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PHOTOCYCLIZATION OF STYRYLPYRIDINES SUBSTITUTED IN THE REACTIVE POSITION

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It is well known that stilbene photocyclizes under U.V. irradiation giving phenanthrene; the reaction mechanism has been the object of many investigations expecially after the last few years (1÷7).

It seems established that the cis isomer of stilbene in its first excited singlet state is responsible for the photocyclization and that in solution the process occurs via the formation of dihydrophenanthrene, which, in the presence of a suitable oxidizers (O_2, I_2), goes through a dark reaction to phenanthrene as the final product.

In relation to photochemical and kinetic studies on the geometrical isomers of styrylpyridines (9), we began similar investigations on the cyclization of 2, 3 and 4-styrylpyridines in order to clarify the behaviour of stilbene-like molecules, in which the presence of heterocyclic nitrogen in different positions can affect the cyclization process. It should be noted that the only available literature information (6-7) was that these compounds did not photocyclize.

In the meantime a communication by Loader et al. (8) reported, contrary to Mallory and his co-workers (6, 7), that 2, 3 and 4-styrylpyridines all photocyclize in cyclohexane giving the corresponding benzoquinolines. As in the stilbene case, the cyclization is accompained by the cis-trans photoisomerization.

With the aim of further elucidate the conditions of the cyclization process, we have continued our study extending it to the four cis-styrylpyridines methyl-substituted in the pyridine ring (3-, 4-, 5-, and 6-CH_3,2-styryl-pyridines).

The compounds were irradiated with an Hanovia, low pressure, mercury lamp, the solution being sufficiently diluted ($\sim 10^{-3}$ M) for the photodimerization process to be practically negligible. The reaction was followed spectrophotometrically.

We have observed in this way that 2, 3 and 4-styrylpyridines photocyclize with good yields to the corresponding benzoquinolines (in agreement with Loader findings) as also do the four isomeric methyl-derivatives.

The behaviour of 3-CH_3,2-styryl-pyridine is of particular interest. This compound has no reactive hydrogen in ortho position with respect to the styryl group; nevertheless, under UV irradiation, it behaves quite similarly to 2-styrylpyridine and to the other methyl-derivatives examined, indicating the phenanthrenic cyclization to be operative in this case too.

The nature of the photoproduct, after purification by alumina chromatography, has been examined very carefully in this case.

The results so obtained show that 1) the photoproduct is the same as obtained from the unsubstituted 2-styrylpyridine; 2) the U.V. and I.R. spectra, melting point, elementar analysis and thin layer chromatographic R_f value are identical to 5,6 benzoquinoline.

Similar results are obtained with 3,6-dimethyl,2-styryl-pyridine. The principal product of irradiation in this case is 2-CH_3, 5,6-benzoquinoline, the same as obtained from 6-methyl,2-styryl-pyridine.

The possibility is then ascertained of obtaining cyclic compounds from styrylpyridines having a substituted reactive position.

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