Tetrahedron Letters No. 5, pp 453 - 454, 1974. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL REACTION OF N,N-DIMETHYL BENZAMIDES AND 1,1-DIPHENYLETHYLENE

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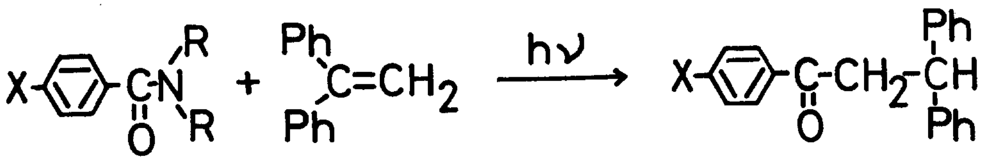
(Received in Japan 7 November 1973; received in UK for publication 28 December 1973)

As a study of photochemical reactions about aromatic amides[1], we wish to report here our new findings that photochemical reactions of N,N-dimethyl benzamides I and 1,1-diphenylethylene II take place easily to give propiophenone derivatives in good yields.

Irradiation of a mixture of N,N-dimethyl benzamide Ia and II gave β,β-diphenyl propiophenone IIIa (70 %) as a sole product[2]. Upon irradiation, N,N-dimethyl anisamide Ib and II yielded the corresponding propiophenone derivative IIIb quantitatively. This type of photochemical cleavage of N-CO bond of the amide group has not previously been reported, although such a bond cleavage has been observed in the photolysis of amides[3].



I II III

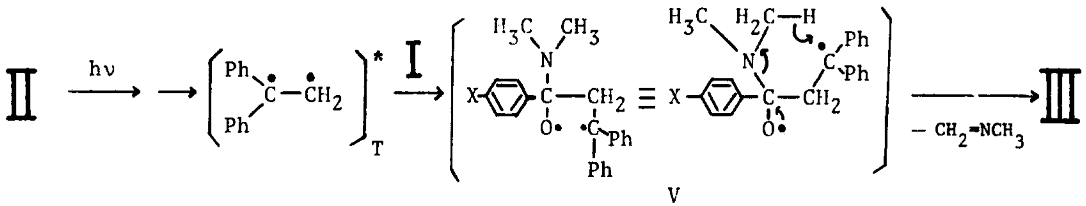
I : a) R= CH_3, b) R= CH_3 , c) R= C_2H_5.
X= H X= OCH_3 X= CN

III : a) X= H, b) X= OCH_3.

On the other hand, no photochemical reaction between II and the aromatic amides having an electron-withdrawing group, such as N,N-diethyl *p*-cyanobenzamide Ic, occurred. It is very notable that the effects of the substituents on the aromatic rings of benzamides were significant in these reactions.

From the efficient quenching effect of piperylene IV on the formation of IIIa and the inefficiency of additive IV on the fluorescence spectrum of II , it was indicated that the reactive species of the reaction would be II in the lowest triplet state. While, the aromatic amides, such as I, would be rather photochemically inert, because N,N-dialkyl benzamides I were neither photolyzed in acetonitrile and benzene nor photoreduced with toluene.

By consideration of the structure of the photoproducts III and the effects of substituents on the formation of III in addition to the above facts, it is reasonable to assume that the propiophenone derivatives IIIa and IIIb may be derived from a 1,4-diradical intermediate V, followed by elimination of N-methyl imine accompanied by hydrogen transfer, as shown below.



a) X= H, b) X= OCH_3.

The present photochemical reaction is the novel one in which the photoexcited olefin attacked to the carbonyl group of amides in the ground states.

The further study on the present reaction of the other amides and olefins are now in progress.

REFERENCES AND FOOTNOTES

1) Y.Katsuhara, H.Maruyama, Y.Shigemitsu, and Y.Odaira, *Tetrahedron Lett.*, 1323 (1973).

2) Photochemical reactions of N,N-dialkyl benzamides I and 1,1-diphenylethylene II (1:1 mixture in acetonitrile) were carried out in quartz tube with a 500 W high pressure mercury arc under a nitrogen atmosphere. Conversions of amides Ia and Ib were controlled within 5 % to inhibit the further reaction of the products IIIa and IIIb. Yields of the photoproducts IIIa and IIIb were based on the unrecovered starting amides Ia and Ib, respectively.

3) I.Rosenthal in " The Chemistry of Amides ", J.Zabicky Ed., Interscience Publishers, London, 1970, Chap. 5.