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A NEW PHOTOREACTION OF BENZOPHENONE OXIME

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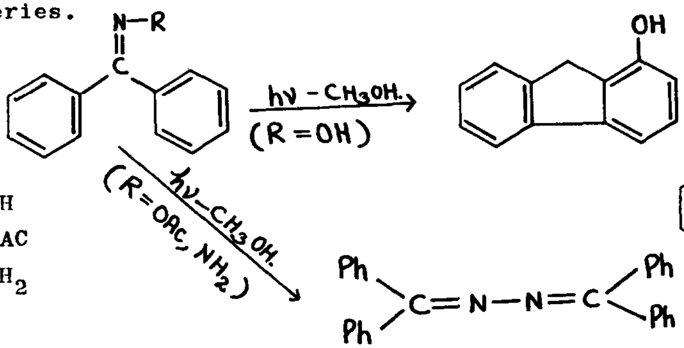
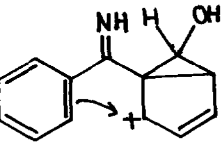
Various groups have studied the photochemistry of oximes of cycloalkanones, aldoximes and hydrazone of benzophenone[1-6] and have reported various types of reactions which these systems undergo. However, we wish to report a new reaction in which the benzophenone oxime undergoes a series of reactions involving hydroxylation, cyclization of the proximate phenyl groups and Wolff-Kischner reduction to give 1-hydroxy fluorene in 30-35% over all yield. This is the first example of intramolecular photosubstitutive cyclization in the benzophenone series.



Ia. R = OH
Ib. R = OAC
Ic. R = NH_2



II

The derivatives of benzophenone under study were the oxime, its O-acetate and the hydrazone. In a general experiment 300 ml of 0.005M solution was irradiated (125 W mercury lamp in immersion type quartz reactor) for various times depending upon the derivative under study. The course of the reaction was followed by thin layer chromatography and in the case of oxime the reaction was stopped after 12 hours. The amount of 1-hydroxy fluorene varied with the solvent, being 30-35% in methanol, but only 10% in isopropanol. The product 1-hydroxy flourene m.p. 120°, lit. m.p 119.5°[7] has been confirmed from its spectral data (IR, NMR) and by the preparation of its acetate m.p 91°, lit. m.p 90°[7]. In the case of Ib and Ic only the benzophenone azine, 25-35% m.p 162°, lit. m.p 163-64°[1,7] was isolated and no cyclized product was obtained. In all these experiments considerable amounts of the benzophenone were isolated. The oxime of m-nitrobenzophenone m.p 124-25° on photolysis for 12 hours gave 50% unreacted oxime as the major product, 10% m-nitrobenzophenone and a small amount of m-amino benzophenone. No cyclized product was however isolated.

The isolation of azine in the case of Ib and Ic, seems to be a result of homolytic cleavage[1,8] but in case of Ia, it appears to be a heterolytic cleavage as no azine was detectable. No cyclization in the case of m-nitrobenzophenone oxime supports the idea that the reaction may involve electrophilic, photosubstitution, in an intermediate like II, formed by cleavage followed by protonation. This intermediate may involve 1-3 hydrogen shifts in a singlet excited state with the elimination of nitrene[2b], to give 1-hydroxy fluorene. During the rearrangement of this intermediate a proton is lost.

There does not seem to be hydrogen abstraction involved in this reaction , as the amount of hydroxy fluorene in isopropanol is reduced to almost one third of what is obtained in methanol. Secondly fluorenene oxime is not an intermediate in this reaction, as under the photolytic conditions, it is found to be completely inery indicating thereby that proximate cyclization is probably not the first step in this sequence of reactions. Further work on mechanism using deuterated systems is in progress.

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