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.

Acknowledgment. The authors are pleased to acknowledge the counsel of Mr. Alan Chaney and his assistance with the preparation of the manuscript.

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A New Synthesis of the Benzothiazole and Benzoxazole Rings

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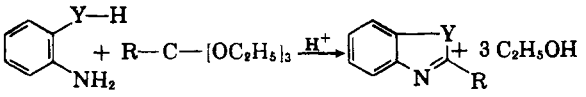
Received May 9, 1960

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.

Acknowledgment. We are indebted to the American Cyanamid Company for the gift of 2-aminobenzenethiol used in this work.

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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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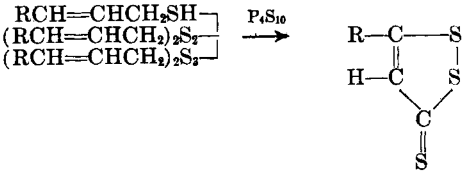
Received May 18, 1960

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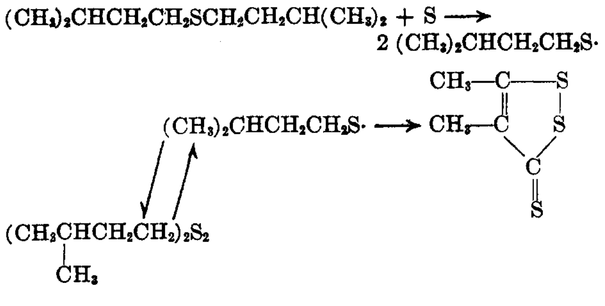
(1) G. A. Barbaglia, *Ber.*, **17**, 2654 (1884).

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

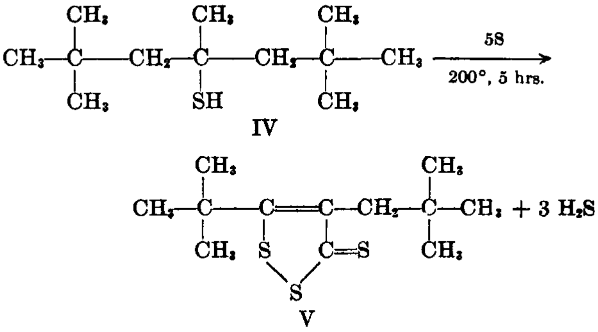
(3) B. Boettcher and A. Luttringhaus, *Ann.*, **557**, 89 (1947).

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

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



During the course of some investigations with thiols we have had occasion to study the reaction of tertiary thiols with sulfur and were surprised to find high yields of 1,2-dithiole-3-thiones. The thiols studied included 2,4,4-trimethyl-2-pentanethiol, II, and 2,2,4,6,6-pentamethyl-4-heptanethiol, IV. Reaction of II with sulfur yielded a mixture of 4-methyl-5-*t*-butyl-1,2-dithiole-3-thione and 4-neopentyl-1,2-dithiole-3-thione identical to that obtained by Spindt[6] from the direct sulfurization of diisobutylene, 2,4,4-trimethylpentene-1, or 2,4,4-trimethylpentene-2.

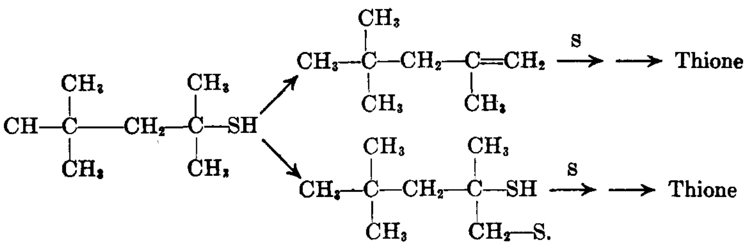


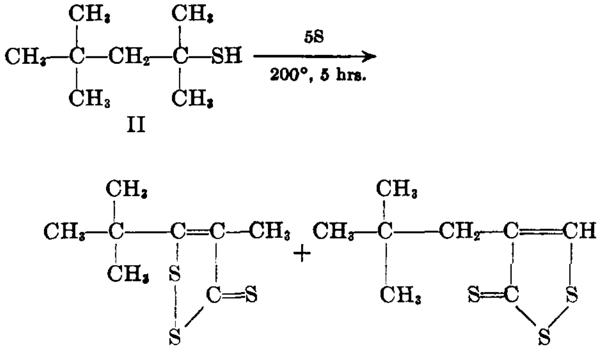
IV

V

Compound V readily formed addition compounds with mercuric chloride, silver nitrate, bismuth chloride, and methyl iodide. Refluxing with alcoholic potassium hydroxide for extended periods of time yielded, among other products, two acids established as pivalic and γ,γ-dimethylvaleric acids. These acids presumably arise by hydrolytic cleavage of thiole ring to a β-keto acid, which readily undergoes base-catalysed C—C ring rupture.

The isolation of the thiones III and V from the indicated thiols suggest two alternatives in the initial reaction path to thione products.





II

IIIa

IIIb

Compound IV with sulfur at 200° gave 4-neopentyl-5-*t*-butyl-1,2-dithiole-3-thione, V identical with the product obtained by the reaction of triisobutylene with sulfur.[7]

Tertiary mercaptans are reported to eliminate hydrogen sulfide at 300°.[8] The presence of excess sulfur may enhance this elimination. Indeed we have found that heating sulfur in an inert solvent at 200°, dropping 2,4,4-trimethyl-2-pentanethiol onto the solution and rapidly removing volatile products in a side-arm takeoff trap produces small amounts of olefin, easily identified as diisobutylene. This observation suggests formation of olefin by loss of hydrogen sulfide before attack at a methyl group. By analogy the thiones from various sulfides reported by Wessely and Siegel must arise by thermal cleavage of the sulfide linkage, formation of a thiol by hydrogen abstraction and elimination of hydrogen sulfide prior to formation of the sulfur-containing intermediates on the route to dithiole-3-thione. In strong support of this suggestion is the observation that 2,4,4-trimethylpentanethiol yielded a mixture of thiones (IIIa and IIIb) in

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(6) R. Spindt, D. Stevens, and W. Baldwin, *J. Am. Chem. Soc.*, **73**, 3693 (1951).

(7) P. Landis and L. Hamilton, *J. Org. Chem.* **25**, 1742 (1960).

(8) C. Thompson, R. Meyer, and J. S. Ball, *J. Am. Chem. Soc.*, **74**, 3284 (1952).

about the same ratio as that obtained from the reaction of diisobutylene and sulfur.

EXPERIMENTAL

Reactions with sulfur. Two techniques were used to react sulfur with tertiary mercaptans. The first utilized the simple process of dropping mercaptan onto heated sulfur at 200° using an addition rate such that all of the low boiling mercaptan and intermediates were efficiently converted to higher boiling products. A second technique used the addition of preformed alkyl-1,2-dithiole-3-thione to the sulfur before addition of the mercaptan. The added thione served to reduce the viscosity of the sulfur, to increase the mutual solubility of the sulfur and mercaptan, and thus to provide increased conversions.

4-Neopentyl-1,2-dithiole-3-thione, IIIb *and 4-methyl-5-t-butyl-1,2-dithiole-3-thione,* IIIa. Sulfur (160 g., 5.0 moles) was placed in a 500-ml. four-necked flask fitted with a stirrer, thermometer, dropping funnel, and efficient condenser. The condenser was connected to a gas meter to measure evolution of hydrogen sulfide. The sulfur was heated and stirred at 200–220° and 2,4,4-trimethyl-2-pentanethiol (146 g., 1 mole) was added dropwise in 4 hr. Heating and stirring was continued for an additional hour at the end of which 3 moles of hydrogen sulfide had been evolved and reaction had essentially ceased. The crude product was vacuum distilled and after a forecut of intermediate sulfur compounds there was obtained 50 g. boiling at 145–155° (3 mm.). This fraction solidified on standing and was separated into two isomers by fractional recrystallization from pentane and ethanol. 4-Neopentyl-1,2-dithiole-3-thione IIIb, m.p. 85–86°, gave no melting point depression with a sample prepared by the method of Spindt, *et al.*[6] 4-Methyl-5-*t*-butyl-1,2-dithiole-3-thione IIIa, m.p. 79–80°, also was identical to that obtained by the method of Spindt.

Anal. IIIa. Calcd. for $C_8H_{12}S_3$: C, 47.01; H, 5.93; S, 47.06. Found: C, 47.05; H, 5.88; S, 47.00.

Anal. IIIb. Calcd. for $C_8H_{12}S_3$: S, 47.06; mol. wt. 204.3. Found: S, 47.19; mol. wt. 205.

4-Neopentyl-5-t-butyl-1,2-dithiole-3-thione, V. Sulfur (160 g.) and 2,2,4,6,6-pentamethyl-4-heptanethiol (212 g.) were placed in a three-necked 500-ml. flask fitted with a thermometer, stirrer, and a reflux condenser which was attached to a gas meter. The reactants were heated at 190–215° for 5 hr. and 67 l. of hydrogen sulfide were evolved. The crude product was vacuum distilled and 68 g. of thione, b.p. 150–170° (0.1–0.03 mm.) was obtained. This product was identical with that obtained from the direct sulfurization of triisobutylene.[7] Confirming analyses include infrared and ultraviolet spectra, metal complexes with mercuric chloride, silver nitrate, bismuth chloride, and methyl iodide, and the alcoholic potassium hydroxide hydrolysis to pivalic and 4,4-dimethylvaleric acids.[7]

Anal. Calcd. for $C_{12}H_{20}S_3$: S, 36.92; mol. wt. 260.5. Found: S, 36.22; mol. wt. 258, 265.

During the course of a large scale reaction (1 l.) of 2,4,4-trimethyl-2-pentanethiol with sulfur in di-*t*-butylbenzene a side-arm take-off trap was attached to the reflux condenser. This allowed removal of small samples of unreacted thiol and low boiling intermediates. Twenty-milliliter samples were thus removed every half hour and examined by vapor phase chromatography. Small (0.4–1.2%) but definite quantities of a C_8-olefin were observed during the entire course of the reaction (5 hr.). The identity of this olefin was confirmed by extraction of 200 ml. of low boiling condensate with aqueous caustic. The small caustic insoluble layer was separated by ether extraction, the ether extract washed with water, dilute caustic, dilute acid, and then dried over anhydrous sodium sulfate. After careful removal of the solvent the residue was distilled using a micro still and there was obtained 1.1 g. of mixed olefin easily identified by infrared as a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. Thermal treatment of the thiol II at reflux temperature gave no evidence for hydrogen sulfide evolution or the consequent formation of olefin.

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Vinylsilicon and 1,2-Dihaloethylsilicon Halogenoids and Esters[1]

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Received February 29, 1960

Earlier publications report the closely related halogenoids and perfluoroester $Si(NCO)_4$,[2] $Si(NCS)_4$,[3] $C_2H_5Si(NCO)_3$,[3] $CH_3Si(NCS)_3$,[3] $C_2H_5Si(NCS)_3$,[3] and $C_2H_5Si(OCOCF_3)_3$.[4] Addition of bromine or chlorine to vinyltrichlorosilane furnishes $CH_2BrCHBrSiCl_3$ and $CH_2ClCHClSiCl_3$ respectively,[5] while only a boiling point at diminished pressure and an analysis for silicon characterize $CH_2{=}CHSi(OCOCH_3)_3$.[6]

An E_2 elimination occurs in $CH_2ClCH_2Si(CH_3)_3$, in which the *beta* chlorine is titrated quantitatively with aqueous alkali.[7] Similarly, an acidic *beta* halogen titrates quantitatively in five new halogenoids and esters of the type $CH_2YCHYSiX_3$, in which Y is chlorine or bromine, presented in this paper.

Table I lists the boiling points, densities, refractive indices, molar refractions (calculated[4] and observed values show an average error of 0.46%), and analyses of the following eleven new compounds: $CH_2{=}CHSi(OCOCF_3)_3$, $CH_2{=}CHSi(OCOC_2F_5)_3$, $CH_2{=}CHSi(OCO\text{-}n\text{-}C_3F_7)_3$, $CH_2{=}CHSi(OCOC_2H_5)_3$, $CH_2{=}CHSi(NCO)_3$, $CH_2{=}CHSi(NCS)_3$, $CH_2BrCHBrSi(OCOCF_3)_3$, $CH_2BrCHBrSi(OCOC_2F_5)_3$, $CH_2BrCHBrSi(OCO\text{-}n\text{-}C_3F_7)_3$, $CH_2BrCHBrSi(NCO)_3$, and $CH_2ClCHClSi(NCO)_3$. There is also adequate data for $CH_2{=}CHSi(OCOCH_3)_3$. These colorless compounds all hydrolyze easily and many decompose sufficiently at the normal boiling point to limit the accuracy of the individual boiling point.

A typical perfluoroester such as $CH_2{=}CHSi(OCOCF_3)_3$ has a higher thermal stability and

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[1] Presented at 15th Southwest Regional A. C. S. Meeting, Baton Rouge, La., December, 1959.

[2] G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **62**, 761 (1940).

[3] H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 3049 (1947); **71**, 1801 (1949); **72**, 196 (1950).

[4] H. H. Anderson and T. C. Hager, *J. Am. Chem. Soc.*, **81**, 1584 (1959).

[5] C. L. Agre and W. Hilling, *J. Am. Chem. Soc.*, **74**, 3895, 3899 (1952).

[6] K. C. Frisch *et al.*, *J. Am. Chem. Soc.*, **74**, 4584 (1952).

[7] L. H. Sommer *et al.*, *J. Am. Chem. Soc.*, **68**, 485 (1946); **70**, 2871 (1948).