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PHOTOCHEMICAL GENERATION AND DECOMPOSITION OF DIBENZOYLANILINE

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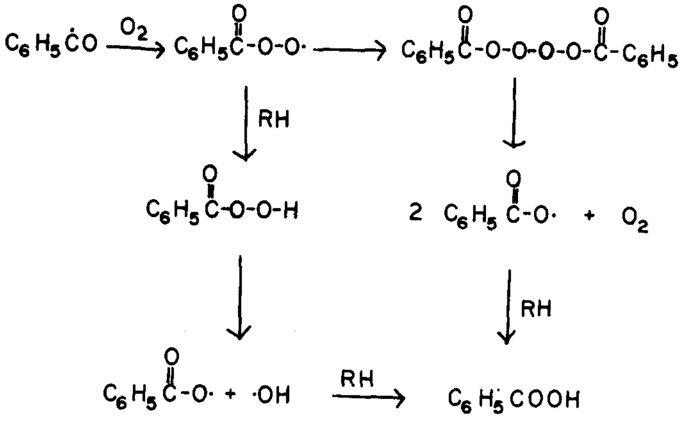
In our studies of the photochemistry of the nitrogen analogs of α,β-unsaturated ketones, we had occasion to irradiate the monoanil of benzil (I). In the presence of benzophenone, an ethereal solution of I, upon irradiation under nitrogen with a water-cooled Hanovia lamp (450 watt) equipped with a Pyrex filter, was found to yield mainly N,N-dibenzoylaniline (II) and benzanilide (III). The latter was found to be the product of secondary photochemical processes, and its formation occurred at the expense of II with increasing periods of irradiation time.

Further investigation of the life time of II in the reaction mixture showed that irradiation in anhydrous ether led to its complete disappearance within 24 hours, while a longer time was required in absolute ethanol or dioxane. Irradiation of II in the absence of sensitizers led to the formation of benzanilide (III), benzoic acid (IV), 2-benzamidobenzophenone (V), 2-aminobenzophenone (VI), 4-aminobenzophenone (VII), and benzamide (VIII).

To determine the origin of these various products, the mixture resulting from the photolysis of II was studied as a function of time, and each of the products was irradiated individually. In this manner it was established that IV, V, and VIII are unreactive under the conditions of the experiment. (The photochemistry of VII has been well established by other investigators,[1] and in view of the small amounts of VI and VII produced, their reaction is of little importance here.) Benzanilide (III), however, yields IV, VI, VII, and VIII. The time studies further showed that formation of these products, except for benzoic acid which forms independently, is a function only of the amount of III being generated.

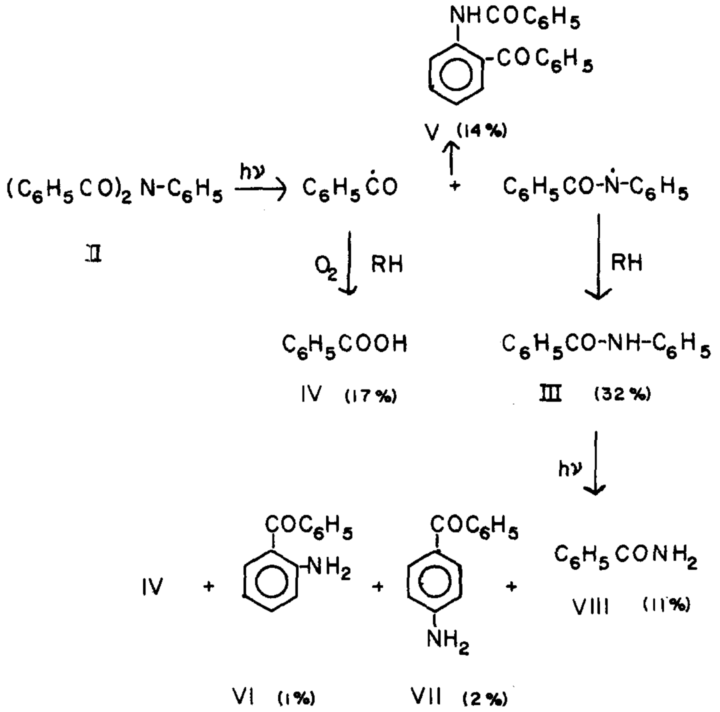
It is interesting that the photolysis conducted in absolute ethanol continues to yield considerable amounts of benzoic acid but no detectable amounts of ethyl benzoate. This fact points to the reaction of benzoyl radicals with oxygen, a process apparently taking place much faster than reaction with the solvent. In support of this conclusion, we have found that irradiation of benzoyl peroxide in absolute ethanol leads to benzoic acid, among other products, but no ethyl benzoate. Further, passing oxygen rather than nitrogen through an ethereal solution during irradiation substantially increases the yield of benzoic acid.

Two possible mechanisms for reaction of the benzoyl radicals follow.



Commercial nitrogen passed through the reaction mixture as a means of agitation can sufficiently account for the presence of the oxygen. Elad and coworkers[2] have already reported the formation of IV, VI, and VII in the photolysis of III. These investigators similarly observed the formation of benzoic acid notwithstanding the use of absolute ethanol as a solvent. Hoffmeister and Tarbell[3] have also reported the formation of benzoic acid, apparently from benzoyl radicals, in benzene.

These results show that the primary photochemical reaction of II consists mainly of the fission of one of the N-CO bonds, leading to III and IV through the abstraction of hydrogen from the solvent and interaction with oxygen, and to V by a radical recombination route. The complete series of reactions is shown below.*



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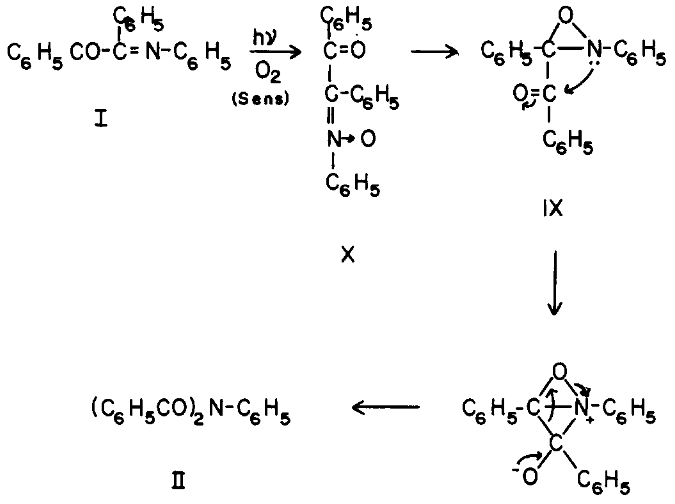
* The yields are based on the amount of the starting material that reacted and were determined by gas-liquid chromatography using an internal standard.

The formation of II from I is unusual, and might be envisaged as consisting of two parts: the formation of 2,3-diphenyl-3-benzoyloxazirane (IX) or N-phenylphenylbenzoylnitrone (X) through a photochemical oxidation, and the subsequent conversion of IX or X into II. The latter reaction has recently been reported by Padwa.[4]



It is becoming apparent that photochemical cleavage and formation of certain amides is a rather facile process, and we are investigating the scope of this process in related materials. The details of the unusual photochemical oxidation of I to II are also being actively investigated in our laboratories.

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