extracted with three 50-ml portions of methylene chloride. The combined extracts, dried and evaporated, gave 5.50 g (82%) of trisulfide **4**, mp 92–94°. Recrystallization from acetone and chloroform–carbon tetrachloride gave bis(2-acetamidoethyl) trisulfide (**4**) with a constant melting point of 95.0–95.5°, $\lambda_{max}^{abs\ EtOH}$ 250 mμ (log ε 3.21); N,N′-diacetylcystamine[2h] has $\lambda_{max}^{abs\ EtOH}$ 245 mμ (log ε 2.55). Infrared spectrum (KBr) showed 3260 (s, br) 3060, 2930, 1630 (s, br), 1530 (s, br), 1420 (s), 1400, 1360 (s), 1300 (s), 1230 (s), 1180, 880 (w), 740, 690, 620, 590, 490 (w), 460 (w), 410 (w), and 320–270 (br) cm^{-1}; N,N′-diacetylcystamine differs from **4** in having bands at 805, 710 (br), 600 (s), 470, and 420, and lacking them at 880, 740, 620, 590, and 490 cm^{-1}.

Anal. Calcd for $C_8H_{16}N_2O_2S_3$: C, 35.80; H, 6.09; N, 10.43; S, 35.84. Found: C, 35.89; H, 5.92; N, 10.30; S, 35.69.

Substitution of potassium hydrosulfide in the foregoing procedure resulted in 26% of **4**, mp 95–95.5°, but only after repeated recrystallization.

Thin layer chromatography of trisulfide **4**, prepared by either of the above methods, on a 250-μ-thick Woelm silica gel G layer developed with acetone gave only one spot (located by exposure to iodine vapor; R_f 0.38).

B. Preparation from Sodium S-(2-Acetamidoethyl) Thiosulfate (10).[25]—An aqueous solution of 11.0 mmoles of sodium hydrosulfide was added to a stirred mixture of 24.3 mmoles of **10**, 65 ml of 0.2 *M* phosphate buffer (pH 8.0), 9 ml of 37% w/v formaldehyde solution, and 200 ml of chloroform. The chloroform layer gave an oil from which crystallization separated only 0.4 g (14%, calculated as **4**) of solid, mp 75–83°. This solid was mainly **4** (thin layer chromatographic R_f 0.38), but repeated recrystallization did not give pure **4**.

C. Attempted Preparation from Sulfur Dichloride.—Sulfur dichloride (50 mmoles) in absolute ether was added (45 min) to 100 mmoles of 2-acetamidoethanethiol[21] in chloroform. Filtration separated 14.5 g of hygroscopic material, which was completely insoluble in acetone and chloroform.

***t*-Butyl Trisulfide (8). A. Gas–Liquid Partition Chromatographic (Glpc) Separations.**—Products in these experiments were separated using an F & M Model 720 instrument (oven, 150°; detection and injection, 250°; flow rate of helium, 60 ml/min; bridge current, 150 ma) with a 30-cm column of 5% silicone gum rubber on Chromosorb P. *t*-Butyl disulfide and *t*-butyl trisulfide (**8**) were readily separated (retention times, 50 and 106 (±4) sec, respectively); their identities were established by peak enhancement using known samples. A third peak found with several preparations (retention time 290 sec) is assumed to be *t*-butyl tetrasulfide because a plot of log (retention volume) *vs.* molecular weight for the three components (assuming the least volatile to be *t*-butyl tetrasulfide) gave a straight line.[26] The composition was calculated by comparing the area of one peak (height × width at one-half height) to the total area of all three peaks (the method was confirmed at ±2% with known mixtures of *t*-butyl di- and trisulfide; pure *t*-butyl trisulfide gave a single peak and hence was stable).

B. Preparation from *t*-Butyl *p*-Toluenethiolsulfonate (7).—A solution of 24.4 g (0.10 mole) of thiolsulfonate **7** in 200 ml of ether and a solution of 0.05 mole of sodium sulfide in 100 ml of water were stirred together for 24 hr. The aqueous phase was separated and washed with ether. The ether extracts were washed with water, dried, and evaporated to give 10 g (95%) of oil comprised of at least 98% of trisulfide **8** (with a trace of *t*-butyl tetrasulfide). Distillation through a 2 × 10 cm Vigreux column gave 6.05 g (58%) of **8**: bp 108–110° (20 mm); $n^{24}D$ 1.5225 [lit.[27] bp 86° (4 mm); $n^{20}D$ 1.5225]; λ_{max}^{hexane} 257 mμ (log ε 3.28); infrared bands (neat) at 2960–2860 (s), 1460 (s), 1390, 1360 (s), 1220, 1160 (s), 1040, 1020 (w), 930 (w), 565 (w), 490, and 280 (s, br); *t*-butyl disulfide has a band at 560 (w) and lacks them at 565 and 490 cm^{-1}. This sample of trisulfide gave only one glpc peak (retention time, 110 sec).

Anal. Calcd for $C_8H_{18}S_3$: S, 45.72. Found: S, 45.81.

Increase in the reaction time to 72 hr resulted in 88% yield of crude trisulfide, shown by glpc to consist of 6% of *t*-butyl disulfide, 94% of *t*-butyl trisulfide (**8**), and a trace of *t*-butyl tetrasulfide. When the thiolsulfonate **7** and potassium sulfide (2:1 molar ratio) in methanol (homogeneous mixture) were allowed to react for 3 hr, 88% of the crude trisulfide **8** resulted, consisting of 83% of trisulfide **8** and 17% of the tetrasulfide.

C. Preparation from 2-Methyl-2-propanesulfenyl Chloride.[28]—2-Methyl-2-propanesulfenyl chloride[29] (0.20 mole) in pentane was stirred with an aqueous solution of sodium sulfide (0.10 mole) for 3 hr. The pentane layer, washed with water, dried, and evaporated gave 18.5 g (88%) of an oil, shown by glpc to consist of 8% of *t*-butyl disulfide, 58% of trisulfide **8**, and 34% of *t*-butyl tetrasulfide. Distillation gave 6.5 g of material with bp 54–75° (0.4 mm); redistillation (21-cm spinning-band column) did not give pure trisulfide **8**.

An identical experiment but with methanol as solvent and potassium sulfide gave 14.0 g (67%) of oil, shown by glpc to consist of 16% *t*-butyl disulfide, 55% trisulfide **8**, and 27% *t*-butyl tetrasulfide.

(25) Procedure based on that described in ref 6.

(26) *Cf.* ref 6.

(27) S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Petrol.*, **39**, 206 (1953).

(28) Procedure somewhat similar to that of ref 7.

(29) W. A. Schulze, G. H. Short, and W. W. Crouch, *Ind. Eng. Chem.*, **42**, 916 (1950).

Thiomethoxymethylation of Phenols by Dimethyl Sulfoxide and Acetic Anhydride

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Burdon, *et al.*,[1a] and Pfitzner, *et al.*,[1b] have found recently that phenols can be thiomethoxymethylated by dimethyl sulfoxide (DMSO) in the presence of dicyclohexylcarbodiimide (DCC) and a proton source.

The authors have found that the same reaction occurred using acetic anhydride instead of DCC at room temperature. Thus, phenol was thiomethoxymethylated to give 2-thiomethoxymethylphenol (I) and 2,6-di(thiomethoxymethyl)phenol (II). Phenyl acetate and a small amount of acetate of I were also obtained (Table I).

TABLE I
THIOMETHOXYMETHYLATION OF PHENOL

Reacn time, hr	Yields of products, % I[a]	II[b]	Phenyl acetate
22	19	Trace	10
46	26	0.8	13
84	37	7.2	14
240	31	20	16

[a] Bp 100–101° (1.2 mm); lit.[1b] bp 73–74° (0.3 mm). [b] Bp 160–162° (4 mm); lit.[1b] bp 119–120 (0.3 mm). Disulfone mp 194–195° (from water). *Anal.* Calcd for $C_{10}H_{14}O_5S_2$: C, 43.17; H, 5.07; S, 23.05. Found: C, 43.43; H, 5.22; S, 22.89.

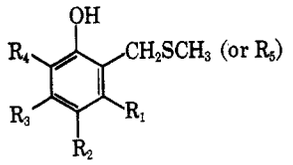
o-, *m*-, and *p*-cresol and 2,4-dimethylphenol gave the corresponding *ortho*-thiomethoxymethylated products (Table II).

Weakly acidic phenols such as those in Table II gave only 2–16% of phenol acetates, but more acidic phenols like *p*-nitrophenol gave the acetate quantitatively. α-Naphthol gave 71% of α-naphthyl acetate and 12% of β-thiomethoxymethyl-α-naphthyl acetate (VIII).

(1) (a) M. G. Burdon and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 4656 (1965); (b) K. E. Pfitzner, J. P. Marino, and R. A. Olofson, *ibid.*, **87**, 4658 (1965).

TABLE II

THIOMETHOXYMETHYLPHENOLS



Phenol	Product		Yield, %	Bp (mm) or mp (°C)	Sulfur, % Calcd	Sulfur, % Found
o-Cresol	III	$R_4 = CH_3$; $R_1 = R_2 = R_3 = H$	25	114–115 (5)[a]	19.05	18.89
	IVa	$R_2 = CH_3$; $R_1 = R_3 = R_4 = H$	36	130 (5)[b]	19.05	19.11
p-Cresol	IVb	$R_4 = CH_2SCH_3$; $R_2 = CH_3$; $R_2 = R_3 = H$	9	165–166 (4)[b]	28.04	27.21
m-Cresol	Va	$R_1 = CH_3$; $R_2 = R_3 = R_4 = H$	16	130–132 (7)[c]	19.05	18.96
	Vb	$R_3 = CH_3$; $R_1 = R_2 = R_4 = H$	18	130–132 (7)[c]		
2,4-Dimethylphenol	VI	$R_2 = R_4 = CH_3$; $R_1 = R_3 = H$	61	130–131 (3)	17.58	17.42
2,6-Dimethylphenol	VII	$R_2 = CH_2SCH_3$; $R_4 = R_5 = CH_3$; $R_1 = R_3 = H$	26	136–138 (5); 43–45[d]	17.58	17.60

[a] Lit.[1a] bp 71 (0.4 mm). [b] Described as oil.[1b] [c] A mixture of Va and Vb (Va:Vb = 1:1.1); relative retention times in vpc, Va:Vb = 1:1.13. [d] Lit.[1b] mp 41–43.

Phenol gave no *para*- or *meta*-substituted products. 2,6-Dimethylphenol which has no available *ortho* positions gave *para*-alkylated product (VII). 2,6-Di-*t*-butylphenol and 2,6-di-*t*-butyl-*p*-cresol were recovered unchanged, and in these cases 45–50% of acetoxymethyl methyl sulfide (IX) was isolated. On the other hand, the other phenols yielded IX in less than 5%. *o*-Cresol may be substituted in *para* position before alkylation of the available *ortho* position, since desulfurization of the product by Raney nickel gave a small amount of 2,4-dimethylphenol (0.3%) besides 2,4,6-trimethylphenol (0.5%) and 2,6-dimethylphenol.

Butyric anhydride, polyphosphoric acid, and phosphorus pentoxide can be substituted for acetic anhydride, although the yields are poor.

A mixture of phenol, DMSO, and phosphorus pentoxide gave 1,3-benzoxathian (14%), I (2%), and salicylaldehyde (X, 0.5%). Compound X may be formed through the Pummerer rearrangement of 2-methylsulfinylmethylphenol which is the oxidation product of I by DMSO.[2] *p*-Nitrophenol, using the same reagent, gave 6-nitro-1,3-benzoxathian (XI, 21%).

A alkoxysulfonium cation is postulated as an intermediate in the oxidation of alcohols by acetic anhydride and DMSO.[3] A phenoxysulfonium cation (XII) may be formed in the reaction of phenol, acetic anhydride, and DMSO, and phenols are thiomethoxymethylated through XII, which was postulated as an intermediate.[1] Decomposition of a complex of benzene diazonium chloride and zinc chloride in DMSO with expectation that XII would be formed[4] gave phenol (76%); I or II could not be detected in the reaction mixture.

(2) R. Oda and Y. Hayashi, *J. Chem. Soc. Japan Pure Chem. Sub.*, **87**, 291 (1966).
(3) J. D. Albright and L. Goldman, *J. Am. Chem. Soc.*, **87**, 4214 (1965).
(4) K. H. Schneid and W. Kampe, *Angew. Chem.*, **77**, 811 (1965).

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Japan Spectroscopic 402G spectrophotometer. The nmr spectra were determined on a Varian A-60 spectrometer.

Thiomethoxymethylation of Phenols.—The thiomethoxymethylation was carried out by allowing a mixture of 0.3 mole of phenols, 0.5 mole of acetic anhydride, and 1.5 mmoles of DMSO to stand at room temperature (15–25°) for 2 days. The reaction mixture was poured into cold water, and the aqueous solution was extracted twice with ether. The combined extract was washed with an aqueous and saturated sodium chloride solution and dried over anhydrous sodium sulfate. After evaporation of the ether the products were distilled *in vacuo* or crystallized. The alkylated products in Tables I and II were identified by their elemental analyses, infrared spectra, nmr spectra, and desulfurization by Raney nickel in methanol to the expected known products.

β-Thiomethoxymethyl-α-naphthyl Acetate (VIII).—After distillation of the α-naphthyl acetate [bp 144–145° (6 mm)], VIII was isolated from the residue, mp 86–87° (from methanol).

Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.30; H, 5.74; S, 13.02. Found: C, 68.55; H, 6.00; S, 12.92.

In the case of 2,4-dimethylphenol, an oil [bp 159–160° (3 mm)] was isolated. The infrared spectrum showed absorption at 1630 and 1650 cm^{-1}. The nmr spectrum exhibited four singlets at 198, 121, 119 and 70 cps (ratio 2:6:3:3) and three multiplets. This material was identified as 2,6-di(thiomethoxymethyl)-4,6-dimethyl-2,4-cyclohexadienone.

Anal. Calcd for $C_{12}H_{18}OS_2$: C, 59.49; H, 7.61; S, 26.42. Found: C, 59.65; H, 7.49; S, 26.14.

6-Nitrobenzoxathian (XI).—To a solution of 25 g (0.194 mole) of *p*-nitrophenol in 100 ml of DMSO, 28.4 g (0.2 mole) of phosphorus pentoxide was added at 10–15°. After stirring at room temperature for 20 hr, the reaction mixture was poured into ice–water and extracted with ether. The extracts were dried and evaporated to yield 12 g of solid. The solid was recrystallized from methanol, mp 136–137° (lit.[1b] mp 135–136°).

Anal. Calcd for $C_8H\,NO_3S$: C, 48.74; H, 3.58; N, 7.11; S, 16.23. Found: C, 48.54; H, 3.62; N, 7.18; S, 16.11.

1,3-Benzoxanthian.—The procedure described above was followed. After evaporation of the ether, the residue was distilled *in vacuo*. Benzoxathian was separated from I by washing out with an aqueous sodium hydroxide solution, bp 104–105° (5 mm) (this was described as an oil[1b]).

Anal. Calcd for C_8H_8OS: S, 21.07. Found: S, 21.54.