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THE PHOTOCHEMISTRY OF N-ACYLDIPHENYLKETIMINES

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Abstract—Irradiation of N-acetyl- and N-benzoyldiphenylketimine (I and III) in 2-propanol affords N-acetyl- and N-benzoylbenzhydrylamine (II and IV), respectively, in quantitative yields. The reactions of I in the presence of such additives as piperylene, diphenyl disulphide and *trans*-anethole have been examined to gain a mechanistic insight. The photoreduction is explained on the basis of a concept of intramolecular chemical sensitization.

Intensive studies of organic photochemistry have been made in the area of α,β-unsaturated carbonyl compounds.[1] N-Acylated ketimines (I and II) described here are formally the α-aza-analog, but to our best knowledge no report has appeared on the photochemistry of this class of nitrogen compounds.[*]

When a solution of N-acetyldiphenylketimine (I)[2] in 2-propanol was irradiated with Pyrex-filtered light, photoreduction to N-acetylbenzhydrylamine (II) was attained in a quantitative yield. Similarly N-benzoyldiphenylketimine (III)[2] gave the calculated amount of N-benzoylbenzhydrylamine (IV).

$$\begin{array}{ccc} Ph_2C{=}N{-}COR + Me_2CHOH & \xrightarrow{h\nu} & Ph_2CHNHCOR + Me_2C{=}O \\ I: R = Me & & II: R = Me \\ III: R = Ph & & IV: R = Ph \end{array}$$

TLC and GLC analyses of each irradiation mixture showed exclusive formation of II and IV, respectively, and none of other expected products such as pinacols or cross-coupled products could be detected. The formation of acetone in the reaction was confirmed as the 2,4-dinitrophenylhydrazone. The photoreduction proceeded almost quantitatively in other hydrogen-donating solvents such as ethanol or cyclohexane, but no reaction occurred in benzene solution.

A thermal nucleophilic addition of alcohols (R'OH) to I (and to III) has been reported to yield V.[2] However, V was

$$\begin{array}{ccc} Ph_2C{=}N{-}COR + R'OH & \xrightarrow{h\nu} & Ph_2C(OR')NHCOR \\ I\ (or\ III) & & V \end{array}$$

shown not to be the precursor of II by an independent irradiation of V ($R = Me$, $R' = Et$). The addition of 2-propanol to I or III proceeded quite slowly on account of

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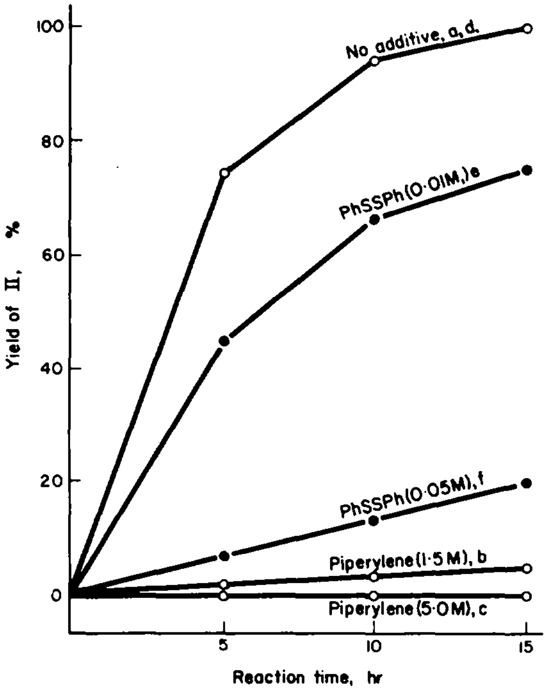
[*] A part of the work has been reported in communication form: T. Okada, M. Kawanisi, H. Nozaki, N. Toshima and H. Hirai, *Tetrahedron Letters*, 927 (1969)

steric factors as previously noted.[2] Thus, the chemical behaviour of I in its electronically excited state is in marked contrast to its behaviour in the ground state. Visible light (>350 nm)* was also effective in the formation of II and IV, which indicated that the longer wavelength chromophores were responsible to the reaction.

Quenching studies

On addition of piperylene, an efficient triplet quencher,[3] the photoreduction of I was greatly retarded. The results of the irradiation conducted under various conditions are shown in Fig 1. Curve *a* shows the percent yields of II in the absence of any additive. Addition of more than 15 molar ratio of piperylene completely suppressed the formation of II (curve *b*).

Addition of diphenyl disulphide as a radical scavenger[4] also retarded the formation of II and these results were included in Fig. 1. Although the thiyl radical derived from diphenyl disulphide could be expected to add to I, any product arising therefrom was not isolated.



These results may suggest that a triplet state of I is involved and the hydrogen abstraction takes place in a radical fashion as recognized in the photoreduction of simple ketones.[5]

The photochemical reaction of I *in the presence of* trans-*anethole*

The photochemistry of *trans*-anethole (A) has recently been disclosed; the reaction

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* Aqueous cupric sulphate solution (10% w/w) was used throughout the work as a filter solution for light of wavelength longer than 350 nm.

in the presence of carbonyl compounds was investigated.[6] To gain further insight into the excited species involved in the photoreduction of I, the behaviour of I in the presence of added A was examined.

A 2-propanol solution of I was irradiated with light (>350 nm) in the presence of A. Concentrations of I and A were both 0·05 M and the light (>350 nm) was absorbed exclusively by I.* The isomerization of A to its *cis*-isomer (*cis*-A) occurred rapidly and a *cis*-A/A ratio of 1·23 was attained after 10 hr. The photoreduction of I also proceeded affording an 87% yield of the reduction product II within 10 hr of irradiation. In benzene, a less hydrogen-donating solvent, no photoreduction was observed, but the energy transfer from I to A still occurred and the *cis*-A/A ratio of 1·30 was obtained after 5 hr. Although measurement of quantum yield was not performed, some qualitative aspects of the reaction may be pointed out. The reactions are formulated as follows, where excited species are indicated by S_1 or T_1. The sensitized isomerization of A to *cis*-A may occur through the T_1 state of A or a phantom triplet.

$$\mathrm{I} + h\nu \rightarrow \mathrm{I}(S_1) \rightarrow \mathrm{I}(T_1) \tag{1}$$

$$\mathrm{I}(T_1) + \mathrm{A} \rightarrow \mathrm{I} + \mathrm{A}(T_1) \tag{2}$$

$$\mathrm{A}(T_1) \rightarrow \mathrm{A} \text{ or } cis\text{-}\mathrm{A} \tag{3}$$

$$\mathrm{I}(T_1) \rightarrow \mathrm{II} \tag{4}$$

A 2-propanol solution of I was irradiated with Pyrex-filtered light in the presence of added A. Concentrations of I and A were both 0·05 M. After 10 hr irradiation, the reduction product II was obtained in a 20% yield, together with an isomeric mixture of A and *cis*-A in a ratio (*cis*-A/A) of 1·33. No dimer of A was detected. The UV spectrum of A shows that it can absorb a considerable fraction of Pyrex-filtered light.‡ The fluorescence spectrum of A measured in 0·05 M ethanol solution indicated a broad band between 310–380 nm with a maximum at 335 nm. Addition of I (25 mole%) to this solution completely quenched the fluorescence. Accordingly, Pyrex-filtered light induces the following reactions in addition to those in Eqs 1, 2, 3 and 4.

$$\mathrm{A} + h\nu \rightarrow \mathrm{A}(S_1) \text{---} ? \rightarrow \mathrm{A}(T_1) \tag{5}$$

$$\mathrm{A}(S_1) + \mathrm{I} \rightarrow \mathrm{A} + \mathrm{I}(S_1) \tag{6}$$

The dimer of A has been known to be produced only in the absence of carbonyl compounds such as benzophenone which effectively quench the S_1 state of A.[6] Similar behaviour was also observed in the present system. This evidence would indicate dual roles for the electronically excited state of I, hydrogen abstraction and triplet energy transfer. Thus, the reactivity of I is quite similar to $n \rightarrow \pi^*$ excited benzophenone, although this parallelism is only qualitative. It should be noted that the ketimines do not form a four-membered ring adduct with the olefinic compounds.

Mechanism of the reaction

Quenching studies and the reactions in the presence of A described above suggest,

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* I: λ(EtOH) 254 (ε 18,900), 280 (6060) and 350 nm (34).†

† In a preliminary report this value was reported to be 120.

‡ *trans*-Anethole: λ_{max}(EtOH) 260 (ε 21,000) and λ(EtOH) 280 nm (3000). No absorption was observed above 315 nm.

but do not require, that the $n \rightarrow \pi^*$ triplet state acts as a chemically reactive species in the photoreduction of I. The mechanism shown in Eqs 7–10 is consistent with the experimental observations. The hydrogen-transfer step (eq 10) is completely analogous to the one observed in the photoreduction of benzophenone in 2-propanol.[5] The *chemical sensitization*[*] mechanism has been proposed in several cases such as the benzophenone-sensitized photoreduction of camphorquinone[7] and of acridine[8] and the photoreduction of N-alkylarylketimines in the presence of carbonyl compounds.[9]

$$Ph_2C{=}N{-}COMe + Me_2CHOH \xrightarrow{h\nu} Ph_2C{=}N{-}\dot{C}(OH)Me + Me_2\dot{C}{-}OH \tag{7}$$

$$\underset{VI}{[Ph_2C{=}N{-}\dot{C}(OH)Me \leftrightarrow Ph_2\dot{C}{-}N{=}C(OH)Me]} \rightleftharpoons \underset{VII}{Ph_2\dot{C}{-}NHCOMe} \tag{8}$$

$$\text{VI and/or VII} \rightarrow \text{I} + \text{II} \tag{9}$$

$$Me_2\dot{C}{-}OH + \text{VI (or VII)} \rightarrow Me_2C{=}O + \text{II} \tag{10}$$

If the mechanism is appropriately applied to the present system, the photoconversion of I to II could be considered to be an example of *intramolecular chemical sensitization.* Direct observation of the radical species VI and/or VII by means of ESR has been accomplished[†] which evidence strongly supports the mechanism.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. IR spectra were obtained in neat liquid film or in Nujol mull on a Shimadzu IR-27-G spectrophotometer. NMR spectra were taken with a JEOL C-60-H spectrometer with CCl_4 as a solvent. UV spectra were taken in EtOH on a Hitachi EPS-2 recording spectrophotometer. Plates of Silicagel G were used for TLC and the spots were visualized with iodine vapour. GLC was performed on SE-30 (18%) on Chromosorb, 2 m, at 130–180° with H_2 carrier.

Materials. N-Acetyldiphenylketimine (I), b.p. 130°/0·1 mm (lit.[2] b.p. 168–171°/1 mm), was prepared by the reaction of diphenylketimine[10] with acetic anhydride. N-Benzoyldiphenylketimine (III),[‡] m.p. 115–117° (lit.[2] m.p. 117°), was prepared by treatment of diphenylketimine[10] with benzoyl chloride and excess pyridine.

Irradiation of N-acetyldiphenylketimine (I). A soln of I (1·0 g, 4·5 mmoles) in 2-propanol (70 ml) was placed in a Pyrex or Vycor vessel and irradiated externally by means of 200 W high pressure Hg arc under N_2 atm at room temp for 50 hr. The reaction mixture was concentrated *in vacuo* to afford an almost pure crystalline mass of N-acetylbenzhydrylamine (II) (1·1 g, ~100%). One recrystallization from EtOH–H_2O gave an analytically pure sample, m.p. 146–146·5° (lit.[11] m.p. 146–147°). (Found: C, 79·70; H, 6·59; N, 6·14. Calc for $C_{15}H_{13}NO$: C, 79·97; H, 6·71; N, 6·22%). The authentic sample of II was prepared by acetylation of benzhydrylamine. The IR and NMR spectra of photoproduct II were superimposable with those of the authentic specimen.

Irradiation of N-benzoyldiphenylketimine (III). A soln of III (1·0 g, 3·5 mmoles) in 2-propanol (70 ml) was irradiated analogously with the above. Concentration of the reaction mixture afforded an almost pure crystalline mass of N-benzoylbenzhydrylamine (IV) (1·0 g, 100%). One recrystallization from EtOH gave an analytically pure sample, m.p. 170–171° (lit.[12] m.p. 172°). (Found: C, 83·60; H, 5·73; N, 4·67. Calc for $C_{20}H_{17}NO$: C, 83·59; H, 5·96; N, 4·88%). Authentic IV was prepared by benzoylation of benzhydrylamine. The IR and NMR spectra of photoproduct IV were superimposable with those of the authentic sample

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[*] As pointed out by Monroe and Weiner,[7] the term "chemical sensitization" may be technically incorrect, since "sensitization" implies energy transfer. However, we favour this term for convenience, implying only "reactions induced by ketyl radical".

[†] Dr. N. Toshima, University of Tokyo, has kindly informed us of the results of an ESR study prior to publication.

[‡] Care should be taken to purify III. Since III gradually forms addition products with alcoholic solvents,[2] recrystallizations from alcohols should be avoided. Sublimation under reduced pressure is generally recommended.

Preparation of V (R = Me, R′ = Et): *ethanol addition product of* I. A soln of I (2·23 g, 10 mmoles) in EtOH (100 ml) was left standing for a week at room temp. Concentration afforded V in an almost quantitative yield. Washing with n-hexane gave the pure sample, m.p. 165–166° (lit.[2] m.p. 166–168°).

2-Propanol did not afford the addition product under identical conditions.

Irradiation of V (R = Me, R′ = Et). A soln of V (0·27 g, 1 mmole) in EtOH (10 ml) was irradiated by Pyrex-filtered light for 50 hr. TLC examination indicated the complete recovery of V and absence of II.

Irradiation of I *in other solvents.* A soln of I (1·0 g, 4·5 mmoles) in solvent (70 ml) was irradiated quite analogously with the procedure in the case of 2-propanol. Irradiation of III was conducted similarly.

Irradiation of I *by light* (>350 nm). A soln of I (1·0 g, 4·5 mmoles) in 2-propanol (70 ml) was irradiated externally by means of a 300 W high pressure Hg arc through aqueous cupric sulphate soln (10% w/w). A similar procedure was employed for III.

Quenching studies in the presence of piperylene. In runs **a**, **b** and **c**, a soln of I (0·1 M) and piperylene (none, 1·5 M and 5·0 M, respectively) in 2-propanol (10 ml) was placed in a Pyrex tube (1·4 cm diameter and 14·5 cm length) and irradiated externally with a 300 W high pressure Hg arc through aqueous cupric sulphate soln (10% w/w) as a filter. The course of the reaction was monitored by GLC. The results are summarized in Fig 1.

Quenching studies in the presence of diphenyl disulphide. In runs **d**, **e** and **f**, a soln of I (0·1 M) and diphenyl disulphide (none, 0·01 M and 0·05 M, respectively) in 2-propanol (10 ml) was placed in a Pyrex tube and irradiated in the same manner. The results are summarized in Fig 1.

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