–S–S– groups to the mono- or dioxide stage is demonstrated to occur in an organism.

Experimental

Ethyl Ethanethiolsulfonate. Method A.—One liter of ethyl acetate and 24.5 g. (0.2 mole) of ethyl disulfide were placed in a three-liter, three-neck flask. The solution was cooled with an ice-bath and while stirring there was added, during fifteen minutes, a solution of 5 moles of 40% peracetic acid in 500 cc. of ethyl acetate. After stirring and cooling for an additional hour the solution was allowed to stand at room temperature overnight. The reaction mixture was stirred with a solution of 30 g. of ferrous sulfate heptahydrate in 150 cc. of water to decompose excess per-acid. The ethyl acetate layer was separated and shaken with sufficient saturated aqueous sodium bicarbonate solution to remove acids. The ethyl acetate extract was dried over anhydrous sodium sulfate and then evaporated under reduced pressure to remove solvent. The liquid residue was distilled, yielding the thiolsulfonate, b. p. 56° at 0.2 mm.; $n^{25}\text{D}$ 1.4972; yield 3.7 g. or 12%.

Anal. Calcd. for $C_4H_{10}O_2S_2$: C, 31.15; H, 6.54. Found: C, 31.42; H, 6.41.

Method B.—Ethyl ethanethiolsulfonate was first prepared by Otto by reaction of an ethyl halide with sodium ethanethiolsulfonate, but few details were given and the compound was poorly characterized.[6,7]

An alcoholic solution of potassium sulfide was prepared by dissolving 0.5 mole of potassium hydroxide in 250 cc. of absolute ethanol, saturating the solution with hydrogen sulfide and adding a second 0.5 mole of alkali to the solution.

Ethanesulfonyl chloride ($n^{25}\text{D}$ 1.4515) was prepared by the method of Lee and Dougherty.[8] To the potassium sulfide solution was added dropwise, during four hours of stirring under anhydrous conditions, a solution of 0.5 mole of ethanesulfonyl chloride in 250 cc. of ethanol. The mixture was cooled with an ice-bath during this period. The mixture was then made alkaline to litmus with alcoholic potassium hydroxide and allowed to stand for fifteen hours at 25° and then heated to 50° for ten minutes. The solution was filtered and the filtrate refluxed for four hours with 0.75 mole of ethyl bromide. After cooling, the solution was filtered, the filtrate concentrated under reduced pressure and the residual thiolsulfonate distilled: yield 23.2 g. or 30%.

Anal. Found: C, 31.07; H, 6.23; $n^{25}\text{D}$ 1.4977.

Reaction with Cysteine.—Unbuffered aqueous solutions of cysteine hydrochloride and the thiolester adjusted to *p*H 6.5 with sodium hydroxide solution were mixed[3] and within a few seconds there appeared a white crystalline precipitate of I where R is ethyl, m. p. 196° dec. The thiosulfinate yielded nearly two moles of I (compare where R is allyl[3]) with no change in *p*H; the thiolsulfonate gave 90% yield for one mole of I and the *p*H dropped to 3.0.

Anal. Calcd. for I, $C_5H_{11}O_2NS_2$: N, 7.75. Found: N, 7.79.

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(6) Otto, *Ber.*, **15**, 122 (1882).

(7) Hilditch, *J. Chem. Soc.*, **97**, 1098 (1910).

(8) Lee and Dougherty, *J. Org. Chem.*, **5**, 83 (1940).

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Further Studies on Oxythiamine

BY MORRIS SOODAK[1] AND LEOPOLD R. CERECEDO

The preparation of oxythiamine from thiamine by deamination with gaseous nitrogen oxides has been previously reported from this Laboratory.[2] In the present communication, we wish to report additional information on this compound.

During the course of this work the thiochrome method was used in following the fate of thiamine, and the Prebluda–McCollum reagent as modified by Melnick and Field[3] served in tracing both the thiamine and oxythiamine, since both compounds give a positive reaction with equal color production. We have found that Melnick and Field[3] and also Rosenberg[4] are incorrect in assuming that the amino group in position 4 of the pyrimidine moiety is necessary for the production of color. Todd and Bergel,[5] and Prebluda and McCollum[6] had already shown that the essential features required for the production of color are the β-hydroxyethyl group on position 5 and a free hydrogen on position 2 of the thiazole moiety. In fact, Bergel and Todd[7] were able to synthesize oxythiamine and showed that it gave a positive formaldehyde–azo reaction. Thus, whereas thiamine gives both positive thiochrome and Prebluda–McCollum reactions, oxythiamine reacts only with the Prebluda–McCollum reagent, and the chloroxy- and bromoxythiamine give neither reaction. Our findings, therefore, confirm those of Todd and Bergel.

Oxythiamine is very similar to thiamine in its chemical properties. Both substances form chloride–hydrochloride salts, picrates and picrolonates, and they can be adsorbed on and eluted from Decalso under similar conditions.[8] Neither compound is attacked by sodium in the presence of glacial acetic acid[9] and both are split by the sulfite treatment of Williams.[10] Thus, by treatment of oxythiamine with sulfite, we have obtained 2-methyl-4-oxypyrimidine-5-methylsulfonic acid.

The ultraviolet absorption spectrum of oxythiamine chloride–hydrochloride was determined for aqueous solutions at neutral and acid reactions, by means of a Model DU Beckman spectrophotometer. Oxythiamine shows two maxima at 223 and 266 mμ, respectively, at *p*H 7.2 (phosphate buffer, 0.02 *M*), and at 221.5 and 265 mμ in 0.02 *M* phosphoric acid. The spectrum is very similar to that of oxychlorothiamine.[11]

Experimental[12]

Picrate and Picrolonate of Oxythiamine.—These compounds were prepared in the usual manner. They were recrystallized several times from an ethanol–water (1:1) mixture.

Oxythiamine picrate, m. p. 102–108°. *Anal.* Calcd. for $C_{12}H_{16}O_2N_3S[C_6H_2OH(NO_2)_3]_2$: C, 39.78; H, 3.00. Found: C, 39.46; H, 2.88.

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(1) Present address: Biochemical Research Laboratory, Massachusetts General Hospital, Boston, Mass.

(2) Soodak and Cerecedo, THIS JOURNAL, **66**, 1988 (1944).

(3) Melnick and Field, *J. Biol. Chem.*, **127**, 505 (1939).

(4) H. R. Rosenberg, "Chemistry and Physiology of the Vitamins," Interscience Publishers, Inc., New York, N. Y., 1942, p. 129.

(5) Todd and Bergel, *J. Chem. Soc.*, 1559 (1936).

(6) Prebluda and McCollum, *J. Biol. Chem.*, **127**, 495 (1939).

(7) Bergel and Todd, *J. Chem. Soc.*, 1504 (1937).

(8) Cerecedo and Hennessy, THIS JOURNAL, **59**, 1617 (1937).

(9) Tolpin, Foy and Cerecedo, *ibid.*, **63**, 2848 (1941).

(10) Williams, Waterman, Keresztesy and Buchman, *ibid.*, **57**, 536 (1935).

(11) Buchman and Williams, *ibid.*, **57**, 1751 (1935).

(12) All melting points are uncorrected. The analyses were performed by Mr. M. Bier.

Oxythiamine picrolonate, m. p. 130–133°. *Anal.* Calcd. for $C_{12}H_{16}O_2N_3S(C_{10}H_8O_5N_4)_2$: C, 48.36; H, 4.03. Found: C, 48.00; H, 4.15.

2-Methyl-4-oxypyrimidine-5-methylsulfonic Acid.—Oxythiamine hydrochloride was treated with sulfite according to the method of Williams and co-workers.[10] After standing with the sulfite for two days (faint Prebluda–McCollum reaction), the solution was adjusted to *p*H 10, the thiazole fragment removed by extraction with chloroform, and the oxysulfonic acid isolated according to the method used by Cline, *et al.*,[13] in their synthesis of this compound.

Anal. Calcd. for $C_6H_8N_2SO_4$: C, 35.29; H, 3.92. Found: C, 35.70; H, 3.84.

The substance was also prepared as follows: The aminosulfonic acid, obtained by treatment of thiamine with sulfite,[10] was treated with the nitrogen oxide gases. The deamination could be easily followed, since the aminosulfonic acid is insoluble, whereas the oxysulfonic acid is rather soluble. The solution was evaporated to dryness *in vacuo*, and recrystallized by solution in water and precipitation with alcohol.[13]

Anal. Found: C, 35.54; H, 4.03.

Bromoxythiamine Bromide Hydrobromide.—One gram of thiamine hydrochloride was dissolved in 20 ml. of glacial acetic acid saturated with dry hydrogen bromide, and sealed in a bomb tube. The mixture was heated at 150–160° for three hours. After removal from the tube, the solution was concentrated *in vacuo* to dryness. The residue was recrystallized several times by solution in methanol and precipitation with absolute ether.[14] The resulting material was washed with ether and dried. It melted at 206–208° with decomposition. The compound does not form thiochrome and does not react with the Prebluda–McCollum reagent.

Anal. Calcd. for $C_{12}H_{16}N_3SOBr_3$: C, 29.38; H, 3.26; Br, 49.00. Found: C, 29.51; H, 3.87; Br, 49.05.

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[13] Cline, Williams, Ruehle and Waterman, THIS JOURNAL, **59**, 530 (1937).

[14] Weil-Malherbe, *Biochem. J.*, **34**, 980 (1940).

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Dichlorovinyltrichlorosilanes

BY G. H. WAGNER AND A. N. PINES

In a recent publication,[1] Agre has described the preparation of "α,β-dichlorovinyltrichlorosilane." In the interest of clarifying the structure of his compound, we would like to record the properties and reactions of two dichlorovinyltrichlorosilanes prepared in this Laboratory. Our data indicate that his compound is β,β-dichlorovinyltrichlorosilane. The properties of our dichlorovinyltrichlorosilanes, I and II, are compared below with Agre's compound.

		Compound I	Compound II	Agre's compound
Boiling point	°C.	163.5–164	162.5–163	159
	Mm.	750	750	729
Density, g./cc. at 25°C.		1.56	1.54	....
$n^{20}D$		1.4958	1.4942	1.4942

Compound I on treatment with concentrated potassium hydroxide gave 1,2-dichloroethylene by fission of the carbon–silicon bond similar to that observed[2] for chloromethyl groups attached to silicon. An explosive gas, probably chloroacetylene, was also formed during this treatment. Compound II, which compares well in its properties with Agre's compound, gave 1,1-dichloroethylene on similar treatment with concentrated potassium hydroxide solution. These reactions indicate that compound I is α,β-dichlorovinyltrichlorosilane and compound II is β,β-dichlorovinyltrichlorosilane. Since the properties of these compounds are almost identical, within experimental error, the part of Agre's proof of structure which is based on a comparison of the physical properties of the compounds obtained from the reaction of trichlorosilane with trichloroethylene and with 1,2-dichloroacetylene is questionable.

Experimental

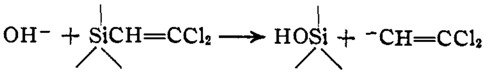
Treatment of Compound I with Concentrated Potassium Hydroxide.—A three-liter flask was fitted with a dropping funnel and a small water condenser. The water condenser was vented to the atmosphere through two traps, one cooled in ice-water and one in Dry Ice and acetone. A solution of 200 g. of potassium hydroxide in 1500 cc. of water was added to the flask. Seventy-seven grams of compound I was added rapidly through the dropping funnel to the potassium hydroxide solution. After heating the mixture for a few minutes at reflux, a water-insoluble liquid formed. This was steam distilled into the traps after shutting off the cooling water to the water condenser. Upon cooling, a violent explosion occurred in the vent lines but 6 g. of material with the following properties was recovered from the traps.

		Unknown	Reported for 1,2-dichloroethylene *cis*	*trans*
Boiling point, °C.		56	48.4	60.3
Density	g./cc.	1.245	1.265	1.29
	°C.	25	15	15
$n^{20}D$		1.4501	1.4490, 15°	1.4519, 15°

Treatment of Compound II with Concentrated Potassium Hydroxide.—Using the same equipment and technique described above, 114 g. of compound II was added to a solution of 300 g. of potassium hydroxide in 700 cc. of water. Upon cooling, a small flash occurred in the vent line; 27.4 g. of material with the following properties was recovered from the traps.

		Unknown	Reported for 1,1-dichloroethylene
Boiling point, °C.		30.5	31.6
Density	g./cc.	1.168	1.218
	°C.	25	20
$n^{20}D$		1.4253	1.4270

The reactions observed here may be formulated in steps as exemplified below for the reaction of β,β-dichlorovinyltrichlorosilane,



$$OH^- + SiCH{=}CCl_2 \longrightarrow HOSi + {}^-CH{=}CCl_2 \quad (1)$$

$$^-CH{=}CCl_2 + H_2O \longrightarrow CH_2{=}CCl_2 + OH^- \quad (2)$$

$$^-CH{=}CCl_2 \longrightarrow CH{\equiv}CCl + Cl^- \quad (3)$$

The first step is an attack of hydroxyl ion on silicon to give the carbanion, $^-CH{=}CCl_2$, which may stabilize itself by reaction with the solvent, reac-

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[1] Agre, THIS JOURNAL, **71**, 300 (1949).

[2] Krieble and Elliott, *ibid.*, **67**, 1810 (1945).