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Photorearrangement of N,N-Diacetyl Derivatives of Aniline and Naphthylamines[1)]

Upon irradiation N-arylamides have been found to undergo "photo-anilide rearrangement,"[2)] analogous to the photo-Fries rearrangement of aryl esters.[2)] In extension of our studies on the photochemistry of amides,[3)] photochemical behaviors of various imide systems are being explored.[1)] A variety of synthetic applications are expected for the photolysis of amides,[3,4,5a)] whereas little has been known about that of diacylamines.[5b)] To our knowledge the only work on the latter[6)] has been reported by Kan and Furey,[7)] in which the photolysis of N,N-dibenzoylaniline was noted. This communication outlines photolysis of diacetyl derivatives of some typical aromatic amines in comparison with that of their monoacetyl derivatives.

Irradiation of **1** (3 mmole) in ethanol (1 l; 3 mM) with low pressure mercury lamps (10W × 4) for 5 hr gave **2** (26%), **3** (11%), **4** (3%), **5** (5%), and **1** (recovered, 20%).[8)] Under similar conditions analogous distribution of the rearranged products was obtained from **5**.[9)] Relative photolytic rate of **1** was estimated to be larger than that of **5** as monitored by disappearance of **1** and **5** in the course of the reaction. It is worth noting that no products were obtained in which the second acetyl group is incorporated to the aromatic ring. **4** was shown to be the secondary product from initially formed **2** by a control experiment.

The photolysis of acetyl derivatives of α-naphthylamine was next examined. In a typical run, irradiation of **6** (2 mmole) in ethanol (200 ml; 10mM) with a 100 W high pressure mercury lamp for 8 hr gave **7** (mp 125.5—127°; 12%), **8** (acetyl derivative=**12**; 3%), **9** and **6** (recovered, 57%).[8)] Under similar conditions, after the irradiation period of 5 hr, **10** (2 mmole; 10 mM in ethanol) afforded **11** (mp 184—185°; 37%), **12** (mp 187.5—188°; 20%), **7** (2.5%), **6** (14%), and **10** (recovered, 4%).[8)] Again with the diacetyl compound the reaction proceeded more rapidly and efficiently.

By contrast, irradiation of acetyl-β-naphthylamine **13** gave only β-naphthylamine **14**, a photolyzed product, as well as recovered **13**, whereby none of the rearranged products were isolated. The photolysis of N,N-diacetyl-β-naphthylamine **15** afforded largely **13** and **14** accompanied by small amount of a keto compound. This marked difference between α- and β-naphthylamine derivatives indicates the existence of strong structure-reactivity relationship in this photochemical rearrangement.

The mechanism of the photo-process has not yet been well clear. However, as elucidated in the case of acetanilide by Shizuka, *et al.*,[10)] predissociation of an acetyl radical from the

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[1)] Photoinduced Reactions. VIII. For Part VII: Y. Kanaoka and K. Koyama, *Tetrahedron Letters*, **1972**, 4517.

[2)] D. Bellus, "Advances in Photochemistry" Vol. 8, ed. by J.N. Pitts, Jr., G.S. Hammond and W.A. Noyes, Jr., Wiley-Interscience, New York, 1971, p. 109.

[3)] Y. Kanaoka and K. Itoh, *Synthesis*, **1972**, 36; "Symposium on Heterocyclic Chemistry," November, 1972, Gifu; Abstracts of papers, p. 85.

[4)] For recent examples, see: M. Fischer, *Tetrahedron Letters*, **1969**, 2881; I. Ninomiya, T. Naito and T. Kiguchi, *ibid.*, **1970**, 4451; D. Elad and G. Friedman, *J. Chem. Soc.* (*C*), **1970**, 893.

[5)] *a*) I. Rosenthal, "The Chemistry of Amides," ed. by J. Zabicky, Wiley Interscience, New York, 1970, p. 289; *b*) O.W. Wheeler and O. Rosado, *ibid.*, p. 335.

[6)] Independent to the present study, a similar work has just appeared; Y. Fujiwara, H. Maruyama, Y. Shigemitsu, and I. Odaira, "Symposium on Photochemistry," November, 1972, Osaka; Abstracts of papers, p. 153.

[7)] R.O. Kan and R.L. Furey, *Tetrahedron Letters*, **1966**, 2573.

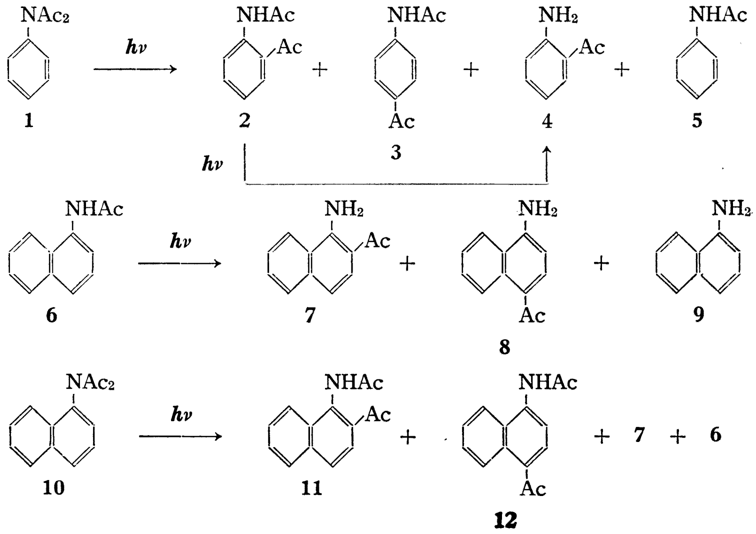
[8)] These products were identified by their elemental analysis and spectral properties (UV, IR, NMR, Mass), or by direct comparison with authentic samples. % shown is isolation yield.

[9)] D. Elad, D.B. Rao and V.I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).

[10)] H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan*, **41**, 2343 (1968); H. Shizuka, *ibid.*, **42**, 52 (1969); *idem*, *ibid.*, **42**, 57 (1969).

diacetylamine followed by its recombination in a solvent cage to *o*- and *p*-rearranged products may be tentatively assumed for this reaction.

In conclusion, the above results indicate that diacetyl (and probably diacyl) derivatives of aromatic amines may generally be more reactive and therefore better substrates than corresponding mono derivatives in the photo-anilide rearrangement, and their photolysis may open a new possible route for the synthesis of certain amino aromatic ketones which are otherwise uneasy to approach. Since the rearrangement competes with oxidative photocyclization when an acyl group is aroyl,[3] the synthetic aspects of the reaction may at present be limited to aliphatic acyl derivatives. The details will be reported in a subsequent publication.



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