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PHOTOCHEMICAL REDUCTION OF 4-NITROPYRIDINE. PREPARATION OF 4,4'-AZOPYRIDINE*

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It has been studied by several workers that nitrobenzene (1,2), α-nitronaphthalene (3), and 4-nitropyridine 1-oxide (4,5) are photoreduced in the hydrogen-donative alcohols to give the corresponding hydroxyamino compounds. Meanwhile, recently, Kaneko has reported that 4-nitropyridine can not be reduced under the same condition as those used for 4-nitropyridine 1-oxide (6). Therefore, it is very interesting to investigate the correlation between the reactivity of the photochemical reduction and formula of the nitro compounds in the photoexcited states.

In this work, we have studied on the photochemical reductions of 4-nitropyridine in 2-propanol with and without hydrochloric acid.

A mixture of 1.24 g (10^{-2} mole) of 4-nitropyridine and 10 ml of concentrated hydrochloric acid was exactly diluted to 2 l with 2-propanol, and irradiated with an immersion-type 130 W high-pressure mercury vapor lamp for 10 hrs. at room temperature under nitrogen atmosphere. The ultraviolet spectroscopy of the reaction mixture showed that the reaction product had an absorption at 273 mμ, but it had no absorption spectrum in a visible region. The resulting solution was evaporated to half of its volume in vacuo, slightly basified with aqueous sodium hydroxide solution, and then evaporated as far as possible. The brown oily residue obtained was dissolved in water, and extracted with chloroform. After evaporation of chloroform, the residue was purified by column chromatography on silica gel with methanol and recrystallized from water. The redish orange needles obtained

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was identified as 4,4'-azopyridine. M.p. 109-110.5 °C (lit. (7) m.p. 108-109 °C); yield 0.269 g (29%). UV spectrum (in 2-propanol), λ_{max} 283 mμ (log ε = 4.20), 453 mμ (2.32); IR spectrum, ν_{max}^{KBr} 1580, 1560, 1400, 1310, 1215, 985, 830 cm^{-1}.

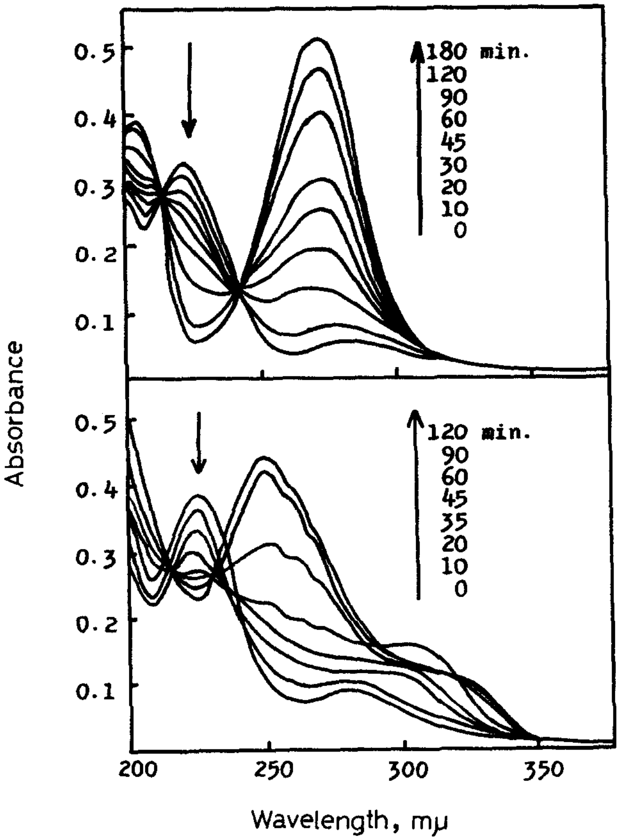

Figure 1. The progressive change of the spectra of 4-nitropyridine on irradiation with a 130 W high-pressure mercury vapor lamp in 2-propanol with and without hydrochloric acid (2 x 10^{-3} mol/l). At room temperature under nitrogen atmosphere.

a. 4 vol% of concentrated hydrochloric acid - 2-propanol solution

b. absolute 2-propanol solution

Numbers refer to irradiation time in minutes.

In a mass spectroscopy, a molecular radical ion M^+ (m/e 184) was presented corresponding to molecular formula $C_{10}H_8N_4$. Found: C, 65.39; H, 4.22; N, 30.16%. Calcd.: C, 65.20; H, 4.38; N, 30.42%.

Figure 1a shows the progressive spectral change during the course of the reaction of 4-nitropyridine in 2-propanol in the presence of hydrochloric acid. The two isosbestic points were observed at 214 and 244 mµ, respectively. The absorption at 273 mµ gradually increased in its intensity with proceeding of the reaction. The ultraviolet spectroscopy directly confirmed that the reaction product (Product A) is not 4,4'-azopyridine. It has been already known that 4-hydroxyaminopyridine 1-oxide is converted by alkali to afford 4,4'-azopyridine 1,1'-dioxide (7). On the other hand, the aromatic nitro compounds are generally photoreduced under the similar condition to give the corresponding hydroxyamino compounds, as described above (1-5). Therefore, it may be reasonable to assume that the "Product A" may be 4-hydroxyaminopyridine hydrochloride, which is subsequently converted by alkali to 4,4'-azopyridine.

Meanwhile, the progressive spectral change during the reaction of 4-nitropyridine in 2-propanol in the absence of hydrochloric acid shows in Figure 1b. In this case, the reaction product had an absorption at 250 mµ, which is different from the case of the reaction in the presence of hydrochloric acid. The product obtained here (m.p.$>$300 °C, brown plates from ethanol) clearly seems not to be 4-hydroxyaminopyridine from the ultraviolet spectroscopy. The further study on the identification of this product is in progress. Further discussion will be reported later in more detail.

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