

Analysis of an aliquot in the vapor fractometer indicated the presence of $100 \pm 3\%$ of each component. No other volatile components were present.

Reaction of Sodium Benzyl Mercaptide (XIX) with Benzyl Thiocyanate (II) and *t*-Butyl Thiocyanate (XII).—To a solution containing 0.805 g. (0.0054 mole) of II and 0.623 g. (0.0054 mole) of XII (in a 1.280-g. mixture of 48.7% *t*-butyl thiocyanate and 51.3% *t*-butyl isothiocyanate) in 40 ml. of acetonitrile was added 0.788 g. (0.0054 mole) of freshly prepared XIX in 40 ml. of acetonitrile. The reaction mixture was kept under a nitrogen atmosphere with magnetic stirring at 50° for 11 hr. The red-orange mixture was cooled, filtered, and the sodium cyanide dried to a constant weight, 0.252 g. (91.5%). The filtrate was

concentrated *in vacuo* and triturated with 8 ml. of dry methanol. The benzyl disulfide (XXI) obtained, 0.950 g. (70.3%), melted at $66\text{--}68^\circ$. A mixture melting point with an authentic sample melted at $67\text{--}69^\circ$.

The residue was analyzed in the vapor fractometer using column 2 and contained 7.2% XXI (total yield 77.5%). Analysis of the oil on column 1 showed the presence of 3.0% 1-phenyl-4,4-dimethyl-2,3-dithiapentane (XIV). The vapor fractogram exhibited three additional components of small peak areas which were not identified.

Acknowledgment.—Preliminary experiments on this work were performed by Mr. William H. Bowers.

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., PROCESS RESEARCH DIVISION, EXPLORATORY RESEARCH SECTION, LINDEN, N. J.]

Reactions of Thiols with Sulfoxides. I. Scope of the Reaction and Synthetic Applications

BY THOMAS J. WALLACE

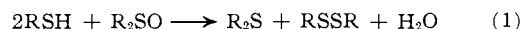
RECEIVED DECEMBER 14, 1963

A detailed study on the oxidation of thiols by sulfoxides has been made. The reaction products are disulfides and sulfides (reduced sulfoxides). Of the sulfoxides investigated, dimethyl sulfoxide and tetramethylene sulfoxide were found to be the most efficient oxidizing agents. The reaction takes place with aliphatic, aralkyl, and aromatic thiols. The order of thiol reactivity was $\text{ArSH} > \text{ArCH}_2\text{SH} > \text{RSH}$. It was also possible to oxidize dithiols by this technique. Thus 1,4-butanedithiol and 1,3-propanedithiol were oxidized to their corresponding 1,2-dithianes. Some limited mechanistic implications are presented and discussed based on the results obtained. Stoichiometrically, it has been established that 2 moles of thiol reacts with 1 mole of sulfoxide to produce 1 mole of disulfide and 1 mole of sulfide. Synthetically, it appears that aromatic thiols are selectively oxidized to their disulfides at room temperature by dimethyl sulfoxide and tetramethylene sulfoxide.

Introduction

Oxidation-reduction reactions involving sulfoxides have been observed with a wide variety of reagents. For example, reduction of dimethyl sulfoxide (DMSO) to dimethyl sulfide occurs in the presence of hydrogen halides, bromine, organic halides, and higher aliphatic sulfides.¹ More recently, it has been found that 1,4-diols can be dehydrated and cyclized to tetrahydrofuran derivatives by adding the diol to a refluxing solution of DMSO.² The above results¹ have established that sulfoxides are weak bases¹ that are capable of oxidizing a variety of acidic (protic) species. In the past few years, we have been interested in the reactions of thiols with a variety of bases.^{3,4} A thorough search of the literature revealed that thiol-sulfoxide reactions have not previously been investigated in detail.⁵ During the preparation of the present manuscript, Yiannios and Karabinos^{5b} reported that DMSO is capable of oxidizing a large number of acidic thiols. These oxidation studies were carried out at $80\text{--}90^\circ$ for 8 hr. in the presence of air. These authors also indicate that α -

toluenethiol and 1-butanethiol are oxidized at the same rate as acidic (ArSH) thiols. Oxidation of benzenethiol by DMSO under nitrogen for 18 hr. produced the same yield of disulfide obtained after 8 hr. of oxidation in the presence of air. Based on this result, Yiannios and Karabinos^{5b} concluded that co-oxidation of the thiol by air did not occur. In the present paper, we wish to report the results of our initial studies on thiol-sulfoxide reactions under nitrogen. Theoretically, an interaction between the two species should yield sulfide, disulfide, and water. This possibility was investigated and found to be true. Under our experimental conditions, it has



been found that the rate of reaction is markedly dependent on the acidity of the thiol. A variation of the reaction temperature has revealed that acidic thiols can be oxidized conveniently at room temperature. It has also been ascertained that, in the absence of air, oxidation of aliphatic thiols at reasonable rates requires temperatures in excess of 100° . In the present paper, the scope, synthetic application, and limitation of various thiol-sulfoxide reactions will be presented.⁶ In a following paper, the kinetic and mechanistic aspects of these reactions will be discussed.

Results

The reaction of thiols with sulfoxides has been investigated under a wide variety of conditions. Reactions were carried out under nitrogen in a micro scale reaction flask equipped with a Vigreux distilling column. In most reactions, an excess of sulfoxide to thiol was employed. In order to simplify the analytical procedure for separating and identifying reaction products,

(6) For a preliminary account see T. J. Wallace, *Chem. Ind. (London)*, 504 (1964).

(1) For a summary see: W. O. Ranky and D. C. Nelson, "Organic Sulfur Compounds," Vol. I, ed. by N. Kharasch, Pergamon Press, New York, N. Y., 1961, Chapter 17.

(2) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

(3) T. J. Wallace, H. Pobiner, and A. Schriesheim, *ibid.*, **29**, 1044 (1964).

(4) T. J. Wallace, N. Jacobson, and A. Schriesheim, *Nature*, **201**, 609 (1964).

(5) (a) One remotely related study is that of Bunnett and co-workers: J. F. Bunnett, E. W. Garbish, and K. U. Pruitt, *J. Am. Chem. Soc.*, **79**, 385 (1957). In a study on activated nucleophilic aromatic substitution reactions these workers found that 2,4-dinitrophenyl phenyl sulfide and phenyl disulfide were by-products of a reaction between 2,4-dinitrophenyl phenyl sulfoxide and piperidine. A detailed study on the mechanism of sulfide and disulfide formation was not undertaken, but it is possible that they could have arisen by an oxidation-reduction reaction involving the thiol anion and the sulfoxide. (b) A study on the reaction of DMSO with acidic thiols has recently been reported: C. N. Yiannios and J. V. Karabinos, *J. Org. Chem.*, **28**, 3246 (1963).

only thiols capable of producing solid disulfide oxidation products were investigated. All disulfides easily precipitated from the reaction mixtures. The identity of each disulfide was determined by its melting point and mixture melting point with an authentic sample. The sulfides produced by sulfoxide reduction were identified by comparing their g.c. retention times with those of authentic sulfides with the aid of an internal hydrocarbon standard.

Initial studies were carried out with 1-hexadecanethiol using dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), diisopropyl sulfoxide (DIIPSO), and di-*n*-butyl sulfoxide (DBSO) as the oxidizing agents at a reaction temperature of $160 \pm 5^\circ$. The reaction conditions employed and the results obtained are summarized in Table I. Based on the yield of hexadecyl disulfide obtained after 4.5 to 5 hr. of reaction, DMSO and TMSO were more efficient oxidizing agents than either DIIPSO or DBSO. In these and subsequent studies with DMSO and TMSO, progress of the reaction was easily followed since their corresponding sulfides readily distilled from the reaction flask as they were formed.

TABLE I
OXIDATION OF 1-HEXADECANETHIOL BY VARIOUS
SULFOXIDES

1-C₁₆H₃₃SH, 0.05 mole; sulfoxide, 0.125 mole; temp., $160 \pm 5^\circ$;
(1-C₁₆H₃₃)₂S₂, m.p. 52–53°

| Sulfoxide | Time, hr. | Mole % yield ^a (1-C ₁₆ H ₃₃) ₂ S ₂ | Method of sulfide identification |
|---------------------|-----------|--|-------------------------------------|
| Dimethyl | 5 | 70 | B.p. and g.c. |
| Tetramethylene | 4.5 | 52 | B.p. and g.c. |
| Diisopropyl | 4.5 | 36 | G.c. |
| Di- <i>n</i> -butyl | 5 | 20 | G.c. |

^a Based on moles of RSSR isolated/theoretical moles of RSSR $\times 100$.

The above results indicated that aliphatic sulfoxides are general oxidizing agents for the conversion of thiols to disulfides. It was next desirable to investigate the generality of the reaction with respect to the thiol. This was done by oxidizing a series of thiols in the presence of excess DMSO at room temperature and $160 \pm 5^\circ$. The pertinent data are summarized in Table II. As indicated, three aliphatic thiols, α -toluenethiol,

TABLE II
SUMMARY OF THIOL OXIDATION STUDIES WITH DIMETHYL
SULFOXIDE

| Thiol (mole) | DMSO, mole | Temp., $\pm 5^\circ$ | Time, hr. | Mole % yield ^a of di- sulfide | M. p., °C., of disul- fide | Lit. m.p., °C. |
|-------------------------------------|------------|----------------------|-----------|---|-------------------------------------|----------------------|
| 1-Dodecane- (0.05) | 0.125 | 160 | 19 | 72 | 33–34 | 34 |
| 1-Octadecane- (0.05) | .125 | 160 | 7 | 72 | 62–63 | 62–63 |
| 1-Hexadecane- (0.05) | .125 | 160 | 12 | 84 | 52–53 | 52–53 |
| α -Toluene- (0.05) | .125 | 160 | 3.5 | 52 | 69–70 | 69–70 |
| 4-Methylbenzene- (0.05) | .125 | R.t. | 24 | 70 | 43–44 | 45 |
| 4-Chlorobenzene- (0.05) | .125 | R.t. | 24 | ~100 | 72–73 | 73 |
| 2-Naphthalene. ^b (0.025) | .125 | R.t. | 24 | 98 | 130–131 | 139 |
| Benzene. ^c (0.30) | .30 | R.t. | 17.5 | 87 | 60 | 60–62 |
| 1-Dodecane. ^c (0.0031) | .0031 | R.t. | 17.5 | Nil | ... | ... |
| 1-Hexadecane. ^c (0.05) | .125 | R.t. | 17.5 | Nil | ... | ... |
| α -Toluene- (0.05) | .10 | R.t. | 48 | 16 | 69–70 | 69–70 |

^a Based on moles of R₂S₂ isolated/theoretical moles $\times 100$.

^b The received material contained about 10% of the 1-isomer.

^c Identical results obtained in two experiments.

and four aromatic thiols were readily converted to their corresponding disulfides. The yield of each oxidation product was dependent on the reaction time employed.

It should be noted that the yield of each product was based on the weight of pure disulfide obtained by recrystallization from acetone. Since all the thiols and sulfoxides investigated were highly soluble in acetone, purification of the disulfide usually required only one recrystallization. Of special interest was the fact that several aromatic thiols were oxidized to their disulfides in high yields at room temperature. For example, benzenethiol yielded 87% of phenyl disulfide in 17.5 hr. However, 1-dodecanethiol did not undergo any appreciable reaction in the same time period, which suggested that the acidity of the thiol was important. This point was further established by investigating the oxidation of benzenethiol, α -toluenethiol, and 1-dodecanethiol in TMSO at room temperature. As shown in Table III, the order of reactivity based on the yield of disulfide was C₆H₅SH > C₆H₅CH₂SH >> 1-C₁₂H₂₅SH.

TABLE III
THIOL OXIDATION STUDIES WITH TETRAMETHYLENE
SULFOXIDE AT ROOM TEMPERATURE

| Thiol (mole) | TMSO, mole | Time, hr. | Mole % yield of disulfide |
|---------------------------|------------|-----------|------------------------------|
| Benzene- (0.30) | 0.30 | 17.5 | 87 |
| Benzene- (0.0028) | .0031 | 19.5 | ~100 |
| α -Toluene- (0.10) | .10 | 24 | 40 |
| 1-Dodecane- (0.0031) | .0031 | 17.5 | Trace ^a |

^a Confirmed by g.c. analysis on a 2-ft. silicone rubber column (see Experimental section for details).




In order to establish firmly the reaction stoichiometry shown in eq. 1, three experiments were performed in which a very accurate determination of the ratio of disulfide to sulfide was made. If 2 moles of thiol react with 1 mole of sulfoxide to produce products, equivalent molar quantities of disulfide and sulfide should be produced. As indicated in Table IV, the molar ratio of RSSR/RSR varied from 0.9 to 1 for the three experiments listed. Hence, the over-all reaction proceeds according to eq. 1.

TABLE IV
STOICHIOMETRIC DATA FOR THIOL-SULFOXIDE REACTIONS

| Experiment | 1 | 2 | 3 |
|-------------------------|--|--|--|
| Temp., °C. | 160 | 160 | ~25 |
| RSH, mole | 1-C ₁₆ H ₃₃ SH, 0.05 | 1-C ₁₆ H ₃₃ SH, 0.05 | C ₆ H ₅ SH, 0.10 |
| R ₂ SO, mole | DMSO, 0.125 | TMSO, 0.125 | TMSO, 0.05 |
| Time, hr. | 12 | 4.5 | 19.5 |
| RSSR, mole | 0.021 | 0.013 | 0.047 |
| RSR, mole | 0.021 | 0.015 | 0.047 |

The last phase of this study was concerned with the oxidation of dithiols by sulfoxides. The dithiols investigated are listed in Table V. In these studies, a

TABLE V
DITHIOL OXIDATION STUDIES

| Dithiol (mole) | Sulfoxide (mole) | Time, hr. | Disulfide, mole % yield |
|-------------------|----------------------|-----------|--|
| 1,4-Butane- (0.1) | Dimethyl (0.1) | 17.5 |  68 |
| 1,4-Butane- (0.1) | Tetramethylene (0.1) | 71 |  89 |
| 1,3-Propane- | Tetramethylene | 20 |  70 |
| 1,2-Ethane- (0.1) | Tetramethylene (0.1) | 21 | Polymer |

^a This could be dimeric. See D. J. Cram and M. Gordon, *J. Am. Chem. Soc.*, **77**, 1810 (1955).

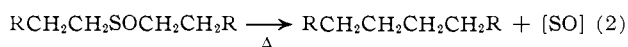
slight modification of the usual reaction conditions was employed. The dithiol was added to an excess of the sulfoxide during a 4-hr. period. If the dithiol and sulfide were mixed completely at the beginning of the

reaction, polymeric rather than monomeric oxidation products were preferentially formed. Using the slow addition technique, 1,4-butanedithiol and 1,3-propanedithiol were oxidized to their corresponding 1,2-dithianes (cyclic disulfides) in 68–89% yield. 1,2-Dithiacyclohexane was identified by its characteristic boiling point and melting point. 1,2-Dithiacyclopentane was identified by g.c. and mass spectral comparison with an authentic sample and its melting point. 1,2-Ethanedithiol gave only polymeric material when oxidized by TMSO.

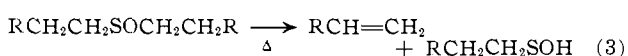
Discussion

The present study has uncovered new data on the oxidation of thiols by sulfoxides. Excellent yields were obtained in all cases when DMSO and TMSO were employed as the oxidizing agents. Synthetically, the reaction is advantageous because it is quite simple to carry out. Since DMSO and TMSO are now widely employed as solvents, the use of such reagents as oxidizing agents is no longer impractical. Both DMSO and TMSO have the added advantage of producing low boiling reduction products, especially DMSO. Thus, if a 2:1 molar ratio of thiol to sulfoxide is employed, a relatively pure oxidation product can be obtained when the reaction temperature is maintained at 120° or above.

As indicated in Table I, DIIPSO and DBSO were less efficient oxidizing agents than DMSO and TMSO. This is apparently due to their decreased thermal stability in comparison to DMSO and TMSO. When each sulfoxide was analyzed by gas chromatography at 200°, TMSO and DMSO were found to be thermally stable. DIIPSO and DBSO gave numerous peaks at this temperature, but at 150° only one peak was observed for both sulfoxides. Under the present reaction conditions, continuous heating at 160° for 4.5 to 5 hr. probably resulted in some thermal decomposition. This would, of course, decrease the oxidizing efficiency of the higher molecular weight sulfoxides. The decomposition could involve either a dethionylation reaction⁷ or

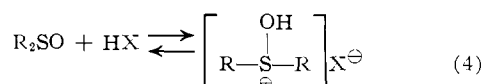


formation of an olefin and unstable sulfenic acids.



These possibilities were not investigated in any detail.

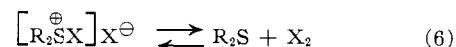
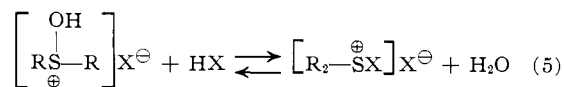
Based on the results summarized in Tables II and III, it is obvious that thiol acidity is of major importance as far as the ease of oxidation is concerned. The observed ease of thiol oxidation was aryl > aralkyl > alkyl. Of course, at sufficiently high temperatures aliphatic thiols are also relatively easy to oxidize. However, this reactivity sequence does allow certain preliminary mechanistic speculations to be made. The present reactions appear to be analogous to the reactions of halogen acids with sulfoxides.¹ Such reactions are believed to proceed by formation of a protonated sulfoxide adduct which is formed in an equilibrium reaction.



The protonated intermediate is then destroyed by

(7) For a summary see H. H. Szmant, "Organic Sulfur Compounds," Vol. I, ed. by N. Kharasch, Pergamon Press, New York, N. Y., 1961, Chapter 16, pp. 163–164.

reaction with another molecule of acid. The stoichiometry observed for the thiol-sulfoxide



reactions (Table IV) is also consistent with a reaction sequence of this type. However, the present results do not allow any definite conclusions on the exact mechanism and the rate-determining step in the reaction to be made. Such conclusions require detailed kinetic studies and these will be presented in a future paper.

Finally, some comments on the application of the reaction to the synthesis of 1,2-dithianes from dithiols should be made. The present reaction represents a simplified route to the five- and six-membered ring 1,2-dithianes. Usually, these compounds are synthesized by slow addition of the dithiol to an aqueous iodine-sodium hydroxide mixture. The volume of the reaction mixture is excessively large, several extraction steps are required to concentrate the product, solvent must be removed by distillation, and the maximum yield of the dithiane is about 30%. Clearly, the present technique gives much higher yields and can be conducted on a much smaller scale. Further, as will be shown in a future paper, lower reaction temperatures can be employed in the presence of a catalytic amount of an aliphatic amine.

Experimental

Reagents.—1-Dodecanethiol, 1-octadecanethiol, and 1-hexadecanethiol were obtained from Columbia Organic Chemicals. Benzenethiol, α -toluenethiol, 4-methylbenzenethiol, and 4-chlorobenzenethiol were obtained from Evans Chemetics Inc. All thiols were reagent grade samples. Temperature-programmed gas chromatographic analysis (F and M Model 609) on a 2-ft. silicone rubber column (30 wt. % silicone rubber on Chromosorb-W) between 75 and 250° indicated that each thiol was at least 98% pure. 2-Naphthalenethiol (Columbia Organic Chemicals) contained 10% of the 1-isomer. Since the boiling points of each isomer differ by a maximum of 2–3° between 15 and 50 mm.⁸ separation was not attempted. Thus, the received material was used. 1,4-Butanedithiol, 1,3-propanedithiol, and 1,2-ethanedithiol were obtained from the Wateree Chemical Co. as ultrapure reagents. All thiol samples were stored in a nitrogen drybox on a continuous basis.

Dimethyl sulfoxide, diisopropyl sulfoxide, and di-*n*-butyl sulfoxide were obtained from Columbia Organic Chemicals. Tetramethylene sulfoxide was obtained from K and K Labs. Each sulfoxide was purified by distillation under reduced pressure over Linde-13X Molecular Sieves. This removed any adsorbed water. The sieves were previously conditioned by calcination under nitrogen at 400° for 4 hr. Each distilled sulfoxide gave only one peak when analyzed by gas chromatography on a 3-ft., 20 wt. % Carbowax (20 M) on Chromosorb-W column. In these analyses, injection port and column temperatures necessary to maintain thermal stability of each sulfoxide were employed. Detailed data on the thermal stability of numerous sulfoxides under these conditions has been published by Cates and Meloan.⁹

Synthesis of Authentic Disulfides.—Each authentic disulfide was prepared according to the method described in Vogel.¹⁰ One-tenth mole of each thiol used was added to 50 ml. of a 15% sodium hydroxide solution in a flask equipped with a nitrogen bubbler and stirrer. Iodine (11.0 g.) was added over a 2-hr. period and each reaction mixture was then stirred overnight.

(8) E. E. Reid, "Organic Chemistry of Divalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y., 1958, Chapter 1, p. 73.

(9) V. E. Cates and C. E. Meloan, *Anal. Chem.*, **35**, 658 (1963).

(10) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans Green and Co., London, 1959.

The insoluble disulfides were isolated by filtration and purified by recrystallization from acetone. The melting point of each recrystallized disulfide agreed with that tabulated by Reid.¹¹ Each authentic disulfide was employed in mixture melting point determinations with the disulfides isolated from the thiol-sulfoxide reactions.

General Procedure for Thiol-Sulfoxide Reactions.—A general procedure was employed for the thiol-sulfoxide reactions listed in Tables I to IV. The thiol and sulfoxide were weighed into a 50-ml. four-necked flask in a nitrogen drybox. The flask was equipped with a magnetic stirring bar, nitrogen bubbler, and thermometer. The flask was sealed, removed from the drybox, and attached to a nitrogen source. A Vigreux column plus a receiver was immediately attached to the reaction flask and the nitrogen flow was initiated. Stirring was initiated and heat was applied by a heating mantle. When the desired reaction temperature was reached, a Thermocap relay (Niagara Electronic Labs) was attached to the thermometer and this temperature was maintained within $\pm 5^\circ$ throughout the entire experiment. In those reactions where dimethyl sulfoxide and tetramethylene sulfoxide were employed as the oxidizing agents, their respective reduction products, *i.e.*, dimethyl sulfide (b.p. 34°) and tetramethylene sulfide (b.p. 121°), easily distilled through the Vigreux column into the receiver. Upon termination of the reaction, the reaction mixture was allowed to cool and stand at room temperature for 1–2 hr. Under these conditions, the acyclic disulfides easily precipitated as crystalline solids. The disulfides were collected by filtration, recrystallized from acetone, and their structures authenticated by m.p. and mixture m.p. determinations using the authentic disulfides prepared above.

In the dithiol oxidations listed in Table V, a slight modification of the above procedure was employed. Instead of mixing both reactants together immediately, the dithiol was added slowly to the hot sulfoxide solution by a dropping funnel over a period of 4 hr. This technique minimized the amount of intermolecular coupling product produced. The monothiols gave essentially the same yield of disulfide under both conditions. The cyclic disulfides were isolated by the above technique. Structural identification of 1,2-dithiacyclohexane was accomplished by its b.p., $87\text{--}88^\circ$ at 34 mm. (reported¹² b.p. $87\text{--}88^\circ$ at 34 mm.), and m.p., 32° (reported¹² m.p. 32°). 1,2-Dithiacyclopentane was identified by its m.p. $73\text{--}74^\circ$,¹³ identical g.c. retention time with an authentic sample, and mass spectral cracking pattern (106 fragment (parent ion), 78 fragment (loss of $\text{CH}_2=\text{CH}_2$), 64 fragment (loss of S_2), and 25 fragment (loss of SCH)) which was identical with that obtained from an authentic sample. The reaction product from tetramethylene sulfoxide and 1,2-ethanedithiol was found to be polymeric. This material melted over a wide range ($105\text{--}115^\circ$), did not dissolve in any common organic solvent, and had an elemental analysis that was inconsistent with a monomeric 1,2-dithiacyclobutane structure.

Anal. Calcd. for $\text{C}_2\text{H}_4\text{S}_2$: C, 26.58; H, 4.37; S, 69.56. Found: C, 28.75, 28.86; H, 5.06, 4.89; S, 64.32.

Identification of Sulfides.—The reduction product of each sulfoxide listed in Table I, *i.e.*, the corresponding sulfide, was carefully identified at least once. The presence of dimethyl sulfide and tetramethylene sulfide was obvious from the observed

boiling points of each sulfide during the reaction (34 and 121° , respectively). Further structural identification was established by gas chromatographic analyses carried out on an F and M Model 609 g.c. unit using the 2-ft. silicone rubber column described above. The unit was equipped with a Minneapolis-Honeywell recorder and a disk integrator (Model 201). The injection port of the unit was maintained at 305° and the inlet pressure of helium was 36 p.s.i.g. The block of the detector was maintained at a constant temperature of 245° . The helium flow through the column was 100 ml./min. when measured at room temperature with a flow meter. For dimethyl sulfide and tetramethylene sulfide, 0.5 ml. of the material collected in the Vigreux receiver was added to 0.5 ml. of mesitylene. A sample of each mixture was injected into the g.c. unit at 150° . The retention times between each sulfide and mesitylene were identical with those obtained with authentic mixtures. Diisopropyl sulfide and di-*n*-butyl sulfide did not distil from their respective reaction mixtures. In these two cases, 1 ml. of mesitylene was injected into the filtrate of each reaction mixture. A sample was withdrawn and injected into the g.c. unit at a column temperature of 200° . The retention times between mesitylene and each sulfide were identical with those observed with authentic diisopropyl sulfide-mesitylene and di-*n*-butyl sulfide-mesitylene mixtures under the same conditions.

Determination of Reaction Stoichiometry. The reaction stoichiometry was deduced from the three experiments listed in Table IV. In these three experiments, meticulous precautions were followed to obtain accurate quantitative data on each disulfide and sulfide produced. In experiments 1 and 2 of Table IV, dimethyl sulfide and tetramethylene sulfide were carefully trapped in a special, calibrated volumetric receiver that was immersed in a Dry Ice-acetone mixture. The moles of each sulfide produced was subsequently determined from the volume of each sulfide at room temperature using known densities. Water, which codistilled under both reaction conditions, forms a distinct, immiscible layer with both sulfides. Thus, it did not interfere with quantitative measurements. Hexadecyl disulfide was isolated from the reaction flask by adding the total contents of the flask to 50 ml. of acetone. This mixture was heated to the boiling point of acetone (55°), allowed to cool, an equal volume of water was added, and the disulfide was collected by filtration and dried to a constant weight. The disulfide isolation technique gave at least 98% disulfide recovery when authentic samples of hexadecyl disulfide and phenyl disulfide were treated under the same conditions. In experiment 3 of Table IV, tetramethylene sulfide did not distil. In this experiment, 0.05 mole of mesitylene was added to the reaction flask. A representative sample was withdrawn by a syringe and injected into the g.c. unit at a column temperature of 150° . Using a predetermined molar response factor¹⁴ between mesitylene and the sulfide, it was possible to compute the moles of sulfide produced during the reaction by measuring the area of the mesitylene and tetramethylene sulfide peaks. Phenyl disulfide was then isolated by the acetone-water dilution technique previously employed. The observed ratios of RSSR/RSR indicated that 1 mole of sulfoxide reacted with 2 moles of thiol to produce 1 mole of disulfide and 1 mole of sulfide.

Acknowledgment.—The author is indebted to Mr. John J. Mahon who performed all of the experimental work and to the Process Research Division of The Esso Research and Engineering Co. for the privilege of publishing this work.

(14) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

(11) E. E. Reid, "Organic Chemistry of Bivalent Sulfur Compounds," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, pp. 395–399.

(12) G. Claesson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4360 (1961).

(13) (a) Reference 11, p. 368, lists the m.p. of this compound as 75° ; several others have also been reported. (b) The dimer is reported to melt at 76° . See D. J. Cram and M. Cordon, *J. Am. Chem. Soc.*, **77**, 1810 (1955).