SYNTHESIS OF 2-MERCAPTO-SUBSTITUTED THIENO[2,3-d]THIAZOLES AND BENZOTHIENO[3,2-d]THIAZOLES

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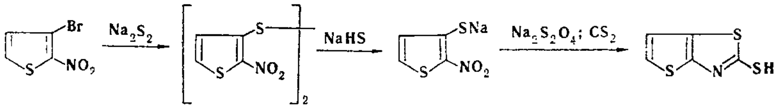
2-Mercaptothieno[2, 3-d]thiazoles were synthesized from bis(2-nitro-3-thienyl) disulfide by successive reduction of, initially, the disulfide bond and the nitro group in the presence of carbon disulfide without isolation of the intermediate 2-nitro-3-mercaptothiophene. 2-Mercaptobenzo-[b]thieno[3, 2-d]thiazole was synthesized by reaction of 3-aminobenzo[b]thiophene hydrochloride with sulfur monochloride and cleavage of the resulting benzo[b]thienothiazothionium chloride with sodium sulfide in the presence of carbon disulfide.

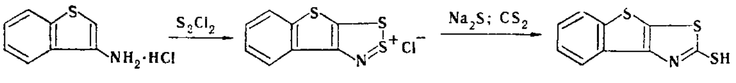
We have previously synthesized 2-mercaptothieno[3,2-d]- and benzo[b]thieno[2,3-d]thiazoles (I and II) by reduction of, respectively, bis(3-nitro-2-thienyl- disulfide with sodium hydrosulfite and bis(2-nitrobenzo[b]-3-thienyl) disulfide with sodium sulfide in the presence of carbon disulfide. However, attempts to similarly obtain 2-mercaptothieno[2,3-d]thiazole (III) were unsuccessful. It might have been assumed that this was associated with the fact that under the conditions of synthesis of bases I and II the nitro group in bis(2-nitro-3-thienyl) disulfide (IV) is reduced more rapidly than the disulfide bond, and the resulting unstable 2-aminothiophene derivative (see [2]) undergoes decomposition.

In fact, we obtained III in 15% yield by selective reduction of the disulfide bond in IV with sodium hydrosulfide and successive treatment of the 2-nitro-3-mercaptothiophene (V) with sodium hydrosulfite in the presence of carbon disulfide:



IV V III

We planned to synthesize 2-mercaptobenzo[b]thieno[3,2-d]thiazole (VI) from 3-aminobenzo[b]thiophene hydrochloride by the Herz reaction via the scheme



VII VI

Benzo[b]thieno[3,2-d]thiazothionium chloride (VII) was obtained in 96% yield by heating 3-aminobenzo[b]-thiophene hydrochloride with sulfur monochloride in benzene. Compound VI was synthesized in 70% yield by the action on the latter of sodium sulfide in aqueous media in the presence of carbon disulfide.

The IR spectra of III and VI do not contain the bands at 2550-2600 cm^{-1} characteristic for the stretching vibrations of the mercapto group but do contain bands at 1510 cm^{-1} (III) and 1525 cm^{-1} (VI) corresponding to the $-NH-\underset{|}{C}=S$. This indicates that III and VI exist in the thione form under ordinary conditions.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds (NaCl prism) were recorded with a UR-10 spectrometer.

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2-Nitro-3-bromothiophene [3]. This compound, with mp 81-83°, was synthesized in 56% yield by the action of a solution of nitric acid (sp. gr. 1.5) in acetic acid on a solution of 3-bromothiophene [4] in acetic anhydride.

Bis(2-nitro-3-thienyl) Disulfide (IV). Sodium disulfide, obtained by fusion of 24.0 g (0.1 mole) of crystalline sodium sulfide and 3.2 g (0.1 g-atom) of sulfur, was added with stirring to a heated (to 50-60°) solution of 41.4 g (0.2 mole) of 2-nitro-3-bromothiophene in 150 ml of 70% ethanol, and the mixture was refluxed with stirring for 2 h. The solid material was removed by filtration, washed with hot alcohol and water, and dried to give 25.6 g (80%) of yellow prisms (from benzene) with mp 211-212°. Found: C 30.0; H 1.0; N 8.8; S 39.6%. $C_8H_4N_2O_4S_4$. Calculated: C 30.0; H 1.2; N 8.8; S 40.0%.

2-Mercaptothieno[2,3-d]thiazole (III). A 9.6-g (0.03 mole) sample of V was added in a stream of nitrogen to a solution of 9.5 g (0.17 mole) of sodium hydrosulfide in 560 ml of 50% methanol, and the mixture was heated with stirring at 45-50° for 1 h. A 5-ml (0.08 mole) sample of carbon disulfide and 31.5 g (0.15 mole) of sodium hydrosulfite were added to the resulting brownish-orange solution of V, and the temperature was raised to 65-70°. After 1 h, another 31.5 g (0.15 mole) of sodium hydrosulfite was added, and heating was continued for 2 h. The mixture was cooled to room temperature and acidified with 15% hydrochloric acid, and the precipitate was removed by filtration. The filtrate was extracted with four 100-ml portions of chloroform, and the chloroform was removed by distillation. The residue was treated with 5% sodium hydroxide solution, the solution was filtered, and the filtrate was acidified with hydrochloric acid. The precipitate was removed by filtration, washed with water, and dried to give 1.56 g (15%) of III. Decolorization with activated charcoal in 70% methanol and recrystallization from the same solvent gave light-yellow prisms with mp 170-171°. IR spectrum (in KBr), cm^{-1}: 1510 (N—$\overset{|}{\mathrm{C}}$=S), 1290 (NH). Found: C 34.3; H 1.5; N 8.1%. $C_5H_3NS_3$. Calculated: C 34.6; H 1.7; N 8.1%.

3-Aminobenzo[b]thiophene Hydrochloride [5]. This compound, with mp > 300°, was obtained in 85% yield by alkaline hydrolysis of 3-acetamidobenzo[b]thiophene and by the action of hydrogen chloride on an ether solution of 3-aminobenzo[b]thiophene.

Benzo[b]thieno[3,2-d]thiazothionium Chloride (VII). A 9.3-g (0.05 mole) sample of 3-aminobenzo[b]thiophene hydrochloride was added gradually with stirring to 67.5 g (0.5 mole) of sulfur monochloride, after which the mixture was stirred at room temperature for 4 h. It was then treated with 40 ml of anhydrous benzene, and the mixture was refluxed for 4 h with periodic stirring. The precipitated material was removed by filtration and washed with benzene to give 11.7 g (95%) of a yellow amorphous powder with mp 261-262°. Found: C 39.3; H 1.7; Cl 14.4; N 5.6%. $C_8H_4ClNS_3$. Calculated: C 39.1; H 1.7; Cl 14.4; N 5.7%.

2-Mercaptobenzo[b]thieno[3,2-d]thiazole (VI). A 2.46-g (0.01 mole) sample of VII and 5 ml (0.08 mole) of carbon disulfide were added to a solution of 6.3 g (0.03 mole) of crystalline sodium sulfide in 8 ml of water, and the mixture was heated and stirred at 60-65° for 2 h. It was then treated with 100 ml of a hot 2% solution of sodium hydroxide, the mixture was filtered, and the filtrate was acidified with 15% hydrochloric acid. The resulting precipitate was removed by filtration and reprecipitated by dissolving in 2% sodium hydroxide solution and acidification of the solution with hydrochloric acid. The precipitate was removed by filtration, washed with water, and dried to give 1.56 g (70%) of light-yellow needles with mp 239-240° (from ethanol). IR spectrum: 1525 (N—C=S), 1280 cm^{-1} (NH). Found: C 48.5; H 2.2; N 6.2%. $C_9H_5NS_3$. Calculated: C 48.5; H 2.3; N 6.3%.

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