moist air. Efforts to prepare monoacyl derivatives of the glassy erythritol arsenite followed by hydrolysis of the arsenic function afforded mixtures which were not separated.

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A New Synthesis of the Benzothiazole and Benzoxazole Rings

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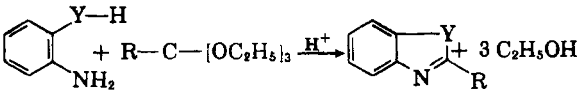
In an attempt to prepare a series of 2-(*N*-alkylamino)benzenethiols, ethyl orthoformate was treated with 2-aminobenzenethiol in a manner similar to that reported in *Organic Syntheses*[1] for the preparation of secondary amines. Although our attempt did not produce the desired product, we did discover a convenient method of preparing 2-substituted benzothiazole and benzoxazole rings (Table I) in 75–85% yields.

Table I lists the compounds prepared by treating 2-aminobenzenethiol or 2-aminophenol with the corresponding ortho-esters.

TABLE I

2-SUBSTITUTED BENZOTHIAZOLE AND BENZOXAZOLE COMPOUNDS



	Y	R	B.P. (mm.)[a] of Heterocycle	
1	S	H	183	(754)
2	S	CH_3	151	(15)
3	S	C_2H_5	132	(18)
4	O	H	182	(753)
5	O	CH_3	91	(18)
6	O	C_2H_5	129	(23)

[a] The physical properties of these compounds were in close agreement with those reported in the literature (Beilstein).

All of the above compounds were prepared according to the following procedure used for the synthesis of benzothiazole.

EXPERIMENTAL

In a 100 ml. round bottomed flask were placed 22 g. (0.17 mole) of 2-aminobenzenethiol, 37 g. (0.25 mole) of ethyl orthoformate, and 0.7 g. (0.007 mole) of concd. sulfuric acid. To the flask was attached a Vigreux column surmounted with a distillation head. The flask was heated in an oil bath and after the temperature reached 115–130° the ethanol began to distill. Heating was continued until the temperature reached 170–180°, at which time all of the ethanol and some yellow material had been removed (*ca.* 1 hr.). About 31 ml. of ethanol was collected. The reaction mixture was kept in the oil bath at 175–185° for an additional 45 min., after which time it was cooled and the product distilled under vacuum.

Anal. Calcd. for C_7H_5NS: C, 62.19; H, 3.73. Found: C, 62.45; H, 3.41.

The infrared spectrum of benzothiazole was identical with that obtained from a commercial product.

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[1] R. M. Roberts and P. J. Vogt, *Org. Syntheses*, **38**, 29 (1958).

Reaction of Tertiary Mercaptans with Sulfur

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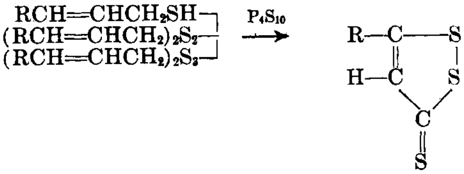
The interesting pseudoaromatic 1,2-dithiole-3-thiones have been prepared by the reaction of sulfur and/or phosphorus pentasulfide with aldehydes,[1] methyl substituted olefins or olefins easily converted to methyl substituted derivatives,[2,3] diolefins,[3] and unsaturated carbonyl compounds.[4] There are also scattered references to the synthesis of these systems from sulfur compounds. Allylic thiols, disulfides, and trisulfides[4] are reported to yield 5-alkyl-1,2-dithiole-3-thiones, I.



I

Wessely and Siegel[5] have reported low yields of thiones by reaction of sulfur with saturated aliphatic sulfides, disulfides and polysulfides. These workers have suggested a cleavage of the sulfide linkage as an initial intermediate on the route to the thione as well as to higher molecular weight products.

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[1] G. A. Barbaglia, *Ber.*, **17**, 2654 (1884).

[2] M. L. Selker and A. R. Kemp, *Ind. Eng. Chem.*, **39**, 895 (1947).

[3] B. Boettcher and A. Luttringhaus, *Ann.*, **557**, 89 (1947).

[4] A. Luttringhaus, H. B. Konig, and B. Bottcher, *Ann.*, **560**, 201 (1947).

[5] F. Wessely and A. Siegel, *Monatsh.*, **82**, 607 (1951).