UDC 547.789.67

SYNTHESIS OF 2-METHYLTHIENO[2,3-b]THIENO[2,3-d]THIAZOLE

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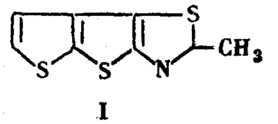
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 4, pp. 619-621, 1965

The synthesis of a new heterocyclic base, 2-methylthieno[2,3-b]thieno[2,3-d]thiazole, is described. It is obtained by oxidizing 2-thioacetylamino[2,3-b]thiophene in alkaline medium with 10% aqueous potassium ferricyanide.

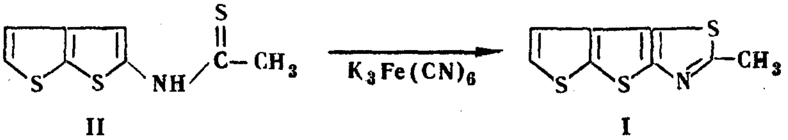
2-Methylthieno[2,3-b]- and 2-methylthieno[3,2-b]thiazoles have previously been synthesized [1, 2].

It has now proved possible to prepare a new heterocyclic base with two condensed thiophene rings, 2-methylthieno-[2,3-b]thieno[2,3-d]thiazole (I).

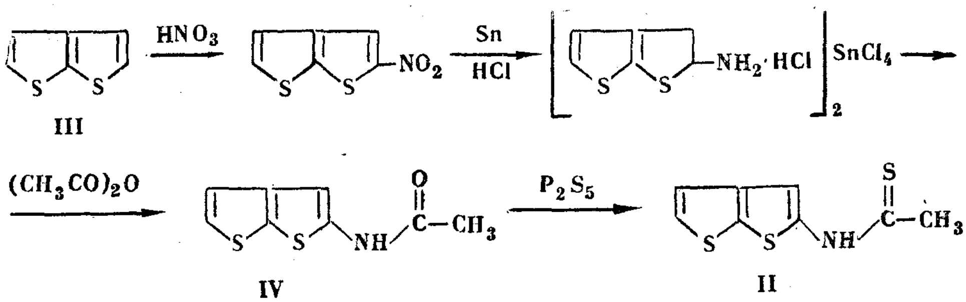


I

I was synthesized by a method [3] involving oxidizing 2-thioacetylaminothieno[2,3-b]thiophene (II) in 2% aqueous sodium hydroxide with 10% aqueous potassium ferricyanide at 1°, the equation being



In its turn II was prepared from thieno[2,3-b]thiophene (III)



The synthesis of III, and the preparation of the double tin salt of 2-aminothieno[2,3-b]thiophene hydrochloride from it, have previously been described [5]. IV was synthesized by reaction of this tin salt with acetic anhydride (yield 55%), and heating IV with phosphorus pentasulfide in dry toluene gave a 31% yield of II. The yield of I (colorless plates, mp 88-89°) was 12%. It readily forms a picrate and methiodide.

Experimental

2-Acetylaminothieno[2,3-b]thiophene (IV). A mixture of 7 g acetic anhydride and 20 ml ether was rapidly added, with stirring, to a suspension of 10 g of the double tin salt of 2-aminothieno[2,3-b]thiophene hydrochloride in 70 ml water at 1°, the temperature at the end of the addition rising to 6°. A solution of 14 g sodium hydroxide in 20 ml water was added, with vigorous stirring, in small portions, the temperature not being allowed to rise above 15°. After completion of the addition, stirring was continued for another 15 min, the whole left at room temperature for 30 min, the ether removed by aspirating air through the mixture, the precipitate filtered off, washed with water, and dried in air. Yield of IV 3.4 g. After recrystallizing from benzene, the yield was 1.7 g (55.7%), colorless plates, mp 226-227°. Found: N 7.13, 7.05%. Calculated for $C_8H_7NOS_2$: N 7.10%.

2-Thioacetylaminothieno[2,3-b]thiophene (VI). A finely-powdered mixture of 10 g IV and 4 g phosphorus pentasulfide was added in small portions, over an hour, to 400 ml vigorously-stirred and boiling dry toluene. Stirring was continued for 2 hr after completion of addition. The toluene was decanted off, and separate small portions of the resinous residue treated with, in all, 500 ml boiling toluene. The toluene solutions were united, cooled, and extracted with 500 ml 4% sodium hydroxide solution (in a few portions). The alkaline solution was energetically stirred and cooled, and dilute (1: 1) hydrochloric acid added until it was acid to congo red. The precipitate was filtered off, washed with water, and dried in air. Yield of II 3. 4 g (31. 4%), mp 161-163°. After recrystallizing from 50% ethanol it formed pale yellow plates, mp 175-176°. Found: N 6. 38, 6. 42%. Calculated for $C_8H_7NS_3$: N 6. 56%.

2-Methylthieno(2, 3-b)thieno(2, 3-d)thiazole (I). 21. 3 g II was dissolved at 45° in 450 ml 2% aqueous sodium hydroxide, the solution energetically stirred, and a solution of 60 g potassium ferricyanide in 540 ml water dropped in at 1°. The mixture was stirred for a further 2 hr, then left overnight. The precipitate was filtered off, the mother liquor extracted with several portions of ether, 3000 ml in all, the ether distilled off, and the residue, plus the precipitate filtered off, were steam distilled. The distillate was extracted with ether, the extract dried over potassium carbonate, and the ether distilled off. On cooling, the residue solidified to a colorless crystalline mass. Yield of I 2. 7 g (12. 6%), mp 79-81°. After recrystallizing from petroleum ether it formed colorless plates, mp 88-89°. Found: N 6. 52, 6. 61%. Calculated for $C_8H_7NS_3$: N 6. 56%. Picrate: yellowish plates mp 146-147° (from ethanol). Found: N 12. 54, 12. 60%. Calculated for $C_8H_5NS_3 \cdot C_6H_3N_3O_7$: N 12. 66%. Methiodide: pale yellow plates mp 217-218° (from ethanol). Found: N 3. 67, 3. 70%. Calculated for $C_{10}H_{10}JNS_3$: N 3. 79%.

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2 February 1965

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UDC 547.825

PYRIDYLETHYLATION OF SOME HETEROCYCLIC THIOAMIDES AND POTENTIAL MERCAPTANS

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 4, pp. 621-624, 1965

2-Pyridylethylation of benzazothiones-2 which are potential mercapto compounds (benzothiazolethione-2, benzoxazolethione-2, 1-methylbenzoimidazolethione-2, benzoimidazolethione-2, 5, 6-dimethylbenzoimidazolethione-2), is described, as well as preparation of 5, 6-dimethylbenzoimidazolethione-2 by direct oxidation of 5, 6-dimethylbenzoimidazole.

Continuing previous work on pyridylethylation of cyclic thioamides [1], 2-vinylpyridine has been reacted with benzothiazolethione-2 (I), benzoxazolethione-2 (II), 1-methylbenzoimidazolethione-2 (III), benzoimidazolethione-2 (IV), and 5, 6-dimethylbenzoimidazolethione-2 (V). These compounds are distinguished by a dual functionality, for they can react at the nitrogen atom of the thioamide group, or at its sulfur atom as mercaptans. Hence thioamides can react with 2-vinylpyridine in two ways