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Photoreactions of Benzoylaminopyridines[1,2]

Photoreactions of anilides have been known and studied for some time.[1,3-5] Photo-Fries type reactions of heterocycles have been rather ignored as a synthetic process except that recent examples of pyridine esters are known.[6] As substrates of such a synthetic photochemical study in heterocyclic series, our attention turned first to the amide derivatives; *i.e.*, N-benzoyl derivatives of aminopyridines.

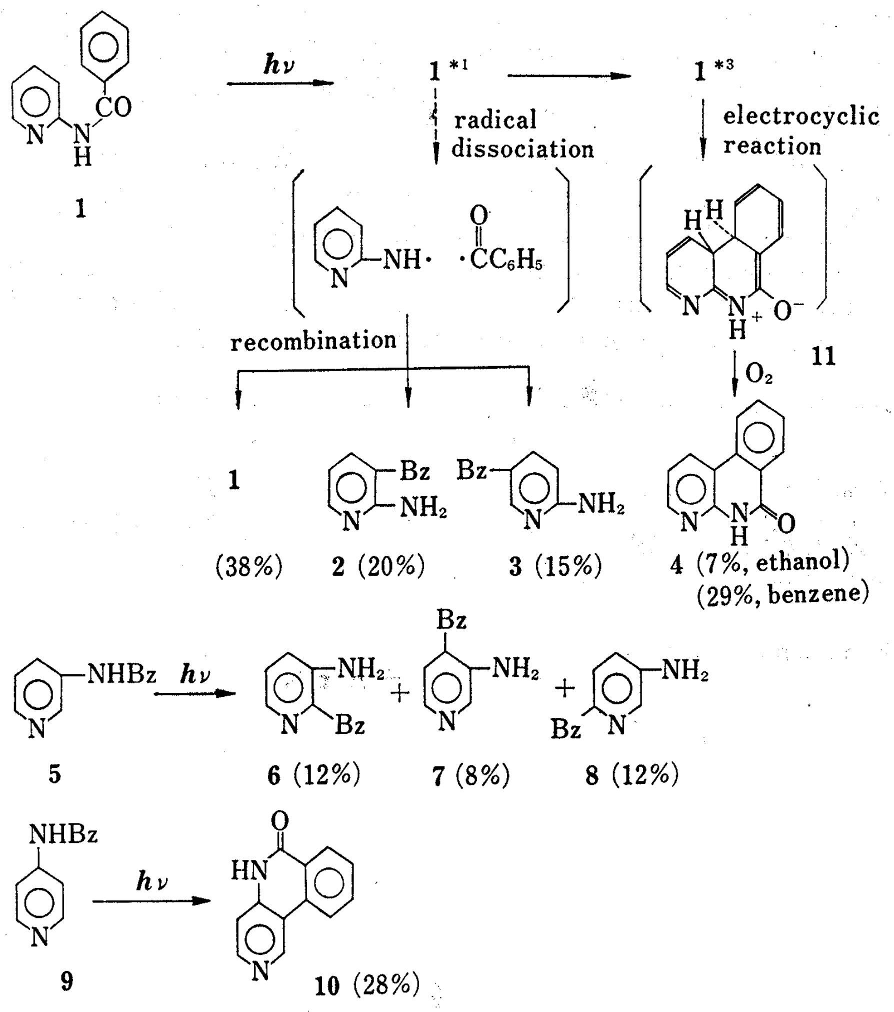

Chart 1[7]

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[1] Photochemistry of the Amide System. IV. Part III: Y. Kanaoka and K. Itoh, *Chem. Comm.*, **1973**, 647.

[2] Photoinduced Reactions. XIV. For Part XIII see ref. 1).

[3] *a*) V.I. Stenberg, "Organic Photochemistry," Vol. 1, ed. by O.L. Chapman, Dekker, New York, 1967, p. 127; *b*) D. Bellus, *Adv. Photochem.*, **8**, 109 (1971); *c*) H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan*, **41**, 2342 (1968); H. Shizuka, *ibid.*, **42**, 52 (1969); *idem*, *ibid.*, **42**, 57 (1969).

[4] Y. Kanaoka and K. Itoh, *Synthesis*, **1972**, 36.

[5] *a*) B.S. Thyagarajan, N. Kharasch, H.B. Lewis, and W. Wolf, *Chem. Comm.*, **1967**, 615; *b*) E. Winterfeldt and H.J. Altmann, *Ang. Chem. Inter. Edn.*, **7**, 466 (1968).

[6] *a*) M.T. LeGoff and R. Beugelmans, *Tetrahedron Letters*, **1970**, 1355; *b*) *Idem*, *Bull. Chim. Soc. France*, **1972**, 1106; *c*) *Idem*, *ibid.*, **1972**, 1115.

[7] Isolation yields (%) are shown in parenthesis. No corrections were made based on the recovered substrate. Bz=benzoyl.

Irradiation of **1**[8] (2.5 mM in ethanol, 10 W × 3 low-pressure mercury lamps, 48 hr) afforded the rearranged products (**2** (mp 144.5—147°), **3** (mp 136—138.5°)), accompanied by a quinolone **4** (mp 275—276°), an oxidatively cyclized product, in which we have recently been interested (Chart 1).[1,4,5] This result may represent the first example of the photo-Fries type reaction of a heterocyclic anilide system. Further, irradiation in ethanol with 250 (±7.5) nm light favored the rearrangement, while with 303 (±7.5) nm in the same solvent the cyclization mainly occurred indicating clear wavelength dependency of these competing reactions. In a preparative experiment **1** was irradiated in benzene (5 mM) with a 100 W high-pressure mercury lamp for 10 hr to give **4** as a sole product. Since photolysis of **1** in degassed ethanol failed to give **4**, the latter probably arises from oxidation of a cyclic intermediate **11**[1] by dissolved oxygen. In contrast to that the formation of **2** and **3** is rather unaffected by adding isoprene (up to 0.1 M), that of **4** is substantially quenched. The above results may be tentatively explained by the mechanism shown in Chart 1. Thus the dual photochemical behavior of **1** may lead, by manipulating the reaction conditions, to the simple synthetic approach either for aminopyridyl ketones or quinolones as required.

By contrast, similar photolysis (5 mM in ethanol, 10 W × 3 low pressure mercury lamps, 12—24 hr) of **5** gave only the rearranged ketones (**6** (mp 97—99°), **7** (mp 125—126°), **8** (N-acetyl derivative, mp 145—146°)), while only **10** (mp 303—304.5°) was obtained from **9**. Such a pronounced structure-dependency of the photochemical reactivities of these heterocyclic anilides, which are readily accessible by combining a variety of acids and amines of heterocyclic series, warrant further synthetic and theoretical investigation.

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[8] All new compounds gave satisfactory analyses, and their structures were supported by spectral (ultraviolet (UV), infrared (IR), nuclear magnetic resonance (NMR), mass) data.