

Ultraviolet spectra of disulfides. The ultraviolet spectra were obtained with the Beckman Recording Spectrophotometer, Model DK, using isoctane as a solvent. The curves are recorded in a thesis,¹ and the maxima: diphenyl disulfide, 241 (4.33), $[\lambda, (\log \epsilon)]$ in $m\mu$ are: 272 (3.57), 302 (3.26); bis-(2,6-dimethylphenyl) disulfide, 225 (4.02), 260 (3.89), 305 (2.78); bis-(2,4,5-triisopropylphenyl) disulfide, 244 (4.18), 285 (3.56), 344 (2.84); bis-(2,4,6-triisopropylphenyl) disulfide, 232 (4.18), 270 (4.07), 310 (3.51). All of the disulfides except diphenyl show a low order of absorption ($\log \epsilon$ ca. 0.2–0.4) at ca. 500–700 $m\mu$, which increases as the ultraviolet region is approached, and are pale yellow. The absorption spectrum of diphenyl disulfide checked well with that recorded.¹²

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(12) H. P. Koch, *J. Chem. Soc.*, 397 (1949); G. Leandri and A. Tundo, *Ann. Chim. (Rome)* **45**, 180 (1955); [*C.A.* **49**, 12,960 (1955)]; R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951, p. 152.

Bis(2-aminoethyl) Dithiolcarbonate Dihydrochloride: Intermediate in the Hydrolysis of 2-Thiazoline-2-thiol

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The acid hydrolysis of 2-thiazoline-2-thiol (I) to 2-aminoethanethiol hydrochloride (II) has been known for some time.^{2,3} When conducted in a sealed container at about 150°, a four to six hour reaction period generally sufficed to give quantitative yields of II. Because we desired some 2-aminoethanethiol hydrochloride, we undertook a study of the hydrolysis in refluxing, concentrated hydrochloric acid. At atmospheric pressure the reaction requires approximately two weeks for completion. Intermediate reaction periods produced a readily separable mixture of 2-aminoethanethiol hydrochloride and a hitherto unreported material, compound III. Reaction times of about twenty-four hours resulted in recovery of substantial amounts of starting material and gave good yields of compound III with practically no 2-aminoethanethiol hydrochloride. The results of several hydrolyses, as summarized in Table I, and the evidence which characterizes compound III as bis(2-aminoethyl) dithiolcarbonate dihydrochloride are reported in this paper.

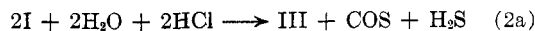
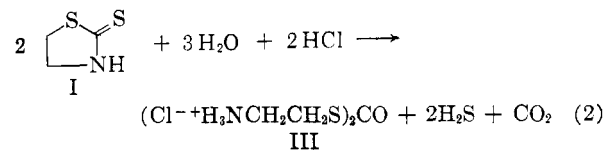
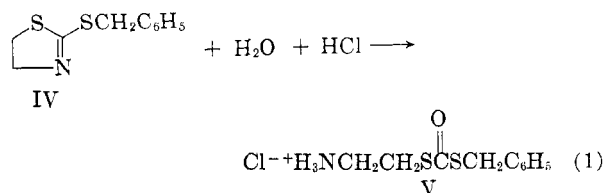
While the facile hydrolysis of 2-alkylthio- or 2-arylthio-2-thiazolines to the corresponding 2-

TABLE I
ACID HYDROLYSIS PRODUCTS OF 2-THIAZOLINE-2-THIOL

Time, Hrs.	Yield, %		
	I	II ^a	III ^a
19.5	61.3	0.0	57.0
20 ^b	60.2	9.9 ^c	71.5
90	12.9	45.2	33.4
336	0.0	94.5	0.0

^a Yields are corrected for recovered I. ^b Conducted with a mixture of 0.5 mole each of I and II. ^c Yield corrected for original II present.

aminoalkyl dithiolcarbonate hydrochlorides^{4,5} (equation 1) is well known, the conversion of



2-thiazoline-2-thiol to a similar type of compound (equations 2 and 2a) has not been reported.

Compound III can be obtained either as a crystalline hydrate or as an anhydrous salt. It is quite soluble in water but is only sparingly soluble in ethanol and common organic solvents. Microanalyses indicate an empirical formula of $\text{C}_5\text{H}_{14}\text{ON}_2\text{S}_2\text{Cl}_2$. Van Slyke amino nitrogen and Volhard chloride determinations further showed that compound III must be a dihydrochloride containing two primary amino groups. An equivalent weight of 126 (chloride content) and a neutral equivalent of 257 indicated that $\text{C}_5\text{H}_{14}\text{ON}_2\text{S}_2\text{Cl}_2$ (M.W. = 253) was very probably the molecular formula. The presence of a single oxygen atom in a carbonyl group was inferred from analytical data and the presence of a strong, infrared absorption band at 1645 cm^{-1} .

The chemical behavior of compound III, which at first may seem incongruous, can best be explained by its formulation as bis(2-aminoethyl) dithiolcarbonate dihydrochloride. It is obtained in highest yield and free from 2-aminoethanethiol hydrochloride in the early stages of the hydrolysis. Like aminoethyl alkyl dithiolcarbonate hydrochlorides generally⁴⁻⁶ III is rather resistant to further acid

(4) J. C. Crawhall and D. F. Elliott, *J. Chem. Soc.*, 3094 (1952).

(5) J. M. Sprague and A. H. Land, *Heterocyclic Compounds*, R. C. Elderfield, ed., John Wiley and Sons, New York, N. Y., 1957, Vol. 5, p. 696.

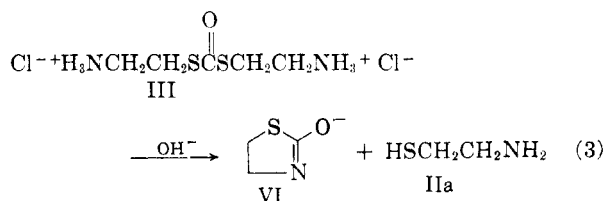
(6) H. C. Crawhall and D. F. Elliott, *J. Chem. Soc.*, 2071 (1951).

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(2) S. Gabriel and E. Leupold, *Ber.*, **31**, 2832 (1898).

(3) E. J. Mills and M. T. Bogert, *J. Am. Chem. Soc.*, **62**, 1173 (1940).

hydrolysis; however, it ultimately is converted quantitatively to 2-aminoethanethiol hydrochloride. While a slightly acidic solution of III does not react with lead acetate or iodine,⁷ in basic solution it undergoes an eliminative-recyclization reaction peculiar only to 2-aminoalkyl substituted dithiolcarbonates.^{4,6} This reaction is illustrated in equation 3.



The formation of the anion of 2-thiazolidinone (VI) accounts for the neutral equivalent of III and the elimination of aminoethanethiol (IIa) gives rise to the quantitative reaction with iodine and a positive sodium nitroprusside test.⁷

Finally, authentic 2-aminoethylbenzyl dithiolcarbonate hydrochloride (V) was prepared and its infrared spectrum was compared with that of III. The correlation of the significant bands, presented in Table II, is excellent. Thus, there is little doubt that this new compound isolated from the acid hydrolysis of 2-thiazoline-2-thiol is bis(2-aminoethyl) dithiolcarbonate dihydrochloride (III).

TABLE II
INFRARED COMPARISON OF COMPOUNDS III AND V

III Bands (cm. ⁻¹)	V Bands (cm. ⁻¹)	Assignment
3360		OH stretch, present only in hydrate
1735	1740	Overtone of 875 and 885 bands respectively
1645	1655	C=O stretch
1600	1585	NH bending in NH ₃ ⁺
1525	1525	
875	885	S—C—S antisymmetric stretch

The isolation of III would seem to indicate that the hydrolysis of 2-thiazoline-2-thiol is considerably more complex than might be anticipated. The resistance of III to further acid hydrolysis may also be the reason for the over-all sluggishness of the reaction. The formation of bis(2-aminoethyl) dithiolcarbonate dihydrochloride in this reaction apparently requires more than one molecule of 2-thiazoline-2-thiol and raises interesting questions regarding the mechanistic path of the process. In the absence of a detailed kinetic examination of this reaction, we are not prepared to speculate further on the probable mechanism for the acid hy-

drolysis of 2-thiazoline-2-thiol to bis(2-aminoethyl) dithiolcarbonate dihydrochloride and 2-aminoethanethiol hydrochloride.

EXPERIMENTAL

Bis(2-aminoethyl) dithiolcarbonate dihydrochloride (III). A mixture of 119 g. (1.0 mole) of 2-thiazoline-2-thiol and 250 ml. of conc. hydrochloric acid was heated under reflux (115°) for 90 hr. The resulting solution, upon prolonged chilling, deposited 15.4 g. (12.9%) of starting material which was removed by vacuum filtration and washed with a small portion of ice-cold water. The filtrate and washings were combined and vacuum concentrated (ca. 90° and 20 mm.) to a pale yellow syrup. This was treated successively with 200 ml. of 1:1 ethanol-benzene, and two 100-ml. portions of ethanol with vacuum concentration after each treatment. The resulting solid was suspended in 100 ml. of hot absolute ethanol and filtered. The filter cake was washed with a total of 250 ml. of absolute ethanol and dried to give 36.8 g. (33.4% corrected for recovered I) of bis(2-aminoethyl) dithiolcarbonate dihydrochloride, m.p. 198.7–199.9° with gas evolution.

Vacuum concentration of the combined filtrate and ethanol wash liquor produced a yellow syrup. This was dissolved in 50 ml. of boiling, absolute ethanol, brought to the cloud-point with anhydrous ether and stored at 5° over night. The resulting, slightly yellow crystalline solid was removed by vacuum filtration, washed with two 100-ml. portions of anhydrous ether, and dried in a desiccator to give 44.7 g. (45.2% corrected for recovered I) of impure 2-aminoethanethiol hydrochloride, m.p. 65.4–67.4° (lit.² m.p. 70.2–70.9°).

A representative analytical sample of III was obtained by dissolving the product obtained in the 19.5 hr. reaction (cf. Table I), m.p. 204.6–205.6° with gas evolution, in a minimum of hot water, filtering, and diluting with approximately 10 volumes of 95% ethanol. After storage at 5°, the solution deposited a nicely crystalline hydrate (infrared band at 3360 cm.⁻¹) which, upon drying at 100° and 0.2 mm. for 24 hr., gave the anhydrous salt (no band at 3360 cm.⁻¹). Both forms melted at 204–205.2° with gas evolution.

Anal. Calcd. for C₈H₁₄ON₂S₂Cl₂: C, 23.72; H, 5.57; N, 11.06; S, 25.32; Cl, 28.00. Found: C, 23.94, 23.69; H, 5.28, 5.54; N, 11.09, 11.40 (Kjeldahl), 14.55, 14.62 (Van Slyke); S, 24.68, 24.97; Cl, 28.02, 28.94 (Carius), 27.68 (Volhard).

Neutral equivalent of III. A solution of 0.4658 g. of III was made basic by the addition of 45.0 ml. of 0.100N sodium hydroxide. After a brief storage period, the solution was back-titrated with 0.100N hydrochloric acid. A total of 26.9 ml. of acid was required to reach the break in the pH titration curve. This corresponds to an initial consumption of 18.1 ml. of base or a neutral equivalent of 257 (C₈H₁₄ON₂S₂Cl₂ = 253).

Titration with standard iodine solution. Bis(2-aminoethyl) dithiolcarbonate dihydrochloride (5.06 g.) was suspended in 150 ml. of 95% ethanol. The suspension was made basic by the addition of 80 ml. of 1N sodium hydroxide, then made up to 250 ml. with ethanol. After storage for 3 hr. at 25°, a 10 ml. aliquot was withdrawn and acidified with 3.3 ml. of 0.100N hydrochloric acid. This sample consumed 7.76 ml. of 0.0985N iodine solution which corresponds to the liberation of 95.6% of the theoretical amount of aminoethanethiol based on equation 3.

Attempted hydrolysis of III. A solution of 10.0 g. of III in 50 ml. of conc. hydrochloric acid was heated under reflux for 46 hr. The resulting solution was vacuum concentrated (90° and 20 mm.) to a yellow solid. This was treated successively with 100 ml. of 1:1 ethanol-benzene and 50 ml. of ethanol with vacuum concentration after each treatment. The resulting solid was suspended in 150 ml. of boiling ethanol and vacuum filtered. The filter cake was washed with

(7) N. D. Cheronis and J. B. Entricken, *Semimicro Qualitative Organic Analysis*, T. Y. Crowel Co., N. Y., 1947, pp. 140–141.

several portions of ethanol, then ether, and dried to give 5.8 g. (58%) of recovered III, m.p. 201.9–203° with gas evolution. Additional small quantities of III separated from the mother liquor; however, no crystalline 2-aminoethanethiol hydrochloride was isolated.

2-Aminoethylbenzyl dithiocarbonate hydrochloride (V). A solution of 2-benzylthio-2-thiazoline⁸ (41.9 g., 0.2 mole) in 500 ml. of 6*N* hydrochloric acid was heated under reflux for 2 hr. After storage at 0° for 1 hr., the crystalline product was removed by suction filtration and dried in a vacuum desiccator. The yield of V, m.p. 172.2–175.2° (lit.,⁴ m.p. 175°), was 43.6 g. (82.8%). A sample recrystallized from hot glacial acetic acid melted at 177.9–178.7°.

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(8) A. H. Goddin, U. S. Patent 2,516,313.

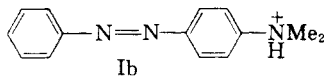
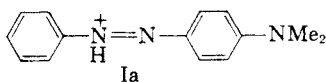
Absorption Spectra of the 4-Dimethylamino Derivatives of Azobenzene and Stilbene

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In neutral solution 4-dimethylaminoazobenzene displays a strong absorption band at 420 $m\mu$ which in acidic solution is replaced by one band at 520 $m\mu$ and another at 320 $m\mu$.¹ Absorption in the 520 $m\mu$ region has been associated with the azonium cation (Ia) to which can be attributed a high degree of stabilization by charge-resonance² while the 320 $m\mu$ peak is considered to be due to the ammonium cation (Ib) essentially because azobenzene in neutral solution also absorbs strongly at 320 $m\mu$.^{1,3}

Further, it has been postulated^{1,3} that both cations exist together in solution as a tautomeric equilibrium mixture (Ia \rightleftharpoons Ib); support for these interpretations has come from several sources.^{4,5,6}



Klotz, Fiess, Chen Ho, and Melody,⁷ however, have questioned the validity of attributing the

(1) G. M. Badger, R. G. Buttery, and G. E. Lewis, *J. Chem. Soc.*, 1888 (1954).

(2) C. R. Bury, *J. Am. Chem. Soc.*, **57**, 2115 (1935).

(3) A. Hantzsch and A. Burawoy, *Ber.*, **63**, 1760 (1930).

(4) G. Cilento, E. C. Miller, and J. A. Miller, *J. Am. Chem. Soc.*, **78**, 1718 (1956).

(5) E. Sawicki, *J. Org. Chem.*, **21**, 605 (1956).

(6) H. H. Jaffe and Si-Jung Yeh, *J. Org. Chem.*, **22**, 1281 (1957).

(7) I. M. Klotz, H. A. Fiess, J. Y. Chen Ho, and M. Melody, *J. Am. Chem. Soc.*, **76**, 5136 (1954).

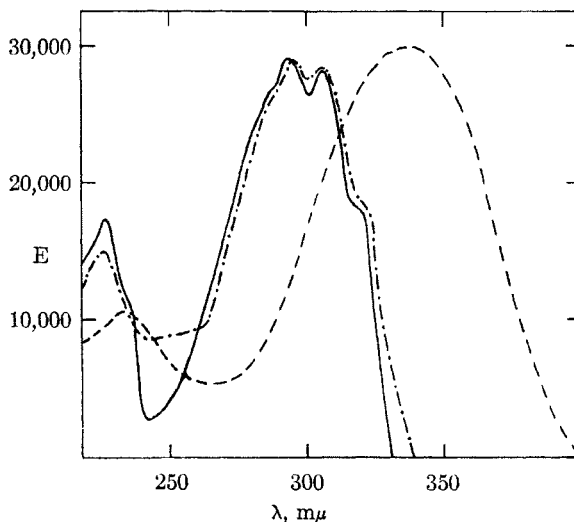
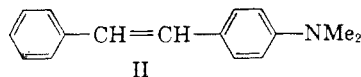


Fig. 1. Absorption spectra: Stilbene in neutral aqueous-ethanol (—); 4-Dimethylaminostilbene in neutral (---) and acidic (2*N* sulfuric acid) aqueous-ethanol (-·-·-)

absorption at 520 $m\mu$ to the ion (Ia) and have attempted to reconcile addition of a proton solely at the dimethylamino- group (Ib) with an absorption shift to longer wave lengths. Criticisms of this view have already been raised by some authors.^{4,8,9}

In an attempt to bring fresh evidence to bear on this question the ultraviolet absorption spectrum of 4-dimethylaminostilbene (II) has been examined in 50% aqueous-ethanol under acidic (2*N* sulfuric acid) and neutral conditions and the separate curves have been compared with that of stilbene in neutral solution. (See Fig. 1.) 4-Dimethylaminostilbene is isosteric with 4-dimethylaminoazo-



benzene but unlike the azo-compound possesses only one basic center and should therefore add a proton only at the dimethylamino- group.

The spectrum of 4-dimethylaminostilbene, as shown, in acidic solution is very nearly identical with that of stilbene in neutral solution and definitely reveals no absorption at wave lengths higher than the main band of the parent free base. These observations fail to lend support to the spectral interpretations suggested by Klotz *et al.*⁷ On the other hand the assignment of the 320 $m\mu$ band, shown by 4-dimethylaminoazobenzene in acidic solution, to the ammonium cation (Ib) is clearly reinforced.

EXPERIMENTAL

Absorption spectra. A Hilger Uvispek Spectrophotometer was used to determine the spectra. The appropriate solvent

(8) E. Sawicki, *J. Org. Chem.*, **22**, 365 (1957).

(9) I. N. Zhmurova, *J. Gen. Chem. (U.S.S.R.)*, **27**, 2745 (1957).