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PHOTOCHEMICAL REDUCTION OF N-ACYLDIPHENYLKETIMINES

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Recent report on the ketone-sensitized photoreduction of N-alkyldiphenylketimines (1) prompts us to record our results on the photochemical reduction of N-acyldiphenylketimines. These compounds are formally aza-analogue of α,ß-unsaturated ketones. To our best knowledge, however, no report has appeared on the photochemistry of the nitrogen compounds.

Irradiation of N-benzoyldiphenylketimine (Ia) (3) (1.0 g) in 2-propanol (4) (70 ml) by means of 200 W high pressure mercury arc (Vycor filter) under N_2 atmosphere for 50 hr gave N-benzoylbenzhydrylamine (IIa) (5) (100%) and acetone (identified as 2,4-DNP). Similarly

$$Ph_2C{=}N{-}COR + Me_2CHOH \xrightarrow{h\nu} Ph_2CHNHCOR + Me_2C{=}O$$

I a: R=Ph II a: R=Ph
b: R=Me b: R=Me

N-acetyldiphenylketimine (Ib) (3) (1.0 g) in 2-propanol (70 ml) was reduced to N-acetylbenzhydrylamine (IIb) (5) (100%) (6).

Light of wavelength longer than 350 nm was equally effective in the formation of II from I. Photoreduction of I was not observed in benzene. In spite of all efforts, the dimeric product was not found among the reaction mixture. The conversion of I to II was completely inhibited in the presence of piperylene (8), an efficient triplet quencher (9). Addition of diphenyl disulfide as a radical scavenger (10) also retarded the formation of II (8). These results may suggest that a triplet state of I is involved and the hydrogen abstraction takes place in a radical fashion in these reactions.

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Fischer proposed the *chemical sensitization* by ketones in the case of the photoreduction of N-alkyldiphenylketimines (1). If the Fischer's mechanism is allowed to apply to the present system, the photoconversion of I to II could be considered to be an example of *intramolecular chemical sensitization* (11) as shown below.

$$Ph_2C{=}N{-}COR + Me_2CHOH \xrightarrow{h\nu} Ph_2C{=}N{-}\dot{C}(OH)R + Me_2\dot{C}OH$$

$$\underset{\text{III}}{\left[Ph_2C{=}N{-}\dot{C}(OH)R \longleftrightarrow Ph_2\dot{C}{-}N{=}C(OH)R\right]} \rightleftharpoons \underset{\text{IV}}{Ph_2\dot{C}{-}NHCOR}$$

$$\text{III and/or IV} \longrightarrow \text{I} + \text{II}$$

$$Me_2\dot{C}OH + \text{III (or IV)} \longrightarrow Me_2C{=}O + \text{II}$$

We are now examining the mechanistic details of this reaction and further photochemical aspects of the compounds which contain the $>C{=}N{-}\underset{|}{C}{=}O$ chromophore in the molecules.

REFERENCES

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2. N. Toshima, H. Hirai and S. Makishima, *Kôgyô Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **72**, 000 (1969).
3. Ia: λ(EtOH) 254 (22700), 280 (12100), and 350 nm (74).
   Ib: λ(EtOH) 254 (18900), 280 (6060), and 350 nm (120).
4. Photoreduction of I proceeded also in ethanol or cyclohexane almost quantitatively.
5. These products were identical with the authentic samples with respect to IR, NMR and mp.
6. A nucleophilic addition of alcohols (R'OH) to I was reported to yield $Ph_2C(OR')NHCOR$ (V) in the ground state (7). However, V was shown not to be the precursor of II by an independent irradiation of V (R=Me, R'=Et).
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8. Addition of piperylene (1.5 *M*) to a solution of Ib (0.1 *M*) in 2-propanol (10 ml) completely quenched the reaction. Similarly addition of diphenyl disulfide (0.01 *M* and 0.05 *M*) to a solution of Ib (0.1 *M*) in 2-propanol (10 ml) decreased the yield of IIb to 76% and 20%, respectively, of the one secured in the absence of such an inhibitor after 15 hr irradiation.
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11. *The intramolecular chemical sensitization* seems to be unprecedent. Intramolecular *physical* sensitization of olefinic double bond by carbonyl function has been recorded in the case of *trans*-5-hepten-2-one (H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965)).