$C_6H_5N(CH_3)_2 \cdot C_6H_5OSO_2Cl$

forms. At higher temperature oxidation occurs and sulfur dioxide is liberated.[3] Attempts to reduce the chlorosulfonated sulfur trioxide salt using zinc and hydrochloric acid gave no identifiable organic product.

The reaction of ammonia on the product which resulted from the action of excess chlorosulfonic acid on the amine sulfur trioxide apparently yields a mixture of amides which could not be separated into individual compounds.

A study of chlorosulfonation in the benzylamine series has been done mainly by Momose.[4] who reports the preparation of the sulfonyl chlorides of *N*-benzylacetamide and *N*-methyl-*N*-benzylacetamide. Momose found a *para* to *meta* ratio in these products of 5:1; there apparently was no detectable *ortho* isomer due to steric hindrance.

EXPERIMENTAL[5]

N,N-Dimethylbenzylamine sulfur trioxide. N,N-Dimethylbenzylamine (91.5 g., 0.68 mole) and chloroform (350 ml.) were placed in a 1-l. three neck flask which was cooled in an ice salt bath. After cooling to 0° and while stirring, 79.7 g. (0.68 mole) of chlorosulfonic acid was added dropwise at such a rate as to keep the temperature between 0 and 10°. After addition of the chlorosulfonic acid the reaction mixture was cautiously and slowly poured over a rapidly stirred ice water mixture to decompose any excess chlorosulfonic acid. The resulting material was then transferred to a separatory funnel and the water layer was removed. The chloroform layer was then washed with several portions of cold water until the washings were free of sulfate and chloride ions as indicated by the addition of barium chloride and silver nitrate to separate portions of the washings. The solvent was then removed by evaporation under reduced pressure. The solid relatively pure *N,N*-dimethylbenzylamine sulfur trioxide was dried by allowing it to stand overnight exposed to the air. The yield was 60 g., 83%. The material was purified by recrystallization from a chloroform-ether solution and melted at 217° dec.

Anal. Calcd. for $C_9H_{13}NO_3S$: S, 14.8; N, 6.50. Found: S, 14.8; N, 6.43.

N,N-Dimethylbenzylamine sulfur trioxide is insoluble in a variety of organic solvents. It is but slightly soluble in chloroform and is hydrolyzed very slowly to sulfate ions by boiling water.

In the absence of solvent the yield of the dimethylbenzylamine sulfur trioxide was only 18%.

The reaction of chlorosulfonic acid with N,N-dimethylbenzylamine sulfur trioxide. To 30 g. (0.139 mole) of *N,N*-dimethylbenzylamine sulfur trioxide was added 155.8 g. (1.34 moles) of chlorosulfonic acid (with stirring) at such a rate that the temperature of the reaction mixture did not rise above room temperature. During the addition there was an immediate liberation of a gas which consisted in part of sulfur dioxide and the formation of a greenish solution. After all the chlorosulfonic acid was added, stirring was continued for 24 hr. during which time no more gas evolution was observed. The reaction mixture was then poured over a rapidly stirred ice water mixture. The fine granular pale yellow crystals were separated and washed with several portions of cold water. The melting point of the crude product was 112–120°. This material contained 20.4% sulfur, 4.47% nitrogen, and 11.3% chlorine. It could not be purified by recrystallization because of its insolubility in all common organic solvents. It must consist of a mixture of substances as its reaction with ammonia produces amides melting in the range 104–260°. Based upon differences in solubility in ethanol, sodium hydroxide, and hydrochloric acid, these latter were separated into three fractions which still were mixtures that could not be separated further into individual pure compounds.

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[3] L. Denivelle, *Bull. Soc. Chem.*, (5), **3**, 2143 (1936).

[4] T. Momose, *Nippon Saikingaku Zasshi* (*Japanese Journal of Bacteriology*), **5**, 119 (1950); also private communication.

[5] Elemental analyses were performed by Drs. Weiler and Strauss, 164 Banbury Lane, Oxford, England.

Transthiazolination: The Rearrangement of 2-(2′-Aminoethylthio)-2-thiazoline

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S-(2-Aminoethyl)isothiourea has been shown by Doherty *et al.*,[1] to undergo rearrangement to 2 mercaptoethylguanidine in neutral aqueous solution, and a cyclic intermediate has been postulated for the reaction. The rearrangement of a number of aminoalkylisothioureas to mercaptoalkylguanidines by this transguanylation reaction has been studied by ion exchange analysis.[2,3] In addition, it was demonstrated by ion exchange analysis that 2-(2′-aminoethylthio)-2-imidazoline underwent transimidazolination to 2-(2′-mercaptoethylamino)-2-imidazoline rapidly at *p*H 7.0; the properties of the compounds involved were not described.

We have found that 2-(2′-aminoethylthio)-2-thiazoline (I) undergoes a similar type of rearrangement, for which a symmetrical bicyclic intermediate can be postulated. The dihydrobromide of I was prepared by the reaction of 2-thiazolidinethione and 2-bromoethylamine hydrobromide in refluxing isopropyl alcohol. When an aqueous solution of I dihydrobromide was neutralized or made weakly alkaline, rearrangement to 2-(2′-mercaptoethylamino)-2-thiazoline (III) occurred. The latter compound readily underwent oxidation in air to the disulfide IV. Color tests on IV, its analytical data, and its infrared spectrum were consistent with its formulation as bis[2-(2′-thiazolinyl-2′-amino)ethyl] disulfide. Proof of this structure was obtained by alternate synthesis.

2-Methylthio-2-thiazoline and 2-mercaptoethylamine hydrochloride in refluxing methanol[4] af-

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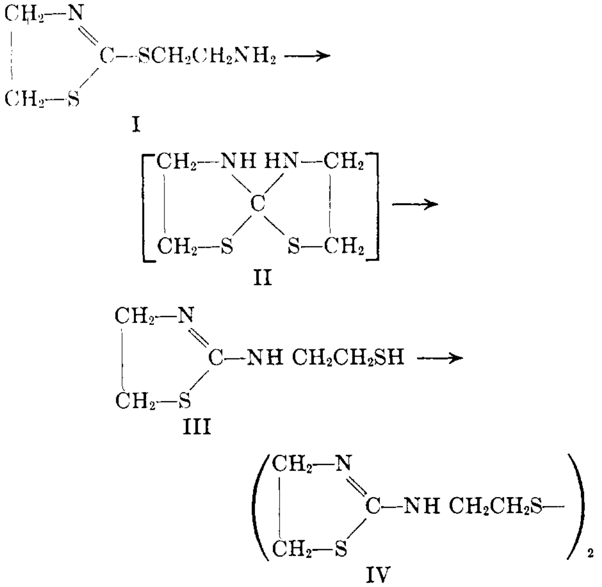
[1] D. G. Doherty, R. Shapira, and W. T. Burnett, Jr., *J. Am. Chem. Soc.*, **79**, 5667 (1957).

[2] J. X. Khym, R. Shapira, and D. G. Doherty, *J. Am. Chem. Soc.*, **79**, 5663 (1957).

[3] J. X. Khym, D. G. Doherty, and R. Shapira, *J. Am. Chem. Soc.*, **80**, 3342 (1958).



forded 2-(2'-mercaptoethylamino)-2-thiazoline hydrochloride (III, HCl). The disulfide obtained from the air oxidation of this mercaptan in alkaline solution proved to be identical to the sample of IV obtained from the rearrangement.

The high yield obtained and the low basicity required indicate that an intratransthiazolination is involved in the rearrangement.[5] The postulated cyclic intermediate for the rearrangement in this case is represented by formula II. In this instance, in which the bicyclic intermediate is composed of similar rings, only one product was obtained. Rearrangements of this kind involving unsymmetrical bicyclic intermediates are being investigated.

EXPERIMENTAL

2-(2'-Aminoethylthio)-2-thiazoline dihydrobromide (I, 2HBr). A solution of 4.76 g. (0.04 mole) of 2-thiazolidinethione and 8.20 g. (0.04 mole) of 2-bromoethylamine hydrobromide in 60 ml. of isopropyl alcohol was refluxed for 4 hr. A solid precipitate began to separate during the refluxing. The cooled mixture yielded 3.50 g. (27%) of colorless product, m.p. 216° dec. Recrystallization from methanol afforded colorless crystals, m.p. 222° dec.

Anal. Calcd. for $C_5H_{12}Br_2N_2S_2$: C, 18.53; H, 3.73; S, 19.78; Br, 49.31. Found: C, 18.61; H, 3.71; S, 19.80; Br, 49.16.

There appeared to be some loss of material during the recrystallization from methanol; the recoveries obtained were low and erratic. The reaction product also gave satisfactory analyses before recrystallization.

When a solution of the dihydrobromide in aqueous ethanol was treated with alcoholic picric acid solution, a yellow crystalline dipicrate, m.p. 132–134°, was obtained.

Anal. Calcd. for $C_{17}H_{16}N_8S_2O_{14}$: C, 32.90; H, 2.60; S, 10.33. Found: C, 33.07; H, 2.65; S, 10.67.

On attempted recrystallization of this picrate from aqueous alcohol rearrangement occurred.[6] The picrate obtained from the recrystallization melted at 191–192° and was identical, by mixed melting point and infrared spectra, to the picrate of 2-(2'-mercaptoethylamino)-2-thiazoline (III).

Bis[2-(2'-thiazolinyl-2'-amino)ethyl]disulfide (IV) *from rearrangement of* I. (a) *At pH 9.1.* To a solution of 500 mg. (1.54 mmoles) of 2-(2'-aminoethylthio)-2-thiazoline dihydrobromide in 7 ml. of water was added two equivalents (3.1 ml.) of 1*N* sodium hydroxide. The resulting solution (*p*H 9.1) was allowed to stand at room temperature for 5 hr., and air was intermittently bubbled through it. A white crystalline precipitate separated slowly. After cooling, filtration yielded 227 mg. (91%) of the disulfide, m.p. 141–143°. Crystallization from 1:1 aqueous ethanol afforded glistening white plates, m.p. 145–146.5°.

Anal. Calcd. for $C_{10}H_{18}N_4S_4$: C, 37.24; H, 5.62; N, 17.37; S, 39.76; mol. wt., 323. Found: C, 37.35; H, 5.68; N, 17.25; S, 39.85; mol. wt., 337 (Rast).

Color tests on the disulfide with nitroprusside reagent and with lead acetate were negative. However, after it had been treated with potassium cyanide[7] or reduced with zinc and hydroxylamine hydrochloride,[8] positive tests for a mercapto group were obtained.

The dipicrate, prepared in ethanol, melted at 239–241°.

Anal. Calcd. for $C_{22}H_{24}N_{10}O_{14}S_4$: C, 33.84; H, 3.10; S, 16.43. Found: C, 33.79; H, 3.03; S, 16.73.

(b) *At pH 7.0.* An aqueous solution of 500 mg. of 2-(2'-aminoethylthio)-2-thiazoline dihydrobromide was treated with 1*N* sodium hydroxide until the *p*H was 7.0. After the solution had stood at room temperature for 42 hr. with occasional aeration, acidification with dilute hydrochloric acid and the addition of ethanolic picric acid solution gave 0.54 g. (90%) of the dipicrate of IV, m.p. 239–241°.

2-(2'-Mercaptoethylamino)-2-thiazoline hydrochloride (III, HCl). A solution of 3.73 g. (0.028 mole) of 2-methylthio-2-thiazoline[4] and 3.18 g. (0.028 mole) of 2-mercaptoethylamine hydrochloride in 75 ml. of methanol was refluxed for 4 hr. The solvent was removed under reduced pressure, and the remaining 6.40 g. of viscous oil was stored under nitrogen at 0–5°.

The ready oxidation of the mercaptan to the disulfide made crystallization difficult. Ultimately, in an atmosphere of nitrogen, a 2.35-g. portion of the 6.40 g. of oil separated from 8.5 ml. of absolute ethanol in clumps of fine white crystals; 1.20 g. (59%), m.p. 99–101°. These were filtered under nitrogen and washed on the filter with acetone. An analytical sample melted at 99.5–101.5°.

Anal. Calcd. for $C_5H_{11}ClN_2S_2$: C, 30.22; H, 5.58; S, 32.26. Found: C, 30.35; H, 5.50; S, 32.47.

This compound gave the usual tests for a mercaptan with nitroprusside reagent and with lead acetate. In addition, the infrared spectra of both this compound and its picrate showed a mercaptan band at $3.9\ \mu$.

The picrate crystallized from ethanol as yellow needles, m.p. 191–192°. From a 0.51-g. portion of the 6.40 g. of concentrate from the reaction there was obtained 0.84 g. (96% yield from 2-methylthio-2-thiazoline) of the picrate.

Anal. Calcd. for $C_{11}H_{13}N_5O_7S_2$: C, 33.76; H, 3.35; S, 16.38. Found: C, 33.75; H, 3.37; S, 16.77.

Bis[2-(2'-thiazolinyl-2'-amino)ethyl] disulfide (IV) *from oxidation of* III. A 0.46-g. portion of the 6.40 g. of viscous concentrate obtained from 2-methylthio-2-thiazoline and 2-mercaptoethylamine hydrochloride was dissolved in 15 ml. of water, and sodium hydroxide was added dropwise until the solution was strongly alkaline (*p*H 10). A precipitate

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(4) A. F. McKay, D. J. Whittingham, and M.-E. Kreling [*J. Am. Chem. Soc.*, **80**, 3339 (1958)] have reported the reaction of 2-methylthio-2-thiazoline with various amines and amino acids.

(5) *Cf.* Refs. 1–3.

(6) It was shown by Doherty, *et al.*, (Refs. 1–3) that although *S*-(2-aminoethyl)isothiourea and related compounds were stable in strongly acidic solution (0.2*N* hydrochloric acid), the rearrangement began to take place under more weakly acidic conditions.

(7) I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

(8) N. D. Cheronis and J. B. Entrikin, *Semimicro Qualitative Organic Analysis*, 2nd Ed., Interscience, New York, 1957, p. 274.

began to separate in a few minutes. After the mixture had stood at room temperature for about 20 hr. with occasional aeration, filtration afforded 0.30 g. (93% yield from 2-methylthio-2-thiazoline) of fine white crystals, m.p. 144–145.5°. Recrystallization from 1:1 aqueous ethanol gave glistening plates, m.p. 145–146.5°. The infrared spectra of this product and of the disulfide from the rearrangement were identical; there was no mixed melting point depression.

The dihydroiodide of the disulfide, m.p. 244.5–246°, was isolated from an attempted preparation of the mercaptan (III) from 2-methylthio-2-thiazoline hydroiodide[4] and 2-mercaptoethylamine in refluxing methanol. The same compound was obtained from IV and hydrogen iodide.

Anal. Calcd. for $C_{10}H_{20}I_2N_4S_4$: C, 20.76; H, 3.49; S, 22.17. Found: C, 20.88; H, 3.57; S, 22.41.

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The Molecular Weights of Some Simple Borolanes and Borinanes[1]

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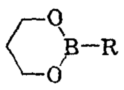
Only a few simple derivatives of the six-membered dioxaborinane ring (I) have been reported in the literature,[2–5] and none of the materials described



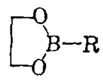
Ia. R = Cl–
Ib. R = n-C_4H_9O-

I

has been characterized by molecular weight determinations. 2-Chloro-1,3,2-dioxaborinane (Ia) was prepared from equivalent amounts of trimethylene glycol and boron trichloride. Conklin and Morris[2] originally described this reaction but did not characterize the chloro compound. Finch, *et al.*,[5] who have prepared Ia independently by a similar method, described it as a viscous liquid, whereas the product obtained in the present work was not a viscous material at room temperature. Reaction of Ia with n-butyl alcohol gave 2-n-butoxy-1,3,2-dioxaborinane (Ib), a reaction which was also noted by Finch. The experimental molecular weights of these borinanes given in Table I show that they are monomeric in benzene solution in the concentration range studied.

A number of related organoboron compounds containing the five-membered dioxaborolane ring (II) have been reported in the literature, and their physical properties have been described in some detail. Although they have generally been assumed to be monomeric in the liquid state, the only simple dioxaborolane for which an experimental molecular weight has been reported is 2-n-butoxy-1,3,2-dioxaborolane (IIc), which was found to be monomeric in cyclohexane solution.[6] The concentration used in this molecular weight determination was not specified.

IIa. R = Cl—
IIb. R = C_2H_5O—
IIc. R = n-C_4H_9O—
IId. R = $(CH_3)_2N$—



II

Recently 2-chloro- (IIa); 2-n-butoxy-(IIc), and 2-dimethylamino-1,3,2-dioxaborolanes (IId) have been prepared in this laboratory, and their physical properties agreed with those reported by previous workers.[2,6,7] It was noted, however, that the chloroborolane, IIa, is an extremely viscous compound with a boiling point which suggests a high degree of association in the liquid state. For example, chlorodimethoxyborane, $(CH_3O)_2BCl$, which has a molecular weight of 108.3 compared to 106.3 for IIa, has a vapor pressure of 1 mm. at $-47°$[8] while IIa boiled at 74° at 1 mm. Cryoscopic molecular weights of the borolanes, IIa, IIc and IId, were determined in benzene solution, and the results are shown in Table I.

The chloro compound (IIa) apparently exists in the dimeric form in benzene solution[9] in the concentration range studied. The only other examples of alkoxyhaloboranes which were reported to be strongly associated in the liquid state are difluoromethoxyborane[10,11,13] and n-butoxydifluoroborane[12] which were originally reported to be dimeric. Later McCusker[13] suggested that these compounds were complexes having the general formula, $(RO)_3B.2BF_3$. However, recent studies

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(1) The research reported in this document was supported in part by Wright Air Development Division of the U. S. Air Force under Contract AF 33(616)-5931.

(2) G. W. Conklin and R. C. Morris, Brit. Patent **790,090** (1958).

(3) P. J. Garner, Brit. Patent **722,538** (1955).

(4) P. J. Garner, U. S. Patent **2,839,564** (1958).

(5) A. Finch, J. C. Lockhart, and J. Pearn, *Chem. & Ind.*, 471 (1960).

(6) J. A. Blau, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 4116 (1957).

(7) R. L. Letsinger and I. H. Skoog, *J. Am. Chem. Soc.*, **76**, 4174 (1954).

(8) E. Wiberg and W. Sutterlin, *Z. anorg. Chem.*, **202**, 1 (1931).

(9) The extremely viscous nature of 2-chloro-1,3,2-dioxaborolane suggests that it is even more highly associated in the pure liquid state.

(10) J. Goubeau and K. E. Lucke, *Ann.*, **575**, 37 (1952).

(11) E. C. Allen and S. Sugden, *J. Chem. Soc.*, 760 (1932).

(12) M. F. Lappert, *J. Chem. Soc.*, 784 (1955).

(13) P. A. McCusker and S. M. Laeticia Kilzer, *J. Am. Chem. Soc.*, **82**, 372 (1960).