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PHOTOREACTIONS OF AROMATIC COMPOUNDS XII[*]

PHOTOINDUCED HYDROLYSIS OF 3-BROMOPYRIDINE

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Whereas m-nitrobromobenzene is remarkably stable when illuminated in alkaline solution[1], 3-bromopyridine has been found to undergo a smooth reaction. The major product is 3-hydroxypyridine as shown by comparing ultraviolet and infrared absorption and melting point of an authentic sample with that of material isolated.

Irradiation with a low pressure Hg lamp of a 4.76×10^{-4} molar solution of 3-bromopyridine in 0.01 N NaOH containing 2% methanol gives a quantum yield of 0.25 for disappearance of bromopyridine and 0.18 for appearance of hydroxypyridine in the first ten percent conversion, Zero order kinetics are observed. A plot of ultraviolet absorption

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[*] No. XI, A. van Vliet, M.E. Kronenberg and E. Havinga, Tetrahedron Letters, in the press.

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spectra taken at various intervals shows the presence of isosbestic points (fig. 1). No reaction occurs in the dark.

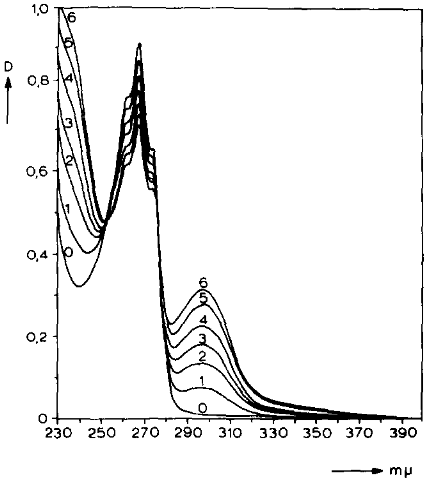

Fig. 1. Photohydrolysis of 3-bromopyridine (3.18×10^{-4} moles l^{-1} in 0.1 N sodium hydroxide) induced by light of 254 mμ. Ultraviolet absorption spectra taken at increasing times of reaction.

The reaction pattern of this photoinduced hydrolysis is complicated as is evident from appearance of 360 mμ absorption and from the sensitivity of the primary product 3-hydroxypyridine to prolonged irradiation. The long wavelength absorption (360 mμ) may be due to dihydropyridines or glutaconaldehyde derivatives and disappears rapidly in the presence of air. Light induced ring opening reactions of pyridines in aqueous base are well known. Actually, Freytag[2] in such studies with bromopyridine derivatives detected bromide ion and postulated formation of hydroxypyridines but did not investigate this further.

In a preparative experiment a mechanically stirred solution containing 1.12 g of redistilled commercial 3-bromopyridine and 5 ml methanol in 2 l of 0.1 N NaOH was irradiated for 16 1/2 hours using a low pressure Hanau NK 6/20 mercury lamp. No precaution was taken to exclude air. The course of the reaction was followed by measuring ultraviolet absorption. The temperature varied between 19 - 28°C. At the end of the irradiation the solution was pale yellow. About one-half of the solvent was removed on a rotating evaporator. The remainder was then extracted several times with ether and acidified with nitric acid to pH 6.8. The aqueous solution was evaporated to dryness on a rotating evaporator and the residue was extracted with dry benzene. The benzene was evaporated to give 150 mg of almost pure 3-hydroxypyridine (ultraviolet and infrared absorption). Recrystallization from benzene gave material with a melting point (124°C; reported[3] 124.5°C) identical to that of an authentic sample. The amount of 3-hydroxypyridine isolated corresponds to 90% of the amount present in solution when the irradiation was stopped. The ultraviolet absorption spectrum of the reaction mixture prior to work-up showed that 0.52 g of the starting material had reacted giving 54% of 3-hydroxypyridine.

3-Chloro- and 3-methoxypyridines slowly decomposed under similar irradiation conditions with little or no observable formation of 3-hydroxypyridine.

An interesting aspect of this work is the difference in the photoreactions of similar nitrobenzenes and pyridines. The quantum yield is high for the photohydrolysis of m-nitroanisole and low for that of 3-methoxypyridine. On the other hand 3-bromopyridine photohydrolyses easily whilst with m-nitro bromobenzene photohydrolysis is almost neglegible.

Another interesting phenomenon is that the addition of sodium bromide slightly increases the quantum yield in the photohydrolysis of 3-bromopyridine but quenches the m-nitroanisole reaction. To date all attempts to demonstrate triplet state intermediates have been unsuccessful.

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1. R.O. de Jongh, unpublished results.
2. H. Freytag, Ber. 69B, 32 (1936).
3. O. Fischer and E. Renovf, Ber. 17, 1896 (1884).