[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORIES, MICHIGAN STATE UNIVERSITY]

Reaction of 2-Alkoxymethylthiiranes with Lithium Aluminum Hydride and with Secondary Amines

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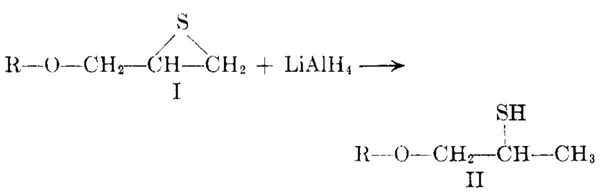
The reduction of 2-alkoxymethylthiiranes with lithium aluminum hydride has been found to result in the formation of 1-alkoxy-2-mercaptopropanes, the isomers expected from normal ring fission. The reaction of triethyl phosphite with the 1-alkoxy-2-mercaptopropanes was found to result in the formation of the corresponding alkyl propyl ethers and triethyl thionophosphate. The reaction of 2-alkoxymethylthiiranes with the secondary amines, piperidine, morpholine, and diethylamine was also investigated. The yield of the amino mercaptan was found to be quite sensitive to the mole ratio of amine to thiirane, the nature of the product formed, the presence or absence of a solvent, and the type of solvent. The reaction of triethyl phosphite with the products isolated from the reactions of amines with 2-alkoxymethylthiiranes were found to result in the formation of amidothionophosphates and alkyl allyl ethers.

This paper is primarily concerned with the nature of the products isolated from the reaction of 2-alkoxymethylthiiranes with lithium aluminum hydride and with secondary amines.

Mousseron and his collaborators[2] first described the reduction of a thiirane by lithium aluminum hydride. They reported that cyclohexanethiol was formed in 85% yield when 2,3-tetramethylenethiirane was treated with lithium aluminum hydride. Bordwell, Andersen, and Pitt,[3] in 1954, reported the unsymmetrically substituted thiiranes, 2-methyl- and 2-*n*-butyl-, were converted to secondary mercaptans, in good yields, by lithium aluminum hydride. On the other hand, Moore and Porter[4] found the reduction of 2-*n*-hexylthiirane by lithium aluminum hydride gave a low yield of the expected octane-2-thiol, but a high yield of polymeric material.

Helmkamp and Schnautz[5] recently reported on the stereochemistry of the lithium aluminum deuteride reduction of 2,3-dimethylthiirane. The reduction was shown to proceed with inversion of configuration.

In the present study, the course of the reaction of several 2-alkoxymethylthiiranes (I) with lithium aluminum hydride was investigated.



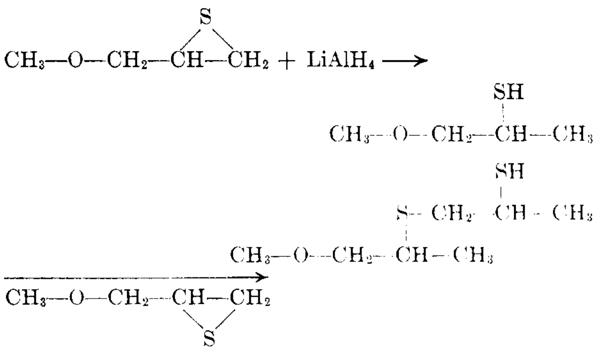
I

II

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5

In accord with the results of previous investigators,[3,4] the reduction products were found to be thiols in which the sulfur atom retained its linkage with the more highly substituted carbon atom (II). The yields of the 1-alkoxy-2-mercaptopropanes were in the range of 75–85%, except in the case of 2-phenoxymethylthiirane. Some polymeric sulfide was produced in all these reactions, but was the sole product obtained in the reduction of 2-phenoxymethylthiirane with lithium aluminum hydride. The observation of polymer formation, although not mentioned by Bordwell and his associates,[3] is in agreement with the recent work by Moore and Porter.[4]

In addition to the formation of monomeric etherthiols and polymeric sulfides, observed in the reduction of 2-alkoxymethylthiiranes by lithium aluminum hydride, a small amount of an impure high boiling liquid was also produced. An approximate molecular weight determination of the higher boiling material formed in the reaction of 2-methoxymethylthiirane with lithium aluminum hydride gave a value of 224. A reasonable explanation for this observation may be the following:



III

The lithium mercaptide formed in the initial ring opening of the thiirane, attacks a second molecule of the thiirane, forming the compound (III) of molec-

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[1] Abstracted in part from the doctoral thesis of R. L. Jacobs, 1959.

[2] M. Mousseron and M. Canet, *Bull. soc. chim., France,* (5) **18,** 792 (1951); M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdour, *Bull. soc. chim., France* (5), **19,** 1042 (1952).

[3] F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Am. Chem. Soc.,* **76,** 1082 (1954).

[4] C. G. Moore and M. Porter, *J. Am. Chem. Soc.,* **80,** 2062 (1958).

[5] G. H. Helmkamp and N. Schnautz, *Tetrahedron,* **2,** 304 (1958).

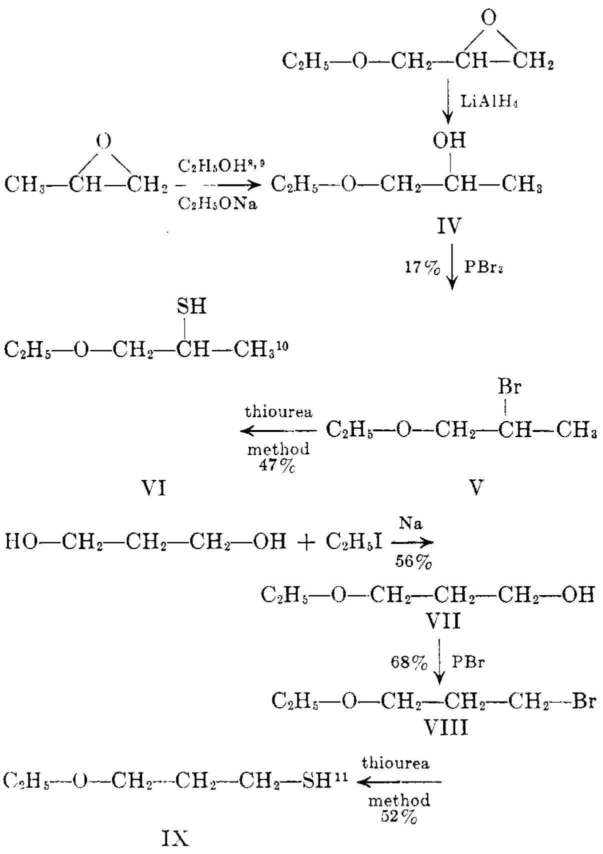
TABLE I

ANALYTICAL DATA FOR THE 1-ALKOXY-2-MERCAPTOPROPANES

1-Alkoxy-2-mercapto-propane	Formula	B.P.	Mm.	n_D^{25}	Yield, %	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
Methoxy	$C_4H_{10}OS$	32–33	27	1.4411	85	45.28	9.43	30.18	45.40	9.63	30.38
Ethoxy	$C_5H_{12}OS$	45–46	25	1.4379	77	50.00	10.00	26.50	49.95	9.92	26.43
Propoxy	$C_6H_{14}OS$	49	13	1.4390	78	53.77	10.53	23.88	53.75	10.54	23.81
Butoxy	$C_7H_{16}OS$	66	13	1.4415	74	57.00	10.81	21.70	56.95	10.92	21.88

ular weight 210. This type of side reaction has frequently been observed in reactions of cyclic sulfides with nucleophilic reagents.[6,7] Further, support for this formulation was found in the fact that the use of excess lithium aluminum hydride increased the yield of the monomeric ether-thiol by several per cent, while decreasing that of the higher boiling material.

To establish the structures of the alkoxypropyl mercaptans produced by the action of lithium aluminum hydride on 2-alkoxymethylthiiranes, unequivocal synthesis of the two possible isomeric products were carried out and a comparison of their properties with those of the reduction product obtained were made. Thus, in the reduction of 2-ethoxymethylthiirane, $C_2H_5—O—CH_2—CHSH—CH_3$ and/or $C_2H_5—O—CH_2—CH_2—CH_2—SH$ could be formed, depending on the direction of ring-opening. Therefore, these two isomers were prepared by unequivocal independent synthesis and compared with the isolated reduction product. The following preparative schemes were employed.



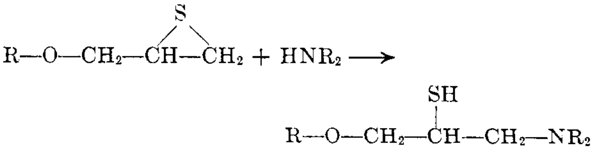
A comparison of the properties of (VI and IX) with those of the reduction production obtained from 2-ethoxymethylthiirane established the reduction product to be identical with VI.

Further evidence in regard to the direction of ring-opening produced by the nucleophilic attack of AlH_4^- on 2-alkoxymethylthiiranes was obtained from similar reactions involving 2-methoxymethylthiirane.

As has been observed previously[11–14] attempts to convert the thiols to solid derivatives, such as 2,4-dinitrochlorobenzene, 3,5-dinitrobenzoyl chloride, 3-nitrophthalic anhydride and mercaptoyldehyde dinitrophenylhydrazones resulted in either viscous liquids or oils when applied to the alkoxy mercaptans prepared in the present study.

Under controlled experimental conditions, excellent yields of substituted amino mercaptans were obtained from the reactions of 2-alkoxymethylthiiranes with the secondary amines piperidine, morpholine, and diethylamine.

By analogy to the findings of Snyder and his associates,[15] the compounds are assumed to consist largely, if not solely, of the secondary mercaptan structure.



R = CH_3, C_2H_5, n-C_3H_7; R_2 = $(C_2H_5)_2$, $(CH_2)_5$, $(CH_2)_4O$

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(6) T. S. Stevens in E. H. Rodd's *Chemistry of Carbon Compounds, Vol. IV*, Elsevier Co., London, England, 1957, part A, Chapter II.

(7) A. Schönberg, Houben-Weyl, *Methoden der Organischen Chemie, Vol. IX*, Verlag, Stuggart, 1955, pp. 148–160.

(8) W. Reeve and A. Sadle, *J. Am. Chem. Soc.*, **72**, 1251 (1950).

(9) H. C. Chitwood and B. T. Freure, *J. Am. Chem. Soc.*, **68**, 680 (1946).

(10) G. G. Urquhart, J. W. Gates, Jr., and R. Conner, *Org. Syntheses*, **Coll. Vol. III**, 363 (1955).

(11) R. W. Bost, L. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

(12) E. Wertheim, *J. Am. Chem. Soc.*, **51**, 3661 (1929).

(13) L. C. Swallen and C. E. Bvord, *J. Am. Chem. Soc.*, **52**, 651 (1930).

(14) H. R. Snyder, J. M. Stewart, and J. B. Fugter, *J. Am. Chem. Soc.*, **69**, 2675 (1947).

(15) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2672 (1947).

The yield of substituted amino mercaptans was sensitive to the mole ratio of amine to thiirane, reaction media (if any), and the nature of the product. Highest yields in the reaction of alkoxymethylthiiranes with piperidine and morpholine were obtained using a 2:1 ratio of amine to thiirane in an inert diluent, such as benzene or ether, in essential agreement with the findings of Branz.[16]

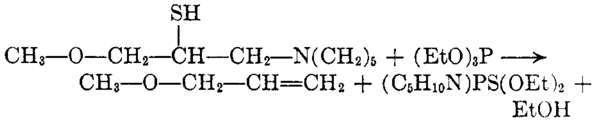
The reaction of diethylamine with alkoxymethylthiiranes in an inert solvent led to the complete recovery of starting materials. Presumably reaction occurred as with other secondary amines, followed by elimination of diethylamine and reformation of the thiirane during attempted isolation, as suggested originally by Wright.[17] In water the expected base-catalysed polymerization[18] of the thiiranes took place.

Since the lithium aluminum hydride reduction of 2-alkoxymethylthiiranes resulted in the formation of several 1-alkoxy-2-mercaptopropanes, and because of our interest[19] in the ability of triethyl phosphite to desulfurize organo sulfur compound, a study of the reaction of triethyl phosphite with the 1-alkoxy-2-mercaptopropanes was conducted. These mercaptans are smoothly desulfurized[19–21] similarly to other mercaptans, converting the sulfhydryl group to hydrogen.

To determine the direction of ring opening of 2-alkoxymethylthiiranes on reaction with secondary amines, an attempt was made to desulfurize the amine mercaptans isolated with triethyl phosphite to convert them to $RO(CH_2)_3NR_2'$ or $ROCH_2CHNR_2'CH_3$, materials obtainable by unequivocal synthesis. However, the desulfurization reaction failed to proceed as anticipated. From the reaction of triethyl phosphite with 1-methoxy-2-mercapto-3-*N*-substituted aminopropanes there was isolated a 60% yield of methyl allyl ether and a viscous residue which on vacuum distillation failed to yield any appreciably amount of low boiling material.

Trialkyl phosphites are known to remove sulfur from many types of organosulfur compounds[19–23] and to be capable of forming compounds with phosphorus to nitrogen bonds[23] by reaction with amines, nitriles, etc. In addition, a rather extensive list of compounds known as amidothionophosphates $(R_2N)PS(OR')_2$, $(RNH)PS(OR')_2$ have been prepared.[23]

In view of these facts, the reaction, using 1-methoxy-2-mercapto-3-piperidinopropane as an example, appears to take the following course:



$$\mathrm{CH_3{-}O{-}CH_2{-}\overset{SH}{\overset{|}{C}}H{-}CH_2{-}N(CH_2)_5 + (EtO)_3P \longrightarrow CH_3{-}O{-}CH_2{-}CH{=}CH_2 + (C_5H_{10}N)PS(OEt)_2 + EtOH}$$

The amidothionophosphate is a known compound,[24] and was obtained in small amounts. The low yield of this material are probably due to the high temperatures and long reaction periods employed. It is known that amidothiophosphates undergo secondary reactions, such as a more or less ready oxidation to the $(R_2N)PO(OR')_2$, thermal decompositions and various disproportionations during attempted purification by distillation.[23]

The reaction of triethyl phosphite with the amino mercaptan isolated from the reaction of 2-methoxymethylthiirane with morpholine likewise produced methyl allyl ether and an unidentified amidothionophosphate or derivative thereof. Similarly, the products obtained from the reaction of 2-ethoxymethylthiirane with both piperidine and morpholine, when treated with triethyl phosphite, produced ethyl allyl ether and presumably an amidothionophosphate.

EXPERIMENTAL[24]

The 2-alkoxymethylthiiranes were prepared from the corresponding alkyl glycidyl ethers and either aqueous potassium thiocyanate or thiourea, following experimental techniques already described.[19] Lithium aluminum hydride obtained from Metal Hydrides Incorporated, was used as received. Piperidine, morpholine, and diethylamine obtained from commercial sources were redistilled just prior to use. Triethyl phosphite obtained from the Virginia-Carolina Chemical Corporation, was purified by distillation from sodium.

Reaction of 2-alkoxymethylthiiranes with lithium aluminum hydride. The reduction of the 2-alkoxymethylthiiranes by lithium aluminum hydride was patterned after the procedure of Bordwell, Andersen, and Pitt.[3] The results are summarized in Table I. In general, small amounts of solid polymeric materials and high boiling liquids were formed in these reductions. A molecular weight determination on the high boiling liquid obtained from the reaction of 2-methoxymethylthiirane with lithium aluminum hydride gave a value of 224. However, in the reduction of 2-phenoxymethyl thiirane, only polymeric sulfide was isolated.

Intermediates. The compounds, 1-methoxy-2-propanol,[8] 1-ethoxy-2-propanol, 1-ethoxy-2-bromo-propane,[25] 3-ethoxy-1-mercaptopropanol,[26] 3-ethoxy-1-bromopropane,[27] and 3-ethoxy-1-mercapto-propane[28] were prepared by procedures described in the literature.

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(16) G. I. Branz, *J. Gen. Chem., USSR*, **21**, 757 (1951).

(17) J. B. Wright, *J. Am. Chem. Soc.*, **79**, 1694 (1957).

(18) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

(19) R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **23**, 1799 (1958).

(20) F. W. Hoffman, R. J. Ess, T. C. Simmons, and R. S. Hanzel, *J. Am. Chem. Soc.*, **78**, 6414 (1958).

(21) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957).

(22) W. G. Emmett and H. O. Jones, *J. Chem. Soc.*, **99**, 713 (1911).

(23) G. M. Kosolapoff, *"Organophosphorus Compounds,"* John Wiley and Sons, Inc., New York (1950).

(24) All melting points and boiling points are uncorrected. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(25) V. S. Abramov and E. N. Nikolaeva, *Zhur. Obschei Khim.*, **20**, 100 (1950) *Chem. Abstr.*, **44**, 5799 (1950).

(26) L. I. Smith and S. A. Sprung, *J. Am. Chem. Soc.*, **65**, 1276 (1943).

(27) E. P. Anderson, J. V. Crawford, and M. L. Sherrell, *Am. Chem. Soc.*, **68**, 294 (1946).

(28) R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3740 (1948).

1-Methoxy-2-bromopropane. To 116 g. (1.29 moles) of 1-methoxy-2-propanol was added dropwise, during 2 hr., 90 g. (0.33 mole) of freshly distilled phosphorus tribromide (b.p. 169–170°/742 mm.). The reaction mixture was stirred an additional 2 hr. and then distilled into 150 ml. of water. The oily layer was separated, washed with water until free of acid, and dried over anhydrous calcium chloride. The crude product was distilled (2 × 30 cm. column packed with $^3/_{16}$-in. glass helices) to obtain a 13% yield of a pure product, b.p. 28–29°/20–21 mm., 49–49.5°/60 mm., n_{D}^{25} 1.4409.

Anal. Calcd. for C_4H_9BrO: C, 31.37; H, 6.00; Br, 52.30. Found: C, 31.57; H, 5.97; Br, 52.07.

1-Methoxy-2-mercaptopropane. A mixture of 60 ml. of 95% ethanol, 12.9 g. (0.17 mole) of thiourea and 11.92 g. (0.17 mole) of 1-methoxy-2-bromopropane was heated at its reflux temperature for 7 hr., cooled to room temperature, and 10 g. (0.25 mole) of sodium hydroxide dissolved in 100 ml. of water was added. The alkaline solution was refluxed for 12 hr., cooled, and acidified with sulfuric acid (7 ml. of concd. sulfuric acid in 50 ml. of water). The acid solution was washed with three 50-ml. portions of benzene. The benzene extracts were combined, dried over anhydrous sodium sulfate and the benzene was removed *in vacuo.* The residual liquid was fractionated (2 × 30 cm. column packed with 3/16-inch glass helices), to obtain a pure product, b.p. 26–27.6°/20–21 mm., 43–43.5°/46 mm., n_{D}^{25} 1.4412. Its 2,4-dinitrophenyl thioether derivative[29] melted at 79.0–80.0°.

Anal. Calcd. for $C_{10}H_{12}N_2O_5S$: C, 44.11; H, 4.41; N, 10.30, S, 11.80. Found: C, 43.91; H, 4.46; N, 10.26; S, 11.92.

A mixed melting point determination with the 2,4-dinitrophenyl thioether derivative of the mercaptan isolated in the reaction of 2-methoxymethylthiirane with lithium aluminum hydride and the derivative described above, showed no depression.

1-Ethoxy-2-mercaptopropane. This mercaptan was obtained in a 47% yield from the corresponding bromide, by interaction with aqueous thiourea, following the procedure described above for preparing 1-methoxy-2-mercaptopropane. The pure product had a b.p. 44°/20 mm., n_{D}^{20} 1.4400. These physical constants are identical to those reported for the product isolated from the reduction of 2-ethoxymethylthiirane with lithium aluminum hydride.

Reaction of 2-alkoxymethylthiiranes with piperidine and morpholine. The following experimental procedure gave the highest yield of a monomeric addition product. To an ice cold solution containing 85 g. (1.0 mole) of redistilled amine dissolved in 75 ml. of benzene or ether was added a cold solution of the 2-alkoxymethylthiirane, 0.5 mole, dissolved in 75 ml. of benzene or ether. The reaction mixture was kept at 0° for an hour, warmed to room temperature, and then heated at its reflux temperature for 2 hr. Excess amine and benzene were removed *in vacuo* and the concentrated residue was fractionated under reduced pressure (40-cm. Vigreux column).

2-Methoxymethylthiirane and piperidine gave a 92% yield of 1-methoxy-2-mercapto-3-piperidinopropane, b.p. 88–90°/2–3 mm., n_{D}^{20} 1.4891.

Anal. Calcd. for $C_9H_{19}NOS$: C, 57.10; H, 10.11; N, 7.40; S, 16.94. Found: C, 57.01; H, 10.03; N, 7.63; S, 16.70.

The hydrochloride salt, prepared by bubbling hydrogen chloride gas into an etheral solution of the alkoxymercaptoamine melted at 130–132°.

Anal. Calcd. for $C_9H_{19}NOS \cdot HCl$: C, 48.87; H, 9.00; N, 6.20; S, 14.20. Found: C, 48.82; H, 8.83; N, 6.24; S, 14.30.

2-Ethoxymethylthiirane and piperidine gave a 90.6% yield of 1-ethoxy-2-mercapto-3-piperidinopropane, b.p. 129–131°/20 mm., n_{D}^{25} 1.4819.

Anal. Calcd. for $C_{10}H_{21}NOS$: C, 60.00; H, 10.34; N, 7:00; S, 16.00. Found: C, 59.98; H, 10.33; N, 7.10; S, 15.95.

Morpholine and 2-methoxymethylthiirane gave an 80.2% yield of 1-methoxy-2-mercapto-3-morpholinopropane, b.p. 35–36°/12 mm., n_{D}^{25} 1.4909.

Anal. Calcd. for $C_8H_{17}NO_2S$: C, 50.21; H, 8.90; N, 7.33; S, 16.75. Found: C, 50.52; H, 8.86; N, 7.60; S, 16.41.

Morpholine and 2-ethoxymethylthiirane gave an 81.3% yield of 1-ethoxy-2-mercapto-3-morpholinopropane, b.p. 66–68°/15 mm., n_{D}^{25} 1.4838.

Anal. Calcd. for $C_9H_{19}N_2OS$: C, 52.68; H, 9.27; S, 15.61. Found: C, 52.89; H, 9.27; S, 15.65.

Reaction of 2-alkoxymethylthiiranes with anhydrous diethylamine. This reaction was carried out in the manner described for the reaction of 2-alkoxymethyl thiiranes with piperidine, using 59.0 g. (0.5 mole) of 2-ethoxymethylthiirane and 170 g. (2.0 moles) of redistilled diethylamine. Attempted product isolation resulted in a nearly quantitative recovery of both reactants unchanged. Heat evolution was observed on mixing the two reagents, indicating that a reaction had occurred. Identical results were obtained with 2-propoxymethylthiirane and diethylamine.

Reaction of 2-propoxymethylthiirane with aqueous diethylamine. To 37 g. (0.5 mole) of freshly distilled diethylamine dissolved in 75 ml. of water was slowly added, with frequent agitation, 20 g. (0.15 mole) of 2-propoxymethyl thiirane. The reaction mixture was then refluxed for 15 hr., transferred to a separatory funnel, and potassium hydroxide pellets were added. The oily layer was separated, and dried over solid potassium hydroxide. Fractionation (short packed column) afforded 36.6 g. of unchanged diethylamine and a viscous yellow polymeric material could not be purified.

Reaction of 1-alkoxy-2-mercapto-3-aminopropanes with triethyl phosphite. In an apparatus previously described,[19] were placed 33.2 g. (0.2 mole) of purified triethyl phosphite and 18.93 g. (0.1 mole) of 1-methoxy-2-mercapto-3-piperidinopropane. The reaction mixture was heated to 150° (b.p. of triethyl phosphite) and distillate was collected at such a rate that its temperature remained in the range 40–44°. On redistillation, (short packed column) a 60% yield of methyl allyl ether was isolated, b.p. 41.2–41.8°/739 mm., n_{D}^{20} 1.3791, n_{D}^{25} 1.3765. Literature values,[30] b.p. 42.5–43°/757 mm., n_{D}^{20} 1.3778–1.3803. The original distillation residue was refractionated under vacuum with a packed column to remove excess triethyl phosphite, and obtain a small amount of material boiling at 135°/10 mm. The amidothionophosphate, $(C_2H_5O)_2PS(NC_5H_{10})$, is reported to boil at 138°/10 mm.[31] The majority of material could not be purified by vacuum distillation, and remained in the flask as a semisolid material.

Similar results were obtained in the reaction of 1-methoxy-2-mercapto-3-morpholinopropane with triethyl phosphite, except that the amidothionophosphate was not isolated. A 57% yield of methyl allyl ether was obtained.

From an equimolar mixture of 1-ethoxy-2-mercapto-3-piperidinopropane and triethyl phosphite there was obtained a 53% yield of ethyl allyl ether, b.p. 65–66°/739 mm., n_{D}^{25} 1.3887. Lit.,[32] b.p. 66–67°/743 mm., n_{D}^{25} 1.3892. A viscous initial distillation residue could not be further purified.

Reaction of 1-ethoxy-2-mercapto-3-morpholinopropane with triethyl phosphite gave a 47% yield of ethyl allyl ether. The amidothionophosphate was not isolated.

Reaction of 1-alkoxy-2-mercaptopropane with triethyl phosphite. Distillation of a mixture containing 12.4 g. (0.12 mole) of 1-methoxy-2-mercaptopropane and 19.4 g. (0.12 mole) of purified triethyl phosphite, by experimental techniques previously described,[19] gave a 94% yield of methyl propyl ether, b.p. 38–39°/742 mm., n_{D}^{20} 1.3563. Lit.,[33] b.p.

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[29] R. W. Bost, L. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

[30] S. C. Irvine, J. A. MacDonald, and C. W. Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

[31] A. Michaelis, *Ann.*, **326**, 129 (1903).

[32] M. T. Rogers and M. B. Panish, *J. Am. Chem. Soc.*, **77**, 4230 (1955).

[33] R. A. Spurr and H. Zeitlin, *J. Am. Chem. Soc.*, **72**, 4832 (1950).

38.3–39°. Triethyl thionophosphate, the other expected product in this reaction, was obtained in an 89% yield. A considerably longer distillation period, 27 hr., was required in this case, as compared to that required in the reaction of 1-methoxymethylthiirane with triethyl phosphite.[19]

The slow distillation (27 hr.) of a mixture composed of 24.0 g. (0.2 mole) of 1-ethoxy-2-mercaptopropane and 33.2 g. (0.2 mole) of triethyl phosphite gave a 91% yield of ethyl propyl ether, b.p. 62–63°/747 mm. Lit.,[34] b.p. 63–63.4°/760 mm. Triethyl thionophosphate was obtained in 83% yield.

Careful distillation (15 hr.) of a mixture composed of 26.8 g. (0.2 mole) of 1-propoxy-2-mercaptopropane and 33.2 g. (0.2 mole) of triethyl phosphite, gave a 65% yield of dipropyl ether b.p. 89–90°/742 mm., n_D^{20} 1.3801. Lit.,[34] b.p. 90–90.5°/768 mm., n_D^{20} 1.3808. Triethyl thionophosphate was also obtained in a 72% yield. Repetition of this reaction with 30 hr. of heating gave an 87% yield of the ether and an 85% yield of the triethyl thionophosphate.

East Lansing, Mich.

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(34) A. I. Vogel, *J. Am. Chem. Soc.*, 617 (1948).

[Contribution from the Central Research Department, E. I. du Pont de Nemours & Co.]

Bis(phenylimino)sulfur

RICHARD CRAMER

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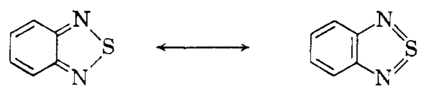
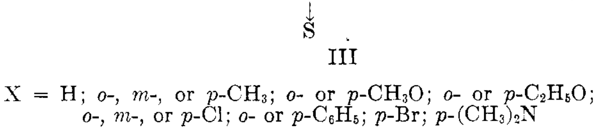
The reaction of aniline with sulfur tetrafluoride or with phenyliminosulfur difluoride yields a metathetical product, $(C_6H_5)_2N_2S$, which is identical with a compound previously obtained through the reaction of thionylaniline with sodium. The new synthetic methods indicate that the structure of the product is $C_6H_5N{=}S{=}NC_6H_5$ and this is supported by additional spectral and chemical evidence.

The first reported compound containing the $>N_2S$ group is piazthiole, obtained in the reaction of thionyl chloride[1] or sulfur dioxide[2] with *o*-phenylenediamine. Piazthiole has generally been formulated as an *o*-quinoid compound (I) but its relative inertness suggests a resonance stabilization to which a benzenoid tetravalent-sulfur structure (II) probably contributes.



I II

In 1956 Goehring and Weiss[3] reported the synthesis of bis(*n*-butylimino)sulfur by the reaction of *n*-butylamine with sulfur tetrachloride. A year later Leandri and Rebora[4] prepared a series of compounds containing the group $>N_2S$ by reaction of a variety of aromatic thionyl imines with metallic sodium (Equation 1). These compounds were



$$4\,XC_6H_4{-}N{=}S{\rightarrow}O + 2\,Na \longrightarrow 2\,XC_6H_4\underset{\underset{S}{\downarrow}}{N}{=}NC_6H_4X + Na_2S_2O_4 \quad (1)$$

III

X = H; *o*-, *m*-, or *p*-CH_3; *o*- or *p*-CH_3O; *o*- or *p*-C_2H_5O; *o*-, *m*-, or *p*-Cl; *o*- or *p*-C_6H_5; *p*-Br; *p*-$(CH_3)_2N$

formulated (III) as analogs of azoxybenzene on the following evidence:

(1) Desulfurization of either III (X = H) or azoxybenzene with zinc yields azobenzene. (2) Reaction of III with alumina also gives azobenzene apparently by an intramolecular reaction since a mixture of homologs (X = H and X = *p*-C_6H_5,) yields azobenzene and *p,p'*-diphenylazobenzene but no phenylazobenzene. (3) Reaction of either III (X = H) or azoxybenzene with hydrogen bromide produces 2,4-dibromoaniline. Subsequently, Leandri *et al.*[5] interpreted the infrared absorption spectrum of the product from thionylaniline and sodium as supporting structure III.

Attempts in this laboratory to learn if aniline and sulfur tetrachloride would yield Leandri's "azothiobenzene" (III) resulted inconclusively in extensive chlorination of aniline. When sulfur tetrafluoride and, subsequently, phenyliminosulfur difluoride became conveniently accessible through syntheses developed by Tullock[6] and Smith[7] and their co-workers, these compounds were used in reactions analogous to the Goehring and Weiss synthesis of bis(*n*-butylimino)sulfur (equations 2 and 3).

$$2\,C_6H_5NH_2 + SF_4 + 4(CH_3)_3N \longrightarrow C_6H_5N{=}S{=}NC_6H_5 + 4(CH_3)_3N{\cdot}HF \quad (2)$$

$$C_6H_5N{=}SF_2 + C_6H_5NH_2 + 2(CH_3)_3N \longrightarrow C_6H_5N{=}S{=}NC_6H_5 + 2(CH_3)_3N{\cdot}HF \quad (3)$$

The products of these reactions had infrared absorption spectra identical with the product from reaction of thionylaniline and sodium; the spectra are

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(1) A. Michaelis and A. Buntrock, *Ann.*, **274**, 253 (1893).

(2) O. Hinsberg, *Ber.*, **22**, 2899 (1889).

(3) M. Goehring and G. Weiss, *Angew. Chem.*, **68**, 678 (1956).

(4) G. Leandri and P. Rebora, *Gazz. chem. ital.*, **87**, 503 (1957).

(5) A. Foffani, G. Leandri, I. Zanow, and C. Carpanelli, *Tetrahedron Letters*, No. 11, p. 21 (1959).

(6) C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 539 (1960).

(7) W. C. Smith, C. W. Tullock, R. D. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.* **82**, 551 (1960).