LETTERS TO THE EDITOR

ARYLATION OF THE PYRIDINE RING IN THE REACTION OF 2-(NITROAMINO)PYRIDINE WITH POTASSIUM PHENOXIDE

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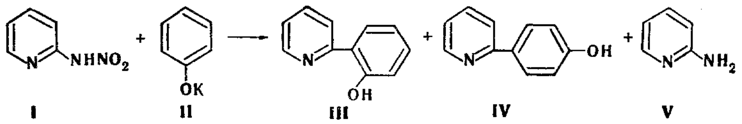
UDC 547.822.7'828

During a study of the reaction of 2-(nitroamino)pyridine (I) with potassium phenoxide (II) we observed a new type of arylation of the pyridine ring. In contrast to the analogous reaction of nitramine I with alkali metal alkoxides, in which the N—N bond undergoes cleavage with simultaneous alkylation and the formation of 2-monoalkylaminopyridines [1], in this case we observed primarily cleavage of the N—C bond, and the pyridine ring was arylated to give a mixture of 2-(o-hydroxyphenyl)- and 2-(p-hydroxyphenyl)pyridines (III, IV). As a side product we obtained up to 18% of 2-aminopyridine (V), which evidently was formed due to thermal cleavage of the HN—NO_2 bond in I. 2-Phenylaminopyridine was not detected in the products by chromatographic mass spectrometry.



This reaction is remotely similar to the known syntheses of unsymmetrical diaryls through diazo compounds and nitrosoacetylamines by the Gomberg—Bachmann—Hey reaction [2] and is evidently realized by a free-radical mechanism. The process was carried out by heating equimolar amounts of reagents I and II in excess phenol at 240-245°C for 7 min. The mixture was acidified, the excess phenol was extracted with chloroform, KOH was added to the aqueous layer to pH 10, and the base was extracted with chloroform. We found that the reaction products contained 65% III (M^+ 171), 35% IV (M^+ 171), and 18% V (M^+ 94) by chromatographic mass spectrometry (with a Varian MAT-112 spectrometer with a column filled with 3% SE-30 on Chromosorb W; the column was 2.1-m long, the temperature was 200°C, the helium flow rate was 20 ml/min, and the emission current was 1.5 A at 70 eV). The compounds had the following retention times: V 1 min, I 5 min, III 7 min, and IV 15 min. By preparative chromatography with a column filled with λ 40/100 silica gel we isolated (by elution with methylene chloride) a mixture (in 60% yield) of hydroxyphenylpyridines III and IV (according to the PMR spectrum the III:IV ratio was 13:7), after which elution with methanol—methylene chloride (1:3) gave aminopyridine V (8%), which was identical to a genuine sample with respect to a mixed-melting-point determination and the IR spectra.

Lowering the reaction temperature to 220°C (20 min) leads to a mixture of 80% I, 9% III, 3% V, and 8% IV (according to data from chromatographic mass spectrometry). The reaction does not take place with sodium phenoxide. Compounds III and IV are also not formed from II and V. Heating phenoxide II with 3- and 4-nitroaminopyridines at 210°C for 10 min to 1 h does not lead to the corresponding arylation products; a further increase in the temperature makes the process uncontrollable.

LITERATURE CITED

1. M. F. Marshalkin and L. N. Yakhontov, Khim. Geterotsikl. Soedin., No. 6, 848 (1981).
2. Organic Reactions [Russian translation], Vol. 2, Inostr. Lit., Moscow (1950), p. 244.v

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0009-3122/82/1802-0212$07.50