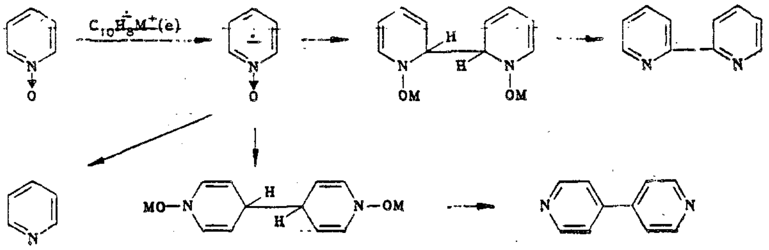
REDUCTIVE DIMERIZATION OF PYRIDINE N-OXIDE

A. S. Kurbatova and Yu. V. Kurbatov

UDC 547.652.1'559.133'821.04:542.953

We have found that the naphthalene anion radical induces reductive dimerization of pyridine N-oxide to give a mixture of 2,2'- and 4,4'-dipyridines. A side reaction which takes place under these conditions is reduction of the N-oxide to pyridine. The nature of the alkali metal employed in this reaction exerts a significant influence on the total yield of dimerization products and on the relative concentrations of the resulting dimeric isomers. The best results were obtained using sodium as the alkali metal. When the reaction was carried out with potassium naphthalenide under analogous conditions, or even at −60°C, a sharp decrease was observed in the yield of dipyridines, due to substantial resinification.



The dimerization reaction apparently occurs via the intermediate participation of an anion radical, in which the electron density is localized predominantly at the 2 and 4 positions [1]. Deoxygenation is apparently the consequence of a two-electron reduction process.

The reaction proposed herein may open up a simple synthesis of dipyridines, which are used as analytical reagents [2] and in the manufacture of herbicides [3].

To a solution of 0.03 mole sublimed naphthalene in 30 ml absolute THF under an atmosphere of purified dry nitrogen was added 0.03 mole of finely divided metal in THF and the mixture was stirred mechanically until all of the metal had dissolved. The resulting greenish solution of the naphthalenide anion radical was added gradually upon cooling to −20°C to a solution of 0.03 mole pyridine N-oxide in 15 ml THF. The solvent was evaporated and the residue was worked up with 5% hydrochloric acid. The resulting naphthalene precipitate was removed by filtration and washed with hydrochloric acid. The filtrate was extracted with ether to remove all traces of naphthalene, then basified with sodium hydroxide (soda) to pH 8 and extracted with ether. The solvent was evaporated and the residue, a mixture of 2,2'- and 4,4'-dipyridines, was separated according to [4]. Dry HCl gas was bubbled through the ether that had been evaporated. The solvent was again removed and pyridine hydrochloride was obtained. The identity of the metal, and yields of 4,4'-dipyridine, 2,2'-dipyridine, and pyridine are summarized below, %: Na, 32, 9. 6; Li, 17, 12, 22; K, 9, 8, 17.

LITERATURE CITED

1. I. Kubota, K. Nishikida, and H. Miyazaki, J. Am. Chem. Soc., 90, 5080 (1968).
2. L. M. Kul'berg, Synthesis of Organic Reagents [in Russian], Goskhimizdat, Moscow, Leningrad (1947), p. 62.
3. N. N. Mel'nikov. E. G. Novikov, and B. A. Khaskin, Chemistry and Biological Activity of Dipyridines and Their Derivatives [in Russian], Khimiya, Moscow (1975), p. 48.
4. G I. Mikhailov and L. I. Mirzakh, Ref. Zh. Khim., 6L203 (1961).

A. Navoi Samarkand State University, Samarkand 703004. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 133-134, January, 1988. Original article submitted August 7, 1987.