

PHOTOCHEMISTRY OF AMIDES AND IMIDES I
 PHOTO-FRIES REARRANGEMENT OF *N*-ARYL IMIDES

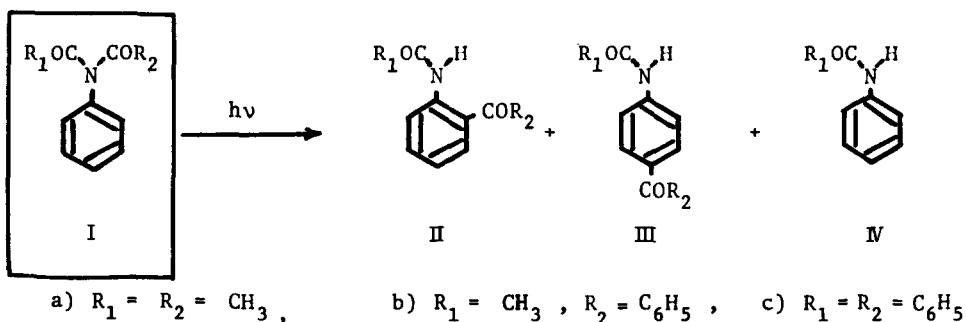
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Practical application of photo-Fries rearrangement of cyclic *N*-aryl imides may provide an effective method for synthesizing various amino-metacyclophanes,¹ which are useful starting materials for the synthesis of other types of metacyclophanes and for catenanes and rotaxanes.

Photochemical reactivity of imide group which holds the key to the above method, however, has not yet been investigated² except for only a few works.³ We wish to report here our preliminary studies on photo-Fries rearrangement of various kinds of *N*-aryl imides.⁴

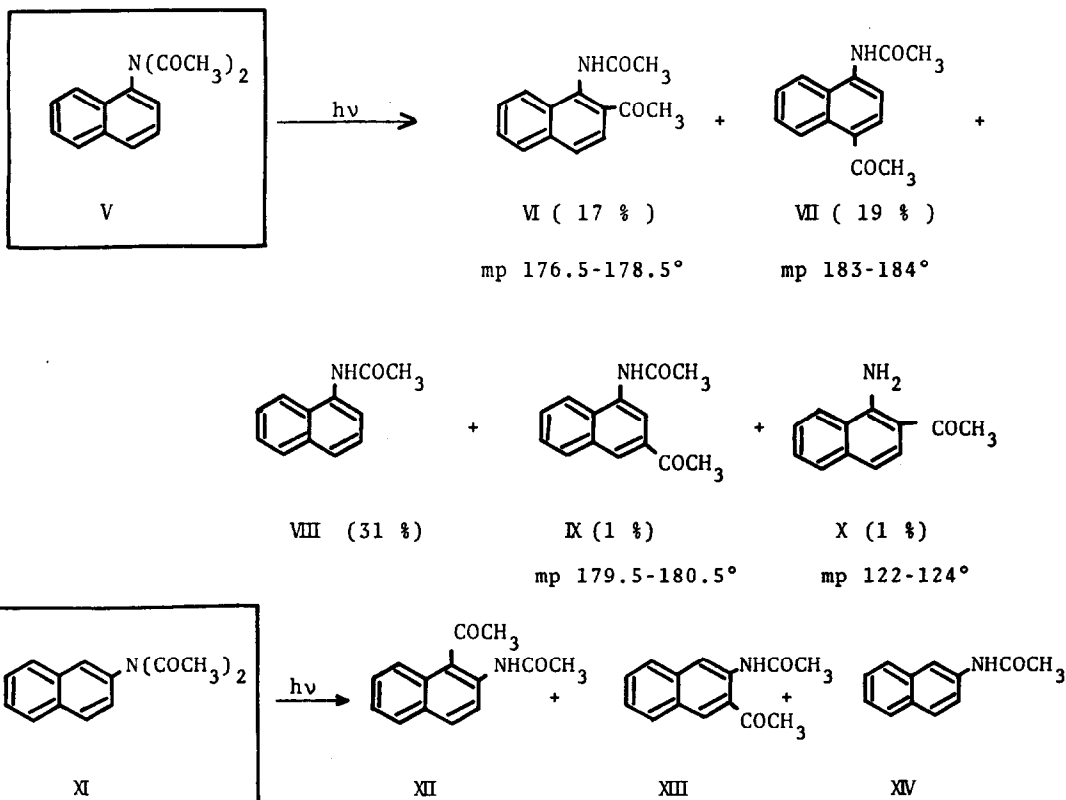
Irradiation of *N,N*-diacetylaniline Ia in a quartz tube for 20 hr, led to the formation of 2-acetaminoacetophenone IIa (30 %), 4-acetaminoacetophenone IIIa (25 %), and acetanilide IVa (45 %).⁵ It is interesting from a synthetic point of view that no secondary photoproducts such as aminoacetophenones and aniline were detected. This is probably because the primary products, IIa and IIIa, would be



excited at the acetophenone moiety rather than at the acetanilide moiety. Another primary product Va, which was found to undergo photo-rearrangement reaction in a moderate quantum yield (*ca.* 0.1),⁶ would have less chance of excitation under the present conditions.

Irradiation of *N*-acetyl-*N*-benzoylaniline Ib through a Pyrex filter gave 2-acetaminobenzophenone IIb (8 %), and 4-acetaminobenzophenone IIIb (16 %) together with Va (54 %), benzanilide Vc (18 %) and benzoic acid (15 %). The above results suggest that predissociation of Ib to benzoyl- and acetanilino groups takes place predominantly over that to acetyl- and benzanilino groups. In contrast, in a quartz tube irradiation of Ib caused only fragmentation to yield Va (57 %), Vc (41 %) and benzoic acid (23 %).

N,N-Dibenzoylaniline Ic,^{7,3a} upon irradiation through a Pyrex filter, yielded 2-benzaminobenzophenone IIc (13 %), 4-benzaminobenzophenone IIIc (17 %) and Vc (29 %), without any formation of secondary photo-products.



Irradiation of *N,N*-diacetyl-1-naphthylamine V through a Pyrex filter for 15 hr gave three major (VI-VIII) and two minor (IX-X) products. We clarified that 2-naphthylamine X was derived from secondary photochemical process of VIII.⁸

Photolysis of *N,N*-diacetyl-2-naphthylamine XI in a similar manner described above yielded 1-acetyl-2-acetaminonaphthalene XII (colorless needles from methanol, mp 119.5-120.5°, 20 %) and 3-acetyl-2-acetaminonaphthalene XIII (pale yellow plates from methanol, mp 189-190°, 2 %) along with 2-acetaminonaphthalene XIV (70 %), the photochemical fragmentation product. No secondary products, such as 1-acetyl-2-naphthylamine, were detected in the present reaction.⁹

From these results, we would like to propose that photo-Fries rearrangement of *N*-aryl imides also proceeds through the formation of radical pairs which follows the predissociation caused by photochemical excitation of the imides, as elucidated in the studies on photo-rearrangement of Na by Shizuka.⁶ For the reason of the formation of fragmentation products in a respectable yield in each case, we presume that the radical pairs XV may be checked from *back* recombination on account of poor electron density on N-atom with an acetyl group, in contrast with the case of the photo-rearrangement of IV.⁶

On the basis of the present data, photo-Fries rearrangement of various cyclic *N*-aryl imides ($n=2,3,8\dots$) is now in progress and will be published shortly.¹⁰

Reaction Scheme

