

halides also react with tertiary hydride donors. The nmr spectrum of the cyclic halide is but slightly affected as the reaction appears to generate tertiary ions which initiate hydride transfer chain reactions with the remaining donor molecules. For example, reaction with 2,2,3-trimethylbutane and 2,3-dimethylbutane leads to immediate exchange broadening of the paraffins spectra (Figure 7). The spectra indicate that methyl migration is rapid in the former system. These halides also initiate the rearrangements of cycloheptane or cyclooctane which however occur slowly at -50° .

Thus in the $AlBr_3$ -chlorobenzene system hydride transfer from tertiary or secondary sources to tertiary

or secondary cations has been observed at quite low temperatures. Spectra of solutions of tertiary halides contain bands consistent with the presence of tertiary cations. The bands may be removed by reaction with hydride donors and hydrocarbons of the proper structures cleanly recovered. High field nmr bands are also present which suggest the presence of protonated alkyl aromatics.

Registry No.—Chlorobenzene, 108-90-7; *t*-amyl chloride, 594-36-5; isobutane, 75-28-5; cycloheptane, 291-64-5; *t*-butyl chloride, 507-20-0; isopropyl chloride, 75-29-6; bromocyclopentane, 137-43-9.

The Formation of Sulfur-Sulfur Bonds by the Chloramination of Thiols¹

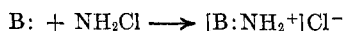
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Chloramine and dimethylchloramine react with cyclohexylmercaptan, thiophenol, 2-mercaptanaphthalene, 2-mercaptopyridine, 2-mercaptoethanol, 1-butanethiol, and 1,2-ethanedithiol with the extraction of the thiol hydrogen atoms and the formation of sulfur-sulfur bonds. There is an indication that the first step in the reaction is the formation of compounds of the type $RSNH_2$ or $RSN(CH_3)_2$. Possible mechanisms for the chloramination reactions are discussed.

It has been well established that the chloramine molecule reacts with electron-donor molecules in accordance with the equation



where B: is the Lewis base. Among the Lewis bases studied are those containing nitrogen, phosphorus, arsenic, or antimony atoms as the basic centers of the molecule. During the past decade, the reactions of chloramines of the type $R_2'NCl$, where $R' = H$ or alkyl, with amines, phosphines, arsines, and stibines have been extensively investigated in this laboratory.²⁻¹³

We were interested in studying the reactions of chloramines with compounds in which sulfur is the electron-donor atom. We hoped that such reactions of $R_2'NCl$ ($R' = H$ or alkyl) with thiols would result in the cleavage of the N-Cl bonds in the chloramine molecules with the formation of sulfenamides of the types $RSNH_2$ and $RSN(CH_3)_2$. Previous work reported in the literature indicating that aqueous solutions of chloramine react with alkali metal mercaptides

to yield insoluble sulfenamides¹⁴⁻¹⁸ supported this suggestion. In all these cases, ammonia was present in excess.

It was our thinking that formation of the disulfide is the initial step in these reactions and that the sulfenamide is obtained by the cleavage of $RS-SR$ to $RSNH_2$ and $RSCl$ followed by the formation of a second molecule of $RSNH_2$ by ammonolysis of $RSCl$. This thinking was based on the reported formation of disulfides by oxidation (by means other than chloramination) of thiols.¹⁹

Therefore, when we observed that cyclohexylmercaptan reacts with dimethylchloramine in ethereal solution to give dicyclohexyl disulfide in good yield, we decided to investigate the series of reactions to determine if the sulfenamides, as well as the disulfides, could be obtained and under what conditions. We were also interested in the possibility of forming $[RSN]_n$ polymers.

Carr and coworkers¹⁵ had found the presence of some disulfides in their oxidation of mercaptides to sulfenamides in aqueous media and had speculated concerning the mechanism of the reactions.

The results of the research we report here show that the disulfide is obtained almost exclusively from the chloramination of thiols in ethereal solution with either chloramine or dimethylchloramine. The presence of ammonia in the reactions with chloramine does not change the result. The results indicate the probability

(1) (a) This research was reported at the 22nd meeting-in-miniature of the Florida Section of the American Chemical Society, Jacksonville, Fla., May 1969.

(2) (a) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, **81**, 2982 (1959). (b) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

(3) D. F. Clemens and H. H. Sisler, *ibid.*, **4**, 1222 (1965).

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(12) L. K. Krannich and H. H. Sisler, *ibid.*, **8**, 1032 (1969).

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(17) I. G. Farbenind, German Patent 586,351 (1933).

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(19) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol I, Chemical Publishing Co., Inc., New York, N. Y., 1958, pp 120-126.

TABLE I
CHLORAMINATION REACTIONS WITH THIOPHENOL AND
CYCLOHEXYLMERCAPTAN IN DIETHYL ETHER

Reactants ^a		Mole ratio (A:B)	Products ^c	Mp or bp, °C (mm)	Yield, %
A	B ^b				
(CH ₃) ₂ NCl	C ₆ H ₅ SH	1:2	C ₆ H ₅ S-SC ₆ H ₅ ^d	57-58 ^e 175-185 ^g (14)	74.3 ^f
C ₆ H ₅ SH ^h	(CH ₃) ₂ NCl	1:1	C ₆ H ₅ S-SC ₆ H ₅ ⁱ	55-56	85.0 ^j
NH ₂ Cl (+ NH ₃)	C ₆ H ₅ SH	1:2	C ₆ H ₅ S-SC ₆ H ₅	55-56	86.0 ^j
C ₆ H ₅ SH ^h	NH ₂ Cl (+ NH ₃)	1:2	C ₆ H ₅ S-SC ₆ H ₅	54-55	93.1 ^j
C ₆ H ₅ SH ^h	NH ₂ Cl (ammonia free)	1:1	C ₆ H ₅ S-SC ₆ H ₅	52-53	80.8 ^j
(CH ₃) ₂ NCl	C ₆ H ₁₁ SH	1:2	C ₆ H ₁₁ S-SC ₆ H ₁₁ ^k	140 (2.1)	86.1 ^j
C ₆ H ₁₁ SH ^h	(CH ₃) ₂ NCl	1:1	C ₆ H ₁₁ S-SC ₆ H ₁₁	150-152 (4)	77.5 ^j
NH ₂ Cl (+ NH ₃)	C ₆ H ₁₁ SH	1:2	C ₆ H ₁₁ S-SC ₆ H ₁₁	190 (18)	56.8 ^j
C ₆ H ₁₁ SH ^h	NH ₂ Cl (+ NH ₃)	1:1	C ₆ H ₁₁ S-SC ₆ H ₁₁	157 (4.3)	87.5 ^j

^a A added dropwise to B. ^b Taken in slight excess of specified mole ratio. ^c Dimethylammonium chloride and ammonium chloride formed from (CH₃)₂NCl and NH₂Cl, respectively, were obtained in almost quantitative yields. ^d Yellow-white needles recrystallized from hot absolute alcohol. ^e Melts to give a yellow liquid; color deepens on heating. ^f Based on chloramine. ^g Solidifies in condenser; hot-water condenser was used. ^h In the initial stages, transient color changes of the reaction mixture were observed (from light yellow to orange red). ⁱ Repeated at a temperature of 0-5; same products were obtained. ^j Based on mercaptan. ^k Yellowish, oily liquid; purity was checked by vpc. ^l Based on mercaptan used; reaction probably was not completed.

that, contrary to our initial expectation, the formation of the sulfenamide is the initial step in the reaction and the disulfide results from reaction of the sulfenamide with additional thiol.

Experimental Section

Materials.—Cyclohexylmercaptan, 2-mercaptopyridine, thiophenol, 2-naphthalenethiol, and diphenyl disulfide were obtained from K & K Laboratories. 1-Butanethiol and dibutyl disulfide were obtained from Eastman Organic Chemicals. 2-Mercaptoethanol and 1,2-ethanedithiol were obtained from the J. T. Baker Chemical Co. The purity of the mercaptans and the disulfides was checked by comparison of indices of refraction, densities, melting or boiling points, and infrared spectra with the corresponding data in the literature. All solvents used were of reagent grade and were stored over calcium hydride. Absolute ethanol was used as received.

Analyses.—The Galbraith Microanalytical Laboratory conducted the elemental analyses. In some cases, the ordinary Kjeldahl procedure for nitrogen analysis was employed in this laboratory. Chlorine analysis was also done in this laboratory. Molecular weights were determined by the cryoscopic method. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared and Nuclear Magnetic Resonance Spectra.—Infrared spectra were recorded with a Beckman Model IR-10 grating infrared spectrophotometer. The spectra of solids were obtained using KBr pellets and those of liquids by using KBr or NaCl disks. The proton magnetic resonance spectra were recorded with a Varian A-60 spectrometer. The spectra of liquids were run as pure samples and those of solids were determined in deuteriochloroform, deuterated acetone, or deuterated dimethyl sulfoxide with tetramethylsilane as internal standard. Infrared data of compounds not previously reported are listed.

Synthesis of Chloramines.—Dimethylchloramine was prepared by a procedure analogous to the Raschig synthesis of chloramine.²⁰ Chloramine was prepared in a generator by an anhydrous method developed by Mattair and Sisler²¹ involving the gas-phase chlorination of ammonia.

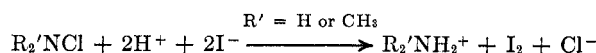
The rates of flow of ammonia, nitrogen, and chlorine in the generator were 1.2, 0.3, and 0.1 mol/hr, respectively, and the production rate of chloramine was ca. 0.1 mol/hr. The ethereal solution of chloramine was freed from ammonia by the method of Gilson and Sisler²² in which the chloramine solution is passed through a column of anhydrous copper sulfate.

Procedure for Chloramination Reactions.—The experimental procedures for most of the reactions studied were similar. The

typical procedure consisted of adding dropwise chloramine solution or dimethylchloramine solution in dry diethyl ether to a solution of the mercaptan in dry diethyl ether with constant stirring. The temperature of the reaction mixture was kept at 25° except as otherwise stated. There was an immediate turbidity followed by the formation of a white precipitate, and dense white fumes were also observed. The reactions were generally exothermic. A water-cooled condenser and magnetic stirrer were used, and air and moisture were kept away using Drierite tubes. After the addition of chloramine was complete, the reaction mixture was stirred overnight, followed by refluxing for periods varying from 1 to 3 hr.

On filtration, generally a white solid was obtained which was dried under vacuum and was identified in most cases as ammonium chloride or dimethylammonium chloride, except in those cases where the disulfides formed are insoluble in diethyl ether.

Excess of mercaptan or chloramine, as the case may be, was removed from the ethereal filtrate. For removing excess mercaptan, fractional distillation or treatment with 2*N* NaOH was carried out. Excess chloramine and ether could be easily removed under reduced pressure. The unused mercaptan was estimated by titration with an alcoholic solution of iodine containing small amounts of pyridine to remove the hydrogen iodide formed. The end point was the appearance of iodine color.²³ Chloramine and dimethylchloramine concentrations in reacting solutions were estimated iodometrically. To a measured volume (5 ml) of ethereal solution of chloramine, ca. 20-40 ml of 50% acetic acid was added followed by excess of potassium iodide. The iodine liberated was titrated against standard thiosulfate solution.



The products obtained were recrystallized from appropriate solvents. The purities of liquids were tested by vapor phase chromatography.

If, as we initially believed, chloramine reacts with mercaptans to form disulfides first, followed by cleavage of sulfur-sulfur bond to give RSNH₂ or RSN(CH₃)₂ and RSCl, the varying mole ratios of chloramine to mercaptan might have given different reaction products. With this point in view, extensive work was carried out with the chloraminations of cyclohexylmercaptan and of thiophenol using varying mole ratios. The results of these experiments are summarized in Table I.

The mole ratios of mercaptans to chloramines in the reactions of 2-mercaptanaphthalene, 2-mercaptopyridine, 2-mercaptoethanol, and 1-butanethiol were kept at slightly in excess of 2:1. These results are summarized in Table II.

The preparations of mixed disulfides by chloramination of a mixture of thiols and the reaction of 1,2-ethanedithiol with dimethylchloramine have been carried out and are discussed separately. A number of experiments were carried out to obtain

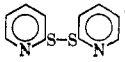
(20) A. Berg, *Ann. Chim. Phys.*, **3**, 319 (1894).

(21) R. Mattair and H. H. Sisler, *J. Amer. Chem. Soc.*, **73**, 1619 (1951).

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(23) D. P. Harnish and D. A. Tarbell, *Anal. Chem.*, **21**, 968 (1949).

TABLE II
CHLORAMINATION REACTIONS WITH 2-MERCAPTONAPHTHALENE, 2-MERCAPTOPYRIDINE,
2-MERCAPTOETHANOL, AND 1-BUTANETHIOL IN DIETHYL ETHER
(THIOL TO CHLORAMINE MOL RATIO > 2:1)

Reactants ^a		Products ^c	Mp or bp, °C (mm)	Yield, %
A	B ^b			
(CH ₃) ₂ NCl	2-Mercaptanaphthalene	β -C ₁₀ H ₇ S-S- β -C ₁₀ H ₇ ^d	135-136	70.6 ^e
NH ₂ Cl (+ NH ₃)	2-Mercaptanaphthalene	β -C ₁₀ H ₇ S-S- β -C ₁₀ H ₇	135-136	94.3 ^e
(CH ₃) ₂ NCl	2-Mercaptopyridine ^f		52	77.6 ^e
NH ₂ Cl (+ NH ₃)	2-Mercaptopyridine		51-52	83.1 ^e
(CH ₃) ₂ NCl	2-Mercaptoethanol ^h	HOCH ₂ CH ₂ S-S-CH ₂ CH ₂ OH ⁱ	25-26	47.6 ^j
NH ₂ Cl (+ NH ₃)	2-Mercaptoethanol	HOCH ₂ CH ₂ S-S-CH ₂ CH ₂ OH	27-28	67.0 ^e
			175-176 (4.5)	
(CH ₃) ₂ NCl	1-Butanethiol	CH ₃ (CH ₂) ₃ S-S-(CH ₂) ₃ CH ₃ ^k	73-74 (1.1)	80.7 ^e
NH ₂ Cl (+ NH ₃)	1-Butanethiol	CH ₃ (CH ₂) ₃ S-S-(CH ₂) ₃ CH ₃	76 (1.75)	74.9 ^e

^a A added dropwise to B. ^b Taken in slight excess of specified mole ratio. ^c Dimethylammonium chloride and ammonium chloride formed from (CH₃)₂NCl and NH₂Cl, respectively, were obtained in almost quantitative yields. ^d Light yellow compound, insoluble in diethyl ether. ^e Based on chloramine. ^f Temperature of the reaction mixture was kept at 0-5°. ^g On evaporation of ether, a dark red, viscous liquid was left which turned into a light red-brown solid. ^h Temperature of the reaction mixture was kept at 10-15°. ⁱ Light yellow liquid with solid particles at 25° (room temperature). ^j Based on mercaptan used. ^k Colorless liquid, turning slightly yellow at higher temperature.

evidence concerning the reaction mechanism. Two of them are described under the heading "General Experiments," and are discussed later.

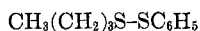
Chloramination of Mixtures of Thiols.—Using procedures analogous to those described, an equimolar mixture of 2-mercaptanaphthalene and thiophenol was treated with a less than equivalent amount of dimethylchloramine. An 80.6% yield of mixtures of diphenyl disulfide, di- β -naphthyl disulfide, and β -naphthylphenyl disulfide based on dimethylchloramine was obtained. The mole ratio of these disulfides in the mixed product was ca. 10.5:9.5:9.0, respectively. β -Naphthylphenyl disulfide, soluble in diethyl ether and obtained by fractional crystallization of absolute alcohol, is a white, crystalline solid melting at 73°. The ¹H nmr spectrum in acetone-*d*₆ gave a very broad complex peak in the aromatic region.

Anal. Calcd for C₁₆H₁₂S₂: C, 71.64; H, 4.48; S, 23.88. Found: C, 71.5; H, 4.57; S, 23.64.

A similar experiment with a mixture of thiophenol and 1-butanethiol gave an overall yield of a mixed disulfide product of 65%. The product contained di-*n*-butyl disulfide, diphenyl disulfide, and *n*-butylphenyl disulfide in a mole ratio of 7.0:7.0:10.0, respectively. Infrared data for the two mixed disulfides, not reported previously, are listed in Table III. *n*-Butylphenyl disulfide was a light yellow liquid, bp 115-118° (2.8 mm). The ¹H nmr spectrum confirms this identification.

TABLE III
INFRARED DATA^a
 β -C₁₀H₇S-SC₆H₅

400 vw, 475 m, 490 m, 605 w, 630 w, 645 vw, 690 s, 745 vs, 820 vs, 850-865 s, 890 sh, 900 m, 920 m, 948 m, 960 sh, 970 m, 1005 w, 1030 s, 1060 w, 1075 m, 1080 sh, 1105 vw, 1140 s, 1150 sh, 1185 vw, 1200 w, 1300 w, 1355 m, 1375 w, 1442 s, 1480 s, 1505 m, 1580 s, 1590 s, 1625 m, 1730 vw, 1860 vw, 2330 vw, 3060 w



695 s, 745 vs, 785 sh, 840 vw, 878 w, 910 sh, 920 w, 970 vw, 1005 w, 1030 s, 1072 m, 1080 sh, 1100 w, 1160 vw, 1182 w, 1225 m, 1268 m, 1304 m, 1330 vw, 1382 m, 1416 m, 1442 s, 1470 sh, 1480 s, 1585 s, 1630-1640 w, br, 1730 vw, 1790 w, 1850-65 w, br, 1940 w, 2880 s, 2935 vs, 2960 vs, 3020 sh, 3068 m



510 w, 585-590 w, br, 680 m, 738 s, 835-45 w, br, 890 vw, 1025 w, 1110 m, 1188 vs, 1250 m, 1340 sh, 1410 s, 1440 w, 1460-1470 w, br, 1610-1640 w, br, 2420 w, 2910 w, 3400-3430 w, br

^a In cm⁻¹. Abbreviations: s, strong; m, medium; w, weak; br, broad; v, very; sh, shoulder.

Anal. Calcd for C₁₀H₁₄S₂: C, 60.6; H, 7.07; S, 32.32. Found: C, 60.75; H, 7.19; S, 32.17.

Reaction of 1,2-Ethanedithiol with Dimethylchloramine.—A 30-ml portion (24.6 mmol) of 0.82 *M* dimethylchloramine solution in diethyl ether was added dropwise to a solution of 5 g (53.2 mmol) of 1,2-ethanedithiol in 100 ml of dry ether taken in a 250-ml, round-bottom flask. There was an immediate white precipitate. After all the addition of chloramine was complete, the reaction mixture was stirred for 24 hr followed by refluxing for 1 hr. White solid, 2.8 g, was obtained on filtration. Dimethylammonium chloride, was separated from it using absolute alcohol, in which it is soluble. A white, amorphous residue, 1.6 g (i), was left. Analysis of i showed that its composition is represented by (CH₂S)_n. The infrared spectral data, as shown in Table III, show evidence of -CH₂S and S-S linkages in i. This substance shrinks at 122-128°, becomes a pasty, viscous, brown mass at 133°, changes color to dark brown and then to reddish brown in the range 165-230°, and melts completely to give dark red liquid at 248°. At 255-260° it gives dark red particles and a yellow sublimate condenses on the upper side of the capillary. Compound i is insoluble in water, benzene, acetone, carbon disulfide, alcohol, chloroform, dioxane, ether, acetonitrile, dimethyl sulfoxide, dimethylformamide, etc. The mass spectrum of i shows well-defined peaks at *m/e* 184, 217, and 229.

Anal. Calcd for CH₂S: C, 26.08; H, 4.34; S, 69.56. Found: C, 26.26; H, 4.69; S, 68.53.

General Experiments. A.—The reaction of benzenethiol and dimethylchloramine in ether (mol ratio 2:1) was carried out in the dark, using the same general procedure as described earlier. Immediately after the addition of dimethylchloramine was complete, the solution was filtered. A white precipitate was retained on the filter and was identified as dimethylammonium chloride. On evaporating the ether, a yellow-white residue was left which was found to be diphenyl disulfide.

B.—Diphenyl disulfide and di-*n*-butyl disulfide were separately treated, under nitrogen atmosphere, with an excess of dimethylchloramine, keeping air and moisture away as far as possible. Prolonged stirring and refluxing produced no sulfenamide derivatives of the type RSN(CH₃)₂ or RSNH₂. It was concluded that cleavage of sulfur-sulfur bonds does not occur by action of chloramines over disulfides. The starting materials in all cases were almost quantitatively recovered.

Results and Discussion

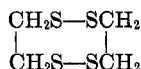
The infrared spectra for the products reported in this study are quite in accordance with their formulation as disulfides of the type RSSR.

The only previous references to the formation of a disulfide by oxidation of 1,2-ethanedithiol are two very old reports of its reaction with halogens.^{24,25}

(24) R. Otto and A. Rössing, *Chem. Ber.*, **19**, 2079 (1886).

(25) H. Fasbender, *ibid.*, **21**, 1470 (1888).

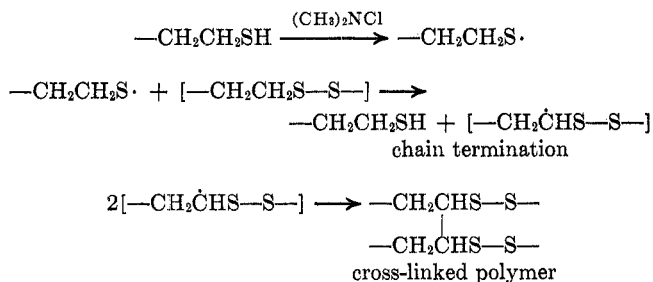
The structure proposed in these reports for the resulting compound is depicted below.



These experiments were repeated using an alcoholic solution of iodine containing 1% pyridine to remove the HI formed and the compound so obtained was identical with compound i described in the Experimental Section. It is clear that this cyclic structure does not correspond to the physical and chemical properties of our product i or those of the product of the earlier reported reaction.^{24,25}

If the structure is that of a linear polymer of the type $[-\text{CH}_2\text{CH}_2-\text{S}-\text{S}-]_n$, the compound should have been soluble in good polymer solvents such as N-methylpyrrolidone, hexafluoroisopropyl alcohol, and hexamethylphosphoramide. It was observed that compound i is insoluble in these solvents even on prolonged stirring. It was also not possible to obtain the simple cyclic disulfide proposed^{24,25} by heating i to ca. 200° in a semimicro sublimation apparatus and trying to condense the product on a cold finger.

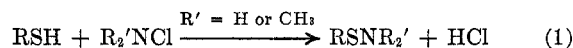
It is suggested that cross linking could have been produced by a mechanism such as the following.



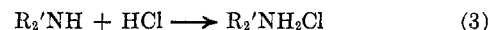
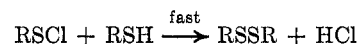
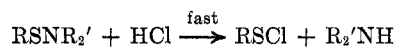
Such a cross-linked polymer would be expected to behave in accordance with our observations for product i.

On the basis of the facts that our chloramination reactions yielded disulfides only, but no sulfenamides $[\text{RSNH}_2$ or $\text{RSN}(\text{CH}_3)_2]$ or sulfonyl chlorides (RSCl), as

reported in the literature,^{14-18,26,27} that the conditions of the reactions and the lack of a probable initiator were not favorable for free radical formation, that the reactions proceeded rapidly in the dark, and that we have shown that the sulfur-sulfur bonds of the disulfides are not subject to cleavage by chloramines, we believe the most probable reaction path for the chloraminations of thiols in ether to be as follows.



or



The failure to isolate the sulfenamides (RSNR₂') probably results from their reactivity toward HCl and toward thiols combined with their solubility in ether. Earlier references¹⁴⁻¹⁸ to the formation of sulfenamides by reactions of chloramines with alkali mercaptides involved experiments in aqueous systems in which sulfenamides are insoluble.

Registry No.—Thiophenol, 108-98-5; cyclohexylmercaptan, 1569-69-3; 2-mercaptanaphthalene, 91-60-1; 2-mercaptopyridine, 2637-34-5; 2-mercaptoethanol, 60-24-2; 1-butanethiol, 109-79-5; β-naphthylphenyl disulfide, 23853-95-4; n-butylphenyl disulfide, 20129-23-1.

Acknowledgment.—We are pleased to gratefully acknowledge the support of this research by the National Science Foundation through Research Project GP-4505 with the University of Florida.

(26) J. B. Billman, J. Garrison, R. Anderson, and B. Wolnak, *J. Amer. Chem. Soc.*, **63**, 1920 (1941).

(27) Reference 19, pp 265, 269, 274.