

Photochemical Formation of Diamides from *p*-Nitrophenylbenzamide

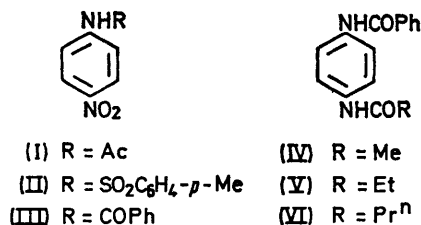
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Summary Photolysis of *p*-nitrophenylbenzamide in alcohols gives *p*-alkanoylaminophenylbenzamide.

ULTRAVIOLET irradiation of amides¹ or arenesulphonamides² of aniline affords the corresponding photo-Fries rearrange-

ment products. Recently, however, irradiation³ of *p*-nitrophenylacetamide (I) in EtOH has been reported to give only unchanged starting material because of the quenching effect of the nitro-group in (I). In the course of our investigation⁴ on photolysis of *p*-toluenesulphonamides, we found that irradiation of an ethanolic solution⁵ of *p*-nitrophenyl-*p*-toluenesulphonamide (II) by a high-pressure mercury lamp (200 w) gave *p*-nitroaniline as well as (II). These findings attracted our attention towards the photochemical behaviour of the title compound (III) and we found that photolysis of (III) in alcohols gave diamides, which were formed by combination of the nitro-group with the alcohols.



Irradiation (7 h; high-pressure mercury lamp,† 400 w) of (III) in EtOH (5 mmole/l) at room temperature (under a nitrogen stream) followed by treatment‡ of the reaction mixture (obtained on removal of the solvent) with CHCl₃ gave *p*-acetylamino-phenylbenzamide (IV) (insoluble fraction) [m.p. 238—239° (MeOH-H₂O) (lit.⁶ m.p. 237—238°)] in 18% yield. In the case of photolysis under an oxygen stream, however, only (III) was obtained.

This finding suggested that combination of the two radicals from the nitro-compound and the hydrogen donor took place. With this fact in mind, photolysis of (III) in other alcohols (PrⁿOH or BuⁿOH) was carried out and similar results were obtained; *p*-propanoylamino- and *p*-butanoylamino-phenylbenzamide§ [(V), m.p. 244—245° (MeOH), and (VI), m.p. 234—235° (MeOH-CHCl₃)] in 22 and 15% yield, respectively, were isolated.

Recently, two examples⁷ of photo-reactions of nitro-compounds with solvents have been reported. The exact reaction pathway of the photolysis is not fully settled at present.

(Received, September 6th, 1971; Com. 1564.)

† An Osawa UV-HT lamp was employed.

‡ Attempted purification of the product in the soluble fraction (CHCl₃) was unsuccessful.

§ Satisfactory analytical data were obtained for the compounds (V) and (VI).

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