REACTION OF 2-NITRO-3-FLUOROPYRIDINE WITH HYDRAZINE
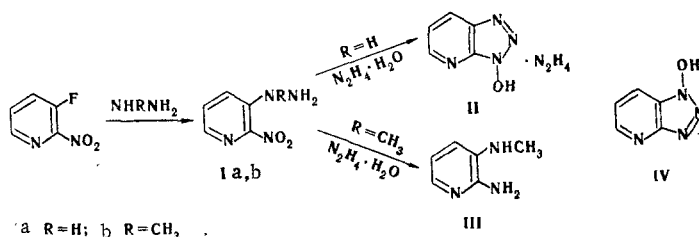
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We have observed that, depending on the conditions, 2-nitro-3-hydrazinopyridine (Ia) or the hydrazinium salt (II) of 3-hydroxytriazolo[4,5-b]pyridine — the aza analog of 1-hydroxybenzotriazole [2] — is obtained in the reaction of 2-nitro-3-fluoropyridine [1] with hydrazine hydrate.

a R=H; b R=CH₃

Hydrazine Ia and salt II (in 15-20% yield) are obtained with a twofold excess of hydrazine in water at no higher than 20°C. Only salt II is obtained when the reaction mixture is heated to 40-50° or when a 15-20-fold excess of hydrazine is present. The 3-hydroxytriazolopyridine base, which was obtained from Ia by the action of hydrazine or other bases (morpholine, sodium carbonate, and NaOH), can be isolated by acidification of an aqueous solution of salt II.

Only 2-nitro-3-hydrazinopyridine (Ib) was obtained by reaction of 2-nitro-3-fluoropyridine with methylhydrazine. Cyclization of Ib to a triazolopyridine is not observed. When 2-nitro-3-methylhydrazinopyridine is heated with a 15-20-fold excess of hydrazine hydrate in water, the $-\overset{|}{N}-N\diagdown$ bond undergoes reductive cleavage to give 2-amino-3-methylaminopyridine (III), identical to the compound described in [3].

This reaction also occurs in the case of 2-chloro-3-nitropyridine, but more severe conditions (refluxing with a 15-20-fold excess of hydrazine hydrate in alcohol for 1 h) are necessary for preparation of the isomeric 1-hydroxytriazolo[4,5-b]pyridine (IV).

The following compounds were prepared [melting points (from water), empirical formulas, λ_{max} (nm) (log ε), and yields (%) given]: Ia, 151-152°, $C_5H_6N_4O_2$, 230 (4.35), 265 (3.73), 413 (3.78), 70-75; Ib, 84-85, $C_6H_8N_4O_2$, 210,(4.08), 250 (3.97), 288 (3.53), 376 (3.09), 65-70; II, 205-206, $C_5H_4N_4O$, 220 (4.10), 280 (3.78), 325 (3.40), 90-95; IV, 209-210, $C_5H_4N_4O$, 220 (4.22), 280 (3.87), 324 (3.50), 75-80.

The results of elementary analysis were in agreement with the calculated values for all of the compounds.

LITERATURE CITED

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2. W. Koenig and R. Geiger, Chem. Ber., 103, 788, 2024 (1970).
3. I. W. Clark—Lewis and M. I. Thompson, J. Chem. Soc., 444 (1957).