

PHOTOCATALYSED CYCLIZATION OF BENZALANILINE

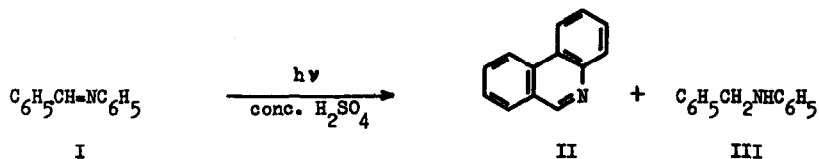
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The formation of dibenzo[c,i]phenanthridine from 1-naphthal-1'-naphthylamine, recently reported¹ as the first example of photooxidative ring closure of an aromatic Schiff base to a phenanthridine, prompts us to record that benzalaniline (I) in solution in concentrated sulphuric acid is photochemically converted to a mixture of phenanthridine (II) and benzylaniline (III).



A solution of benzalaniline (76 mg.) in 98% "Analar" sulphuric acid (100 ml.) was irradiated for 72 hr with a Philips 125 W mercury-quartz lamp in a water-cooled Pyrex photochemical reactor.² Solutions in sulphuric acid-water mixtures could not be employed due to rapid hydrolysis of the Schiff base. The mixture, after dilution with ice and neutralization with sodium hydroxide, was extracted with benzene. Evaporation of the solvent yielded a brown-yellow gum (58 mg.) which was redissolved in benzene and chromatographed on a column of silica. Elution with a mixture of ether (10% v/v) and benzene caused benzylaniline to separate as the first band

(yellow fluorescence) from the more strongly adsorbed phenanthridine (blue-yellow fluorescence). The residue remaining after evaporation of the first chromatographic fraction was identified as benzylaniline by its conversion with phenylisothiocyanate to *N*-benzyl-*N,N'*-diphenylthiocarbamide (23 mg.) m.p. 107°; this was identical (mixed melting point and infrared spectrum) with the thiocarbamide prepared from an authentic sample of benzylaniline. Likewise the residue (29 mg.) m.p. 103° from the second fraction was identified as phenanthridine by comparison with an authentic sample.³

The quantum efficiency of the photochemical reaction of benzylaniline under these conditions is markedly lower than that of azobenzene in 22 N sulphuric acid² but the two reactions are otherwise comparable.

In view of the fact that no phenanthridine is formed when benzylaniline is irradiated in hexane⁴ and that formation of benzylaniline accompanies the cyclization of benzylaniline in concentrated sulphuric acid, this Schiff base appears to be more closely related in photochemical behaviour to azobenzene and its derivatives^{2,5} than to the stilbenes.⁶ Azo compounds when irradiated under strongly acidic conditions give rise to benzidine-rearrangement products in addition to benzo[*c*]cinnolines^{2,5} but the conversion of stilbene to phenanthrene appears not to be accompanied by formation of bibenzyl.⁷ On the other hand, the presence of dissolved oxygen was shown to be necessary for the photocatalysed cyclization of 1-naphthal-1'-naphthylamine in benzene.¹ Disproportionation in this case does not therefore play an apparently significant role.

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7. According to Stegemeyer (loc. cit., 1962) no bibenzyl can be detected spectroscopically, but see also R. Srinivasan and J.C. Powers, J.Chem. Phys., 39, 580 (1963).