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TWO-WAYS PHOTOCYCLIZATION OF 3-STYRYLPYRIDINE

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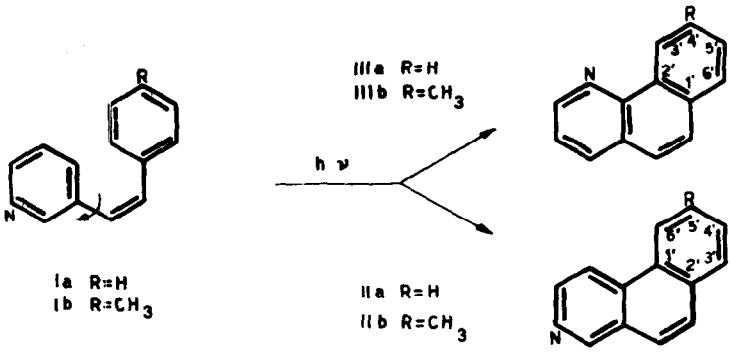
In a previous communication [1], we have exposed some results obtained in our investigations on the photocyclization of styrylpyridines, with particular reference to the behaviour of 3 CH_3, 2-styrylpyridine, which gives the corresponding benzoquinoline though having a substituted reactive position.

In the progress of this study a careful investigation of the behaviour of 3-styrylpyridine (Ia) has been carried out. Such a compound photocyclizes easily, as shown by Loader and coll. [5], and seems to be of particular interest because, contrary to the 2 and 4 isomers, it is structurally susceptible to photocyclize in two ways, giving besides the 5,6-benzoisoquino-

line (IIa) the 7,8-benzoquinoline (IIIa). The latter photoproduct, however, has no previously been identified.



The cis 3-styrylpyridine was irradiated in n-hexane, using the same experimental arrangement as described previously [1]. The oxygen saturated solutions were photolyzed by a duration of $\sim$ 150 h and the photoproducts separated by an alumina column.

The thin layer chromatographic analyses revealed, besides the 5,6-benzoisoquinoline (hR_f=52), a fluorescent compound with hR_f=70. The eluent used was n Butanol-acetic acid-water (80:20: :20) ml.

Repeated purifications and examination of the U.V. spectra have shown unequivocally the latter photoproduct to be the 7,8- -benzoquinoline. The n-hexane U.V. spectra of the compounds

obtained are shown in fig. 1.

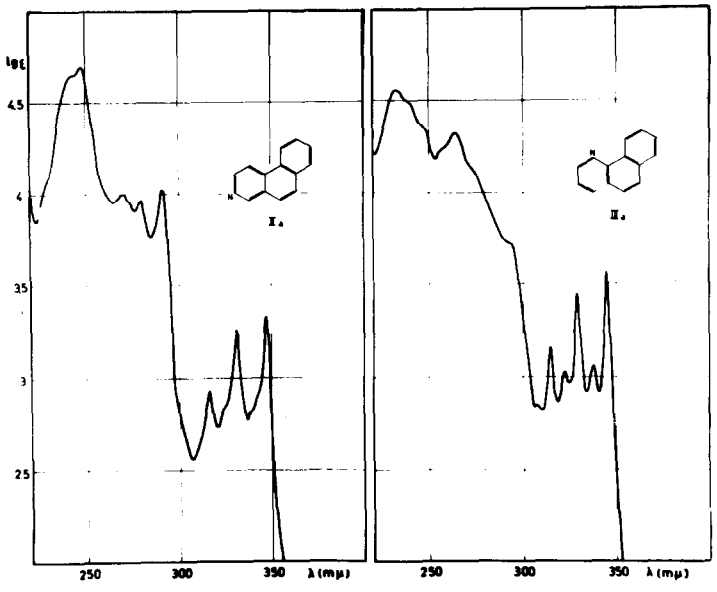


Fig. 1

The ratio of the two benzoquinolines was found to be approximately 4/1 in favour of the 5,6-benzoisoquinoline. 4'-CH_3 3-styrylpyridine (Ib) behaves in a quite similar way giving the correspondings 2'-CH_3, 5,6-benzoisoquinoline (IIb; hR_f=51) and 4'-CH_3, 7,8-benzoquinoline (IIIb; hR_f=69) see fig. 2. The occurence of simultaneous photocyclizations has been found also in the case of styrylthiophenes [3] and substituted

stilbenes [4].

The possibility of obtaining isomeric photoproducts in the photocyclization appears to be of importance in relation to the study of the relative reactivity in non-conformationally equivalent positions.

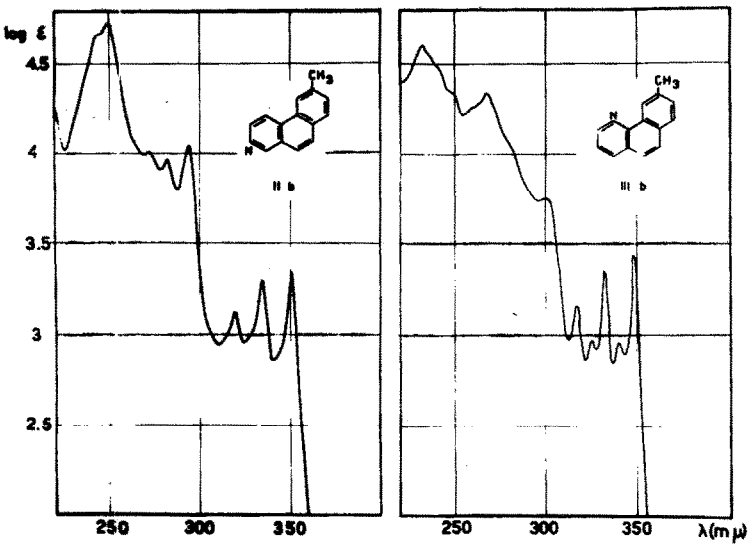


Fig. 2

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