α-(Iodomethyl)chalcone (14).—To a solution of 3.01 g (0.010 mole) of **3** in 50 ml of dry acetone was added a solution of 2.25 g (0.015 mole) of NaI in 100 ml of dry acetone. After standing for 24 hr the acetone was evaporated and the residue was extracted with ethyl ether. The ether extract was washed with water, dried, and evaporated to give a product which after recrystallization from petroleum ether produced yellow crystals: mp 75–76°; λ_{max} 255, 290 mμ (ϵ 15,000, 17,100) in isooctane; $\nu_{C=O}$ 1660 cm^{-1}; there were nmr signals at 2.1–2.8 (ten aromatic protons), 3.03 (one benzal proton), 5.59 (two α-iodomethyl protons).

Anal. Calcd for $C_{16}H_{13}IO$: C, 55.19; H, 3.76; I, 36.45. Found: C, 55.14; H, 3.84; I, 36.52.

α-(Chloromethyl)chalcone (15).—A 1.50-g (0.0050 mole) sample of **3** and 4.98 g (0.030 mole) of tetraethylammonium chloride were added to 25 ml of acetonitrile and heated under reflux for 16 hr. The acetonitrile was evaporated and the product was extracted with ether. Evaporation of the ether and recrystallization from petroleum ether gave white crystals (0.75 g, 58% yield): mp 62–63°; λ_{max} 261, 281 mμ (ϵ 14,200, 17,000) in isooctane; $\nu_{C=O}$ 1660 cm^{-1}; nmr 2.0–2.7 (ten aromatic protons), 2.75 (one benzal proton), 5.37 (two α-chloromethyl protons).

Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.85; H, 5.11; Cl, 13.81. Found: C, 74.84; H, 5.21; Cl, 13.93.

Relative Rates of Rearrangement of 10 to 11 in Various Solvents.—Three nmr sample cells labeled A, B, and C, each containing 100 mg of **10** and 0.5 ml of solvent, benzene, carbon tetrachloride, or deuteriochloroform, respectively, were allowed to stand for 6 days. Periodic analysis by nmr showed that the relative rates of rearrangement of the contents of cells A, B, and C were roughly 1:2:10.

Reaction of 10 with Morpholine.—A 2.93-g (0.010 mole) sample of **10** was dissolved in 50 ml of pentane and 8.71 g (0.010 mole) of morpholine was added. After standing for 48 hr the pentane was evaporated *in vacuo* and the residue was taken up in ether, which after water washing, drying, and evaporation gave 2.8 g (91% yield) of **6**. Periodic nmr analysis during the course of the reaction showed the presence of only **10** and **6**.

Reaction of 11 with Morpholine.—When the above described experiment was repeated using **11** in place of **10**, 90% of the starting material was returned; but when the pentane was replaced by 25 ml of methanol and the reaction mixture was allowed to stand at room temperatur for 3 days **11** was quantitatively converted to the morpholino analog **6**.

It was found that **6** was unchanged after standing 4 days in a methanol solution containing 10 molar equiv of *t*-butylamine.

Registry No.—**1**, 14182-01-5; **2**, 14181-91-0; **3**, 14181-92-1; **4**, 14181-93-2; **6**, 14182-00-4; **6** hydrochloride, 14271-42-2; **7** hydrochloride, 14182-02-6; **8**, 14181-94-3; **9**, 14181-95-4; **10** hydrochloride, 14271-48-8; **11** hydrochloride, 14182-03-7; **12** hydrochloride, 14181-96-5; **13**, 14181-97-6; **13** hydrochloride, 14181-98-7; **14**, 14271-43-3; **15**, 14181-99-8.

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The Versatility and the Mechanism of the *n*-Butylamine-Catalyzed Reaction of Thiols with Sulfur

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The *n*-butylamine-catalyzed reaction of alkyl thiols with sulfur has been investigated in detail. By proper selection of reaction variables, alkyl di-, tri-, or in some cases tetrasulfides can be formed in good yields. These variables are (1) moles of thiol/g-atoms of sulfur ratio, (2) polarity of solvent, (3) reaction time, and (4) temperature. The appropriate combination is selected after consideration of the steric requirements of the thiol. The reaction probably proceeds by a mechanism similar to that proposed for the interaction of both inorganic and organic thiophilic nucleophiles with sulfur. Intermediates were isolated. The intermediates were identified by nmr spectroscopy even in complex mixtures of the reactants.

The base-catalyzed reaction of thiols with sulfur is well known; however, it has found little utility, because a mixture of alkyl polysulfides is the usual consequence.[1,2]

A major obstacle preventing a detailed investigation of the mechanism and scope of this reaction has been lack of a reliable analytical tool. A method which would permit analysis of the polysulfide mixtures at ambient temperatures was needed, since the higher polysulfides are known to undergo disproportionation at elevated temperatures.

Recently, Grant and Van Wazer[3] utilized nuclear magnetic resonance to analyze mixtures of alkyl polysulfides. They showed that as the number of sulfur atoms increased the chemical shifts of the α-protons are shifted downfield. Their technique seemed to be an appropriate analytical procedure to use in a study of the thiol–sulfur reaction. Indeed, this method has proven an effective tool, particularly for the *t*-butyl system, since only one type of proton and hence one peak for each polysulfide is observed. For this reason and because it reacts at a convenient rate, *t*-butyl thiol was selected for most of the mechanistic studies. Once an insight into the reaction was obtained using nmr, a gas chromatography (gc) method was developed. This was especially useful for alkyl polysulfides, such as the isopropyl or *sec*-butyl compounds where splitting of the α-protons made nmr analysis more difficult.

Our recent report showed that alkyl trisulfides could be obtained by the controlled reaction of most thiols with sulfur.[4] The versatility of this general base-catalyzed reaction has been expanded to include the formation of alkyl di-, tri-, or in some cases tetrasulfides in good yields. Several variables must be considered when a particular alkyl polysulfide is desired. These variables are (1) the moles of thiol/g-atoms of sulfur ratio, (2) the polarity of the solvent, (3) the reaction time, and (4) temperature. The

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(1) For a review of polysulfide chemistry, see E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p 387.

(2) W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 9.

(3) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).

(4) B. D. Vineyard, *J. Org. Chem.*, **31**, 601 (1966).

TABLE I

ALKYL DISULFIDES FROM THIOLS AND SULFUR IN METHANOL[a]

$$2RSH + S \longrightarrow RS_2R + H_2S$$

	Reactants[b]			Products, wt %[c]		
Thiol RSH	Moles of thiol/ g-atoms of sulfur	Temp, °C	Time, hr	RS_2R	RS_3R	RS_4R
n-C_4H_9SH	2.5	62	3	97.5	2.5	
i-C_4H_9SH	2.5	62	3	95.0	5.0	
sec-C_4H_9SH	2.5	62	3	92.3	7.7	
i-C_3H_7SH	2.5	53	5	89.5	9.7	0.8
n-C_3H_7SH	2.5	62	3	98.5	1.5	

[a] For physical properties, see ref 1, Chapter 7. [b] *n*-Butylamine was the catalyst (~2 mole % based on thiol). [c] Yields determined by gas chromatography (see Experimental Section).

TABLE II

ALKYL TRISULFIDES[a]

$$2RSH + 2S \longrightarrow RS_3R + H_2S$$

	Reactants[b]				Products, wt %[d]		
Thiol RSH	Moles of thiol/ g-atoms of sulfur	Solvent	Temp, °C	Time, hr[c]	RS_2R	RS_3R	RS_4R
i-C_4H_9SH	1.25	CH_2Cl_2	25	0.66	11.0	71.0	18.0
n-C_4H_9SH	1.25	CH_2Cl_2	25	0.66	10.0	70.0	19.0
n-C_3H_7SH	1.25	CH_2Cl_2	25	0.66	8.3	64.0	24.0
sec-C_4H_9SH	1.50	CH_2Cl_2	53	2.5	4.5	88.0	7.5
i-C_3H_7SH	1.50	CH_2Cl_2	50	3.5	9.8	83.0	7.2
t-C_4H_9SH	1.25	CH_3OH	63	3.0	0.5	93.0	6.5
t-$C_5H_{11}SH$	1.25	CH_3OH	63	3.0	2.0	91.0	7.0

[a] For physical properties see ref 1 and 4. [b] *n*-Butylamine was the catalyst (~2 mole % based on thiol). [c] See Experimental Section for rate of thiol addition. [d] Yields were determined by gas chromatography. The *t*-butyl and isobutyl product mixtures were checked by nmr (see Experimental Section). In the primary thiol runs a small amount of higher polysulfide was still present.

necessary combination of conditions, which must be closely adhered to, is selected after a consideration of the steric requirements of the alkyl thiol. In general, increasing steric hindrance in the alkyl thiol requires more severe conditions for optimum results. This will be reiterated in the ensuing discussion.

Disulfides.—Disulfides can be formed in excellent yields from primary and secondary thiols, but tertiary alkyl thiols do not afford the disulfide because of adverse steric requirements. Thus, an excess of a relatively nonhindered thiol reacts with sulfur in a polar solvent to give disulfides in greater than 90% yields. The preferred technique is to add the thiol (25% excess over the stoichiometric amount required for disulfide formation) to a slurry of sulfur and the *n*-butylamine catalyst in methanol at room temperature. The resulting solution is then refluxed for 3 to 5 hr. If the moles of thiol/g-atoms of sulfur ratio is less than 2 (stoichiometric for disulfide), a mixture of polysulfide results. Disulfides formed in this study are summarized in Table I.

Trisulfides.—Trisulfides can be formed from all alkyl thiols, although respectable yields are obtained only by a careful choice of conditions. If the thiol is primary, a minimum moles of thiol/g-atoms of sulfur ratio (1.25), a nonpolar solvent, ambient temperature, and short reaction time is required. Increasing any of the above variables or use of polar solvents results in a decreasing trisulfide/disulfide product ratio. If the thiol/sulfur ratio is appreciably less than 1.25, an horrendous mixture of polysulfides is obtained. For secondary thiols, somewhat similar conditions can be used; however, a larger excess of thiol, higher temperatures, and longer reaction times facilitate trisulfide formation without a significant increase in disulfide.

For the *t*-alkyl thiols polar solvents and elevated temperatures are prerequisites for an efficient conversion to the trisulfides. Steric requirements prevent the reaction from proceeding to disulfide, hence an excess of the *t*-thiol is an advantage. Table II summarizes the alkyl trisulfides prepared, including conditions for their formation.

TABLE III

ALKYL TETRASULFIDES FROM *t*-THIOLS AND SULFUR IN METHYLENE CHLORIDE[a]

$$2RSH + 3S \longrightarrow RS_4R + H_2S$$

	Reactants[b]			Products, wt %[c]		
Thiol RSH	Moles of thiol/ g-atoms of sulfur	Temp, °C	Time, hr	RS_2R	RS_3R	RS_4R
t-C_4H_9SH	1	25	5		10	90
t-$C_5H_{11}SH$	1	25	7		8	92

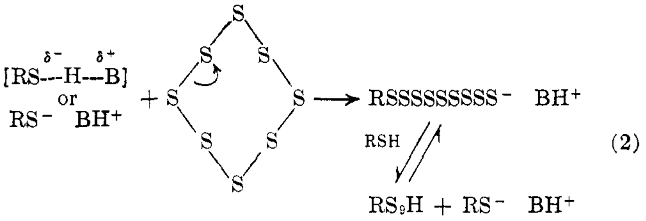
[a] Physical properties of *t*-butyl tetrasulfide are given in ref 1, Chapter 7. No attempt was made to purify *t*-amyl tetrasulfide. [b] *n*-Butylamine was the catalyst (~2.5 mole % based on thiol). [c] Yields of the *t*-butyl products were determined by nmr, and the *t*-amyl product composition was obtained by gas chromatography (see Experimental Section). Trace amounts of higher polysulfides were still present.

Tetrasulfides.—Tetrasulfides are the predominant products only from *t*-alkyl thiols, and then only if the most moderate conditions are used. Ambient temperatures and nonpolar solvents are essential. In addition, the moles of thiol/g-atoms of sulfur ratio must be greater than the stoichiometric (2 to 3) for tetrasulfide formation. A 33% excess of thiol results in approximately 90% yields (based on sulfur) of tetrasulfide, if the reaction is stopped once the maximum tetrasulfide level is reached. Allowing the reaction to continue results in increasing amount of trisulfide at the expense of tetrasulfide. Higher polysulfides persist if the thiol–sulfur ratio is less than the stoichiometric. The alkyl tetrasulfides prepared are given in Table III.

Mechanism.—The base-catalyzed thiol–sulfur reaction probably proceeds by a mechanism similar to that proposed for inorganic nucleophiles and sulfur.[5,6] Such a reaction sequence is presented in Chart I. Interaction of the thiol with base is probably the first step; then nucleophilic attack by the thiolate or developing thiolate on sulfur opens the eight-membered sulfur ring forming a linear alkyl hydrogen polysulfide (step 2). Reaction of the thiolate on the alkyl hydrogen sulfur chain occurs forming a mixture of alkyl polysulfides (step 3). Further random attack by the thiolate on the alkyl polysulfides can occur until steric factors and conditions intercede to govern the nature of the final product (step 4).

Chart I

$$\mathrm{RSH + B: \rightleftharpoons [\overset{\delta^-}{RS}\cdots\overset{\delta^+}{H}\cdots B] \rightleftharpoons RS^-\ BH^+} \quad (1)$$



(2)

$$\mathrm{RS_9H + RS^-\ BH^+ \longrightarrow RS_nR + HS^-\ BH^+} \quad (3)$$
$$n = 2\text{–}9$$

$$m\mathrm{RS_nR} + 2z[\mathrm{RS^-\ BH^+}] \longrightarrow y\mathrm{RS_xR} + z\mathrm{H_2S} + 2z\mathrm{B}: \quad (4)$$
$$x = 2, 3, \text{ or } 4$$

for example, when $n = 4$, $x = 3$, then $m = 2$, $z = 1$, and $y = 3$

This mechanistic interpretation is consistent with the following observations. (1) A red-orange color, which diminishes as the reaction proceeds, develops immediately upon addition of the thiol to a slurry of sulfur, amine, and an inert solvent. This color is suggestive of a polysulfide anion (see step 2, Chart I). Although sulfur in primary or secondary amine solvents gives highly colored solutions,[7] this interaction is apparently retarded in our heterogeneous system. The color does not develop until the thiol is added. Kinetic evidence for the interaction of amines with thiols is presented by Bartlett and co-workers.[8] (2) From a study of the *t*-butyl thiol–sulfur system, the intermediate alkyl penta-, hexa-, and heptasulfides were identified by nmr and their disappearance was followed by a resultant increase in *t*-butyl tri- and tetrasulfides (see Figure 1). (3) *t*-Butyl tetrasulfide is converted to trisulfide by interaction with *t*-butyl thiol and base. This is shown by the specific example given in step 4 of Chart I. (4) Polar solvents markedly enhance the reaction rate, indicating ionic species involved in the rate steps.

The proposed reaction scheme agrees with that presented by Foss[9] and later by Bartlett[10,11] concerning ring opening of the sulfur molecule by nucleophilic reagents (*e.g.*, cyanide ion and tertiary phosphines). Intermediate sulfur chains were not observed indicating that they are extremely reactive.

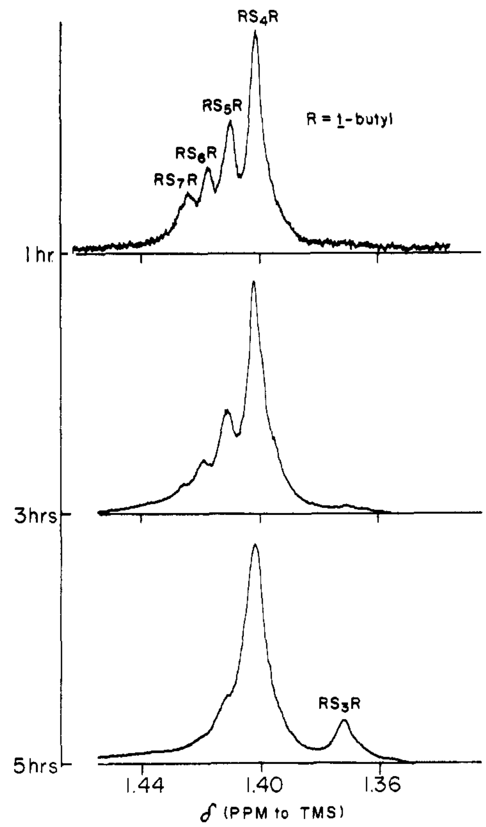


Figure 1.—Nmr spectra in deuteriochloroform showing the *t*-butyl thiol–sulfur reaction with time.

We isolated intermediate alkyl polysulfides, but did not observe any alkyl hydrogen polysulfides ($\mathrm{RS_xH}$). This suggests that the alkyl polythiolates are more thiophilic than the alkyl thiolates. The oxibase scale, which is a measure of relative nucleophilicity, might be used to test this postulate.[12]

Experimental Section

General Procedure for Alkyl Disulfides.—A primary or secondary alkyl thiol (0.188 mole) was added in approximately 1 to 1.5 hr to a slurry of 2.4 g (0.075 g-atom) of sulfur, 0.3 g (0.004 mole) of *n*-butylamine, and 15 ml of methanol at 25°. The solution was heated slowly to reflux and held there for 3 hr. If the thiol was added or heat applied too rapidly, vigorous evolution of hydrogen sulfide removed thiol by entrainment. After completion of reflux, the methanol and thiol were stripped under a reduced pressure of 15–20 mm. The residual product after filtration was analyzed by gc, and then the alkyl disulfide was purified by distillation. Yields of disulfide were 90–98%, based on sulfur.

General Procedures for Alkyl Trisulfides. A. From Primary Thiols.—The primary thiol (0.188 mole) was added in 2 hr to a slurry of 4.8 g (0.15 g-atom) of sulfur, 0.3 g (0.004 mole) of *n*-butylamine, and 15 ml of methylene chloride at 25°. After stirring for an additional 40 min, the mixture was worked up immediately or 0.5 ml of concentrated hydrochloric acid was added to stop the reaction. If the latter procedure is employed, the mixture is dried thoroughly over anhydrous $\mathrm{Na_2SO_4}$ before removing the methylene chloride and thiol at reduced pressure. The residual product after filtration was analyzed by gc, and the alkyl trisulfide was purified by fractional distillation at a pressure of 1 mm or less. Crude yields of trisulfide were approximately 70%, based on sulfur.

Strict adherence to these conditions is essential. Longer reaction times result in increasing amounts of disulfides, while from shorter cycles higher polysulfides are still prevalent.

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(5) F. G. A. Stone and W. A. G. Graham, "Inorganic Polymers," Academic Press Inc., New York, N. Y., 1962, pp 149–154.

(6) R. E. Davis, *Surv. Progr. Chem.*, **2**, 189 (1964).

(7) R. E. Davis and H. F. Nakshbendi, *J. Am. Chem. Soc.*, **84**, 2085 (1962).

(8) P. D. Bartlett, E. F. Cox, and R. E. Davis, *ibid.*, **83**, 103 (1961).

(9) O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950).

(10) P. D. Bartlett, and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

(11) P. D. Bartlett and R. E. Davis, *ibid.*, **80**, 2513 (1958).

(12) For a review of the oxibase scale read the discussion by R. E. Davis, ref 6, pp 199–212.

B. From Secondary Thiols.—A *sec*-thiol (0.225 mole) was added in 1.5–2 hr to a slurry of 4.8 g (0.15 g-atom) of sulfur, 0.3 g (0.004 mole) of *n*-butylamine, and 15 ml of methylene chloride at 25°. The resulting mixture was stirred at 25° until a homogenous solution resulted, which was usually 0.5 to 1.5 hr. At this time the rapid evolution of hydrogen sulfide had subsided; then the solution was heated slowly to reflux (50–55°). After refluxing for 2–4 hr, the material was worked up in the usual manner. The crude product was analyzed by gc, then the trisulfide was recovered by fractional distillation at reduced pressures. *sec*-Alkyl trisulfides were obtained in approximately 85% yields, based on sulfur.

C. From Tertiary Thiols.—A *t*-thiol (0.188 mole) was added in approximately 1.5–2 hr to a slurry of 4.8 g (0.15 g-atom) of sulfur and 0.3 g (0.004 mole) of *n*-butylamine in 15 ml of methanol at 25°. The homogenous solution was heated slowly to reflux (62–64°). After refluxing for 3–4 hr, the solution was worked up in the usual manner. The residual product, containing greater than 90% trisulfide, was analyzed by gc or nmr. The alkyl trisulfides were purified by fractional distillation at a reduced pressure of 1 to 2 mm.

General Procedure for Alkyl Tetrasulfides.—A *t*-thiol (0.15 mole) was added in approximately 1.5–2 hr to a slurry of 4.8 g (0.15 g-atom) of sulfur, 0.3 g (0.004 mole) of *n*-butylamine, and 15 ml of methylene chloride at 25°. The mixture was stirred until a homogenous solution resulted, usually 4–8 hr. After stirring for an additional 40 min, the solution was worked up the usual manner. The residual product contained approximately 90% *t*-alkyl tetrasulfide, as determined by gc or nmr. Distillation of only the lower alkyl tetrasulfides should be attempted, since at temperatures greater than 130° disproportionation is quite pronounced.

Interaction of *t*-Butyl Tetrasulfide with *t*-Butyl Thiol. Formation of *t*-Butyl Trisulfide.—*t*-Butyl thiol (7.9 g, 0.088 mole) was added over 40 min to a solution of 12.1 g (0.05 mole) of *t*-butyl tetrasulfide (99%), 0.3 g of *n*-butylamine, and 15 ml of methanol at 25°. Hydrogen sulfide evolution began immediately upon thiol addition. The solution was heated slowly to reflux (61–62°) and held for 3 hr, then cooled and stripped at 25° and 20 mm for 30 min. Filtration of the slightly hazy material yielded 15 g (quantitative for trisulfide formation) of residual product. Gc and nmr indicated that the product was greater than 95% *t*-butyl trisulfide.

Interaction of *n*-Propyl Disulfide with *n*-Butyl Thiol.—A solution of 7.28 g (0.0486 mole) of *n*-propyl disulfide, 4.32 g (0.0486 mole) of *n*-butyl mercaptan, 0.3 g of *n*-butylamine, and 15 ml of methanol was heated at reflux (62–63°) for 5 hr. The solution remained completely colorless. Stripping the cooled (20–25°) solution at 15–20 mm for 30 min yielded 7.85 g of a clear residual product. Gc analysis gave 34.9% n-$C_3H_7S_2C_3H_7$-n, 46.2% n-$C_3H_7S_2C_4H_9$-n, and 15.8% n-$C_4H_9S_2C_4H_9$-n. Complete random interchange occurred.

Identification of Intermediates in *t*-Butyl Thiol–Sulfur Reaction.—*t*-Butyl thiol (13.5 g, 0.15 mole) was added in 1.5 hr to a slurry of 4.8 g (0.15 g-atom) of sulfur, 0.3 g of *n*-butylamine, and 15 ml of methylene chloride at 25°. The solution was homogenous in approximately 4 hr and hydrogen sulfide evolution had subsided. A sample was removed each hour, stripped at 25° and 20 mm for 20 min, then the residual product was dissolved in deutrated chloroform and analyzed by nmr. A 1-hr spectrum indicated a mixture of *t*-butyl tetra-, penta-, hexa-, and heptasulfides. After 3 hr the higher polysulfides had decreased and at 5 hr only a trace of polysulfides higher than tetra remained, and *t*-butyl trisulfide was appearing. These nmr spectra, at different concentrations, are shown in Figure 1. Protons chemical shifts for the *t*-butyl polysulfides in parts per million to tetramethylsilane follow: RS_3R 1.371, RS_4R 1.402, RS_5R 1.412, RS_6R 1.419, and RS_7R 1.425 (R = *t*-butyl).

Analytical Procedures. Nuclear Magnetic Resonance.—A Varian A-60 high-resolution nuclear magnetic resonance spectrometer was used. The chemical shifts reported in this paper were determined by use of modulation side bands. Semiquantitative yields were obtained in the *t*- and isobutyl polysulfides systems from the protons nearest the sulfur. The yields were calculated from either the areas, as determined by planimeter, or from peak heights with necessary allowance being made for the difference in molecular weights. Chemicals shifts for a series of alkyl polysulfides were reported earlier.[3,4]

Gas Chromatography.—An F & M Model 5750 gas chromatograph was employed. The 0.25 in. × 0.5 m glass column[13] was packed with 15% SE-52 silicone rubber gum on 50 to 60 mesh gas pack EP-S (AW-DMCS dedusted). Injector block temperature was maintained at 150°, column temperature at 110°, and detector block at 200°. A 0.001-ml sample was injected "on-column" and helium was the eluent at a flow rate of 60 cc/min. The calibration technique involved applying area correction factors and normalization. Absence of disproportionation was confirmed by analyzing a synthetic mixture containing *n*-butyl disulfide, isopropyl trisulfide, and *t*-butyl tetrasulfide. If interconversion had occurred, individual polysulfides with different alkyl groups would have appeared. Since only trace amounts of these mixed alkyl polysulfides were observed, it was concluded that the alkyl di-, tri-, and tetrasulfides are stable under these conditions.

The compounds that separated along with their retention times in minutes are *n*-propyl di- (1.0), tri- (3.1), and tetrasulfide (10.0); isopropyl di- (0.9), tri (2.6), and tetrasulfide (3.5); isobutyl di- (2.2), tri- (7.1), and tetrasulfide (21.2); *sec*-butyl di- (2.0), tri- (7.4), and tetrasulfide (21.8); *t*-butyl di- (1.3), tri- (3.6), and tetrasulfide (13.4); *t*-amyl[14] di- (2.3), tri- (5.9), and tetrasulfide (18.2).

Registry No.—*n*-Butylamine, 109-73-9; i-C_4H_6SH, 513-44-0; n-C_4H_6SH, 109-79-5; n-C_3H_7SH, 107-03-9; *sec*-C_4H_9SH, 513-53-1; i-C_3H_7SH, 75-33-2; t-C_4H_9SH, 75-66-1; t-$C_5H_{11}SH$, 1679-09-0.

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[13] Stainless steel column or injection block causes disproportionation of the alkyl polysulfides, especially the tetrasulfides. Gas chromatography is not practical for the alkyl polysulfides higher than tetrasulfides.

[14] Gas chromatography column temperature was 125°.