$\Delta^{5,12}$-17-Ethyletiojervadiene-3,11-dione-17,20-diol 3-Ethylene Ketal 21-Acetate (VII).—A solution of V (650 mg., m.p. 236–239°) in pyridine (15 ml.) and acetic anhydride (13 ml.) was allowed to stand at room temperature for 13 hr. The mixture was poured into iced water (100 ml.) and the product was extracted with two 100-ml. portions of chloroform. The chloroform solution was washed with two 100-ml. portions of water, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The solid residue was recrystallized twice from acetone to yield $\Delta^{5,12}$-17-ethyletiojervadiene-3,11-dione-17,20-diol 3-ethylene ketal 21-acetate (VII) as needles (660 mg.), m.p. 240–241°, $[\alpha]^{33}_{D}$ −165° (*c* 0.59, chloroform); λ_{max} 251 mμ (ε 14,000); 2.83, 2.88, 5.78, 5.84, 6.12, 8.00, 9.00, 9.20 μ.

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 69.74; H, 7.96. Found: C, 69.52: H, 8.07.

Oxidation of $\Delta^{5,12}$-17-Ethyletiojervadiene-3,11-dione-17,20-diol 3-Ethylene Ketal (V) to $\Delta^{5,12}$-Etiojervadiene-3,11,17-trione 3-Ethylene Ketal (VIII).—A solution of V (250) mg., m.p. 236–239°) in pyridine (5 ml.) was added to the complex prepared from chromium trioxide (300 mg.) and pyridine (15 ml.). The mixture was stirred for 30 min. at room temperature and then allowed to stand overnight in the refrigerator. The mixture was poured into ice-water (150 ml.) and extracted with two 75-ml. portions of ether. The ethereal extract was washed with 2 *N* hydrochloric acid (75 ml.), 1 *N* sodium hydroxide solution (50 ml.), water (50 ml.), and dried over anhydrous sodium sulfate. Evaporation to dryness yielded a solid residue, which was crystallized twice from acetone–isopropyl ether to yield $\Delta^{5,12}$-etiojervadiene-3,11,17-trione 3-ethylene ketal (VIII), 95 mg., m.p. 176–178°. The melting point was not depressed by admixture of an authentic sample,[1] and the ultraviolet and infrared spectra were superimposable upon those of the authentic sample.

The Dehydrohalogenation of S,S′-(β-Chloroethyl) Dithiolcarbonate[1]

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Received July 31, 1963

During a recent investigation of the cyclopolymerization of S,S′-divinyl dithiolcarbonate (I), a detailed study of the dehydrohalogenation of S,S′-(β-chloroethyl) dithiolcarbonate was conducted. Rigorous purification and identification of the reaction products has necessitated a revision in the physical constants previously reported[2] for I, and has revealed a sulfonium ion rearrangement occurring in competition with the expected dehydrohalogenation.

S,S′-(β-Chloroethyl) dithiolcarbonate (II) can be prepared by reaction of phosgene with ethylene sulfide.[2] Dehydrohalogenation of II with potassium *t*-butoxide yielded a mixture of S,S′-divinyl dithiolcarbonate (I), S-vinyl-O-*t*-butyl thiolcarbonate (III), S-(β-chloroethyl)-O-*t*-butyl thiolcarbonate (IV), S-β-(vinylmercapto)ethyl-S-vinyl dithiolcarbonate (V), and S-vinyl-S′-β-(chloroethyl) dithiolcarbonate (VI). The composition of the product mixture was dependent on the reaction conditions; the formation of V was favored by lower reaction temperatures as illustrated in Table I.

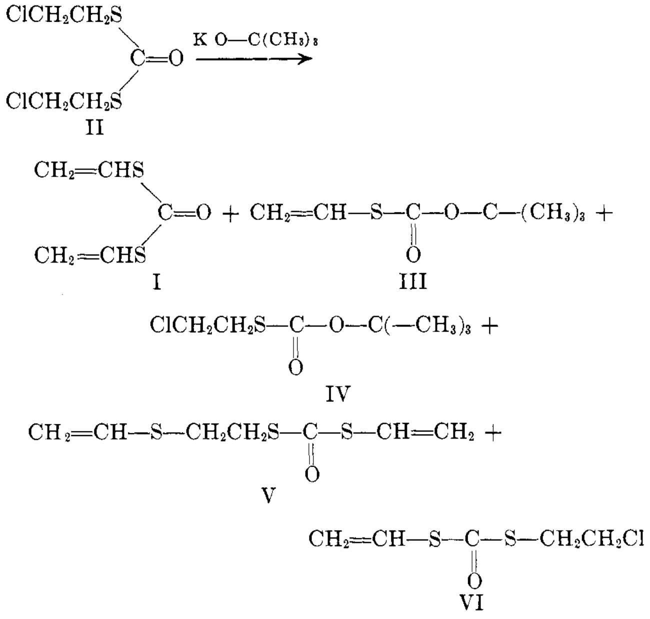


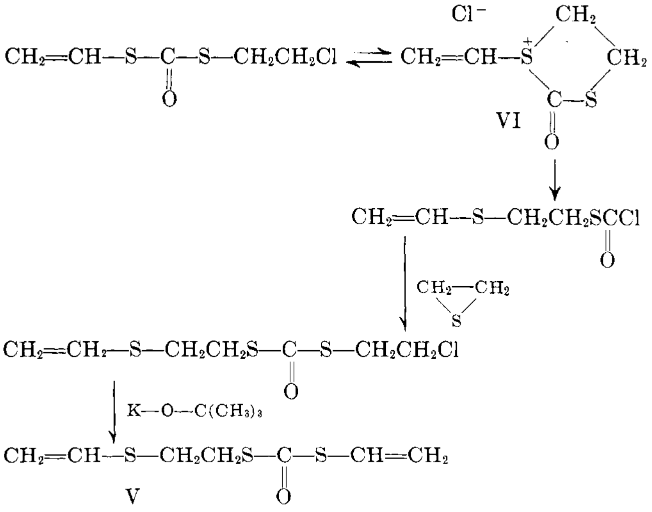
TABLE I

DEHYDROHALOGENATION OF S,S′-(β-CHLOROETHYL) DITHIOLCARBONATE (II)

Reaction conditions		Yield of products, %			
Pot temperature, °C.	Stirring[a] time, hr.	I	III	IV + VI	V
85	3	9.8	13.1	5.4	13.0
85	2	18.5	17.5	14.5	6.5
85	1	20.6	5.8	18.1	9.1
75	1	20.0	11.6	16.0	9.3
55	1	15.3	19.1	8.4	22.0

[a] After addition was completed.

Although the formation of V under the conditions of dehydrohalogenation was not anticipated, a mechanism for its formation can be proposed. The existence of cyclic sulfonium ions has been documented by Fuson and co-workers[3–5] and a similar intermediate should be applicable to this situation as illustrated.



The mechanism is indigent upon the presence of ethylene sulfide; however, ethylene sulfide is a byproduct from the formation of S-vinyl-O-*t*-butyl thiol-

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[1] This is the 26th in a series of papers concerned with new monomers and polymers; for the previous paper in this series, see C. G. Overberger, H. Kayé, and G. Walsh, *J. Polymer Sci.*, in press.

[2] H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **44**, 418 (1961).

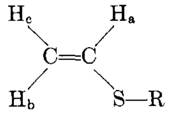
[3] R. C. Fuson, C. C. Price, and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1946).

[4] R. C. Fuson and A. J. Speziale, *J. Am. Chem. Soc.*, **71**, 1582 (1949).

[5] R. C. Fuson and J. H. Koehneke, *J. Org. Chem.*, **14**, 706 (1949).

TABLE II

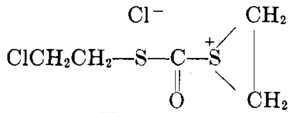
NUCLEAR MAGNETIC RESONANCE[a] AND INFRARED DATA ON S-VINYL COMPOUNDS



R	H_a (τ)	J_{ab} (c.p.s.)	J_{ac} (c.p.s.)	H_b (τ)	H_c (τ)	Other protons (τ)	$\underset{\underset{\displaystyle O}{\|}}{-C-}$ (cm.$^{-1}$)	—C-H stretch (cm.$^{-1}$)
$\underset{\underset{\displaystyle O}{\|}}{C}-O-C-(CH_3)_3$	3.30^b	17.5	9.8	4.58^c	4.84^c	8.55	1725, 1715	3080, 3014 2930
$\underset{\underset{\displaystyle O}{\|}}{C}-S-CH=CH_2$	3.10^b	17.3	9.2	4.40	4.65^c		1750, 1658	3080, 3025
$\underset{\underset{\displaystyle O}{\|}}{C}-S-CH_2CH_2-S-CH=CH_2$	3.06^b	17.5	9.6	4.39	4.65^c	6.90^d	1740, 1653	3080, 3010 2930
$CH_2CH_2-S-\underset{\underset{\displaystyle O}{\|}}{C}-S-CH=CH_2$	3.63^b	18.3	10.0	4.56	4.84^c			
$\underset{\underset{\displaystyle O}{\|}}{C}SCH_2CH_2Cl$	3.26^b	17.4	9.6	4.47	4.69^c	6.54^d	1740, 1655	3080, 2930

[a] Samples run neat; tetramethylsilane, internal standard. [b] Quartet. [c] Doublet. [d] Center of complex multiplet.

carbonate (III) which can be envisioned as proceeding through a three-membered sulfonium ion (VII)



VII

with subsequent elimination of ethylene sulfide and esterification of the S-(β-chloroethyl) chlorothiolformate intermediate to yield IV. IV would dehydrohalogenate readily under the conditions of reaction.

A dehydrohalogenation of II conducted in the presence of an added excess of ethylene sulfide yielded V and higher boiling yellow oils. Elemental and infrared analysis of the crude oil was consistent with the incorporation of several molecules of ethylene sulfide to cyclic intermediate VI. This aspect of the reaction was not pursued further.

Since there was some confusion concerning the identity of I and V due to the similarity of their elemental analyses, n.m.r. and mass spectra were used to assign the proper structures. The n.m.r. spectra and pertinent infrared absorptions for I, III, V, and VI are reported in Table II.[6] The n.m.r. spectra of I and III are remarkably simple, consisting of a quartet and a triplet characteristic of vinyl protons with the addition of a single methyl proton peak in the spectrum of III. The n.m.r. spectrum of V clearly indicates two types of vinyl groups and contains a complex multiplet in the methylene region which is typical of A_2B_2 type spectra predicted by Pople[7] for 1,2 asymmetrically substituted ethanes. The infrared spectrum of I and V are nearly identical with the exception of a strong methylene absorption at 2930 and 1425 cm.$^{-1}$ in the spectrum of V.

The molecular weight of compound I was 146 and this appears as the principal peak of its mass spectrum (Table III)[8] along with the expected fragmentation products. A significant principal peak could not be obtained for V but fragmentation similar to I was observed and the isotopic distribution of the fragment with mass 178 was indicative of an ion containing three sulfur atoms.

TABLE III

MASS SPECTROMETER FRAGMENTATION OF S,S′-DIVINYL DITHIOLCARBONATE (I) AND S-[(β-VINYLSULFIDE)ETHYL]-S′-VINYL DITHIOLCARBONATE (V)

m/e	Relative intensity I	Relative intensity V
25	3.2	1.9
26	14.6	12.6
27	72.0	59.2
28	10.6	16.7
29	1.0	1.9
32	8.0	7.5
33	5.2	4.1
35		4.8
41	1.9	6.3
45	20.0	100.0
46	1.9	7.6
47	2.0	19.6
53		9.6
57	22.2	17.0
58	73.5	63.0
59	100.0	98.8
60	14.5	19.1
61	8.8	12.0
63		16.7
64	3.6	5.6
65	0.7	6.6
73	2.5	7.8
84	3.2	1.5
85	18.9	8.6
86	1.7	26.0
87	52.8	68.5
88	2.3	4.6
89	2.5	3.3
91		38.0
92		2.9
93		3.6
118	21.1	8.1
119	1.3	46.3
120	2.5	3.9
121		4.2
123		3.6
146	7.8	
147	0.6	8.6
148	0.7	0.6
178		7.9
179		0.9
180		1.2

S,S′-Divinyl dithiolcarbonate has been cyclopolymerized to a soluble polymer. The details of polymerization and subsequent hydrolysis of the resultant polymer will be reported elsewhere. The polymerization conditions and physical constants previously reported[2] for poly-S,S′-divinyl dithiolcarbonate actually apply to the polymer for S-β-(vinylmercapto)-ethyl-S′-vinyl dithiolcarbonate (V).

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(6) The authors wish to thank Mr. H. Talts for running the infrared and n.m.r. spectra.

(7) J. A. Pople, W. G. Schneider, and H. S. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 379.

(8) The authors wish to thank the American Cyanamid Co. and Mrs. R. H. Barritt for running and interpreting the mass spectra.

Experimental[9]

Preparation of S,S'-(β-Chloroethyl) Dithiolcarbonate (II).—A modification of the procedure of Ringsdorf and Overberger[2] was used. Ethylene sulfide was prepared by the method of Searles and Lutz[10] in 45% yield, b.p. 55–56°. To a mixture of 98 g. (1.0 mole) of phosgene and 0.5 ml. of pyridine was added 60 g. (1.0 mole) of ethylene sulfide over a period of 4 hr. The reaction temperature was maintained below 8°. (Caution: the reaction is extremely exothermic but may have an induction period. Not more than 15 g. of ethylene sulfide should be added before the exothermic reaction is observed.) The reaction temperature was then allowed to rise to 50° and an additional 60 g. of ethylene sulfide [total amount, 120 g. (2.0 moles)] was added. The mixture was heated at 50° for 3 hr. after addition was completed. Fractional distillation of the reaction mixture yielded a forerun of S-(β-chloroethyl) chlorothiolformate, 26.8 g. (17%), b.p. 67–69° (5 mm.), lit.[2] b.p. 67.5° (5 mm.), and S,S'-(β-chloroethyl) dithiolcarbonate (II), 142.5 g. (65%), b.p. 124–126° (2.0 mm.). The product solidified on standing and was recrystallized from methanol, m.p. 40–41°, lit.[2] b.p. 96–97° (0.1 mm.), m.p. 40–41°.

Dehydrohalogenation of S,S'-(β-Chloroethyl) Dithiolcarbonate (II).—A 1.5-*M* solution of potassium *t*-butoxide was prepared by dissolving 26.4 g. (0.67 g.-atom) of potassium metal in 450 ml. of anhydrous *t*-butyl alcohol. A solution of II, 70 g. (0.32 mole) in 100 ml. of *t*-butyl alcohol was heated to 60°, and the potassium *t*-butoxide solution was added slowly. The temperature rose to 75° during addition. The mixture was maintained at 75° for 1 hr., then cooled to room temperature. After neutralization with glacial acetic acid, the potassium chloride formed during the reaction was removed by centrifugation. The solvent was evaporated under reduced pressure and a trace of hydroquinone was added as an inhibitor.

The residue was fractionally distilled through a 30-cm. spinning band column to yield the following components.

(a) S-Vinyl-O-*t*-butyl thiolcarbonate (III), 6.0 g. (11.6%), had b.p. 60.5–61° (15 mm.), $n^{25}\text{D}$ 1.4642. Dehydrohalogenation of S-(β-chloroethyl) chlorothiolformate gave b.p. 50° (6 mm.), $n^{21.2}\text{D}$ 1.4601.[11]

Anal. Calcd. for $C_7H_{12}O_2S$: C, 52.47; H, 7.55; S, 20.01. Found: C, 52.45; H, 7.46; S, 19.79.

(b) S,S'-Divinyl dithiolcarbonate (I), 9.5 g. (20%), had b.p. 77–77.5° (16 mm.), $n^{25}\text{D}$ 1.5780.

Anal. Calcd. for $C_5H_6OS_2$: C, 41.2; H, 4.12; S, 43.8. Found: C, 41.13; H, 4.22; S, 43.62.

(c) S-(β-Chloroethyl)-O-*t*-butyl thiolcarbonate (IV), 9.1 g. (14.5%), had b.p. 48–49° (0.5 mm.), $n^{25}\text{D}$ 1.4722; lit.[11] b.p. 51–52° (0.9 mm.), $n^{21.2}\text{D}$ 1.4693.

Anal. Calcd. for $C_7H_{13}ClO_2S$: C, 42.74; H, 6.66; S, 16.30; Cl, 18.05. Found: C, 42.85; H, 6.65; S, 16.45; Cl, 18.01.

The n.m.r. spectrum consisted of a complex multiplet centering around 6.61 and a single peak at 8.52 τ.

Since there was a discrepancy between the refractive index observed and that which was previously reported,[11] compound IV was independently synthesized by the following procedure. S-β-(Chloroethyl) chlorothiolformate, 35.7 g. (0.25 mole), was added to a solution of *t*-butyl alcohol, 18.5 g. (0.25 mole), and pyridine, 20 g. (0.25 mole) in 100 ml. of chloroform. The mixture was refluxed for 24 hr., cooled, and washed sequentially with water, 5% hydrochloric acid, 5% sodium carbonate, and water. After drying the chloroform solution with anhydrous magnesium sulfate, the solvent was evaporated under reduced pressure.

Distillation of the residue through a 30-cm. spinning band column yielded S-β-(chloroethyl)-O-*t*-butyl thiolcarbonate, 30 g. (60%), b.p. 72° (5.0 mm.), $n^{25}\text{D}$ 1.4719. The purity was checked by redistilling at a different pressure, b.p. 100° (14 mm.), $n^{25}\text{D}$ 1.4719. From the results, it is apparent that the refractive index reported here is a better value.

Anal. Calcd. for $C_7H_{13}ClO_2S$: C, 42.74; H, 6.66; S, 16.30; Cl, 18.05. Found: C, 42.76; H, 6.62; S, 16.03; Cl, 18.06.

(d) S-Vinyl-S'-β-chloroethyl dithiolcarbonate (VI), 0.9 g. (1.5%), had b.p. 83.5–84° (2.0 mm.), $n^{25}\text{D}$ 1.5684.

Anal. Calcd. for $C_5H_7ClOS_2$: C, 32.88; H, 3.83; S, 35.05; Cl, 19.45. Found: C, 32.94; H, 3.81; S, 34.76; Cl, 19.43.

(e) S-β-(Vinylmercapto)ethyl-S'-vinyl dithiolcarbonate (V), 6.0 g. (9%), had b.p. 112–113° (1.8 mm.), $n^{25}\text{D}$ 1.5958; by the same procedure but reported[2] as S,S'-divinyl dithiolcarbonate it had b.p. 73–74° (0.04 mm.), $n^{21.2}\text{D}$ 1.5967. Further purification by eluting from a "florisil" column with hexane and redistillation yielded a fraction, b.p. 109.5–110° (0.5 mm.), $n^{25}\text{D}$ 1.5998.

Anal. Calcd. for $C_7H_{10}OS_3$: C, 40.74; H, 4.85; S, 46.62; mol. wt., 206. Found: C, 40.76; H, 4.86; S, 46.59; mol. wt., 210.

Dehydrohalogenation of II in Presence of Ethylene Sulfide.—Ethylene sulfide, 10 g. (0.16 mole), and II, 35 g. (0.16 mole), were dissolved in 100 ml. of *t*-butyl alcohol and heated to 50°. A 1.5-*M* solution of potassium *t*-butoxide, 250 ml., was added at a rate which maintained the temperature between 50° and 60°. The mixture was stirred for 2 hr. after addition was completed and was worked up as described above.

Fractional distillation of the residue under reduced pressure yielded a forerun of I, 2.0 g. (8.5%), and IV, 2.5 g. (8.0%), a fraction composed primarily of V, 3.5 g. (11.0%), and a pale yellow oil, 5.0 g. (12.0%), b.p. 158–164° (0.2 mm.), $n^{25}\text{D}$ 1.6114.

Anal. Calcd. for $C_9H_{14}OS_4$: C, 40.6; H, 5.27; S, 48.2. Found: C, 40.32; H, 4.98; S, 47.26.

Acknowledgment.—We gratefully acknowledge the support of this work by the National Institute of Health under Grant No. AI-01425-09, and by the United States Air Force under Contract No. AF33-(616)-6866, monitored by the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

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Reactions of Thionyl Chloride with 2,6-Dimethylphenol

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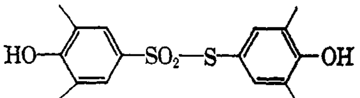
Received September 30, 1963

The reactions of phenols with thionyl chloride result in the formation of nuclear substitution products[1] in addition to chlorosulfinates. For example, bis(4-hydroxyphenyl) sulfide and tris-(4-hydroxyphenyl)-sulfonium chloride are reported[2] to be obtained as the major products of the phenol–thionyl chloride reaction. Where aluminum chloride was added, the corresponding sulfoxides[3] were formed. The preparation of a thiolsulfonate using the above reaction, however, has not been reported. In this report there is described the reaction of 2,6-dimethylphenol with excess thionyl chloride leading to the preparation of 3,5-dimethyl-4-hydroxyphenyl 3,5-dimethyl-4-hydroxybenzenethiolsulfonate (I). The structure of I was established by



I

the synthesis of its dimethyl ether by an independent route. Furthermore, the treatment of 2,6-dimethylphenol with thionyl chloride to yield the sulfoxide and the sulfide is described.

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