NEW INSTANCE OF DIRECT AMINATION IN THE PYRIDINE SERIES

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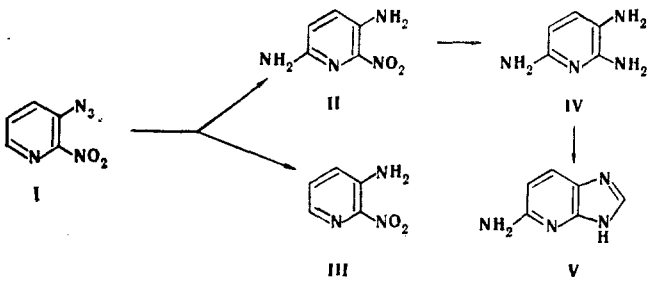
We have established that the direct amination of the pyridine ring is possible when there are acceptor groups in the molecule.

Thus 2-nitro-3,6-diaminopyridine (II), with mp 210-212°C, was obtained as the chief product as needles (from water) in 43% yield when 2-nitro-3-azidopyridine (I) was refluxed for 30 min with ammonium hydroxide. Amination under these conditions is accompanied by reduction of the azide group. 2-Nitro-3-aminopyridine (III) was also identified in the reaction medium by thin-layer chromatography (TLC). It may be assumed that the reduction that accompanies amination is due to the delivery of hydrogen atoms by the intermediate.



The site of incorporation of the amino group in the 6 position in II was proved by its reduction to 2,3,6-triaminopyridine (IV) and cyclization of the latter with formic acid to give 5-aminoimidazo[4,5-b]pyridine, which was identical to the compound described in [1]. Signals of two pyridine protons at 7.45 and 6.95 ppm, which, according to the spin–spin coupling constants correspond to the 4-H and 5-H protons (J = 8.65 Hz), are observed in the PMR spectrum of II.

Let us note that we obtained the starting 2-nitro-3-azidopyridine (I) by the diazo reaction from 14 mmole of 2-nitro-3-aminopyridine in 35 ml of 50% sulfuric acid with a solution of 17 mmole of sodium nitrite in 4 ml of water with the subsequent addition of an aqueous solution of 20 mmole of sodium azide; the product was obtained in 78-80% yield and had mp 40-42°C (needles, from water) and IR bands at 2220 and 2247 cm^{-1} (N_3). Ghosh and Whiterhouse [2] were unable to isolate this compound.

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

LITERATURE CITED

1. B. H. Graboyes and A. R. Day, J. Amer. Chem. Soc., 79, 6426 (1957).
2. P. B. Ghosh and M. W. Whiterhouse, J. Med. Chem., 12, 505 (1969).

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