REACTIONS OF POLYHALOPYRIDINES. 9*. PERFLUOROALKYLATION OF 2,3,5,6-TETRAFLUORO-4-MERCAPTOPYRIDINE WITH COMPOUNDS OF XENON CONTAINING FLUORINE

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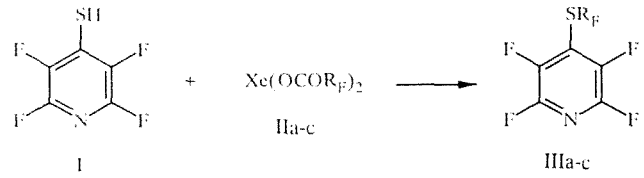
We showed recently that the decomposition of xenon bisperfluoroalkanecarboxylates in the presence of thiols may lead to the perfluoroalkylation of the latter [2]. This method of perfluoroalkylation is preferable for thiols with electron-accepting substituents stable in the presence of such strong oxidizing agents as compounds of xenon (II) and sensitive to the action of nucleophilic reagents.

In the present report we give results of an investigation of the perfluoroalkylation of 2,3,5,6-tetra-fluoro-4-mercapto-pyridine (I) using compounds of xenon containing fluorine. New derivatives of tetrafluoropyridine, viz., 2,3,5,6-tetrafluoro-4-perfluoroalkylthiopyridines (IIIa-c), were obtained in 25-50% yield on carrying out the thermolytic conversion of the xenon bisperfluoroalkanecarboxylates (IIa-c) in the presence of compound (I). The xenon derivatives (IIa-c) were synthesized by the action of xenon difluoride with perfluoroalkanecarboxylic acids either previously (method A) or *in situ* (method B) [2]. Method A is preferred for perfluoromethylation [compound (IIIa)]. Method B provides higher yields for compounds (IIIb, c).



I IIIa-c

II, III a R_F=CF_3, b R_F=C_2F_5, c R_F=C_3F_7

Compounds (IIIa-c) are colorless liquids, stable on storage. The ^{19}F PMR spectra of compounds (III) are characterized by the presence of both two signals for the tetrafluoropyridine fragment at −10 ppm and −53-54 ppm and of signals for the perfluoroalkyl groups. Molecular ions were present in the mass spectra.

2,3,5,6-Tetrafluoro-4-trifluoromethylthiopyridine (IIIa) C_6F_7NS. Yield 25% by method A [2]. Eluent was pentane. bp 126°C. ^{19}F NMR spectrum ($CDCl_3$): −54.05 (2F); −9.72 (2F) (Py); 37.64 (3F) (SCF_3).

2,3,5,6-Tetrafluoro-4-pentafluoromethylthiopyridine (IIIb) C_7F_9NS. Yield 49% by method B [2]. Eluent was pentane. bp 145°C. ^{19}F NMR spectrum ($CDCl_3$): −53.42 (2F); −10.02 (2F) (Py); −12.43 (2F); −6.19 (3F) (SC_2F_5).

2,3,5,6-Tetrafluoro-4-heptafluoropropylthiopyridine (IIIc) $C_8F_{11}NS$. Yield was 52% by method B. Bp 170-171°C. ^{19}F NMR spectrum ($CDCl_3$): −53.28 (2F); −10.01 (2F) (Py); −46.67 (2F); −7.84 (2F); −2.96 (3F) (SC_3F_7).

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