Reactions of olefin sulfides. I. Oxidation of trimethylene sulfide. II. Preparation of sulfenyl halides from propylene and trimethylene sulfide

Charles Howard Burnside

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REACTIONS OF OLEFIN SULFIDES

I. OXIDATION OF TRIMETHYLENE SULFIDE

II. PREPARATION OF SULFENYL HALIDES FROM PROPYLENE AND TRIMETHYLENE SULFIDE

by

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B.A., Dakota Wesleyan University, 1947

Presented in partial fulfillment of the requirements for the degree of Master of Science

MONTANA STATE UNIVERSITY

1952
This thesis has been approved by the Board of Examiners in partial fulfillment of the requirements for the degree of Master of Science.

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Chairman of the Board of Examiners

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Date June 5 1952
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PART I

OXIDATION OF TRIMETHYLENE SULFIDE
INTRODUCTION

The reactions of the four-membered heterocyclic sulfides have not been extensively studied. That these strained rings will open is to be expected, but by analogy with the four-membered carbocyclic compounds, these rings would be expected to be more stable than those of the three-membered heterocyclic sulfides. This has been shown to be the case. Both trimethylene sulfide and B, B-dimethyl trimethylene sulfide will form salts with mercuric chloride.\(^1,2\) These cyclic sulfides will also form sulfones when treated with 30 per cent hydrogen peroxide or potassium permanganate.\(^1,2,3\) Three-membered cyclic sulfide rings, due to strain, suffer cleavage of the carbon-sulfur bond on peroxide oxidation.\(^4\)

Cleavage of the carbon-sulfur bond has been accomplished by treating the four-membered ring sulfides with various reagents. Methyl iodide cleaves the ring at the carbon-sulfur bond\(^3,5,6\) to give, in the case of trimethylene sulfide, 3-iodopropyl dimethyl sulfonium iodide.\(^5\) It has been postulated that this cleavage proceeds through an unstable cyclic sulfonium intermediate.\(^6\) Trimethylene sulfide has been reported to polymerize in the presence of nitric acid and hydrochloric acids.\(^1,6\) The ring has also
been opened by heating to 200°C with ammonia, trimethylene sulfide yielding 3-aminopropane-1-thiol. Grishkevich and Trokhimovski have also claimed ring cleavage when trimethylene sulfide was heated to 200°C with water; however, the products of the reaction were not identified. Bost and Conn reported that trimethylene sulfide forms an addition compound with bromine which was, however, unstable, decomposing even at -15°C. They failed to identify the decomposition products.
CHAPTER I

DISCUSSION OF THE WORK

The 3-membered sulfide ring in propylene sulfide is opened by such oxidizing agents as 30 per cent hydrogen peroxide, nitric acid, and the halogens, chlorine and bromine. With the halogens the nature of the cleavage products obtained varied with the solvent used.\(^4,7\) In aqueous chlorine 1-chloro-propane-2-sulfonyl chloride was formed. Addition of chlorine or bromine to propylene sulfide in anhydrous solvents gave quantitative yields of bis-(1-methyl-2-halo-ethyl) disulfides. With 30 per cent hydrogen peroxide, in addition to a primary cleavage and oxidation product, 2-hydroxypropane-1-sulfonic acid, sulfuric acid was formed by the complete cleavage and oxidation of the sulfur atom.

In this work the oxidation of trimethylene sulfide by these same oxidizing agents has been studied. As with propylene sulfide, the reaction of halogens produces different types of products in aqueous and non-aqueous solution. When a calculated molar equivalent of chlorine was passed into a chloroform solution of trimethylene sulfide, bis-(3-chloropropyl)disulfide (I.) was produced in accordance with the following equation:

\[
\text{CH}_2\text{CH}_2\text{CH}_2 + \text{Cl}_2 \rightarrow \text{ClCH}_2\text{CH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{CH}_2\text{Cl} \quad \text{(I.)}
\]
Sulfur analysis on (I) substantiates the structure shown. Treatment of (I) with excess piperidine, followed by anhydrous hydrogen chloride yielded a solid derivative, bis-(3-piperidinopropyl)disulfide dihydrochloride, (II)

\[
\text{ClCH}_2\text{CH}_2\text{CH}_2\text{S}_2 + 4 \text{C}_5\text{H}_{10}\text{N} \xrightarrow{\text{HCl}} \text{C}_5\text{H}_{10}\text{NCH}_2\text{CH}_2\text{CH}_2\text{S}_2 \cdot 2\text{HCl} + 2 \text{C}_5\text{H}_5\text{NHHCl} \]

Similarly trimethylene sulfide reacted readily with a molar equivalent of bromine to give an addition product which, however, was unstable to heating and could not be distilled without decomposition. The crude product was shown to be bis-(3-bromopropyl)disulfide by converting it to a solid derivative identical with (II) on treatment with piperidine followed by hydrogen chloride. Sulfur analysis on a sample of the crude bromine addition product, though not in close agreement with the calculated value, also substantiates the structure given.

Three-chloropropane-1-sulfenyl chloride(III) has been prepared by the addition of a chloroform solution of trimethylene sulfide to liquid chlorine, reversing the order of addition described above. This reacts with trimethylene sulfide to give (I). Hence, the sulfenyl halide is probably an intermediate in the reaction in which the halogen is added to the sulfide. A probable mechanism for addition of halogen to trimethylene sulfide may be as follows:
When trimethylene sulfide and chlorine were reacted in 75 per cent acetic acid solution, the physical constants of the liquid product were found to be in close agreement to those of 3-chloropropane-1-sulfonyl chloride which has been prepared by another method. Furthermore, the sulfonamide derivative of (IV) was prepared and found to have a melting point identical with that of 3-chloropropane-1-sulfonamide as reported by Kharasch et al. In confirmation of some work reported by Bost and Conn it was found that treatment of trimethylene sulfide in petroleum ether with an acetic acid solution of the calculated amount of 30 per cent hydrogen peroxide followed by a short heating period gave trimethylene sulfone. If, however, the petroleum ether was eliminated, and the sulfide was heated at reflux with excess 30 per cent hydrogen peroxide for about seven hours, cleavage of the ring occurred. As with results reported for propylene sulfide, much of the sulfur was completely cleaved and oxidized to sulfuric acid.
A mixture of trimethylene sulfide and 30 per cent hydrogen peroxide, in 12 per cent excess, was refluxed seven hours. The resulting sulfonic acid was isolated as the barium salt. Sulfate ignition analysis of the salt failed to give any conclusive results. Classification tests of the salt indicated the presence of a carbon-carbon double bond and the absence of a hydroxyl group. This was unexpected.

Treatment of the crude barium sulfonate with phosphorus pentachloride gave $\Delta^1$-propene-3-sulfonyl chloride (V).

\[
(CH_2=CHCH_2SO_3)_2Ba + 2PCl_5 \rightarrow 2CH_2=CHCH_2SO_2Cl + 2POCl_3 + BaCl_2
\]

(V) was not analyzed, but converted into a methyl anilide derivative, $\Delta^1$-propene-3-sulfonmethylanilide (VI).

\[
CH_2=CHCH_2SO_2Cl + 2 C_6H_5NHCH_3 \rightarrow CH_2=CHCH_2SO_2N(CH_3)C_6H_5 + C_6H_5NHCH_3 \text{ HCl}
\]

Analysis of (VI) was evidence that the unsaturated structures assigned to (V) and (VI) were correct.

In another experiment, the trimethylene sulfide-hydrogen peroxide mixture was refluxed for five and one-half hours. Isolation of the barium salt and conversion to the sulfonyl chloride yielded (V) and a very small amount of a different sulfonyl chloride having a refractive index, $n_D^{20}$ 1.4859. A satisfactory amide could not be prepared from the latter, however, its refractive index is quite close to that of (IV). This would seem to indicate, that in
peroxide oxidation, a small amount of 3-hydroxypropane-l-sulfonic acid is formed. It is quite probable that 3-hydroxypropane-l-sulfonic acid is the oxidation product, which is in turn dehydrated in the strong acid solution to give \( \Delta^1 \)-propene-3-sulfonic acid.
CHAPTER II

EXPERIMENTAL

Preparation of trimethylene sulfide. The sulfide was prepared by a modification of the procedure of Bennet and Hock.5

A solution of 160 g. sodium sulfide (hydrate) in 160 cc. of water and 200 cc. of methanol was divided into two portions, one third being boiled and stirred in a flask fitted with a reflux condenser, while the remaining two thirds and 100 g. of trimethylene bromide were simultaneously added dropwise over a period of one hour. Following the addition, stirring and refluxing were continued for another hour. The reaction mixture was cooled and extracted five times with ether. The combined extracts were washed with water and with saturated brine, dried overnight over a large amount of anhydrous calcium chloride, filtered, and distilled through a glass bead filled column to give an average yield of 45 per cent of product, b.p. 90-93° (680-685 mm.); nD20 1.5070.

Addition of chlorine to trimethylene sulfide in anhydrous solvents. (Preparation of bis-(3-chloropropyl)disulfide [I]). A solution of 5 g. of trimethylene sulfide in 25 cc. of chloroform was stirred and cooled in a cold
water bath. Two and four-tenths g. of chlorine was passed in beneath the surface of the solution. Air was then blown through the mixture and the solvent evaporated at the aspirator. The crude was distilled at 1 mm. pressure. The fraction boiling from 110-120° was collected and redistilled to yield 3.6 g. (25 per cent) oily product, b.p. 113-115° (1 mm.); nD 1.5450.

Anal:
Calcd. for C6H12S2Cl2 %C,32.87 %H,5.52 %S,29.25
Found %C,33.03 %H,5.22 %S,29.57

A solid derivative (II) of the bis-(3-halopropyl) disulfide was prepared as follows: An ethanol solution of 2 g. of the bis-(3-halopropyl)disulfide and 4 molar equivalents of piperidine was refluxed for four hours. The solution was cooled and diluted with water. The mixture was extracted with ether, the extract washed twice with water and dried by shaking with anhydrous sodium sulfate. The solvent was evaporated at the aspirator leaving a yellow oil. The oil was taken up in absolute alcohol and dry hydrogen chloride was passed in. The solution was evaporated to a few cc.'s and ether added to precipitate the derivative. The solid was taken up in alcohol, colorized with "Norite," and then precipitated again by the addition of ether. Recrystallization from an alcohol-ether solution gave white crystals m.p. 210-212° (decomp).0.

Anal:
Calcd. for C_{16}H_{34}S_{2}Cl_{2}N_{2}  \%^{\text{C}}1, 18.21;  \%^{\text{S}}, 16.46

Found  \%^{\text{C}}1, 13.03;  \%^{\text{S}}, 16.30

Addition of bromine to trimethylene sulfide in anhydrous solvent. (Preparation of bis-(3-bromopropyl) disulfide). A solution of 3.8 g. of trimethylene sulfide in 20 cc. of chloroform was stirred and cooled in a cold water bath. Bromine (1.3 cc.) in 10 cc. of chloroform was added dropwise over a period of 20 minutes. The solvent was evaporated at the aspirator. Attempts to distill the crude at 1 mm. resulted in decomposition. A sample that had become colored on standing was analyzed to show that the compound was the one expected.

Anal:
Calcd. for C_{6}H_{12}S_{2}Br_{2}  %S, 20.81;  %S found, 22.07

A piperidine derivative was prepared from the crude, as described above, m.p. 209-211°.

Chlorine oxidation of trimethylene sulfide in 75 per cent acetic acid. (Preparation of 3-chloropropone-1-sulfonyl chloride (IV). Chlorine was introduced beneath the surface of a chilled 80 cc. solution of 75 per cent acetic acid. When the solution was saturated, 5.8 g. of trimethylene sulfide was added dropwise and chlorine introduction was continued at such a rate that there was always an excess of chlorine present. The addition of chlorine was continued for five minutes after all the sulfide had been added. Air was then blown through the reaction mix-
ture to remove excess chlorine. The mixture was diluted with 400 cc. of water, extracted with ether, the extract dried one-half hour over anhydrous sodium sulfate, and the solvent stripped at the water aspirator. The crude product was then distilled in vacuo to yield 10 g. (72%) of product, b.p. 82-85°C (1 mm.); n_D 1.4890. The reported physical constants for 3-chloropropane-1-sulfonyl chloride are b.p. 117-118°C (15 mm.); n_D 1.4900.

The amide derivative was prepared as follows:

Ether (150 cc.), cooled in an ice bath, was saturated with ammonia, 1 cc. of the 3-chloropropane sulfonyl chloride in 10 cc. of ether was added and ammonia was then passed through the solution for five minutes. The mixture was allowed to stand for thirty minutes. The precipitated ammonium chloride was filtered off and the solvent evaporated at the aspirator. Recrystallization of the crude product from an ether-petroleum ether solution gave white crystals, m.p. 62-64°C. Three-chloropropane-1-sulfonamide has been reported to have m.p. 63°C.10

Hydrogen peroxide oxidation of trimethylene sulfide.

A. Preparation of trimethylene sulfone. The procedure was essentially that of Bost and Conn.1 A solution of 30 per cent hydrogen peroxide in acetic acid was added in portions to a solution of trimethylene sulfide in petroleum ether. When the reaction subsided, the mixture was refluxed for one hour. The solvent was evaporated at the steam cone. Re-
crystallization from ethanol yielded white crystals, m.p. 74-75°.

B. Preparation of the barium sulfonate. A solution of 11.6 g. of trimethylene sulfide in 80 cc. of acetone was placed in a cold water bath and stirred. To this was added dropwise 12 per cent excess of 30 per cent hydrogen peroxide at such a rate that the reaction would not become violent. Stirring in the cold water bath was continued 15 minutes after all the hydrogen peroxide had been added. The mixture was then heated in a hot water bath for seven hours. The mixture was cooled and a water solution of sulfur dioxide added to destroy excess peroxide. The acetone was removed at the aspirator, the mixture neutralized with barium hydroxide solution and the barium sulfate filtered off. Carbon dioxide was passed in until the solution was saturated. The solution was boiled and filtered to remove barium carbonate. The filtrate was evaporated to dryness on the steam cone to yield 15½ g. of tan salt. The salt gave a negative ceric nitrate alcohol group test, and a positive permangate test for unsaturation. Sulfate analysis of the salt was inconclusive.

C. A solution of 9 g. of trimethylene sulfide was treated with 30 per cent hydrogen peroxide as in B except that heating was limited to five and one-half hours, and following this the mixture was steam distilled. The undistillable residue was then treated with sulfur dioxide, barium
hydroxide, and carbon dioxide as before, and the barium salt isolated as in B.

**T}reatment of the crude barium sulfonate salt from peroxide oxidation with phosphorus pentachloride (V).** The dried barium salt (10 g.) from procedure C was mixed with 30 g. of phosphorus pentachloride in a flask fitted for reflux. When fumes were no longer evolved, the mixture was placed on the steam cone and heated for one hour. Chloroform (40 cc.) was added and the mixture refluxed for one and one-half hours. The mixture was then allowed to stand overnight. Any solid lumps were broken up and the mixture poured onto cracked ice. The chloroform layer was separated, washed twice with ice water, dried for two hours over calcium chloride, and the solvent evaporated at the aspirator. The crude was distilled at 8 mm. pressure to yield 1 g. of product, b.p. 63-65°; \( n_D^{20} \) 1.4542. Less than one-half cc. of after run was obtained by heating the side arm of the distilling flask, \( n_D^{20} \) 1.4859. A dark tarry residue remained in the flask. Phosphorus pentachloride treatment of the salt from procedure B yielded only the lower boiling product b.p. 64-66° (8 mm.); \( n_D^{20} \) 1.4541. The refractive index of the higher boiling fraction corresponds closely to that of 3-chloropropane-1-sulfonyl chloride and this is presumed to be 3-chloropropane-1-sulfonyl chloride.

A methyl aniline derivative (VI) of the main product (\( n_D^{20} \) 1.4542) was prepared as follows: An ethanol solu-
tion of 1 g. of the sulfonyl chloride, two molar equivalents of methyl aniline, and one molar equivalent of anhydrous sodium carbonate was refluxed three and one-half hours. Dilute hydrochloric acid was then added to the cooled mixture. The mixture was extracted with ether, the extract washed with dilute hydrochloric acid, and dried by shaking with anhydrous sodium sulfate. The solvent was evaporated at the aspirator and the solid residue was recrystallized twice from a methanol-water solution to yield white crystals, m.p. 66.5-68°.

Anal:

Calcd. for C_{10}H_{13}SO_{2}N  \%S, 15.15; \%C, 56.85; \%H, 6.20

Found  \%S, 15.55; \%C, 56.46; \%H, 7.08
CHAPTER III

SUMMARY

The four membered sulfide ring in trimethylene sulfide was opened by the action of oxidizing agents.

Chlorine and bromine in anhydrous solvents yielded bis-(3-halopropyl)disulfides. From these, the solid derivative bis-(3-piperidinopropyl)disulfide dihydrochloride was prepared.

Aqueous chlorine was shown to yield 3-chloropropane-1-sulfonyl chloride.

A barium sulfonate was isolated from the hydrogen peroxide mixture, which was converted to $\Delta^1$-propene-3-sulfonyl chloride. From this was prepared the solid derivative $\Delta^1$-propene-3-sulfonmethylanilide.
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INTRODUCTION

Only in recent years have the alkyl sulfenyl halides been prepared and their reactions studied. Three general methods for their preparation have been employed. In each case, the reaction is carried out in the cold due to the instability of the sulfenyl halide product.

The classical method of preparation is the treatment of a disulfide with a free halogen. With alkyl disulfides, this procedure is accompanied by halogenation and mixtures of compounds are obtained. However, 2-chloroethyl-1-sulfenyl chloride has been successfully prepared from bis(2-chloroethyl)disulfide in this way. The corresponding chloro sulfenyl bromide could not be isolated. Isolation of these sulfenyl halide compounds is difficult, as decomposition occurs readily, giving the corresponding disulfides through splitting out a molecule of halogen between two molecules of sulfenyl halide. Mercury mercaptides and the halogens react to give sulfenyl halides. A third general method of preparation is the cleavage of the sulfur nitrogen bond in thioamides with halogen acids.

The sulfenyl halides are extremely reactive. They will react with olefins to form halogen substituted sulfides.
with amides to produce thioamides,\textsuperscript{1,3,4} with sulfur to produce poly sul-
rides and thiosulfonic esters.\textsuperscript{2} Water decomposes them giving disul-
rides and thiosulfonic esters.\textsuperscript{2} When treated with mercap-
tans or alcoholates, sulfenyl halides react to give, respect-
ively, disulfides\textsuperscript{3} and sulfenic esters.\textsuperscript{1,3} Metals, such as mag-
nesium or mercury, convert them into the corresponding disulfides.\textsuperscript{1} Oxidation with nitric acid converts them to sulfonic acids.\textsuperscript{2}
CHAPTER I
DISCUSSION OF THE WORK

The work described here pertains to a new preparation of haloalkyl sulfenyl halides by the action of chlorine and bromine on propylene sulfide and tri methylene sulfide, and some new reactions of these sulfenyl halides.

Stewart and Cordts\textsuperscript{5} have shown that addition of chlorine and bromine to propylene sulfide in anhydrous solvents produced bis(1-methyl-2-haloethyl)disulfides. It appeared possible that this reaction might proceed through a haloalkyl sulfenyl halide intermediate, the intermediate sulfenyl halide then reacting rapidly with excess propylene sulfide to form the disulfide product isolated.

\[
\text{CH}_3\text{CHCH}_2\text{X} + \text{CH}_3\text{SCHCH}_2\text{S} \rightarrow \text{CH}_3\text{CHCH}_2\text{X} \]

To ascertain whether such a sequence of reactions did occur, the method of addition was reversed, adding the cyclic sulfide slowly to a calculated molar equivalent of halogen. A chloroform solution of propylene sulfide, when added to a solution of liquid chlorine in chloroform at the temperature of a dry ice-acetone bath reacted to give 1-chloropropane-2-sulfenyl chloride (I), an orange oil, in
accordance with the following equation:

\[
2\text{CH}_3\text{CHCH}_2^+ + \text{Cl}_2 \rightarrow 2\text{CH}_3\text{CHCH}_2\text{Cl}
\]

In addition to product (I) an after run consisting probably of other more highly halogenated sulfenyl halides was also produced. (I) was separated from the mixture by fractional distillation at low pressure. Direct analysis of (I) was not made and attempts to prepare a solid derivative of (I) with methyl aniline failed. When (I) was added to a chloroform solution of propylene sulfide it lost its bright orange color. The reaction resulted in what has been termed normal cleavage of the carbon sulfur bond in propylene sulfide to yield bis(1-methyl-2-chloro ethyl)disulfide (II), the constants agreeing closely to those reported for this compound by Stewart and Cordts.\textsuperscript{5}

\[
\text{CH}_3\text{CHCH}_2\text{Cl} + \text{CH}_3\text{CHCH}_2^+ \rightarrow \text{CH}_3\text{CHCH}_2\text{Cl}
\]

Similarly, when propylene sulfide was added slowly to a chloroform solution of one molar equivalent of bromine cooled in an ice bath, a red orange oil, 1-bromopropane-2-sulfenyl bromide (III) was formed.

\[
2\text{CH}_3\text{CHCH}_2^+ + \text{Br}_2 \rightarrow 2\text{CH}_3\text{CHCH}_2\text{Br}
\]

(III) could not be isolated in a pure state. Attempted distillation in a vacuum resulted in decomposition. The decomposition product was later identified as bis(1-methyl-2-
bromoethyl)disulfide (IV) which has been prepared previously. When propylene sulfide was treated with an equivalent amount of crude (III), the sulfinyl halide color disappeared and normal cleavage of the carbon-sulfur bond in the sulfide occurred, giving bis(1-methyl-2-bromoethyl)disulfide (IV) the constants agreeing closely with those previously reported for this compound. Derivatives of (II) and (IV) were prepared by treating each, first with piperidine, and then with dry hydrogen chloride. The derivative in each case was the dihydrochloride salt of bis-(1-methyl-2-piperidinoethyl) disulfide (V). The melting points were in close agreement with those reported previously for this compound.

\[
\begin{align*}
\text{CH}_3\text{CHCH}_2\text{Cl} & \quad + \quad 4\text{C}_5\text{H}_{10}\text{N} \\
\text{CH}_3\text{CHCH}_2\text{Cl} & \quad \text{then} \quad \text{HCl} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CHCH}_2\text{NC}_5\text{H}_{10}\text{HCl} & \quad + \quad 2\text{C}_5\text{H}_{10}\text{N.HCl} \\
\end{align*}
\]

The piperidine hydrochloride derivatives of (II) and (IV) had identical melting points. Mixed melting points showed no depression. Mixed melting points of these derivatives with the piperidine derivative, prepared from a known sample of bis(1-methyl-2-chloroethyl)disulfide, produced no depression.

In preparing a sulfinyl chloride from trimethylene sulfide, the procedure, as described for (I), was unsuccessful. More highly halogenated products and decomposition products, which were not identified, were obtained. To reduce the amount of halogenation of the alkyl groups, a few
crystals of a free radical inhibitor, hydroquinone, were used. The procedure, when repeated with this modification, gave 3-chloropropane-1-sulfenyl chloride (VI, an orange oil.

\[ 2\text{CH}_2\text{CH}_2\text{CH}_2 + \text{Cl}_2 \rightarrow 2\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SCl} \]

(VI)

In addition to (VI) an after run of some small amount of more highly halogenated products and also disulfides, was apparently obtained, though this material was not characterized. (VI) was not directly analyzed but was added to a chloroform solution of an equivalent amount of trimethylene sulfide yielding the addition product bis(3-chloropropyl) disulfide (VII), which has been described in Part I of this paper. (VII), when treated with piperidine and hydrogen chloride, gave a derivative having a melting point identical with that of bis(3-piperidinopropyl)disulfide dihydrochloride also described in Part I of this paper.

A sample having the characteristic sulfenyl halide odor and color, obtained by treating propylene sulfide with liquid chlorine, was dissolved in 80 per cent acetic acid. Through this solution was bubbled an excess of chlorine. This reaction gave a sulfonyl chloride of somewhat higher refractive index than that reported for either 2-chloropropane-1-sulfonyl chloride or 1-chloropropane-2-sulfonyl chloride. It was assumed that this material was a mixture and contained some more highly halogenated propane sulfonyl chloride, in addition to the expected 1-chloropropane-2-sulfonyl chloride.
CHAPTER II

EXPERIMENTAL

Preparation of propylene sulfide. Prepared by the method of Snyder, Stewart, and Ziegler.

Preparation of trimethylene sulfide. Prepared as described by Bennet and Hock, and in Part I of this paper.

Addition of propylene sulfide to a solution of liquid chlorine. (Preparation of 1-chloropropane-2-sulfenyl chloride (II)). A solution of 3.2 cc. of liquid chlorine in 10 cc. of chloroform was cooled in an acetone-dry ice bath and 5.7 g. of propylene sulfide in 40 cc. of pre-cooled chloroform was added dropwise over a period of ten minutes. The mixture was allowed to warm to room temperature. Argon was bubbled through the mixture and the solvent evaporated at the aspirator leaving an orange oil. This was distilled at 4½ mm. to yield:

3.6 cc. of orange forerun, b.p. 40-50°
2.5 cc. of orange middle run, b.p. 50-64°
1/2 cc. of orange after run, b.p. 65-75°

A dark higher boiling residue remained in the flask. The fraction 40-50° was redistilled at 6 mm. pressure to yield 2 g. (17 per cent) or orange liquid b.p. 44-47°, nD 1.5200 which on the basis of the following reaction product's
constants is fairly pure 1-chloropropane-2-sulfenyl chloride.

**Reaction of 1-chloropropane-2-sulfenyl chloride** and propylene sulfide (II). A solution of 2 g. of the sulfenyl chloride in 20 cc. of chloroform was added dropwise to a chloroform solution of 1 g. of propylene sulfide, which was agitated during the addition. When the addition was completed the solvent was evaporated at the aspirator, leaving a colorless crude product. This was distilled to yield 1½ g. (50 per cent) of product, having constants b.p. 96-98° (1 mm.); n<sub>D</sub> 1.5430 which agree closely with those reported for bis(1-methyl-2-chloroethyl)disulfide.

**Addition of propylene sulfide to bromine.** (Preparation of 1-bromopropane-2-sulfenyl bromide (III)). A solution of 4 g. of propylene sulfide in 25 cc. of chloroform was added dropwise with stirring, over a period of 25 minutes, to a solution of 2.7 cc. of bromine in chloroform, which was cooled in an ice bath. The solvent was evaporated at the aspirator, leaving a red orange oil. Attempts to distill this oil at 7 mm. pressure resulted in decomposition of the sulfenyl halide. The light tan decomposition product, b.p. 146-149°; n<sub>D</sub> 1.5849 was obviously bis-(1-methyl-2-bromoethyl)disulfide the constants being in close agreement with those reported earlier for this compound.

The crude sulfenyl bromide was prepared as described above from 4 g. of propylene sulfide. A chloroform solu-
tion of this red orange crude product was added dropwise with stirring, over a period of 30 minutes, to a chloroform solution of 4 g. of propylene sulfide. The solvent was evaporated at the aspirator to yield a tan oil. This was distilled at 1 mm. to yield 7.6 g. of yellow oil boiling in the range 109-112°. This fraction was redistilled, argon being admitted through the ebulliator, to yield 6.1 g. of yellow oil b.p. 107-110°; n_D^19 1.5848, these constants being in close agreement to those of bis(1-methyl-2-bromoethyl) disulfide reported earlier.5

Addition of trimethylene sulfide to a solution of liquid chlorine. (Preparation of 2-chloropropane-1-sulfenyl chloride (VI)). A stirred solution of 2½ cc. of liquid chlorine in 10 cc. of chloroform, to which a few crystals of hydroquinone had been added, was cooled in a dry ice-acetone bath. To this, a solution of 4 g. of trimethylene sulfide in 40 cc. of pre-cooled chloroform, was added dropwise over a period of 10 minutes. The creamy reaction mixture was allowed to warm, argon was blown through the mixture and the solvent was evaporated at the aspirator. The orange-colored crude product was distilled at reduced pressure to yield about 3 cc. of orange oil b.p. 48-55° (3½ mm.) and an after run of yellow oil which began to distill at 80°. The pressure was reduced to 1 mm. and the after run collected to a temperature of 120°. The orange oil fraction was redistilled at 4 mm. to yield 2.3 g. (30 per cent) of product, b.p.
51-53°; n_D^20 1.5190, which on the basis of the following reaction product's constants is fairly pure 3-chloropropane-1-sulfenyl chloride.

**Reaction of 3-chloropropane-1-sulfenyl chloride and trimethylene sulfide (VII).** A solution of 2.3 g. of the sulfenyl chloride in 20 cc. of chloroform was added dropwise with stirring to a solution of 1.2 g. of trimethylene sulfide in 20 cc. of chloroform. The solvent was evaporated at the aspirator leaving a yellow oil. This was distilled at 1 mm. pressure to yield 1.9 g. (54 per cent) of pale yellow product b.p. 111-115°; n_D^20 1.5458, the constants being in close agreement with those for bis-(3-chloropropyl)disulfide reported in Part I of this paper.

**Preparation of the piperidine hydrochloride derivatives (V).** A solution of 2 g. of the bis-(halopropyl)disulfide and four molar equivalents of piperidine in absolute alcohol was refluxed for four hours. The mixture was cooled, diluted with water, and extracted with ether. The extract was washed five times with water to remove excess piperidine and its hydrochloride and then dried overnight over anhydrous sodium sulfate. The solvent was evaporated at the aspirator leaving a yellow oil. This was taken up in ether and treated with dry hydrogen chloride. The precipitated product was recrystallized twice from alcohol by precipitation with ether:

Bis-(l-methyl-2-piperidionethyl)disulfide dihydro-
chloride, m.p. 225-226° (decomp.) This melting point agrees with that reported for the compound as prepared by a different method.\(^5\)

Bis-3-piperidinopropyl)disulfide dihydrochloride, m.p. 209-211° (decomp.) This melting point agrees with that reported in Part I of this paper for the compound as prepared by a different method.
 CHAPTER III

SUMMARY

Haloalkyl sulfenyl halides were prepared by adding propylene sulfide and trimethylene sulfide in an inert solvent to bromine and liquid chlorine.

These sulfenyl halides were shown to react with the corresponding 3- and 4-membered cyclic sulfides to yield bis(halopropyl)disulfides of known structure. They were also shown to be oxidized by chlorine water to the corresponding sulfonyl halides.
BIBLIOGRAPHY


