added *trans*-stilbene (2.31 g., 0.0128 mol.) and 3.74 g. of I. The reaction mixture was refluxed 2 hr., during which time the solution turned dark. The reaction mixture was aspirated to dryness, dissolved in benzene, and chromatographed on a column of alumina (2.5 × 20 cm.) using a 50% by volume mixture of benzene and mixed alkanes (b. range 50–60°) to elute the first fraction. Methanol was gradually added to elute the second fraction.

Fraction (1) gave 2.8 g., m.p. 133–134°.

Fraction (2) gave 0.7 g., m.p. 122–125°. The separations indicate that two distinct products are formed. Both products gave negative Beilstein tests, and had similar infrared spectra but 2 showed an absorption maximum in the 5.9μ region while 1 did not.

Elemental analysis of 1 indicated that it was the vinyl sulfide (compound II, in text).

Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.47; H, 3.73. Found C, 63.70; H, 3.55.

Elemental analysis of 2 indicated that it was the β-acetoxy compound.

Anal. Calcd. for $C_{22}H_{18}N_2O_6S$: C, 60.26; H, 4.14. Found: C, 60.33; H, 4.01.

Reaction of 2,4-dinitrobenzenesulfenyl chloride with 1,1-diphenylethylene. Reaction of 5.0 g. of I and 3.3 g. of 1,1-diphenylethylene, in 40 ml. of dry acetic acid for 24 hr. at room temperature yielded crude II, which after recrystallization from 95% ethanol yielded 5.5 g. of product, m.p. 134–135° (80%).

Anal. Calcd. for $C_{20}H_{14}N_2O_4S$: C, 63.47; H, 3.73. Found: C, 63.70; H, 3.55.

This product was identical with the one from *trans*-stilbene, as shown by infrared spectra and mixture melting point.

Acetolysis of the 1:1 adduct in refluxing acetic acid. To a refluxing solution of dry acetic acid was added 2.1 g. of 1:1 adduct. The reaction mixture was refluxed 4 hr. Employing a similar chromatographic procedure as above, it was found that the 1:1 adduct was converted into 70% vinyl sulfide, II, and 10% of the acetoxy compound of fraction 2. A 10% loss in work-up was sustained.

Acetolysis of the 1:1 adduct with sodium acetate and acetic acid. To a refluxing solution of dry acetic acid was added 5.0 g. of anhydrous sodium acetate and 1.6 g. of 1:1 adduct. The reaction mixture was refluxed 4 hr. The yellow reaction mixture was aspirated nearly to dryness and poured onto ice. The yellow material was collected and recrystallized from methanol. The product melted at 125–126°; yield, 1.4 g.; 89%.

Desulfuration and reduction of the vinyl sulfide with Raney nickel. A solution of 4.0 g. (0.011 mol.) of the vinyl sulfide was dissolved in 50 ml. of absolute ethanol containing 15 g. of Raney nickel. The solution was refluxed 2 hr. on the steam bath. About 5 g. more of catalyst was added, and refluxing continued an additional hour. The mixture was filtered through diatomaceous earth, and the catalyst washed with two 15-ml. portions of absolute ethanol. The washings were added to the filtrate, which was then concentrated in an air stream to dryness. The dark oil was distilled under reduced pressure yielding a colorless oil, b.p. 110°/2 mm., m.p. −8° (1.0 g., 57%).

Oxidation of the vinyl sulfide. The vinyl sulfide (4.0 g., 0.011 mol.) was added to an aqueous solution of potassium dichromate. Concentrated sulfuric acid was added to the solution. An hour later, the solution was poured onto ice. The white crystals were collected and reprecipitated from 95% ethanol with ice to give 1.6 g. of product, m.p. 47–48° (84%). This product was shown to be benzophenone by infrared spectra and mixture melting point.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
UNIVERSITY PARK
LOS ANGELES 7, CALIF.

Organic Disulfides and Related Substances. II. 2,4,6-Triisopropylphenyl Disulfide, the 2,4,5-Isomer, and Related Compounds[1]

D. E. PEARSON, DRURY CAINE, AND LAMAR FIELD

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The first disulfide named in the title is new, the second has been mistaken for the first, and in our opinion, the disulfides and related compounds deserve further study and comment.

Triisopropylbenzene made from propylene and benzene with sulfuric acid as a catalyst has been shown to consist mainly of the 1,2,4-isomer.[2] Evidently, Costanza and co-workers[3] believed that the commercial mixture was mainly the symmetrical 1,3,5-isomer for the properties of their sulfonyl chloride and disulfide made from the hydrocarbon, reported as the 2,4,6-isomers, agreed well with the physical properties of our 2,4,5-isomers. Our confidence in the correctness of the structures given here is based on three facts: (1) The equilibration of a trialkylbenzene with large amounts of aluminum chloride (which provided our 1,3,5-triisopropylbenzene) gives predominantly the symmetrical 1,3,5-isomer, as this isomer is the strongest Lewis base and forms the most stable Lewis salt.[2,4,5] (2) The hydrocarbon obtained from the equilibration in this work differed considerably in physical properties from the original hydrocarbon. And both hydrocarbons gave derivatives which had sharp melting ranges and were distinctly different from each other. (3) 2,4,5-Triisopropylbenzenesulfonyl chloride (I) and its 2,4,6-isomer (II) were made by the method of Newton and agreed well in physical properties and derivative formation with his descriptions.[6]

The study of models of 2,4,6-triisopropylbenzenesulfonyl chloride (II) suggested that the chlorosulfonyl group would be tilted out of the ring plane so that the rear of the group would be more exposed to the attack of a nucleophilic reagent than that of the 2,4,5-isomer which is in the plane of the ring and is hindered by a ring substituent. The solvolysis of such sulfonyl chlorides has been shown

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[1] Supported in part by funds provided by the Office of Ordnance Research, U. S. Army. Abstracted from the M.S. thesis of D.C., Vanderbilt University, January, 1956. Paper I. L. Field and J. E. Lawson, *J. Am. Chem. Soc.*, **80**, 838 (1958).

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to proceed by a concerted (SN-2) mechanism.[7] If one assumes that the steric inhibition of resonance of a sulfur atom with the benzene ring is a negligible influence[8] and that the attack of water is made on the sulfur atom on the side opposite to the chlorine atom, one would predict a faster rate of hydrolysis for the 2,4,6-isomer than for the 2,4,5-isomer. The results in the Experimental show that the 2,4,6-isomer does hydrolyze almost twice as rapidly as the 2,4,5-isomer.

The sulfonyl chlorides were reduced to the thiols by lithium aluminum hydride and the latter reoxidized without isolation to the disulfides. We were expecting that 2,4,6-triisopropylphenyl disulfide in comparison with phenyl disulfide would show a substantial difference in ease of formation from the thiol or in ultraviolet absorption properties. Neither expectation was realized. Both the 2,4,5- and 2,4,6-disulfides formed with ease, and the absorption spectra, given in the Experimental, showed differences that could be attributed merely to inductive properties of alkyl groups alone. Apparently, groups larger than an isopropyl or phenyl[9] are necessary to prevent or hinder disulfide formation.

EXPERIMENTAL[10]

1,2,4-Triisopropylbenzene. Triisopropylbenzene (Distillation Products Industries, Technical) was separated by very slow distillation through a 10-in. carborundum-packed column. The middle fractions of constant refractive index were taken as the desired compound, b.p. 238–240° (754 mm.), n_D^{20} 1.4915, reported[11] b.p. 240–242° at 753 mm., n_D^{20} 1.4924.

1,3,5-Triisopropylbenzene. 1,2,4-Triisopropylbenzene (n_D^{20} 1.4915) was isomerized to the 1,3,5 isomer by the method of Newton[2] and others.[4] The first isomerization with anhydrous aluminum chloride appeared to be incomplete as judged from refractive indices of the distillate. The distillate therefore was subjected to a second isomerization with aluminum chloride. The 1,3,5-triisopropylbenzene fraction obtained by isolation and distillation had b.p. 228–230° (754 mm.) and a constant refractive index, n_D^{20} 1.4884, reported[4] n_D^{20} 1.4882.

2,4,5-Triisopropylbenzenesulfonyl chloride (I). This compound, made by the method of Newton,[6] was less pure (m.p. 137–140°) than that of Newton, m.p. 141.5–142.2°. Derivatives of I, however, checked well with the literature[6]: sulfonamide m.p. 155–156°, sulfonanilide m.p. 187–188°. Recrystallization of I from isooctane proved wasteful, but small portions could be purified by partial hydrolysis. I (6 g.) was dissolved in 100 ml. of 80% aqueous acetone, and the solution held at 50° for 1 hr., diluted with water to the point of cloudiness, and cooled. After filtration, drying, and recrystallization from isooctane, 3.5 g. of I was obtained, m.p. 141–141.8°.

2,4,6-Triisopropylbenzenesulfonyl chloride (II). This compound, made by the method of Newton,[6] melted at 95–97°, reported[6] m.p. 97.2–98.4°. Derivatives checked well with the literature:[6] sulfonamide m.p. 118.5–119.5°; sulfonanilide m.p. 163–164°. Partial hydrolysis of 6 g. of II (as with I) gave 2.8 g. of pure II, m.p. 96.8–97.5°.

2,4,5-Triisopropylphenyl disulfide (III) *and the 2,4,6-isomer* (IV). Compound I (18 g., 0.06 mole) was dissolved in 180 ml. of absolute ether contained in a 3-necked flask fitted with condenser, stirrer, and dropping funnel and protected from moisture by calcium chloride tubes. Lithium aluminum hydride (5.3 g., 0.14 mole) in 115 ml. of ether was added dropwise over a period of 25 min. to the stirred solution of I. The initial hydride concentration in ether was determined by weighing the residue from a 5-ml. aliquot. Vigorous refluxing and hydrogen evolution were noted during the addition. After a reflux period of 4 hr., 50 ml. of an equal mixture of benzene and ethanol was cautiously added dropwise to destroy excess hydride. Following this addition, about 200 ml. of 10% aqueous sulfuric acid was added to dissolve the lithium salts, and 75 ml. of benzene was added to dissolve the thiol. The benzene solution was separated from the aqueous acid solution and washed free of acid with aqueous sodium bicarbonate. For oxidation to the disulfide, 8.8 g. (0.07 mole) of iodine in 50 ml. of benzene was added to the thiol in benzene. After standing for 8 hr., during which time it was washed twice with water to remove hydrogen iodide, the mixture was washed with a 5% sodium bisulfite solution to destroy excess iodine, dried with sodium sulfate, and evaporated. A dark oil was obtained which solidified after immersion in Dry Ice and scratching. Recrystallization from 40 ml. of methanol gave large yellow plates of III, 7 g., 50%, m.p. 75.4–76.2°.

Anal. Calcd. for $C_{30}H_{46}S_2$: C, 76.53; H, 9.85. Found: C, 76.64; H, 9.83.

2,4,6-Triisopropylphenyl disulfide (IV). IV was made in the same manner as the previous disulfide except that the compound crystallized without cooling in Dry Ice: light yellow plates, 8.4 g., 60%, m.p. 91.2–92.0°. Costanza *et al.* report m.p. 79–79.5°.[3]

Anal. Calcd. for $C_{30}H_{46}S_2$: C, 76.53; H, 9.85. Found: C, 76.90; H, 10.05.

Ethyl 2,4,5-triisopropylbenzenesulfonate (V) *and the 2,4,6-isomer* (VI). By dissolving the appropriate sulfonyl chloride in alcohol and allowing the solution to stand at 50° overnight, the ethyl ester was obtained in over 70% yields. The 2,4,5-ester (V), recrystallized from hexane, melted at 99–100°.

Anal. Calcd. for $C_{17}H_{28}O_3S$: C, 65.34; H, 9.03. Found: C, 65.61; H, 9.18.

The 2,4,6-isomer, recrystallized from hexane, melted at 58–59°.

Anal. Calcd. for $C_{17}H_{28}O_3S$: C, 65.34; H, 9.03. Found: C, 64.98; H, 8.87.

Hydrolysis rates of the sulfonyl chlorides, I *and* II. About 0.6 g. samples (weighed accurately) were added to 125 ml. of 80% by volume of acetone, 20% water held at 51.8°. Aliquots (25 ml.) were taken at .5 hour intervals at the beginning and hour intervals near the end of the hydrolysis. The aliquots were quenched with 25 ml. of acetone cooled to ice temperature and titrated with standard base using a *p*H meter to detect the end-point. Duplicate runs were made, and the average values, as pseudo first-order rate constants at 51.8° in 80% aqueous acetone, are given below:

Sulfonyl Chloride	k_1 (min.$^{-1}$)	Half-life (min.)
2,4,5-Triisopropylbenzene-(I)	2.3×10^{-3}	301
2,4,6-Triisopropylbenzene-(II)	3.9×10^{-3}	178
4-Bromobenzene-	15.0×10^{-3}	46

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Ultraviolet spectra of disulfides. The ultraviolet spectra were obtained with the Beckman Recording Spectrophotometer, Model DK, using isooctane as a solvent. The curves are recorded in a thesis,[1] and the maxima: diphenyl disulfide, 241 (4.33), [λ, (log ε)] in mμ 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 (284): 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 ε *ca.* 0.2–0.4) at *ca.* 500–700 mμ, which increases as the ultraviolet region is approached, and are pale yellow. The absorption spectrum of diphenyl disulfide checked well with that recorded.[12]

VANDERBILT UNIVERSITY,
DEPARTMENT OF CHEMISTRY
NASHVILLE 5, TENN.

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

RICHARD J. GAUL[1] AND WINFRIED J. FREMUTH

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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.

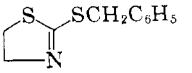
TABLE I

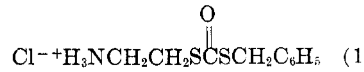
ACID HYDROLYSIS PRODUCTS OF 2-THIAZOLINE-2-THIOL

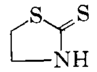
Time, Hrs.	Yield, %		
	I	II[a]	III[a]
19.5	61.3	0.0	57.0
20[b]	60.2	9.9[c]	71.5
90	12.9	45.2	33.4
336	0.0	94.5	0.0

[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.

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


IV $+ H_2O + HCl \longrightarrow$


$$Cl^{-}\,{}^{+}H_3NCH_2CH_2SC(=O)SCH_2C_6H_5 \quad (1)$$
V

2 
I $+ 3H_2O + 2HCl \longrightarrow$

$$(Cl^{-}\,{}^{+}H_3NCH_2CH_2S)_2CO + 2H_2S + CO_2 \quad (2)$$
III

$$2I + 2H_2O + 2HCl \longrightarrow III + COS + H_2S \quad (2a)$$

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 $C_5H_{14}ON_2S_2Cl_2$. 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 $C_5H_{14}ON_2S_2Cl_2$ (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 generally[4-6] III is rather resistant to further acid

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(1) Address correspondence to Department of Chemistry, John Carroll University, Cleveland 18, Ohio.

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