

PHOTOCHEMICAL REDUCTION OF N-ACYLDIPHENYLKETIMINES

T. Okada\*, M. Kawanisi, H. Nozaki

Department of Industrial Chemistry, Kyôto University

Kyôto, Japan

and

N. Toshima, H. Hirai

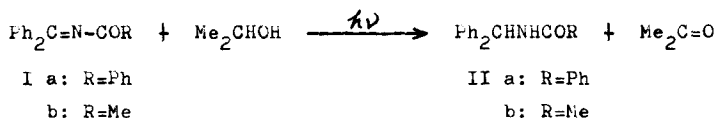
Department of Industrial Chemistry, University of Tokyo

Tokyo, Japan

(Received in Japan 17 January 1969; received in UK for publication 4 February 1969)

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  $\alpha,\beta$ -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-benzoylbenzhydramine (IIa) (5) (100%) and acetone (identified as 2,4-DNP). Similarly

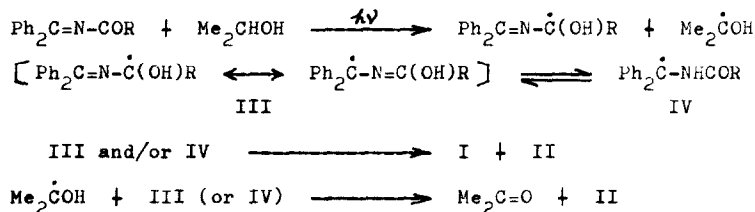


N-acetyldiphenylketimine (Ib) (3) (1.0 g) in 2-propanol (70 ml) was reduced to N-acetylbenzhydramine (IIb) (5) (100%) (6).

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.

\* To whom inquiries should be addressed.

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.



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

#### R E F E R E N C E S

1. M. Fischer, Chem. Ber., **100**, 3599 (1967): One group of ours has recently reported that diphenylketimine is photochemically reduced to benzhydrylamine in 2-propanol without sensitizer (2).
2. N. Toshima, H. Hirai and S. Makishima, Kôgyô Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.), **72**, 000 (1969).
3. Ia:  $\lambda(\text{EtOH})$  254 (22700), 280 (12100), and 350 nm (74).  
Ib:  $\lambda(\text{EtOH})$  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 ( $\text{R}'\text{OH}$ ) to I was reported to yield  $\text{Ph}_2\text{C}(\text{OR}')\text{NHCOR}$  (V) in the ground state (7). However, V was shown not to be the precursor of II by an independent irradiation of V ( $\text{R}=\text{Me}$ ,  $\text{R}'=\text{Et}$ ).
7. J. E. Banfield, G. M. Brown, F. H. Davey, W. Davies and T. H. Ramsay, Australian J. Sci. Research, **A1**, 330 (1948).
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.
9. G. S. Hammond and P. A. Leermakers, J. Phys. Chem., **66**, 1148 (1962).
10. S. G. Cohen and S. Aktipis, J. Am. Chem. Soc., **88**, 3587 (1966).
11. The intramolecular chemical sensitization seems to be unprecedented. 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)).