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REACTIONS OF POLYHALOGENOPYRIDINES.
10.* PERFLUOROALKYLATION OF BIS(TETRAFLUORO-4-PYRIDYL) DISULFIDE

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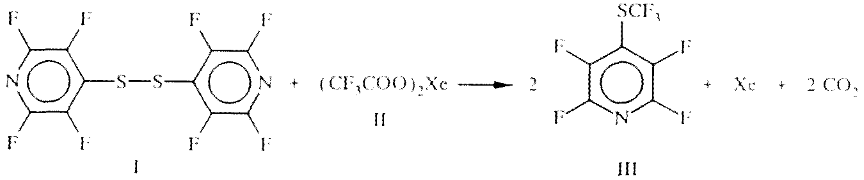
In the previous communication, we described the perfluoroalkylation of 4-mercaptotetrafluoropyridine by xenon bisperfluoroalkylcarboxylates to 4-perfluoroalkylthiotetrafluoropyridines with yields of 25-52%. The process is accompanied by transformation of the initial thiol into bis(tetrafluoro-4-pyridyl) disulfide (I).

In the present work, by varying the conditions for the thermolysis of xenon bistrifluoromethylcarboxylate (II) in the presence of compound (I) we were able to detect its transformation into the required 4-trifluoromethylthiotetrafluoropyridine (III). The highest yield (41%) was obtained with simultaneous generation of the xenonates *in situ* and their thermolysis (method B [2]) at 50-60°C.

It was also determined that the optimum molar ratios of the reagents were: Disulfide (I):XeF_2:CF_3COOH = 1:2:(3-4).



4-Trifluoromethylthio-2,3,5,6-tetrafluoropyridine (III) (C_6F_7NS). To a stirred solution of the disulfide (I) [3] at 50-60°C in a fourfold excess of trifluoroacetic acid, we added in portions two equivalents of xenon difluoride. The end of the reaction was determined by the end of the release of gas. The reaction mixture was cooled, poured into water, neutralized with sodium bicarbonate, and extracted with methylene chloride. The solution was dried with sodium sulfate, evaporated, and chromatographed on a column of silica gel with pentane as eluant or distilled. The yield was 41%; bp 126°C. Published data [1]: bp 126°C.

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REFERENCES

1. A. M. Sipyagin, I. V. Efremov, I. A. Pomytkin, S. A. Kashtanov, and N. N. Aleinikov, Khim. Geterotsikl. Soedin., No. 9, 1291 (1994).
2. A. M. Sipyagin, I. A. Pomytkin, S. V. Pal'tsun, and N. N. Aleinikov, Khim. Geterotsikl. Soedin., No. 1, 58 (1994).
3. R. E. Banks, R. N. Haszeldine, D. R. Karsa, F. E. Rickett, and I. M. Young, J. Chem. Soc. (C), No. 3, 1660 (1969).

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*For Communication 9, see [1].

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