Photochemical Cyclisation of Benzanilides

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THE cyclisation of stilbene derivatives under ultraviolet irradiation[1] has stimulated a valuable series of publications describing similar syntheses. Azobenzene,[2] stilbazoles,[2] Schiff bases,[3] 2-styrylthiophen,[4] and 1-styrylpyridinium cation[5] have been successfully subjected to photochemical cyclisations. The common feature of all the systems listed above is the presence of a *formal double bond* between the atoms (C=C, C=N, N=N) linking the two aromatic ring systems involved.

Here we report the first instance of a photochemical cyclisation† of an amide, benzanilide to yield phenanthridone, where an NH–CO function replaces the doubly linked atoms. This inquiry has an important bearing on a concurrent study by us into the stereochemistry of an α-sulphonyl carbanion.‡

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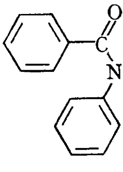
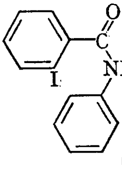
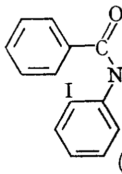
† Irradiations were made with a (W-K)^2-low-pressure, cold cathode mercury arc; *cf.* Brochure 900, Nuclear Supplies, P.O. Box 312, Encino, California.

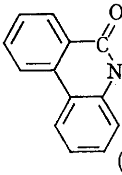
‡ We are currently investigating the photochemical behaviour of benzenesulphonanilide, with the possibility of obtaining biphenylenesultam, in order to determine the stereochemistry of α-sulphonyl carbanion system.

Irradiation of benzene solutions of benzanilide (I), the anilide (II) of *o*-iodobenzoic acid, and the benzoyl derivative (III) of *o*-iodoaniline gave phenanthridone, (IV), albeit in varying yields.


(I)


(II)


(III)


(IV)

The Table presents the optimal results obtained, selected from several similar runs, in which the periods of irradiation and the amounts of catalysts were varied. From runs 1 and 2 it is seen that iodine is essential for the ring closure (I) → (IV).

An analysis of the results in the Table reveals the following features:

(i) Benzanilide, in the presence of external iodine, cyclises to phenanthridone, affording even greater yields than (II), which carries an iodine in the molecule.

(ii) The anilide of *o*-iodobenzoic acid (II) not only yields less phenanthridone, but also less phenylated product than the benzoyl derivative of *o*-iodoaniline.

(iii) As distinct from other investigations,[6] intramolecular cyclization and homolysis of an aryl C–I bond appear to proceed *simultaneously and independently*. This is emphasized by the photochemical results obtained with (II) and (III).

(iv) In benzene solution, during the photolysis of *o*-iodobenzanilide, hydrogen transfer occurs competitively with phenylation and cyclisation, yielding benzanilide.

A complete study of the mechanistic details of the photolysis of (I), (II), and (III) and the related sulphonyl system will be presented later. The study, being the first in the photochemical cyclisations of anilides, offers scope for possible photochemical modifications in related amide systems.

TABLE

Reactant	Molar concentration	Time	Products[a,b]
(I)	0·03 Molar, in benzene; 0·5 mole I_2 added	148 hr.	Starting material, 57·1% Phenanthridone, 20% Unknown components, *ca.* 10%
(I)	0·03 Molar, in benzene; No iodine added	92 hr.	Phenanthridone, 0·3% Unknown components, *ca.* 1% Unchanged benzanilide (major component)
(II)	0·03 Molar, in benzene; No iodine added	126 hr.	Starting material, 50·8% Phenanthridone, 9·0% 2-Phenylbenzanilide, 14·9% Benzanilide, 5% Unknown compounds, *ca.* 5%
(III)	0·03 Molar, in benzene; No iodine added	160 hr.	Phenanthridone, 47·7% Benzoyl derivative of 2-phenylaniline, 58·5% Starting material, 0·56%

[a] Analyses were made by v.p.c. methods. Because of the insolubility of phenanthridone, dimethylformamide was a required solvent, on $\frac{1}{8}$ in.—three foot, 2% "Versamid-900" on 100—120 mesh "Gas Chrom-Q" columns.

[b] In these photolyses, a considerable deposit forms on the walls of the reaction tube. It is necessary to remove this repeatedly during the period of reaction, by physical means, aided by dimethylformamide. The deposits contain considerable phenanthridone, which was retrieved and accounted for as product.

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[1] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, 1964, **86**, 3094.
[2] C. E. Loader, M. V. Sargent, and C. J. Timmons, *Chem. Comm.*, 1965, 127; G. E. Lewis, *Tetrahedron Letters*, 1960, No. 9, 12.
[3] M. P. Cava and R. H. Schlesinger, *Tetrahedron Letters*, 1964, 2109.
[4] W. Carruthers and H. N. M. Stewart, *Tetrahedron Letters*, 1965, 301.
[5] R. E. Doolittle and C. K. Bradsher, *J. Org. Chem.*, 1966, **31**, 2616.
[6] S. M. Kupchan and H. C. Wormser, *J. Org. Chem.*, 1965, **30**, 3792.