TRANSFORMATION OF THE THIENO[2',3':2,3]THIENO[2,3-c]PYRIDINE SYSTEM BY NUCLEOPHILIC ATTACK

A. R. Kirilash, T. V. Stupnikova,
N. A. Klyuev, and S. N. Baranov

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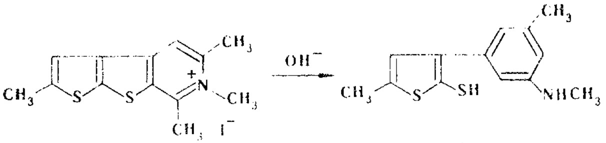
The recently synthesized thieno[2',3':2,3]thieno[2,3-c]pyridine heterocyclic system has remained virtually uninvestigated [1]. The presence of a pyridine ring makes it possible to expect facile reaction of this quaternized system with nucleophilic reagents, particularly isomerizational recyclization of the ring, similar to that for isoquinoline derivatives, of which this compound is a heteroanalog [2].

In fact, when methiodide I is heated with a methanol solution of alkali in a sealed ampul at 120°C, the pyridine ring is opened with subsequent formation of a new benzene ring at one of the side methyl groups. It is interesting that cleavage of the C—S bond in the adjacent thiophene ring is cleaved simultaneously, as a result of which N-methyl-5-(2-methyl-5-mercapto-4-thienyl)-m-toluidine (II) is formed:



I

II

Opening of the thiophene ring occurs as a result of attack by the nucleophile on the sulfur atom, which has free d orbitals, to give an intermediate anion, as described in [3].

Methiodide, I, with mp 224-225°C (from ethanol), was obtained in 95% yield; II, with mp 273-274°C (from ethanol), was obtained in 40% yield; PMR spectrum: 2.4 (s, 3H, thiophene CH_3); 2.6 (s, 3H, benzene CH_3); 3.5 (s, 3H, N—CH_3); 6.84, 7.29, 7.30 ppm (aromatic protons); M^+ 249. The IR spectra were in agreement with the assumed structures. The results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

1. N. N. Alekseev and S. V. Tolkunov, Khim. Geterotsikl. Soedin., No. 10, 1424 (1979).
2. A. N. Kost, V. I. Terenin, L. G. Yudin, and R. S. Sagitullin, Khim. Geterotsikl. Soedin., No. 9, 1272 (1980).
3. S. Gronovits and T. Fried, in: Five-Membered Aromatic Heterocycles [in Russian], Zinatne, Riga (1979), p. 152.

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