500), 305 (415), 320 (280); MS *m/e* 293 (M^+), 251, 236, 182, 146, 105 (base), 91, and 77.

Preparation of *N*-(α-*tert*-Pentylbenzylidene)-*p*-anisamide (17). A solution containing 7.1 g of bromobenzene in 40 ml of ether was added to a three-neck flask which contained 1.1 g of magnesium turnings in 10 ml of ether. After heating at reflux for 1 hr, a solution containing 4.0 g of 2,2-dimethylbutyronitrile[41] in 40 ml of benzene was added to the solution. The above mixture was heated at reflux for 4 hr and stirred for an additional 12 hr at room temperature and then quenched with 3.72 g of *p*-anisoyl chloride in 30 ml of ether. After heating the mixture for 4 hr, it was cooled and quenched with 30 ml of a saturated ammonium chloride solution. The aqueous layer was extracted with ether and the combined ethereal extracts were dried over magnesium sulfate and concentrated under reduced pressure to give 7.4 g of an orange oil. The crude oil was purified by thick layer chromatography using a 50% ether–pentane mixture as the eluent. The major component of the mixture (R_f 0.3) (60%) was a clear oil whose structure was assigned as *N*-(α-*tert*-pentylbenzylidene)-*p*-anisamide (**17**) on the basis of its spectral data: ir (neat) 3.30, 5.95, 6.01, 7.90, 8.51, 9.02, 9.31, 9.70, 9.93, 10.15, 11.02, 11.71, 12.01, 12.60, 12.95, 13.52, and 14.25 μ; NMR ($CDCl_3$) δ 7.45–6.90 (9 H, m), 3.68 (3 H, s), 1.24 (6 H, s), 1.68 (2 H, q *J* = 7.6 Hz), 1.02 (3 H, t, *J* = 7.6 Hz); uv (cyclohexane) 215 nm (ε 28,400) and 262 (19,000); MS *m/e* 176, 105 (base), 91, and 77.

Irradiation of *N*-(α-*tert*-Pentylbenzylidene)benzamide. A solution containing 347 mg of *N*-(α-*tert*-pentylbenzylidene)benzamide (**13**) in 150 ml of cyclohexane was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Vycor filter for 10 hr. Removal of the solvent left a yellow oil which was purified by thick layer chromatography. The major band isolated from the thick layer plate using a 50% ether–pentane mixture as the eluent (R_f 0.5) was a white solid, mp 123–124°, whose structure was assigned as *N*-(α-*tert*-pentylbenzyl)benzamide (**14**) on the basis of the following data: ir (KBr) 2.90, 3.40, 6.11, 6.35, 9.2, 9.35, 9.70, 10.81, 11.35, 12.50, 12.96, 13.70, 14.23, and 14.70 μ; NMR ($CDCl_3$) δ 7.65–7.20 (m, 10 H), 5.00 (d, 1 H, *J* = 9.2 Hz), 1.36 (2 H, d, *J* = 7.6 Hz), 6.65 (1 H, d, *J* = 9.2 Hz), 0.96 (6 H, s), 0.90 (3 H, t, *J* = 7.6 Hz); MS *m/e* 281 (M^+), 211, 105 (base), 91, and 77.

Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.12; H, 8.17; N, 4.77.

An authentic sample of *N*-(α-*tert*-pentylbenzyl)benzamide (**14**) was independently prepared by the sodium borohydride reduction of *N*-(α-*tert*-pentylbenzylidene)benzamide (**13**). To a solution containing 300 mg of **13** in 25 ml of 95% ethanol was added 124 mg of sodium borohydride. The mixture was stirred for 12 hr at room temperature and the solvent was removed under reduced pressure. The residual oil was taken up in ether and washed with a 10% hydrochloric acid solution followed by water. The ethereal layer was dried over magnesium sulfate and the ether was removed under reduced pressure to give 254 mg of a white solid, mp 123–124°, whose physical properties were identical in every detail with those of the sample of *N*-(α-*tert*-pentylbenzyl)benzamide isolated from the photolysis of **13**.

Irradiation of *N*-[α-(1,1-Dimethylbutyl)benzylidene]benzamide. A solution containing 200 mg of *N*-[α-(1,1-dimethylbutyl)benzylidene]benzamide (**15**) in 150 ml of 2-propanol was irradiated under an argon atmosphere using a 450-W Hanovia lamp equipped with a Vycor filter for 12 hr. Removal of the solvent left a pale yellow oil which was purified by thick layer chromatography. The major component (60%) (R_f 0.47) was a white solid, mp 147–148°, whose structure was assigned as *N*-[α-(1,1-dimethylbutyl)]benzamide (**16**) on the basis of the following data: ir (KBr) 2.90, 6.07, 6.72, 7.20, 7.40, 8.75, 9.65, 10.81, 11.30, 12.45, 13.51, 14.15, and 14.55 μ; NMR ($CDCl_3$) δ 7.75–7.30 (10 H, m), 6.78 (1 H, d, *J* = 9.2 Hz), 5.08 (1 H, d, *J* = 9.2 Hz), 1.31 (4 H, m), 0.94 (6 H, s), and 0.88 (3 H, t, *J* = 2 Hz); MS *m/e* 295 (M^+), 211, 105 (base), 91, and 77.

Anal. Calcd for $C_{20}H_{25}NO$: C, 81.31; H, 8.53; N, 4.72. Found: C, 81.29; H, 8.60; N, 4.72.

An authentic sample of *N*-(α-(1,1-dimethylbutyl)benzyl)benzamide was independently prepared by the sodium borohydride reduction of **15**. To a solution containing 390 mg of **15** in 25 ml of 95% ethanol was added 165 mg of sodium borohydride. The mixture was stirred for 12 hr at room temperature and the solvent was removed under reduced pressure. The residual oil was taken up in ether and washed with a 10% hydrochloric acid solution followed by water. The ethereal solution was dried over magnesium sulfate and the ether was removed under reduced pressure to give 200 mg of a white solid, mp 147–148°, whose physical properties were identical in every detail with those of the sample of *N*-[α-(1,1-dimethylbutyl)benzyl]benzamide isolated from the irradiation of **15**.

Irradiation of *N*-(α-*tert*-Pentylbenzylidene)-*p*-anisamide (17). A solution containing 150 mg of *N*-(α-*tert*-pentylbenzylidene)-*p*-anisamide in 200 ml of cyclohexane was irradiated under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Vycor filter for 12 hr. Removal of the solvent left a pale yellow oil which was purified by thick layer chromatography. The major photoproduct was a white, crystalline solid, mp 118–120°, whose structure was assigned as *N*-(α-*tert*-pentylbenzyl)-*p*-anisamide (**18**) on the basis of the following data: ir (KBr) 3.01, 3.36, 6.10, 7.35, 7.70, 8.51, 9.02, 9.46, 9.72, 11.85, 13.11, 13.90, and 14.30 μ; NMR ($CDCl_3$) δ 7.68 (2 H, d, *J* = 8.0 Hz), 6.82 (2 H, d, *J* = 8.0 Hz), 7.24 (5 H, s), 6.64 (1 H, d, *J* = 9.2 Hz), 5.04 (1, H, d, *J* = 9.2 Hz), 3.76 (3 H, s), 1.36 (2 H, q, *J* = 7.6 Hz), 0.94 (6 H, s), and 0.86 (3 H, t, *J* = 7.6 Hz); uv (95% ethanol) 252 nm (ε 14,500); MS *m/e* 309, 281, 266, 224, 196, 135 (base), and 107.

Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.13; H, 8.09; N, 4.50. Found: C, 76.85; H, 8.07; N, 4.15.

An authentic sample of *N*-(α-*tert*-pentylbenzyl)-*p*-anisamide was prepared by the sodium hydride reduction of *N*-(α-*tert*-pentylbenzylidene)-*p*-anisamide using the procedure outlined above for the reduction of *N*-(α-*tert*-pentylbenzylidene)benzamide (**15**). The white solid obtained from the borohydride reduction of **17**, mp 118–120°, was identical in every detail with the sample of **18** isolated from the irradiation of *N*-(α-*tert*-pentylbenzylidene)benzamide (**17**).

Quantum Yield Determinations. Solutions were prepared in various solvents as described in the Results and Discussion, and 3.0 ml of each was placed in separate culture tubes (13 × 100 mm). Each sample was degassed to 0.005 mm and sealed in vacuo. In a given run all tubes were irradiated in parallel for the same length of time in a merry-go-round apparatus which assured that each sample absorbed the same intensity of light. Cyclopentanone solutions were used as the chemical actinometer for which a quantum yield of 0.38 was used[43] giving a reproducible light intensity of 2.10×10^{16} quanta sec^{-1}. Analyses were performed on a Hewlett-Packard Model 5750 gas chromatograph using a 10% FS-1265 Diasaport S column at 210–235.[6] The mole ratio:area ratio response of the instrument was calibrated for each aroylimine and internal standard used, so that yields of product could be measured accurately. The conversions were run to 10% or less. The mass balance in these runs were generally better than 95%.

Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer equipped 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. The emission spectra were measured in a methanol–ethanol (4:1) or methylcyclohexane glass. The solvent was checked for emission each time a spectra was recorded. No interference due to solvent was found at any time. All compounds having short radiative lifetimes were measured by photographing the decay curve on an oscillograph. The chopper speed was adjusted manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted vs. time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime (τ_0).

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Registry No.—**9**, 36728-20-8; **12**, 55030-00-7; **13**, 55030-01-8; **14**, 55030-02-9; **15**, 55030-03-0; **16**, 55030-04-1; **17**, 55030-05-2; **18**, 55030-06-3; *n*-butyl bromide, 109-65-9; benzonitrile, 100-47-0; benzoyl chloride, 98-88-4; bromobenzene, 108-86-1; 2,2-dimethylbutyronitrile, 20654-46-0; 2,2-dimethylvaleronitrile, 20654-47-1; *p*-anisoyl chloride, 100-07-2.

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A Convenient Synthesis of Protiated and Specifically Deuterated Secondary Azoalkanes

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A convenient synthesis of secondary azo compounds is reported. The method involves addition of chlorine to the azine or hydrazone in CH_2Cl_2 followed by reduction of the dichloro- or chloroazoalkane with $LiAlH_4$ or $LiAlD_4$ in ether. The preparation of a variety of symmetrical secondary azoalkanes demonstrates the applicability of the technique. The procedure is applicable to the synthesis of (*sec*-alkylazo)alkanes and presumably of (*sec*-alkylazo)-2,4,6-trichlorobenzenes. The isotope purity of the azoalkane is fixed by that of the azine or hydrazone precursor and of the $LiAlD_4$.

Secondary deuterium isotope effects[2] in and the rates[3] of thermolysis of secondary azoalkanes have been extensively utilized in investigations of the mechanism of azo compound pyrolysis and of the effect of substituents on the energetics of free-radical formation. We report a convenient synthesis of secondary azoalkanes and their specifically deuterated congeners possessing essentially the maximum number of atoms of deuterium.

The classical method (Scheme I) for the synthesis of symmetrical (eq 1) or unsymmetrical (eq 2) secondary azoalkanes involves catalytic reduction of the corresponding azine or hydrazone to the hydrazine followed by oxidation;