[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

LEVINSTEIN MUSTARD GAS. IV. THE *bis*(2-CHLOROETHYL) POLYSULFIDES[1]

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Mustard gas made by the Levinstein process is known to contain a considerable amount of material which has a high sulfur content and which has been thought to consist of the *bis*(2-chloroethyl) polysulfides (1). The present work deals with the identification and a study of some properties of these substances. The problem has been attacked not only by attempts to isolate pure compounds from the high-boiling fraction obtained by the Levinstein process but also by the preparation of the polysulfides by synthetic methods.

THE SYNTHESIS OF THE POLYSULFIDES

The synthesis of *bis*(2-chloroethyl) disulfide was carried out by converting monothioglycol to *bis*(2-hydroxyethyl) disulfide and treating the latter with concentrated hydrochloric acid.

$$2\ HOCH_2CH_2SH + H_2O_2 \rightarrow (HOCH_2CH_2)_2S_2 + 2\ H_2O$$
$$(HOCH_2CH_2)_2S_2 + 2\ HCl \rightarrow (ClCH_2CH_2)_2S_2 + 2\ H_2O$$

The procedure was essentially that of Bennett (2). The last step has been modified so as to be continuous, greatly facilitating the preparation of large amounts of material. This method is of especial value in the synthesis of vesicant compounds; for example, *bis*(2-chloroethyl) sulfide, 1,2-*bis*(2-chloroethylthio)ethane, and 2-chloroethyl 2-chloro-*n*-propyl sulfide have been prepared in yields of 85, 92, and 61%, respectively.

bis(2-Chloroethyl) trisulfide was isolated by Mann, Pope, and Vernon (3) from the product obtained by the reaction between sulfur monochloride and ethylene at 60°. It has now been prepared by a straightforward synthesis from ethylene chlorohydrin and sodium polysulfide followed by treatment of the resulting glycol with thionyl chloride.

$$2\ HOCH_2CH_2Cl + Na_2S_3 \rightarrow (HOCH_2CH_2)_2S_3 + 2\ NaCl$$
$$(HOCH_2CH_2)_2S_3 + 2\ SOCl_2 \rightarrow (ClCH_2CH_2)_2S_3 + 2\ SO_2 + 2\ HCl$$

The trisulfide is a white, crystalline compound melting at 30.5–31.5°. Distillation of the crude reaction product yielded a considerable quantity of the disulfide. Later it was found that the pure trisulfide actually decomposes under the influence of heat to give *bis*(2-chloroethyl) disulfide.

bis(2-Chloroethyl) pentasulfide was isolated first in studies of the hydrolysis

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of mustard gas which had been made by the Levinstein process. It was noticed that hydrolysis with water appeared to be incomplete. The method of "exhaustive" hydrolysis was then developed for the isolation of the polysulfides corresponding to mustard gas. It consisted in subjecting a mixture of Levinstein mustard gas and water to vigorous agitation. The progress of the hydrolysis was followed by titration to determine hydrogen or chloride ion concentration. When the rate of hydrolysis had become negligibly small, the unhydrolyzed residue was found to amount to about 30% by weight of the original mustard gas. The composition of the residues from various samples varied from values corresponding to those for the hexasulfide to those for the nonasulfide.

The unhydrolyzed residues were observed to deposit sulfur slowly. Because sulfur dissolves only slightly in Cellosolve, whereas polysulfides are fairly soluble, the possibility suggested itself of using this solvent as a means of separating the excess sulfur rapidly from the polysulfides. When the Levinstein residue was treated with Cellosolve, sulfur separated in crystalline form and, in addition, a small amount of viscous oil remained undissolved. This oil had the composition, indicated by analysis, of a higher polysulfide such as $(ClCH_2CH_2)_2S_{11}$. It invariably deposited sulfur within a few days and took on the appearance of yellow, crystalline sulfur.

The Cellosolve solution was washed with water to remove the Cellosolve; the water-insoluble oil was dried in ether solution and then freed from the ether. A clear, amber oil was obtained, which consisted almost entirely of *bis*(2-chloroethyl) pentasulfide.

It is impossible to purify the pentasulfide by ordinary distillation because of its thermal instability; nevertheless the volatile materials such as the disulfide can be removed by steam-distillation, either before or after treatment with Cellosolve. However, due to autosulfurization of the pentasulfide, which is described later, stripping with Cellosolve after distillation is always necessary. The purest pentasulfide obtained was an amber liquid of high refractive index (n_D^{20} 1.6853) which could not be induced to crystallize, even at −80°.

Oils which had the composition of the higher sulfides were made also by treatment of *bis*(2-chloroethyl) trisulfide with sulfur under mild conditions and by heating the corresponding disulfide with sulfur under more drastic conditions. When these oils were stripped of excess sulfur by the Cellosolve treatment they resembled the Cellosolve-stripped Levinstein residues in appearance, odor, refractive index, density, and composition. Also, polarographic studies revealed the same reduction potential for the synthetic pentasulfides as for that isolated from Levinstein mustard gas.

PROPERTIES OF THE POLYSULFIDES

A few of the properties of the *bis*(2-chloroethyl) polysulfides have been mentioned in the preceding section; notably, the sulfurization of the di- and trisulfides with sulfur and the stripping of the higher polysulfides to *bis*(2-chloroethyl) pentasulfide with Cellosolve. A number of the reactions presently to be mentioned also have been of value in the synthesis of the polysulfides.

Sulfurization. Following the suggestion of Dr. E. Emmett Reid (4) that alkyl polysulfides might be better sulfurizing agents than sulfur itself, experiments were run in which *bis*(2-chloroethyl) disulfide, trisulfide, and pentasulfide were heated with methyl tetrasulfide. The assumption was made that at the temperature and pressure employed, the volatile methyl trisulfide would be removed as it was formed, allowing the reaction to proceed to completion. In this way *bis*(2-chloroethyl) pentasulfide and higher polysulfides identical with the polysulfides obtained by other methods were prepared from the trisulfide and pentasulfide.

$$(ClCH_2CH_2)_2S_3 + 2\ (CH_3)_2S_4 \rightarrow (ClCH_2CH_2)_2S_5 + 2\ (CH_3)_2S_3$$

bis(2-Chloroethyl) disulfide was not sulfurized by methyl tetrasulfide under the same conditions.

The autosulfurization of *bis*(2-chloroethyl) pentasulfide also is a reaction which falls into this category. When the pentasulfide was subjected to steam distillation, the distillate was found to contain the corresponding trisulfide. The residue had the composition of polysulfides higher than the pentasulfide. Evidently, under these conditions autosulfurization of the pentasulfide occurred, the removal of the trisulfide forcing the reaction to proceed.

$$(ClCH_2CH_2)_2S_5 \rightarrow (ClCH_2CH_2)_2S_{5+x} + (ClCH_2CH_2)_2S_3$$

It was mentioned that when the non-hydrolyzable Levinstein residues were stripped with Cellosolve, not only sulfur, but also a gum was obtained which had the analytical composition of a high polysulfide, $(ClCH_2CH_2)_2S_{11}$. It was found that when *bis*(2-chloroethyl) trisulfide or pentasulfide was heated with sulfur, and the reaction mixtures subsequently extracted with Cellosolve and ether, there remained viscous oils which had the composition indicated by analysis of high polysulfides of the order of the dodecasulfide or greater. These polysulfides were often stable for days at room temperature even in the presence of sulfur, although the presence of ammonia caused their rapid degradation to the pentasulfide and sulfur (see section on Stripping).

The fact that the higher sulfides readily give up sulfur suggested that they might not be definite compounds but merely solutions of sulfur in the pentasulfide. This hypothesis seems untenable in view of the observation that when mixtures of finely divided sulfur and the pentasulfide were shaken for extended periods at room temperature, less than one gram atom of sulfur dissolved.

Stripping. It has been seen that sulfurization is a most important reaction of the polysulfides; by the same token, the reverse procedure, stripping, plays a prominent rôle in the chemistry of these unusual compounds.

It had been discovered by other investigators (5) that treatment of the high-boiling fraction of Levinstein mustard gas with moist, gaseous ammonia caused rapid precipitation of sulfur. Examination of the analytical data showed that the residual oil corresponded closely in composition to *bis*(2-chloroethyl) pentasulfide. This report has been confirmed, although it appears that ammonia-stripping is not as efficacious as the Cellosolve method already described. With ammonia alone some sulfur seems to remain dissolved in the pentasulfide.

Although *bis*(2-chloroethyl) pentasulfide is stable to moist ammonia and to Cellosolve alone, it is readily stripped to the trisulfide by ammonia in the presence of either Cellosolve or ether. The degradation of the pentasulfide to the trisulfide by steam-distillation has already been mentioned in another connection.

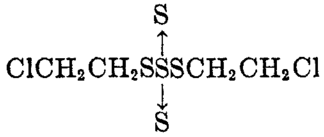
Up to this point no reference has been made to *bis*(2 chloroethyl) tetrasulfide. The evidence that such a compound actually exists is meager. The only indication of a true level of stability for a polysulfide of this composition was found in a study of the stripping of the pentasulfide with boiling acetone. In experiments using *bis*(2-chloroethyl) pentasulfide from several different sources, the limit of degradation appeared to be at the tetrasulfide level.

STRUCTURE OF THE POLYSULFIDES

The linear structure for *bis*(2-chloroethyl) disulfide follows from its method of synthesis. The stability of the corresponding pentasulfide and trisulfide and the degradation of the former to the latter indicate that these compounds are related structurally. The disulfide, known to be linear, takes up an atom of sulfur only with difficulty. Then two additional atoms of sulfur may be added with comparative ease to produce the pentasulfide, degradation of which yields the trisulfide. These facts may be explained plausibly by assuming that a sulfur atom enters the disulfide molecule to produce a linear trisulfide.

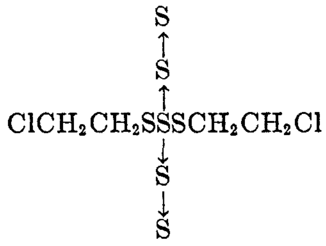
$$ClCH_2CH_2SSCH_2CH_2Cl + S \rightarrow ClCH_2CH_2SSSCH_2CH_2Cl$$

The trisulfide then easily takes up two additional sulfur atoms to yield the pentasulfide, the newly added sulfur being joined to the central sulfur atom as in the following formula.



$$ClCH_2CH_2S\overset{\overset{S}{\uparrow}}{\underset{\underset{S}{\downarrow}}{S}}SCH_2CH_2Cl$$

The structure of the higher polysulfides could be of the following type.



$$ClCH_2CH_2S\overset{\overset{\overset{\overset{S}{\uparrow}}{S}}{\uparrow}}{\underset{\underset{\underset{\underset{S}{\downarrow}}{S}}{\downarrow}}{S}}SCH_2CH_2Cl$$

This type of structure is in accord with the facts that sulfur atoms are naturally chain-forming and that the polysulfides above the pentasulfide readily lose sulfur. The gradual conversion of plastic sulfur, $S\mu$, which is supposed to consist of long sulfur chains, to the stable λ-sulfur is accelerated by ammonia (6). This may be related to the observed stripping of higher polysulfides to the pentasulfide by ammonia.

bis(2-CHLOROETHYL) DISULFIDE

Reports of the existence of *bis*(2-chloroethyl) disulfide in Levinstein mustard gas are in disagreement. This is not at all surprising in view of the tendency of the higher polysulfides to decompose under the influence of heat to give the trisulfide which in turn is degraded to the disulfide by distillation. It is apparent that any reliable method for determining the amount of the disulfide in the Levinstein product must involve only mild conditions.

There is one report (5) that Levinstein mustard gas contains about 6% of *bis*(2-chloroethyl) disulfide. If this were true, about 20% of the non-hydrolyzable portion of the product and an even greater proportion of the stripped residue would consist of the disulfide, since it has been found to resist hydrolysis under the conditions employed. Analysis of the stripped residue indicated that the proportion of *bis*(2-chloroethyl) disulfide was much lower than this figure.

It was observed that the refractive indices of mixtures of the disulfide and pentasulfide, and of the disulfide and trisulfide, followed a linear relationship with respect to the mole fraction of the constituents. Thus, measurement of the refractive indices of the stripped residue from the hydrolysis of Levinstein mustard gas, and of the steam-distillate of the residue, indicated the presence of 1 to 1.8% of the disulfide in the crude mustard gas. This value is in good agreement with that obtained by MacInnes and Belcher (7) by analysis of a fraction from the molecular distillation of Levinstein mustard gas.

Crystalline derivatives of *bis*(2-chloroethyl) disulfide were prepared using thiosalicylic acid, potassium morpholyldithiocarbamate, and piperidine. All but the last are useful for the identification of the disulfide. Attempts to prepare similar derivatives of *bis*(2-chloroethyl) trisulfide gave intractible solids or oils, from which no pure compound could be isolated.

EXPERIMENTAL

Preparation of bis(2-chloroethyl) disulfide. The preparation of this compound was carried out by a modification of a method used by Bennett (2). Five hundred three grams of 30% hydrogen peroxide was added slowly, with stirring, to 624 g. of monothioglycol over a period of two hours. The temperature was maintained at 50–60° by careful cooling. After the addition was complete the reaction mixture was allowed to stand for two hours; then it was heated on a steam-cone under reduced pressure to remove the water. The crude *bis*(2-hydroxyethyl) disulfide was mixed with 2800 ml. of concentrated hydrochloric acid and the mixture heated on a steam-cone for one and one-half hours. The aqueous layer was decanted and the dichloride distilled through a heated, packed 12-inch column. The yield of *bis*(2-chloroethyl) disulfide, boiling at 97–98° (0.4 mm.), was 580 g., or 94%; n_D^{20} 1.5656.

For large scale production the last step has been modified so as to be continuous. A diagram of the apparatus used is shown in Fig. 1. One hundred grams of the glycol was added from the dropping-funnel over a period of forty minutes to 130 ml. of concentrated hydrochloric acid, with constant bubbling of gaseous hydrogen chloride through the solution. The temperature, initially at 75°, soon rose to 90° where it remained for the duration of the reaction. The chloride which separated was removed continuously by the suction provided by the vacuum line. The yield of the dichloro disulfide obtained by this procedure was 94%.

Preparation of bis(2-chloroethyl) trisulfide.[3] A solution of sodium trisulfide was prepared by dissolving 256 g. of sulfur in 960 g. of sodium sulfide nonahydrate and 1300 ml. of water. To this red solution was added over a period of one-half hour, with stirring, 644 g. of ethylene chlorohydrin. Heat was evolved, and the flask was cooled with ice-water. The crude glycol, *bis*(2-hydroxyethyl) trisulfide, began to separate when about two-thirds of the chlorohydrin had been added. After an additional four hours of stirring the oily layer was removed, and water and excess chlorohydrin were distilled under reduced pressure.

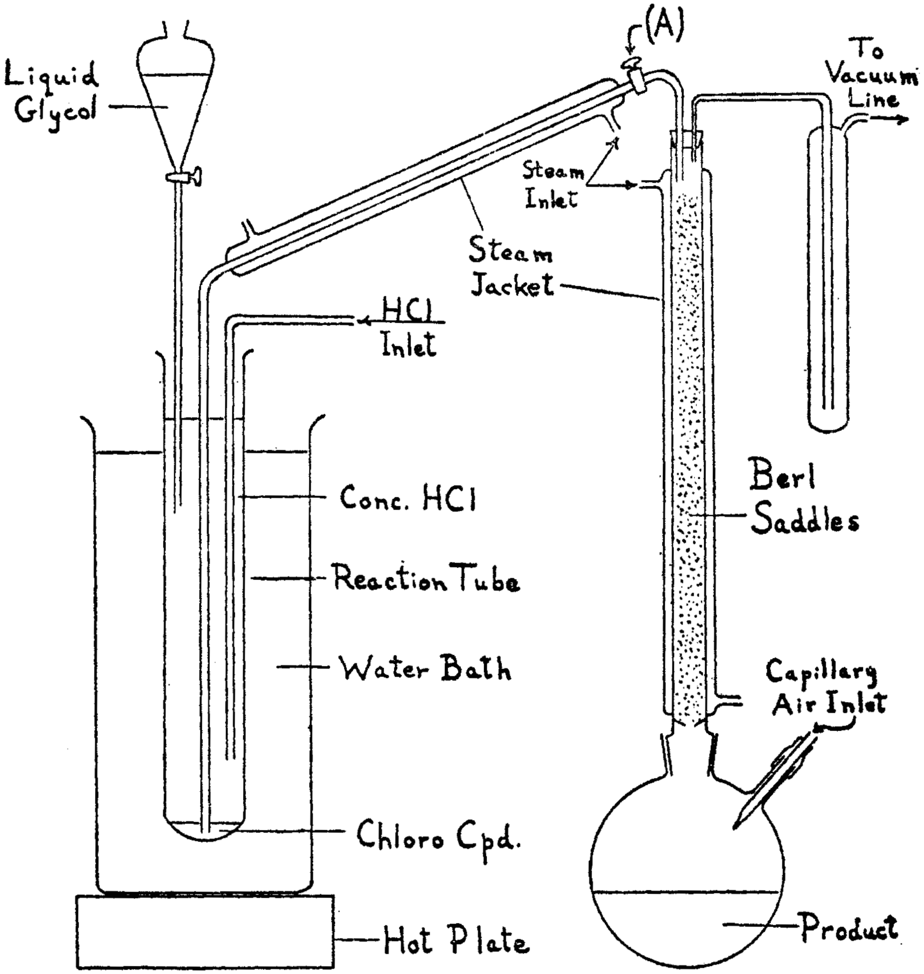


FIG. 1

The residual glycol, which corresponded to an 80% yield, was converted to the chloride

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[3] From a British Chemical Warfare report it appears that a similar procedure was developed independently by Kinnear and Harley-Mason.

by the use of thionyl chloride in chloroform solution (8). When the reaction was complete, the chloroform and excess thionyl chloride were removed at water-pump pressures and the crude chloride fractionally distilled at a pressure of 0.01 mm. The fractions with refractive indices between 1.59 and 1.62 were combined and crystallized from absolute ethanol; the white, crystalline trisulfide melted at 30.5–31.5°; n_D^{20} 1.6110. Mann, Pope, and Vernon (3) report the melting point 27°. From 600 g. of crude chloride about 200 g. of the pure solid was obtained.

Anal. Calc'd for $C_4H_8Cl_2S_3$: C, 21.54; H, 3.62; Cl, 31.80; S, 43.13.
Found: C, 21.78; H, 3.57; Cl, 31.55, 31.76; S, 43.14.

Preparation of bis(2-chloroethyl) pentasulfide. a. *From Levinstein mustard gas.*[3] A sample of Levinstein mustard gas (1210 g.) was stirred vigorously with water for eleven days. The water was changed frequently during this period until finally the hydrogen ion concentration became negligible, indicating the hydrolysis of *bis*(2-chloroethyl) sulfide to be complete. The unhydrolyzed polysulfide residue, amounting to 29.1% of the total weight of mustard used, was dissolved in Cellosolve. The precipitated sulfur (77.5 g.) and a small amount of viscous oil were removed by filtration and the Cellosolve subsequently washed out with water. The composition of the polysulfide originally present was $(ClCH_2CH_2)_2S_{7.6}$, based on the weight-percent of residue obtained and $(ClCH_2CH_2)_2S_{7.5}$, based on the amount of sulfur obtained by stripping. The crude pentasulfide (n_D^{20} 1.6763) had the following composition.

Anal. Calc'd for $C_4H_8Cl_2S_5$: C, 16.72; H, 2.81.
Found: C, 17.93; H, 2.74.

It was purified by steam distillation (to remove any disulfide and trisulfide present) followed by stripping with Cellosolve. During the steam distillation, fractions of the distillate were collected and the refractive index of the oil was determined. When the index of the oil reached 1.61 (approximately the value for the trisulfide) the distillation was halted. The weight of oil was 10% of the total weight of the crude pentasulfide taken. The residue had the index 1.685. After being stripped with Cellosolve, the water-insoluble oil was dried in ether solution and the ether removed *in vacuo* at 30°. The light amber pentasulfide amounted to 70% of the original crude pentasulfide; n_D^{20} 1.6853; d_4^{20} 1.5013. It did not freeze at −80°.

Anal. Calc'd for $C_4H_8Cl_2S_5$: C, 16.72; H, 2.81; Cl, 24.74; S, 55.74.
Found: C, 16.98; H, 2.82; Cl, 23.76; S, 56.64.

b. *By sulfurization of bis(2-chloroethyl) trisulfide with sulfur.* The trisulfide was heated with sulfur in the molecular proportions to produce the penta-, hexa-, octa-, and decasulfides. The heating was varied from six to thirty-six hours and the temperature from 115° to 140°. In every case a homogeneous product was obtained, which when allowed to stand in a refrigerator for several days deposited sulfur. The amount of sulfur deposited closely approached that taken in excess of the amount required to produce the pentasulfide. Several samples, the composition of which had approached that of the pentasulfide, were observed to deposit no more sulfur over a period of three weeks. Treatment of the polysulfides with Cellosolve as described in the previous experiment removed further small amounts of sulfur. The resulting pale yellow oils had properties (refractive index, density, and composition) which corresponded closely to those of *bis*(2-chloroethyl) pentasulfide.

c. *By sulfurization of bis(2-chloroethyl) disulfide with sulfur.* It was found that when the disulfide was heated with sulfur under conditions which were adequate to sulfurize the trisulfide, most of the sulfur was reprecipitated on cooling. However, when the mixture was heated at higher temperatures (145–150°) for twenty to thirty hours a polysulfide was formed which had the same properties as that obtained from *bis*(2-chloroethyl) trisulfide. Here, as before it was observed that sulfur precipitated slowly until the composition of the residual oil approached that of *bis*(2-chloroethyl) pentasulfide.

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[3] This procedure was developed from preliminary experiments conducted by Dr. Orville H. Bullitt, Jr.

Isolation of a high polysulfide from Levinstein mustard. When the residue from the hydrolysis of Levinstein mustard gas is stripped with Cellosolve, there is obtained, in addition to sulfur, a small amount of Cellosolve-insoluble oil. A portion of this dark, viscous oil was filtered, washed well with water, and dried in carbon disulfide solution over magnesium sulfate. After removal of the drying agent and solvent a sample was analyzed.

Anal. Calc'd for $C_4H_8Cl_2S_{11}$: C, 10.0; H, 1.7; S, 73.5; Cl, 14.8.
Found: C, 10.1; H, 1.8; S, 75.9; Cl, 14.7.

The material slowly deposited crystalline sulfur on standing.

Preparation of methyl tetrasulfide.[4] This compound was prepared by a modification of the method of Levi and Baroni (9) for ethyl tetrasulfide. Equimolar quantities of sulfur and sulfur monochloride were heated on a steam-cone for five hours. Carbon disulfide was added and methyl mercaptan introduced. The addition was continued for some time after the evolution of hydrogen chloride had ceased. The carbon disulfide was evaporated, and the residue was heated for sixteen hours and distilled *in vacuo*. The fraction boiling at 56–69° (1 mm.) was collected; n_D^{20} 1.6403. The yield was 25%. Redistillation gave the pure tetrasulfide; b.p. 68–70° (1.5 mm.); n_D^{20} 1.6621; d_4^{25} 1.3008.

Anal. Calc'd for $C_2H_6S_4$: C, 15.20; H, 3.81.
Found: C, 15.43; H, 3.68.

Attempted sulfurization of bis(2-chloroethyl) disulfide with methyl tetrasulfide. The disulfide (0.05 mole) was mixed with methyl tetrasulfide (0.15 mole) and treated in a manner similar to that described for the sulfurization of *bis*(2-chloroethyl) trisulfide. At a bath temperature of 90° and a pressure of 1 mm. the liquid distilled completely. The refractive indices of the various fractions indicated that they consisted of mixtures of *bis*(2-chloroethyl) disulfide and methyl polysulfides.

Sulfurization of bis(2-chloroethyl) trisulfide with methyl tetrasulfide. A mixture of methyl tetrasulfide (0.14 mole) and *bis*(2-chloroethyl) trisulfide (0.06 mole) was warmed at 35–40° (3–4 mm.) in a distillation apparatus. After a few hours the receiver, which was immersed in Dry Ice, contained material of refractive index, n_D^{20} 1.5999 (methyl trisulfide, n_D^{20} 1.5890). The slow distillation was continued at 60° (1 mm.) for five hours; distillate n_D^{20} 1.6180; residue n_D^{20} 1.6684. Finally the temperature was increased to 120° for two hours at the same pressure. The oil which remained, n_D^{20} 1.6840, had only a slight odor of methyl polysulfide. It was dried in ether solution and the solvent evaporated. The yield of pale yellow pentasulfide was 50%; n_D^{20} 1.6850.

Sulfurization of bis(2-chloroethyl) pentasulfide with methyl tetrasulfide. A mixture of *bis*(2-chloroethyl) pentasulfide and two molecular equivalents of methyl tetrasulfide was heated at 75° for four hours, and then distilled at water-pump pressure in a nitrogen atmosphere. Finally, the temperature of the bath was raised to 130° for several hours. The residue was a clear, brown, viscous liquid ($n_D^{20} > 1.74$) whose weight corresponded to a 97% yield of *bis*(2-chloroethyl) heptasulfide. It deposited sulfur upon standing overnight. The resulting oil was shown by analysis to have an average composition of $(ClCH_2CH_2)_2S_{6.3}$.

Anal. Calc'd for $C_4H_8Cl_2S_7$: C, 13.66; H, 2.28.
Found: C, 14.57; H, 2.46.

This material was insoluble in acetone, alcohol, and ether, but soluble in chloroform and carbon disulfide. Stripping with moist ammonia (see below) reconverted it to the original *bis*(2-chloroethyl) pentasulfide (n_D^{20} 1.6740).

The above experiment was repeated using amounts of methyl tetrasulfide calculated to yield the octasulfide and nonasulfide. The results were analogous, except that the polysulfides formed were relatively less stable. For example, the nonasulfide deposited sulfur on standing only a few hours to give a compound whose composition corresponded closely to that of *bis*(2-chloroethyl) heptasulfide.

Anal. Found: C, 13.89; H, 2.15.

Autosulfurization of bis(2-chloroethyl) pentasulfide. The residue from the steam distilla-

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[4] This compound was prepared by Dr. Curtis W. Smith.

tion of a 10-g. sample of the pentasulfide, which had been distilled until 400 ml. of aqueous distillate had been collected, was dried by filtration and allowed to stand for one week. No sulfur precipitated, so the clear, amber oil (n_D^{20} 1.702) was submitted for analysis. It had the average composition $(ClCH_2CH_2)_2S_{5.5}$.

Anal. Calc'd for $C_4H_8Cl_2S_{5.55}$: C, 15.80; H, 2.64.
Found: C, 15.80; H, 2.67.

Another sample of the pentasulfide which had been steam-distilled more extensively yielded a residue whose composition corresponded to $(ClCH_2CH_2)_2S_{5.8}$.

Anal. Calc'd for $(ClCH_2CH_2)_2S_{5.8}$: C, 15.36; H, 2.54.
Found: C, 15.38; H, 2.49.

Sulfurization of bis(2-chloroethyl) pentasulfide with sulfur. Ten grams of the pentasulfide was heated with 9.0 g. of sulfur at 110° for three days. When the mixture was cooled and allowed to stand for several hours, it deposited a large amount of sulfur which was removed by filtration. The filtrate was shaken with Cellosolve, and the residue extracted several times with ether; the insoluble oil was dried *in vacuo*. The composition of the resultant red, viscous oil approximated that of the dodecasulfide.

Anal. Calc'd for $C_4H_8Cl_2S_{12}$: C, 9.17; H, 1.57.
Found: C, 9.43; H, 1.52.

Solubility of sulfur in polysulfides. a. *bis(2-chloroethyl) trisulfide.* Finely divided sulfur, obtained by filtration of a suspension of "milk of sulfur" (10), was shaken with a sample of the trisulfide (n_D^{20} 1.6125) for several days. The amount which dissolved was estimated by difference to be 4.58%. The resulting solution (n_D^{20} 1.6216) was stripped with Cellosolve. The amount of sulfur recovered indicated a solubility of 4.18%. The average of these results indicates that *bis*(2-chloroethyl) trisulfide dissolved up to 4.4% of its weight of sulfur, which is equivalent to one-third of an atom.

b. *bis(2-Chloroethyl) pentasulfide.* In a similar manner a sample of crude pentasulfide (n_D^{20} 1.6758) dissolved up to 7.4% (average value) of its weight of sulfur. This corresponds approximately to two-thirds of an atom. The index of refraction of the saturated solution was n_D^{20} 1.6850.

Stripping of polysulfides. It has already been shown in the preparation of *bis*(2-chloroethyl) pentasulfide from Levinstein mustard gas that the higher polysulfides are stripped to the pentasulfide with Cellosolve. Stripping of polysulfides also has been accomplished by the following methods.

a. *With moist ammonia.* A sample of *bis*(2-chloroethyl) pentasulfide, synthesized from the trisulfide, was treated with moist ammonia gas for several hours. No sulfur precipitated.

In a similar manner a portion of the polysulfide residue remaining from the exhaustive hydrolysis of Levinstein mustard gas was treated with moist ammonia gas for several hours. The sulfur which precipitated was removed by filtration. The composition of the stripped residue, n_D^{20} 1.672, was that of the pentasulfide.

Anal. Calc'd for $C_4H_8Cl_2S_5$: Cl, 24.74. Found: Cl, 24.8.

In another experiment it was noticed that subsequent treatment of the stripped residue with Cellosolve yielded an additional amount of sulfur, 5.2% by weight. This indicates that some sulfur must have remained dissolved in the pentasulfide after treatment with ammonia.

b. *With ammonia in the presence of Cellosolve or ether.* A sample of *bis*(2-chloroethyl) pentasulfide was dissolved in moist ether and the solution was saturated with ammonia. The sulfur which precipitated was removed by filtration and the process repeated until there was no further separation of sulfur, even when the solution was cooled to 0°. The resulting ether solution was dried and the solvent evaporated. The composition of the red oil (n_D^{20} 1.6244) was estimated from the amount of sulfur obtained to be $(ClCH_2CH_2)_2S_{3.5}$. Analysis indicated a composition closer to that of *bis*(2-chloroethyl) trisulfide.

Anal. Calc'd for $C_4H_8Cl_2S_{3.2}$: C, 20.89; H, 3.51.
Found: C, 20.97; H, 3.50.

A similar result was obtained when Cellosolve was used instead of ether. It was found necessary to use at least 40 ml. of Cellosolve in order to strip completely a 15-g. sample of the pentasulfide.

c. *With acetone.* A 4.0-g. sample of *bis*(2-chloroethyl) pentasulfide (n_D^{20} 1.6855) isolated from Levinstein mustard gas was boiled under reflux for two days with 100 ml. of acetone. The precipitated sulfur was removed by filtration and the filtrate allowed to reflux for another two-day period. A small additional amount of sulfur separated. The total weight of sulfur recovered (0.460 g.) indicated the composition of the product to be approximately that of *bis*(2-chloroethyl) tetrasulfide. The refractive index of the oil after removal of the acetone was n_D^{20} 1.6545.

Anal. Calc'd for $C_4H_8Cl_2S_4$: C, 18.92; H, 3.16; Cl, 27.78; S, 50.24.
Found: C, 19.04; H, 3.27; Cl, 26.56; S, 51.11.

A sample of pentasulfide (n_D^{20} 1.6858) obtained from Levinstein mustard gas prepared at 20° was subjected to the same treatment. The amount of sulfur obtained was 0.457 g.; the residual yellow oil, n_D^{20} 1.6480, had the following composition.

Anal. Found: C, 19.45; H, 3.06; S, 50.41.

When the experiment was repeated with a sample of the pentasulfide (n_D^{20} 1.6852) prepared from *bis*(2-chloroethyl) disulfide, 0.460 g. of sulfur again was obtained. The composition of the resulting oil, n_D^{20} 1.6520, again corresponded closely to that of the tetrasulfide.

Anal. Found: C, 19.27; H, 3.34; S, 51.19.

d. *With steam.* Ten-gram samples of *bis*(2-chloroethyl) pentasulfide prepared from Levinstein mustard gas, from *bis*(2-chloroethyl) disulfide and sulfur, and from the trisulfide and sulfur were subjected to steam distillation. In each case a pale yellow oil collected slowly in the receiver. Except for the first few drops, the index of refraction of this oil remained nearly constant. After about 3 ml. of oil had distilled, it was separated, dried in ether solution, and the ether removed. The refractive indices (n_D^{20}) of the distillates from the three different sources were 1.622, 1.605, and 1.611, respectively. One of these oil-distillates (n_D^{20} 1.611) was examined more thoroughly. It melted at 13° and its chlorine content corresponded closely to that of *bis*(2-chloroethyl) trisulfide. (The pure trisulfide melts at 30.5–31.5°; n_D^{20} 1.6110.)

Anal. Calc'd for $C_4H_8Cl_2S_3$: Cl, 31.8 Found: Cl, 31.4.

Stability of bis(2-chloroethyl) trisulfide toward heat. A sample of pure *bis*(2-chloroethyl) trisulfide was placed in a distillation apparatus and heated at 145–160° at a pressure of 0.5 mm., under which conditions the trisulfide would not distil, but any lower-boiling material would be removed. The distillate proved to be *bis*(2-chloroethyl) disulfide, n_D^{20} 1.5690. The residue in the distilling flask was shown to be a mixture of sulfur and polysulfides from which no trisulfide could be isolated.

Attempted hydrolysis of bis(2-chloroethyl) disulfide and trisulfide. Five grams of the disulfide and five grams of the trisulfide each were shaken with 100-ml. portions of water for one week under conditions similar to those employed in the hydrolysis of Levinstein mustard gas. Very little hydroysis occurred, as evidenced by the low chloride-ion concentration in the aqueous layer.

Estimation of the amount of bis(2-chloroethyl) disulfide present in Levinstein mustard gas. A 1208-g. sample of Levinstein mustard gas was subjected to exhaustive hydrolysis and the residue stripped with Cellosolve as in the preparation of *bis*(2-chloroethyl) pentasulfide. It was assumed that the stripped residue contained no polysulfides other than the disulfide and the pentasulfide. This assumption is believed to be a reasonable one in view of the ease of sulfurization of the trisulfide, etc. by the higher polysulfides. This residue weighed 288 g.; n_D^{20} 1.6740. It was observed experimentally that an almost linear relationship exists between refractive index and weight-per cent for mixtures of the di- and penta-sulfide. On this basis, with n_D^{20} 1.6835 for the pentasulfide and n_D^{20} 1.5656 for the disulfide, the stripped residue must have contained 7.5% of *bis*(2-chloroethyl) disulfide. Therefore, the sample of Levinstein mustard gas used contained 1.8%.

The stripped residue was submitted to steam distillation until the refractive index of the oil distillate reached that of *bis*(2-chloroethyl) trisulfide, which undoubtedly was being formed from the stripping of the pentasulfide (see above). From the weight and refractive index of the oil distillate the amount of disulfide present was estimated and found to be equivalent to about 1% of the original Levinstein mustard gas. The lower result in this case can be attributed to losses due to volatilization and partial hydrolysis of the disulfide at 100°. The total loss in the steam distillation was 5%.

Reactions of bis(2-chloroethyl) disulfide. a. *With thiosalicylic acid.* Three and one-tenth grams of the disulfide was added slowly to a solution of 5.5 g. of commercial 90% thiosalicylic acid and 2.6 g. of sodium hydroxide in 150 ml. of 95% ethanol. The mixture was heated under reflux for one hour, allowed to cool, and poured into 400 ml. of water. Acidification with dilute hydrochloric acid precipitated the *bis*(2-thiosalicylethyl) disulfide. It was collected on a filter and dissolved in a solution of sodium bicarbonate. The salt solution was extracted with ether and the disalicyl derivative reprecipitated by the addition of dilute acid. Two recrystallizations from ethanol gave 5.1 g. of product melting at 175–182°. After repeated recrystallization from ethanol the compound melted at 185–186°.

Anal. Calc'd for $C_{18}H_{18}O_4S_4$: C, 50.67; H, 4.25.
Found: C, 50.89; H, 4.21.

b. *With potassium morpholyldithiocarbamate.* A solution of 7 g. of the disulfide in 50 ml. of methanol was added, with stirring, to a solution of 16.5 g. of potassium morpholyldithiocarbamate (11) in 125 ml. of methanol and 15 ml. of water. The mixture was warmed on a steam-cone for two hours and allowed to stand overnight. The precipitate was removed by filtration and the filtrate concentrated to yield a second crop of crystals. The product crystallized from 95% ethanol in fine needles; m.p. 109–110°; yield 15 g., or 92%.

Anal. Calc'd for $C_{14}H_{24}N_2O_2S_6$: C, 37.81; H, 5.42.
Found: C, 37.94; H, 5.27.

c. *With piperidine.* The disulfide was added to an excess of piperidine in boiling petroleum ether solution and the mixture allowed to reflux for thirty-six hours. The piperidine hydrochloride was removed and the filtrate washed with water to get rid of excess piperidine. The *bis*[2-(N-piperidyl)ethyl] disulfide was extracted with dilute hydrochloric acid and recovered by treating the acid solution with sodium hydroxide, followed by extraction with petroleum ether. After evaporation of the solvent the product remained as an oil; n_D^{28} 1.5478; yield 53%.

Two grams of the oil was dissolved in petroleum ether and treated with dry hydrogen chloride. The dihydrochloride, which separated as a white solid, was immediately collected and recrystallized from absolute ethanol; m.p. 236°.

Anal. Calc'd for $C_{14}H_{10}Cl_2N_2S_2$: C, 46.52; H, 8.37.
Found: C, 43.54; H, 8.00.

From the analysis it seemed probable that 2-chloroethyl 2-(N-piperidylethyl) disulfide was present as a contaminant.

SUMMARY

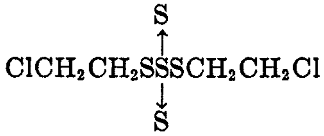
Methods have been given for the preparation of *bis*(2-chloroethyl) disulfide, trisulfide, and pentasulfide.

Exhaustive hydrolysis of Levinstein mustard gas has been found to yield a residue which is thought to be a mixture of higher *bis*(2-chloroethyl) polysulfides. The pentasulfide has been prepared by subjecting this mixture to steam distillation and to stripping with Cellosolve or ammonia. The same compound has been made by sulfurization of the corresponding di- and tri-sulfides with sulfur and of the trisulfide with methyl tetrasulfide.

bis(2-Chloroethyl) pentasulfide has been stripped to the trisulfide by ammonia

in the presence of Cellosolve or ether and to the tetrasulfide by boiling acetone. Steam distillation of the pentasulfide was found to cause its degradation to the trisulfide.

It has been concluded that both the disulfide and trisulfide possess the linear rather than the angular structure. The following structure is proposed for the pentasulfide.



$$\mathrm{ClCH_2CH_2S\overset{\overset{S}{\uparrow}}{\underset{\underset{S}{\downarrow}}{S}}SCH_2CH_2Cl}$$

Urbana, Ill.

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