[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Vinyl Sulfides. IV. Ketene Mercaptals

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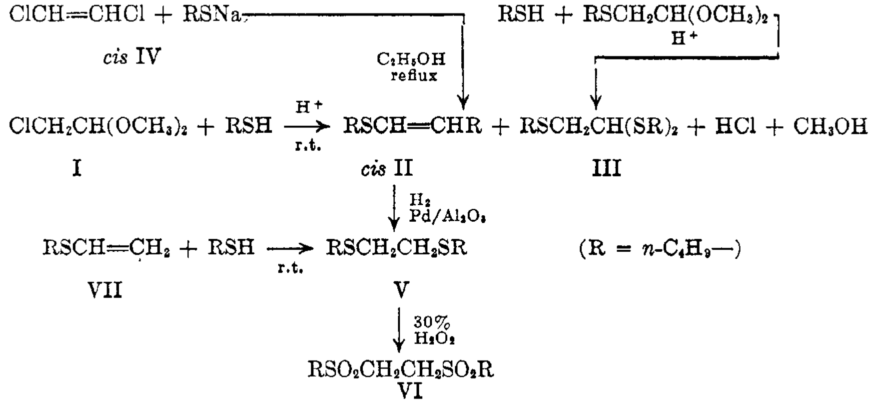
Ketene mercaptals (VIII) have been prepared in essentially quantitative yield by reaction of *n*-alkylmercaptoacetaldehyde dialkyl mercaptal (III) with acetylene under vinylation conditions. Dialkyl disulfides react with vinyl sulfides in the presence of iodine to produce III.

Ketene mercaptals, of the general formula $CH_2{=}C(SR)_2$, have been relatively unknown. Rothstein[1] has reported the preparation of methyl ketene diethyl mercaptal by the abnormal dehydrohalogenation of β-chloropropionaldehyde diethyl mercaptal. This proposed ketene dimercaptal structure has since been questioned by Parham.[2] Ketene dimethyl mercaptal has been disclosed[3] as a pyrolysis product in a patent concerned with sulfur-containing carboxylic esters, and was obtained as a liquid (b.p. 80°/10 mm.). No structure proof is available and the occurrence of ketene dimethyl mercaptal from the lengthy synthesis described has been questioned recently by Arens.[4]



By reaction of ethylmercaptoacetaldehyde diethyl mercaptal with potassium *t*-butoxide in *t*-butyl alcohol, Arens[4] recently obtained ketene diethyl mercaptal in 55% yield, along with other products.

Early studies in this laboratory directed toward the synthesis of ketene mercaptals followed the same route originally proposed by Arens—the dehydrohalogenation of a haloacetaldehyde dialkyl mercaptal, analogous to the preferred method of preparation of ketene acetals.[5] The preparation of chloroacetaldehyde dioctyl mercaptal has been reported.[6]

The reaction of chloroacetaldehyde dimethyl acetal (I) with *n*-butyl mercaptan did not yield chloroacetaldehyde di-*n*-butyl mercaptal despite considerable variation in reaction conditions and work-up procedures. Two products, *cis*-1,2-bis-(*n*-butylmercapto)ethylene (II) and *n*-butylmercaptoacetaldehyde dibutyl mercaptal (III) were isolated. The relative amounts of these products varied with the ratio of mercaptan to I. At the lower levels the ethylene compound (II) is appreciable but at a mercaptan/acetal ratio of 3, III was the only product recovered. The conversion of I to II and III is due to the formation of a cyclic sulfonium intermediate.[2]

An authentic sample of II was prepared by the reaction[7] of sodium *n*-butyl mercaptide with *cis*-1,2-dichloroethylene (IV). Both samples of II were hydrogenated separately to 1,2-bis(*n*-butylmercapto)ethane (V) and the separate reduction products oxidized with hydrogen peroxide to 1,2-bis(*n*-butylsulfonyl)ethane (VI). Both samples of VI showed no depression in melting point with an additional sample of VI obtained by oxidation of authentic V, which had been obtained by addition of *n*-butyl mercaptan to *n*-butyl vinyl sulfide (VII). An authentic sample of III was prepared by the acid-catalyzed reaction of *n*-butylmercaptoacetaldehyde with *n*-butyl mercaptan.[8]

The acid-catalyzed reaction of mercaptans with I is accompanied by evolution of hydrogen chlo-

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(1) E. Rothstein, *J. Chem. Soc.*, 1550 (1940).

(2) W. E. Parham, J. Heberling, and H. Wynberg, *J. Am. Chem. Soc.*, **77**, 1169 (1954).

(3) J. D. Kendall and H. D. Edwards, U. S. Pat. **2,493,071** (Jan. 3, 1950).

(4) H. C. Volger and J. F. Arens, *Rec. Trav. Chim.*, **76**, 848 (1957).

(5) S. M. McElvain and J. Beyerstadt, *J. Am. Chem. Soc.*, **58**, 529 (1936).

(6) E. Schiom, U. S. Pat. **2,369,619** (Feb. 13, 1945).

(7) J. Cusa and McCombie, *J. Chem. Soc.*, 767 (1937).

(8) W. E. Parham, H. Wynberg, and F. L. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953).

ride. Early in the study various bases in aqueous solution were employed to remove dissolved acid before distillation. While, in general, this technique was reasonably satisfactory, neutralization with an alcoholic system was expected to be more thorough.

When a crude product mixture from the reaction of *n*-butyl mercaptan and I (2:1 mole ratio) was added to *t*-butyl alcohol containing potassium *t*-butoxide equivalent to I, the expected products II and III were obtained. In addition, however, a small quantity of ketene dibutyl mercaptal (VIII) was isolated.

Further study showed that VIII was obtained from III by elimination of *n*-butyl mercaptan. Reaction of pure III with an equivalent quantity of potassium *t*-butoxide in *t*-butyl alcohol gave VIII in 72% conversion, 92% yield.[3]

$$\mathrm{III} + \mathrm{KOC_4H_9}\text{-}t \xrightarrow{t\text{-}\mathrm{C_4H_9OH}} \underset{\mathrm{VIII}}{\mathrm{CH_2{=}C(SC_4H_9)_2}} + \mathrm{KSC_4H_9}$$

While the stoichiometric reaction of III with potassium *t*-butoxide is sufficiently useful for a laboratory preparation, methods of performing the elimination catalytically were considered. A successful catalytic system requires the irreversible removal of the mercaptide ion as it is formed. This was accomplished readily by use of acetylene to form *n*-butyl vinyl sulfide (VII). Conversion to the mercaptal and vinyl sulfide was 92%.

$$\underset{\mathrm{III}}{\mathrm{RSCH_2CH(SR)_2}} + \mathrm{HC{\equiv}CH} \xrightarrow[\mathrm{R'OH}]{^{-}\mathrm{OR'}} \underset{\mathrm{VIII}}{\mathrm{CH_2{=}C(SR)_2}} + \underset{\mathrm{VII}}{\mathrm{CH_2{=}CHSR}}$$

$$\begin{gathered}90\text{–}120° \\ 500 \text{ p.s.i.g.} \\ \mathrm{R} = n\text{-}\mathrm{C_4H_9}\text{—} \qquad \mathrm{R'} = t\text{-}\mathrm{C_4H_9}\text{—}\end{gathered}$$

No extensive study of reaction parameters was made. Reaction conditions are similar to those devised by Reppe for vinylation of mercaptans.[10] *t*-Butyl alcohol was employed as solvent solely because of its rather slow rate of vinylation. Further study has shown that the relatively mild reaction conditions required permitted the use of almost any alcohol.

The ketene mercaptal (VIII) was hydrogenated over palladium-alumina catalyst to acetaldehyde di-*n*-butyl mercaptal (IX), which was also prepared independently from acetaldehyde. Melting points and mixed melting points of separate samples of 1,1-di(*n*-butyl sulfonyl)ethane (X) obtained by oxidations of IX showed no depression. Infrared spectra of the various vinyl chlorides were employed as model systems for comparison with the related sulfur compounds. A similar comparison has been used in the study of *cis*-1,2-bis(*p*-tolylthio)-ethylene.[11] The C=C stretching bonds which were useful in this study are summarized in Table I.

$$\begin{tikzcd}
\mathrm{CH_2{=}C(SC_4H_9)_2} \arrow[d, "\mathrm{H_2}"', "\mathrm{Pd/Al_2O_3}"] & & \mathrm{CH_3CHO} \arrow[d, "\mathrm{H^+}"', "\mathrm{C_4H_9SH}"] \\
\mathrm{CH_3CH(SC_4H_9)_2}\ (\mathrm{IXa}) \arrow[d, "\mathrm{H_2O_2}"] & & \mathrm{CH_3CH(SC_4H_9)_2}\ (\mathrm{IXb}) \arrow[d, "\mathrm{H_2O_2}"] \\
\underset{\text{m.p. }70°}{\mathrm{CH_3CH(SO_2C_4H_9)_2}\ (\mathrm{Xa})} \arrow[dr] & & \underset{\text{m.p. }70°}{\mathrm{CH_3CH(SO_2C_4H_9)_2}\ (\mathrm{Xb})} \arrow[dl] \\
& \text{mixed m.p. }70° &
\end{tikzcd}$$

$\mathrm{C_4H_9SO_2CH_2CH_2SO_2C_4H_9}$ m.p. 180°

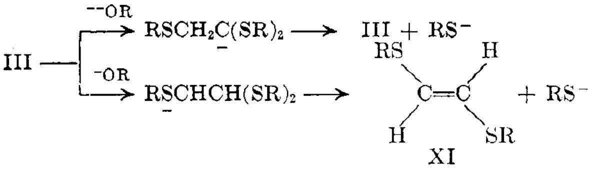
TABLE I

CHARACTERISTIC C=C STRETCHING BONDS

R = *n*-C_4H_9—

Compound	C=C Stretching, cm.$^{-1}$	Intensity
$CH_2{=}CHCl$	1610	S
$CH_2{=}CCl_2$	1611 1553	S M
$ClCH{=}CHCl$ (*cis*)	1582	S
$ClCH{=}CHCl$ (*trans*)	1650	M-W
$CH_2{=}CHSR$	1587	S
$CH_2{=}C(SR)_2$	1580 1550	M-S M-S
$RSCH{=}CHSR$ (*cis*)	1547	M-S

The *trans*-1,2-dichloroethylene (XI) was included in the infrared studies as inspection of atomic models in III implied considerable steric hindrance around the carbon center from which initial proton removal is required to produce VIII. Elimination in the opposite direction would have produced XI, for which the constants were not available.



XI

The higher band (1611 cm.$^{-1}$) of the vinylidene chloride doublet is assigned to the C=C stretching vibration and occurs at approximately the same frequency as the C=C stretching band in vinyl chloride. Similarly, the higher band (1580 cm.$^{-1}$) in the ketene mercaptal (VIII) doublet[12] represents the C=C stretching vibration and occurs at almost the same frequency as the C=C stretching band in the vinyl sulfide. In both vinylidene chloride and the ketene mercaptal, the lower band of

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(9) Arens obtained ketene diethyl mercaptal in 55% yield, using almost two moles of base per mole of ethylmercaptoacetaldehyde diethyl mercaptal, *cf.* Ref. 4, p. 853.

(10) J. W. Reppe and F. Nicolai, Ger. Pat. **624,845** (Jan. 30, 1936); U. S. Pat. **2,073,589** (March 9, 1937).

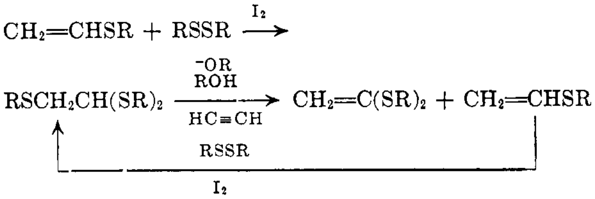
(11) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).

(12) Arens reports a split C=C band at 1560 and 1580 cm.$^{-1}$ for ketene diethyl mercaptal (ref. 4, p. 853).

the doublet is assigned to the first overtone of the 775 cm.$^{-1}$ vibration.

Several other spectral features substantiate the ketene mercaptal structure. A weak, resolved band in the C—H stretching region at 3100 cm.$^{-1}$, characteristic to the $\mathrm{CH_2{=}C}$— structure, was found in both the vinyl sulfide and the ketene mercaptal. A single strong band in the skeletal region of the ketene mercaptal corresponds to a band in the vinylidene chloride spectrum.

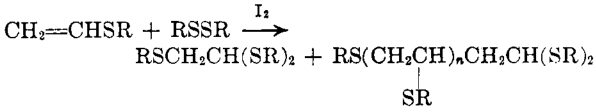
While I is a satisfactory source of III, from which the ketene mercaptals can be obtained by base-catalyzed reaction with acetylene, a more direct route to III is desirable. The addition of disulfides to styrene in the presence of iodine is a smooth, high yield reaction.[13] Consideration of the structural relationship of vinyl sulfides to III and an awareness that the behavior of vinyl sulfides in some addition reactions was similar to that of styrene prompted a study of the addition of disulfides to vinyl sulfides. Furthermore, success in this reaction would provide a process for the preparation of ketene mercaptals from acetylene and disulfides in which the vinyl sulfide would be employed as a "carrier" and recycled after regeneration.



$$\mathrm{CH_2{=}CHSR + RSSR \xrightarrow{I_2}}$$

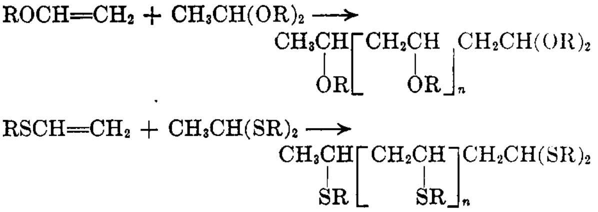
$$\begin{tikzcd} \mathrm{RSCH_2CH(SR)_2} \arrow[r, "\mathrm{^-OR}\ \mathrm{ROH}", "\mathrm{HC{\equiv}CH}"'] & \mathrm{CH_2{=}C(SR)_2 + CH_2{=}CHSR} \arrow[l, bend left, "\mathrm{RSSR}"', "\mathrm{I_2}"] \end{tikzcd}$$

In the presence of catalytic amounts of iodine, disulfides react with vinyl sulfides to give n-alkylthioacetaldehyde dialkyl mercaptals. The reaction, however, is less clean-cut than is the reaction of disulfides with styrene. In addition to n-alkylmercaptoacetaldehyde dialkyl mercaptals, telomeric products involving the reaction of two or more moles of vinyl sulfide per mole of disulfide are obtained. More extensive studies of telomer formation from mercaptals and vinyl sulfides and of addition of disulfides to other olefinic centers are in progress. The appearance of telomers is



$$\mathrm{CH_2{=}CHSR + RSSR \xrightarrow{I_2} RSCH_2CH(SR)_2 + RS(\underset{\substack{|\\ SR}}{CH_2CH})_{n}CH_2CH(SR)_2}$$

attributed to reaction of the n-alkylthioacetaldehyde dialkyl mercaptals and appears to be similar to the preparation of polymers by reaction of acetals with vinyl ethers.[14]



$$\mathrm{ROCH{=}CH_2 + CH_3CH(OR)_2 \longrightarrow \underset{\substack{|\\ OR}}{CH_3CH}\left[\underset{\substack{|\\ OR}}{CH_2CH}\right]_{n}CH_2CH(OR)_2}$$

$$\mathrm{RSCH{=}CH_2 + CH_3CH(SR)_2 \longrightarrow \underset{\substack{|\\ SR}}{CH_3CH}\left[\underset{\substack{|\\ SR}}{CH_2CH}\right]_{n}CH_2CH(SR)_2}$$

EXPERIMENTAL

Reaction of n-butyl mercaptan with chloroacetal. Dry hydrogen chloride was passed into a solution of n-butyl mercaptan (90 g., 1.0 mole) and chloroacetal until absorption ceased. The crude product, in two layers, was washed with aqueous sodium carbonate until the water effluent was basic. The oil layer was dried over potassium carbonate, filtered, and distilled.

The first fraction, an off-white liquid (13 g., 0.069 mole, 14% yield, b.p. 92–95%/0.35 mm., n_{D}^{25} 1.5216) was *cis*-1,2-(n-butylmercapto)ethylene (II).

Anal. Calcd. for $\mathrm{C_{10}H_{20}S_2}$: C, 58.76; H, 9.86; S, 31.37. Found: C, 58.98; H, 10.00; S, 31.10.

A quantity (40.8 g., 0.20 mole) of II from several similar preparations was dissolved in isopropyl alcohol (100 cc.) containing a commercial palladium–aluminum oxide catalyst (3 g.). The solution was contacted with hydrogen in a rocking autoclave under 950–1080 p.s.i.g. at 90–109° and a total pressure drop of 470 p.s.i.g. (calcd. 500 p.s.i.g.) was observed. 1,2-Bis(n-butylmercapto)ethane (V) (36 g., 0.16 mole, 78% yield) was recovered.

A sample (5 g.) of V from the hydrogenation was oxidized with 30% hydrogen peroxide (75 ml.) by heating in a steam bath for 3 hr. 1,2-Bis(n-butyl sulfonyl)ethane (VI, 4.4 g.) was isolated as white platelets and recrystallized from ethanol (m.p. 180–180.6°). A sample of V, obtained as a by-product in the vinylation of n-butyl mercaptan, was oxidized to VI. A melting point of the mixed bissulfones was not depressed.

An authentic sample of *cis*-1,2-bis(n-butylthio)ethylene (II) was prepared by refluxing *cis*-1,2-dichloroethylene with sodium n-butyl mercaptide in ethanol. II was obtained as a water-white liquid (70% yield, b.p. 90–92°0./4 mm., n_{D}^{0} 1.5232, n_{D}^{25} 1.5210, d_{20}^{20} 0.9577, d_{25}^{25} 0.9546).

Anal. Calcd. for $\mathrm{C_{10}H_{20}S_2}$: C, 58.76; H, 9.86; S, 31.37. Found: C, 58.83; H, 10.03; S, 31.31.

The infrared curve of the authentic sample was identical with II prepared from chloroacetal. The authentic sample also was converted to V and VI (m.p. and mixed m.p. 180–180.6°).

The second product (43 g., 0.146 mole, 29.2% yield, b.p. 129°/0.35 mm., n_{D}^{20} 1.5149, n_{D}^{25} 1.5121, a_{20}^{20} 0.9735, d_{2}^{25} 0.9710) was n-butylmercaptoacetaldehyde di-n-butyl mercaptal (III).

Anal. Calcd. for $\mathrm{C_{14}H_{30}S_3}$: C, 57.08; H, 10.27; S, 32.65; $\mathrm{M_D}$, 90.85. Found: C, 57.25; H, 10.24; S, 32.39; $\mathrm{M_D}$, 91.39.

A sample of III was prepared by reaction of equimolar portions of n-butylthioacetaldehyde dimethyl acetal and n-butyl mercaptan, catalyzed with p-toluenesulfonic acid (1%). Physical properties of this product (n_{D}^{20} 1.5138, n_{D}^{25} 1.5121, d_{20}^{20} 0.9735, d_{25}^{25} 0.9701) compared satisfactorily with III obtained from chloroacetal.

Anal. Calcd. for $\mathrm{C_{14}H_{30}S_3}$: C, 57.08; H, 10.27; S, 32.65; $\mathrm{M_D}$, 90.85. Found: C, 57.35; H, 10.36; S, 32.72; $\mathrm{M_D}$, 91.35.

A summary of acid-catalyzed reactions of n-butyl mercaptan with chloroacetals, showing the effect of ratios on product, is given in Table II.

Ketene di-n-butyl mercaptal (VIII). *The stoichiometric reaction.* n-Butylmercaptoacetaldehyde di-n-butyl mercaptal (29.5 g., 0.1 mole) was added at reflux to a solution of potassium metal (3.9 g., 0.1 mole) in t-butyl alcohol (50 cc.). Reflux was continued for 3 hr. during which period the solution turned dark black. t-Butyl alcohol (36 g.) was

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[13] B. Holmberg, Arkir-Kerns, *Mineral Geol.*, **13B**, No. 14 (1939); *Chem. Abstr.* **34**, 2341 (1940).

[14] J. W. Copenhaver, U.S. Patent **2,165,962** (July 11, (1939)).

TABLE II

ACID-CATALYZED REACTION OF *n*-BUTYL MERCAPTAN WITH CHLOROACETALS

R = *n*-C_4H_9—

RSH Moles	Chloroacetal		Conditions	RSCH=CHSR Moles	$RSCH_2CH(SR)_2$ Moles	Total Yield, Based on	
	R′	Moles				RSH	Chloroacetal
1	C_2H_5	0.5	[a]	0.069	0.146	57.6	43.0
1	C_2H_5	0.5	[b]	0.046	0.146	53.0	38.4
1	CH_3	0.5	[c]	0.069	0.146	57.6	43.0
3	CH_3	1.0	[c]	0.167	0.722	80.0	88.9
3	CH_3	1.0	[d]	0.041	0.744	77.1	78.5
9	CH_3	3.0	[c]	—	2.67	89.0	89.0

[a] Concd. hydrochloric acid (3 drops), distill ethanol. [b] Dry hydrogen chloride to saturation, wash two-layer crude with aqueous sodium carbonate. [c] *p*-Toluenesulfonic acid (1%), stand 2–5 days, wash with aqueous sodium hydroxide. [d] *p*-Toluenesulfonic acid (1%), distill methanol.

stripped from the solution *in vacuo*, leaving a slush-like material. After addition of water (100 ml.) the residue was extracted with ether (2 × 50 cc.). The ether was stripped and the residue flash distilled (21 g., b.p. 72°/0.55 mm.–135°/0.45 mm.) into a receiver cooled in Dry Ice–acetone. This material was redistilled to give VIII (15 g., 0.074 mole, 74% conversion) as an off-white liquid (n_D^{20} 1.5107, n_D^{25} 1.5077, d_{20}^{20} 0.9496, d_{25}^{25} 0.9470).

Anal. Calcd. for $C_{10}H_{20}S_2$: C, 58.76; H, 9.86; S, 31.38; M_D, 63.91. Found: C, 59.04; H, 9.97; S, 31.38; M_D, 64.60.

Distillation residues were unconverted III (6 g., 0.0204 mole, 20.4% of charge). The yield of VIII was 92%.

Ketene di-n-butyl mercaptal. The catalytic reaction using acetylene as an aid to elimination. n-Butylmercaptoacetaldehyde di-*n*-butyl mercaptal (467 g., 1.59 mole) and a solution of potassium metal (6.2 g., 0.159 g.-atom) in *t*-butyl alcohol (125 ml.) were added to a 1-l. stirred autoclave. The gas space was flushed with nitrogen and acetylene. The mixture was heated to 120° and acetylene (61 g., 2.34 moles) was pressed in from a calibrated reservoir over a period of 1.25 hr. The reaction was exothermic.

The dark reaction mixture was flash distilled into a Dry Ice-acetone cooled receiver to give a light yellow distillate (577 g., b.p. 110°/0.75 mm., pot temperature 158°) and a dark brown solid residue (29 g.).

After removal of *t*-butyl alcohol and *t*-butyl vinyl ether, *n*-butyl vinyl sulfide (177 g., 1.52 moles, 96% yield, b.p. 54.8°/32 mm.–53°/29 mm., n_D^{25} 1.4714) was obtained.

A small (1 g.) intermediate fraction was removed and VIII (299 g., 1.46 moles, 92% yield, b.p. 60.5°/0.07 mm., n_D^{20} 1.5103, n_D^{25} 1.5077, d_{20}^{20} 0.9562, d_{25}^{25} 0.9538), was obtained as a white, mobile liquid.

Anal. Calcd. for $C_{10}H_{20}S_2$: C, 58.76; H, 9.86; S, 31.37; M_D, 63.91. Found: C, 58.85; H, 9.76; S, 30.96; M_D, 64.10.

A portion (30 g., 0.146 mole) in isopropyl alcohol (110 cc.) was hydrogenated over palladium-aluminum oxide (2 g.) at 102–110° under 800–1000 psig. Approximately 98% of theoretical gas absorption was obtained. The isopropyl alcohol was removed by distillation, and acetaldehyde di-*n*-butyl mercaptal (22 g., 0.107 mole, 73% yield) was obtained as a mobile, colorless liquid (b.p. 64.7–65°/0.11 mm., n_D^{25} 1.4889). Whitner and Reid[15] report b.p. 105°/3 mm., n_D^{20} 1.4900, d_{25}^{25} 0.9342.

Corresponding data for pure 1,2-bis(*n*-butylmercapto)-ethane are: b.p. 70.5–71.2°/0.08 mm., n_D^{20} 1.4963, n_D^{25} 1.4948, d_{25}^{25} 0.9342.

A portion (0.5 g., 0.024 mole) of the acetaldehyde di-*n*-butyl mercaptal from VIII was added during 12 min. to a cool (5–10°) solution of acetic anhydride (16.5 g., 0.16 mole) in 35% hydrogen peroxide (29 g., 0.30 mole), previously held for 5 min. at 45–60°. The batch was immersed in ice water overnight. The crude product was poured onto 75 ml. of cracked ice and crystals, which precipitated, were collected on a filter. The product was recrystallized from 50% ethanol to give 1,1-di(*n*-butyl sulfonyl)ethane (4.5 g., 0.017 mole, 70% yield) as white crystals (m.p. and mixed m.p. 69–70°).

Addition of disulfides to vinyl sulfides (VII). A homogeneous solution of VII (127.8 g., 1.10 mole), *n*-dibutyl disulfide (178.4 g., 1.0 mole) and iodine (1.5 g.) was stirred at room temperature for 5 days. Some slight exotherm was noted on mixing the reactants. The crude reaction products were washed with aqueous sodium hydroxide (1*N*) until the iodine color was removed. The oil layer was separated and distilled through a modified Claisen.

The first fraction was *n*-dibutyl disulfide (103 g., 0.58 mole, 58% recovery). The second product was *n*-butylmercaptoacetaldehyde di-*n*-butyl mercaptal (III) (61 g., 0.21 mole, 21% yield).

No *n*-butyl vinyl sulfide was recovered unchanged and that (0.89 mole) not accounted for by III appeared as telomers in the distillation residue (133 g.). The *n*-butyl disulfide unrecovered (0.21 mole) also appeared in the residue, indicating an average *n*-butyl vinyl sulfide/*n*-butyl disulfide ratio of 4.2. In a similar but smaller scale preparation a crude product of molecular weight 355 was isolated (b.p. 175–190°/0.04 mm.).

Slow addition of the vinyl sulfide to the disulfide provides a better product distribution. Methyl vinyl sulfide (34.3 g., 0.46 mole) was added dropwise over a 1-hr. period to a stirred solution of iodine (0.8 g.) in dimethyl disulfide (43.5 g., 0.46 mole) at room temperature. Stirring was continued for an additional 6 hr., and the reaction mixture stood for 3 additional days at room temperature. After washing with 10% sodium hydroxide until the iodine color disappeared, the organic layer was distilled through a modified Claisen to give methylmercaptoacetaldehyde dimethyl mercaptal (42 g., 0.25 mole, 54.2% yield) as a water-white liquid, b.p. 68–69°/0.5 mm., n_D^{25} 1.5715, d_{25}^{25} 1.135.

Anal. Calcd. for $C_5H_{12}S_3$: C, 35.67; H, 7.19; S, 57.14; M_D, 49.29. Found: C, 35.94; H, 7.22; S, 56.99; M_D, 48.87.

In addition, 1,1,3,4-tetra(methylmercapto)butane (17 g., 0.07 mole, 30.3% yield) was obtained a light yellow liquid, b.p. 116°/0.23 mm., n_D^{25} 1.5743, d_{25}^{25} 1.141.

Anal. Calcd. for $C_8H_{18}S_4$: C, 39.62; H, 7.48; S, 52.89; M_D, 71.14. Found: C, 39.90; H, 7.71; S, 52.90; M_D, 70.34.

Acknowledgment. Infrared spectral data were obtained by Miss Helen Miklas.

PHILADELPHIA, PA.

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[15] T. C. Whitner and E. E. Reid, *J. Am. Chem. Soc.*, **43**, 639 (1921).