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

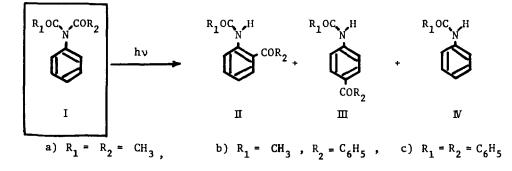
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Practical application of photo-Fries rearrangement of cyclic N-aryl imides may provide an effective method for synthesizing various amino-metacyclophanes,<sup>1</sup> which are useful starting materials for the synthesis of other types of metacyclophanes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

Photochemical reactivity of imide group which holds the key to the above method, however, has not yet been investigated<sup>2</sup> except for only a few works.<sup>3</sup> We wish to report here our preliminary studies on photo-Fries rearrangement of various kinds of N-aryl imides.<sup>4</sup>

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 Na (45 %).<sup>5</sup> 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

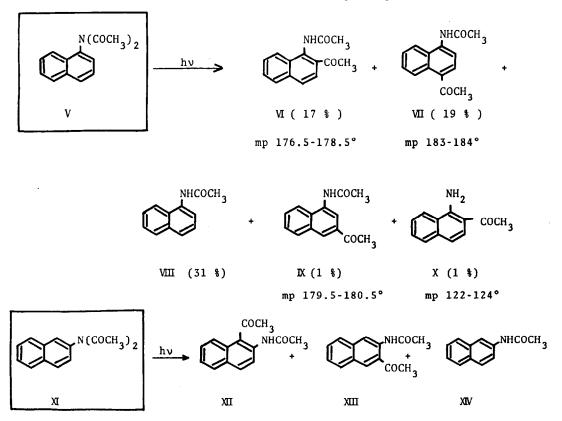


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excited at the acetophenone moiety rather than at the acetanilide moiety. Another primary product Na, which was found to undergo photo-rearrangement reaction in a moderate quantumn yield (ca. 0.1),<sup>6</sup> would have less chance of excitation under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

Irradiation of N-acetyl-N-benzoylaniline Ib through a Pyrex filter gave 2acetaminobenzophenone IIb (8 %), and 4-acetaminobenzophenone IIIb (16 %) together with Na (54 %), benzanilide Nc (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 Na (57 %), Nc (41 %) and benzoic acid (23 %).

N,N-Dibenzoylaniline Ic,<sup>7,3a</sup> upon irradiation through a Pyrex filter, yielded 2-benzaminobenzophenone IIc (13 %), 4-benzaminobenzophenone IIIc(17 %) and Nc (29 %), without any formation of secondary photo-products.



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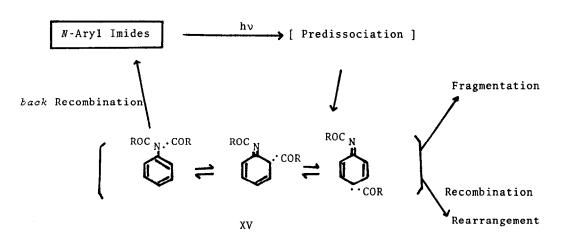
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Irradiation of N,N-diacetyl-1-naphthylamine V through a Pyrex filter for 15 hr gave three major (VI-VIII) and two minor (IX-X) products. We clarified that 2-naphthylamine X was derived from secondary photochemical process of VIII.<sup>8</sup>

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 XII (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.<sup>9</sup>

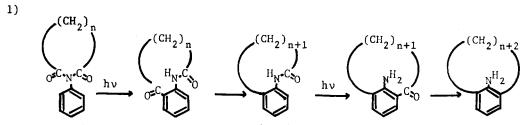
From these results, we would like to propose that photo-Fries rearrangement of *N*-aryl imides also proceeds through the formation of radical pairs which follows the predissociation caused by photochemical excitation of the imides, as elucidated in the studies on photo-rearrangement of Na by Shizuka.<sup>6</sup> 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 N.<sup>6</sup>

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

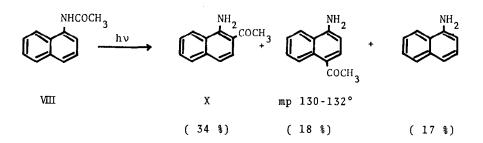


Reaction Scheme

## **REFERENCES AND NOTES**



- 2) Y.Kanaoka et al., personal communication; Chem. Pharm. Bull. 21, 453 (1973).
- 3) (a) R.O.Kan and R.L.Furey, *Tetrahedron Lett.*, 2573 (1966). (b) Y.Kanaoka and K.Koyama, *ibid.*, 4517 (1972). (c) Y.Kanaoka, Y.Migita, Y.Sato and H.Nakai, *ibid.*, 51 (1973).
- 4) Photolyses of N-aryl imides were carried out in acetonitrile solutions with a 500 W high pressure mercury arc under a nitrogen atmosphere. For all new compounds described in the present letter, satisfactory analytical and spectral data were given.
- 5) Yields are based on the reacted starting imides.
- H.Shizuka and I.Tanaka, Bull. Chem. Soc. Japan, <u>41</u>, 2343 (1968). H.Shizuka, ibid., <u>42</u>, 52 (1969); <u>42</u> 57 (1969).
- 7) In their paper,<sup>3a</sup> Kan and Furey didn't describe the formation of MC which was one of the main products in the present work.
- 8) Irradiation of VIII in an acetonitrile solution through a Pyrex filter for 10 hr gave X along with the other products as shown below.



- 9) Amide XIV was found to be almost photochemically inert. Photolysis of XW, under the same conditions described in ref. 6, led to the formation of small amounts of 1-acety1-2-naphthylamine and polymeric substance.
- 10) Succinanil which is one of cyclic N-aryl imides (n=2), upon direct irradiation, didn't convert at all. A rapid back reaction would take place because of its small ring size, and as a result, succinanil appeared to be photochemically inert.