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SOME TRANSFORMATIONS OF 2-(2-HYDROXY-3-CHLOROPROPYLTHIO)BENZOTHIAZOLE

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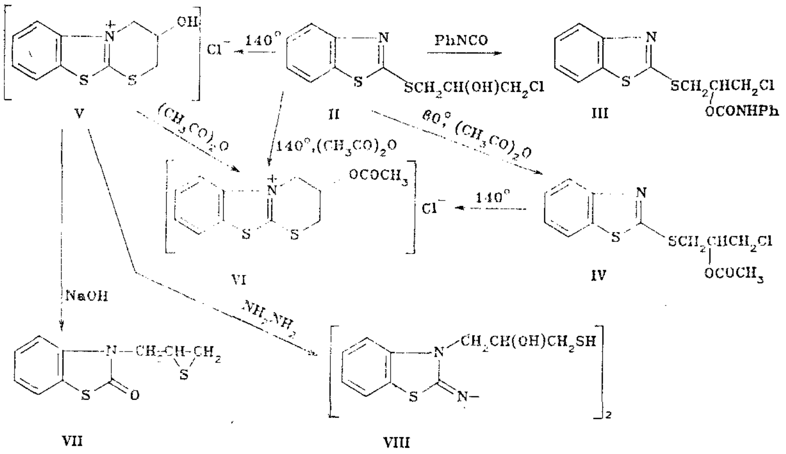
The reaction of phenyl isocyanate and acetic anhydride with 2-(2-hydroxo-3-chloropropylthio)benzothiazole was studied. At 140°C, this benzothiazole cyclizes with the formation of quaternary salt which readily reacts with hydrazine and alkali.

Many derivatives of benzothiazoline-2-thione (I) are biologically active which have, in particular, defoliating [1] and fungicide properties [2].

In a search for new pesticides, we studied some chemical transformations of 2-(2-hydoxy-3-chloropropylthio)benzothiazole (II) obtained in the reaction of thione I with 1-chloro-2, 3-epoxypropane [3].



The hydroxyl group of thiazole II reacts with phenyl isocyanate and acetic anhydride with the formation of 2-(2-phenylcarbamoyloxy-3-chloropropylthio)benzothiazole (III) and 2-(2-acetoxy-3-chloropropylthio)benzothiazole (IV), respectively. Heating thiazole II in xylene solution at reflux leads to cyclization and the formation of quaternary salt V. This salt reacts with acetic anhydride upon heating in glacial acetic acid at reflux and gives a quantitative yield of 5-acetoxy-4,5-dihydro-6H-benzothiazolo[2,3-b]thiazonium chloride (VI) which may also be obtained by the acetylation of thiazole II at 140°C or cyclization of acetoxy derivative IV.

Quaternary salt V readily reacts with alkali to form 3-(2,3-epithiopropyl)benzothiazolin-2-one (VII) and with hydrazine to form the azine of 3-(2-hydroxy-3-mercaptopropyl)benzazolin-2-one (VIII).

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Benzothiazole II has slight fungicide properties while III has growth regulating properties.

EXPERIMENTAL

The IR spectra were taken in KBr pellets on a UR-20 spectrophotometer. The UV spectra were taken on a Hitachi EPS-3T spectrometer in ethanol. The PMR spectra were taken on a Joel C-60-HL spectrometer with HMDS as internal standard. The purity and individual nature of the compounds obtained was monitored by thin-layer chromatography on Silufol-254.

2-(2-Phenylcarbamoyloxy-3-chloropropylthio)benzothiazole (III). A sample of 2.6 g (0.01 mole) thiazole II and 2.38 g (0.05 mole) phenyl isocyanate in 25 ml absolute benzene was heated at 70-80°C for 3 h. One half of the solvent was evaporated. The crystalline precipitate was filtered off to yield 3.6 g (94%) III with mp 113-114°C (from 1:2 benzene—petroleum ether). UV spectrum: λ_{max} (log ε): 297 (4.07), 290 (4.00), 300 nm (3.90). IR spectrum: 1710 (C=O), 3320 cm^{-1} (NH). PMR spectrum (in CF_3CO_2H): 3.52 (2H, s, CH_2—Cl), 3.60 (2H, s, CH_2—S), 5.22 (1H, m, CH—O), 6.92 and 7.52 ppm (9H, s, aromatic protons). Found: N, 7.47%. Calculated for $C_{17}H_{15}ClN_2O_2S_2$: N, 7.39%.

2-(2-Acetoxy-3-chloropropylthio)benzothiazole (IV). A mixture of 2.6 g (0.01 mole) thiazole II, 1.02 g (0.01 mole) acetic anhydride, and two drops sulfuric acid in 30 ml benzene was heated at reflux for 4 h. The solution was washed with water and dried over calcium chloride. Evaporation of the benzene solvent gave 2 g (66%) acetoxy derivative IV with mp 56-57°C (from petroleum ether). UV spectrum, λ_{max} (log ε): 280 (4.01), 290 (3.94), 301 nm (3.80). IR spectrum: 1730 cm^{-1} (C=O). PMR spectrum (in CF_3CO_2H): 1.80 (3H, s, CH_3), 3.55 (4H, br.s, CH_2—Cl, CH_2—S), 5.20 (1H, m, CH—O), 7.48 and 7.68 ppm (4H, s, aromatic protons). Found: N, 4.81%. Calculated for $C_{12}H_{12}ClNO_2S_2$: N, 4.64%.

5-Hydroxy-4,5-dihydro-6H-benzothiazolo[2,3-b]thiazonium chloride (V). A sample of 1.3 g (0.05 mole) thiazole II in 10 ml o-oxylene was heated at reflux for 3 h. The mixture was cooled and the precipitate was filtered off and washed with chloroform to yield 1.1 g (88%) V with mp 245-246°C (from absolute ethanol). UV spectrum, λ_{max} (log ε): 312-318 nm (4.05). IR spectrum: 3380-3400 cm^{-1} (OH). PMR spectrum (in CF_3CO_2H): 3.4 (2H, br.s, CH_2—S), 4.28 (2H, d, CH_2—N), 4.85 (1H, m, CH—O), 7.38 ppm (4H, s, aromatic protons). Found: N, 5.54%. Calculated for $C_{10}H_{10}ClNOS_2$: N, 53.9%.

5-Acetoxy-4,5-dihydro-6H-benzothiazolo [2,3-b]thiazonium chloride (VI). A solution of 0.5 g (1.9 mmole) and 1.02 g (0.01 mole) acetic anhydride in 5 ml glacial acetic acid was heated at reflux for 3 h. The acetic anhydride and acetic acid were distilled off to yield 0.45 g (88%) VI with mp 221-222°C (from absolute ethanol). UV spectrum, λ_{max} (log ε): 308-312 nm (4.05). IR spectrum: 1750 cm^{-1} (C=O). PMR spectrum (CF_3CO_2H): 3.50 (2H, br.s, CH_2—S), 4.50 (2H, br.s, CH_2—N), 5.80 (1H, m, CH—O), 7.52 ppm (4H, s, aromatic protons). Found: N, 4.66%. Calculated from $C_{12}H_{12}ClNO_2S_2$: N, 4.64%.

3-(2,3-Epithiopropyl)benzothiazolin-2-one (VII). A sample of 0.4 g (0.01 mole) 20% aqueous sodium hydroxide was added to a solution of 2.6 g (0.01 mole) quaternary salt V in 50 ml water and 50 ml ether with vigorous stirring. After 30 min, the organic layer was washed with water and dried over magnesium sulfate. The ether was distilled off. The oily residue crystallized upon standing to yield 2 g (90%) VII with mp 50-51°C (from hexane) [3].

Azine of 3-(2-hydroxy-3-mercaptopropyl)benzothiazolin-2-one (VIII). A sample of 3 g (0.06 mole) 80% hydrazine hydrate was added dropwise with stirring to a solution of 2.6 g (0.01 mole) quaternary salt V in 30 ml water. The oil formed was separated. Benzene was added and the crystals were separated to yield 1.6 g (33%) VIII with mp 184-185°C (from acetone). UV spectrum, λ_{max}: 322, 349 nm. IR spectrum: 2540 (SH), 3330 (OH), 1580 and 1610 cm^{-1}(C=N). PMR spectrum (in CF_3CO_2H): 2.50 (2H, br.s, CH_2—S), 4.30 (2H, d, CH_2—N), 4.50 (1H, m, CH—O), 7.35 ppm (8H, s, aromatic protons). Found: N, 11.69%. Calculated for $C_{20}H_{22}N_4O_2S_4$; N, 11.71%.

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