equal molal quantity of trimethylene oxide with 5 drops of 40% sulfuric acid and heated for six hours on the steam-bath. The benzylethylene oxide was recovered unchanged. This is in accordance with the results obtained by Wurtz with ethylene oxide and acetaldehyde.[5]

Summary

1. Few of the dioxolanes based on phenyl-, methylphenyl- and phenoxypropanediol have a marked agreeable odor.
2. None of the compounds has a jasmine-like odor.

BURLINGTON, VERMONT

[CONTRIBUTION FROM THE MEDICAL RESEARCH DIVISION, CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]

CHLORINATION OF β,β-DICHLORO-ETHYL SULFIDE. I[1]

BY W. E. LAWSON AND T. P. DAWSON

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The only feasible methods for the destruction of Mustard Gas, or β,β-dichloro-ethyl sulfide, involve the use of chlorine. Small amounts in the laboratory may be oxidized with nitric acid to the sulfoxide, which is non-vesicant, that is, does not cause blistering of the skin, and under certain conditions clothing may be demustardized with live steam, but these are practically the only instances of other means for its destruction.

The ease and rapidity with which β,β-dichloro-ethyl sulfide is chlorinated suggests a preliminary addition of the chlorine followed by a molecular rearrangement involving substitution of one atom of chlorine and elimination of one molecule of hydrogen chloride[2] according to the equations

$$(ClCH_2CH_2)_2S + Cl_2 \longrightarrow (ClCH_2CH_2)_2SCl_2$$
$$(ClCH_2CH_2)_2SCl_2 \longrightarrow ClCH_2CHClSCH_2CH_2Cl + HCl$$

Certain facts that give support to this view have already been published. The sulfide is promptly oxidized to the sulfoxide by nitric acid;[3] it reacts with chloramine-T to form an addition product, $(ClCH_2CH_2)_2S = NSO_2\text{-}C_6H_4CH_3$;[4] and it adds bromine to form a dibromide and perbromide.[5]

One paper on the chlorination of β,β-dichloro-ethyl sulfide has appeared, besides a number of chemical warfare studies. Mann and Pope[6] chlorinated the compound to different stages with gaseous chlorine and

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[5] Wurtz, *Ann.*, 120, 328 (1861).

[1] Published by permission of the Chief of the Chemical Warfare Service.

[2] It is with pleasure that we acknowledge that this suggestion was first made by Professor E. Emmet Reid of Johns Hopkins University in a discussion with one of us on the chlorination of Mustard Gas.

[3] Helfrich and Reid, THIS JOURNAL, 42, 1208 (1920).

[4] Mann and Pope, *J. Chem. Soc.*, 121, 1052 (1922).

[5] Gibson and Pope, *ibid.*, 117, 271 (1920).

[6] Mann and Pope, *J. Chem. Soc.*, 121, 594 (1922).

isolated three compounds which they termed α,β,β′-trichlorodiethyl sulfide, α,β,β,β′-tetrachlorodiethyl sulfide and α,α,β,β,β,β′-hexachlorodiethyl sulfide. McCrumb and Reeves[7] found that more than the theoretical quantity of hydrogen chloride was evolved on chlorination, and isolated a chloro-ethylchlorovinyl sulfide, without, however, determining the position of the chlorine atoms. Our own experience leads us to believe that it was a mixture of two isomeric compounds. Pfanstiel and Peakes[8] also noted the evolution of hydrogen chloride in more than the theoretical amount on chlorinating the sulfide.

Our study of the chlorination of β,β-dichloro-ethyl sulfide was divided into three parts: (1) isolation of the intermediate addition product in chlorination; (2) preparation of the lower chlorinated derivatives; (3) tabulation of the different compounds theoretically possible in chlorination.

Isolation of Intermediate Addition Product

On treating a solution of β,β-dichloro-ethyl sulfide in carbon tetrachloride with chlorine at a temperature of —5 to 0°, the intermediate addition product in the process of chlorination, β,β-dichloro-ethyl sulfonium chloride, $(ClCH_2CH_2)_2SCl_2$, crystallizes from solution in white needles. The chlorine may be added directly or as a solution in carbon tetrachloride. No hydrogen chloride is liberated during this treatment. The compound is unstable at room temperature. It decomposes simultaneously in two ways, forming dichloro-ethyl sulfoxide and trichlorodiethyl sulfide, the main reaction being the formation of the latter. Solution in 95% alcohol, however, yields chiefly the sulfoxide.

Preparation of Chlorinated Sulfides

It was considered that the isolation and decomposition of β,β-dichlorodiethyl sulfonium chloride would give a very pure α,β,β′-trichlorodiethyl sulfide, one probably less contaminated by other chlorinated derivatives than the compound described as such by Mann and Pope.[6] On distillation of this relatively pure trichlorodiethyl sulfide, great quantities of hydrogen chloride were evolved and no definite boiling point was observed. After ten distillations, two distinct fractions were obtained boiling at 73.5–74.5° (4 mm.) and 69.5–70.5° (4 mm.), respectively. Analysis showed both to have the same empirical formula, corresponding to chloroethylchlorovinyl sulfide. Both compounds were oxidized by dilute nitric acid to form β-chloro-ethane sulfonic acid, from which ammonium β-chloro-ethane sulfonate was obtained in small needles melting at 200°. This proved the presence of a β-chloro-ethyl group in each of the above compounds and left only the position of the chlorine on the vinyl group

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[7] McCrumb and Reeves, Chemical Warfare Report.

[8] Pfanstiel and Peakes, Chemical Warfare Report.

in doubt. The higher-boiling compound had a sweet odor; the lower-boiling isomer had the penetrating odor of α,α-dichloro-ethyl sulfide, though the odor was not as strong. The α-chlorovinyl derivative should have a lower boiling point than the corresponding β-chlorovinyl compound. Both compounds were treated with the sodium salt of β-naphthol; the β-chloro-ethyl-β-chlorovinyl sulfide reacted with two moles, while the β-chloro-ethyl-α-chlorovinyl sulfide reacted with but one.

This would seem to complete the proof of structure, but as the proof was inferential rather than direct, the preparation and decomposition of α-bromo-β,β′-dichlorodiethyl sulfide was carried out following the method described for its chlorine analog. Decomposition during distillation was very great, but there was finally obtained a compound free from bromine having a boiling point of 77–77.5° (4 mm.), as compared with 73.5–74.5° (4 mm.) for the same compound in a slightly purer state made by chlorination instead of bromination. The only possible formula for this compound is β-chloro-ethyl-β-chlorovinyl sulfide, which is in accord with the inferential proof already given.

Compounds Theoretically Obtainable by Chlorination of Dichloro-ethyl Sulfide

The instability of α,β,β′-trichlorodiethyl sulfide and its decomposition on distillation to give the two isomers, β-chloro-ethyl-β-chlorovinyl and β-chloro-ethyl-α-chlorovinyl sulfides, affords an explanation for the failure of Mann and Pope[6] to isolate pentachlorodiethyl sulfide. They considered their products to have been α,β,β′-trichlorodiethyl sulfide, analyzing 2.6% hydrogen with a theoretical value of 3.6; α,β,β,β′-tetrachlorodiethyl sulfide, analyzing 1.8% hydrogen with a theoretical value of 2.6; and α,α,β,β,β,β′-hexachlorodiethyl sulfide, analyzing 1.3% hydrogen with a theoretical value of 1.4.

We have found that α,β,β′-trichlorodiethyl sulfide is so unstable that it is absolutely impossible to isolate it by distillation at pressures as low as 3.5 mm. of mercury. The compound isolated by Mann and Pope could not, therefore, have been the trichlorodiethyl sulfide. If, however, we postulate the splitting out of hydrogen chloride from tetrachlorodiethyl sulfide to give a chloro-ethyldichlorovinyl sulfide, and if we explain similarly the decomposition of pentachlorodiethyl sulfide to give chloro-ethyltrichlorovinyl sulfide, there is afforded an explanation for the low hydrogen values obtained by them in analyzing their tri- and tetrachlorinated derivatives, and also for their inability to isolate the pentachloro derivative.

By assuming the instability of the chlorinated ethyl group after chlorination of β,β-dichloro-ethyl sulfide, the following list of compounds is theoretically possible.

TABLE I

CHLORINATION OF DICHLORO-ETHYL SULFIDE (1)

Initial comp., no.	Treatment	Compound formed No.	Formula	See note	B. p., °C. (corr.) 4 mm. pressure
I	$\mathrm{Cl_2}$ by subst.	II	$\mathrm{ClCH_2CHClSCH_2CH_2Cl}$	(1)	Unstable
II	By vac. dist.	III	$\mathrm{ClCH:CHSCH_2CH_2Cl}$	(1)	73.5–74.5
		IV	$\mathrm{CH_2:CClSCH_2CH_2Cl}$	(1)	69.5–70.5
III	$\mathrm{Cl_2}$ by add.	V	$\mathrm{Cl_2CHCHClSCH_2CH_2Cl}$	(3)	118.5–119/3.5
IV	$\mathrm{Cl_2}$ by add.	VI	$\mathrm{ClCH_2CCl_2SCH_2CH_2Cl}$	(4)	Unstable
I	$\mathrm{2Cl_2}$ by subst.	VI			
V	By vac. dist.	VII	$\mathrm{ClCH:CClSCH_2CH_2Cl}$	(2)	79.5–80.5
		VIII	$\mathrm{Cl_2C:CHSCH_2CH_2Cl}$	(3)	90–91/3
VI	By vac. dist.	VII			
VII	$\mathrm{Cl_2}$ by add.	IX	$\mathrm{Cl_2CHCCl_2SCH_2CH_2Cl}$	(3)	Unstable
VIII	$\mathrm{Cl_2}$ by add.	X	$\mathrm{Cl_3CCHClSCH_2CH_2Cl}$	(4)	Unstable
I	$\mathrm{3Cl_2}$ by subst.	IX			
IX, X	By vac. dist.	XI	$\mathrm{Cl_2C:CClSCH_2CH_2Cl}$	(2)	98.0–98.5
XI	$\mathrm{Cl_2}$ by add.	XII	$\mathrm{Cl_3CCCl_2SCH_2CH_2Cl}$	(2)	131–132
I	$\mathrm{4Cl_2}$ by subst.	XII			

(1) Prepared in this paper.
(2) Prepared by Mann and Pope.
(3) Prepared but will be published in subsequent paper.
(4) Not prepared.

Both of the chloro-ethyl chlorovinyl compounds are irritating and slightly vesicant, but by no means comparable to their parent compound, β,β-dichloro-ethyl sulfide. The higher chlorinated derivatives, saturated or unsaturated, are non-vesicant. This is also in accord with the findings of Mann and Pope.

Experimental Part

Preparation of β,β-Dichloro-ethyl Sulfonium Chloride

A sample of β,β-dichloro-ethyl sulfide weighing 15.98 g. was diluted with 50 cc. of pure, dry carbon tetrachloride in a 500cc. Pyrex boiling flask whose paraffined stopper bore a stirrer, thermometer, dropping funnel, and an exit tube filled with calcium chloride. A solution of chlorine in dry carbon tetrachloride containing 7.13 g. of chlorine was also prepared. Flasks and solutions were chilled to —5°, after which the chlorine solution was slowly added, the temperature being maintained at —5 to 0°. A white precipitate appeared very soon after the addition of the chlorine solution was begun and increased in amount as more chlorine was added. The precipitate was filtered off on a Büchner funnel, washed with cold carbon tetrachloride, and transferred to a small Erlenmeyer flask. In about three minutes the mass began to liquefy; the reaction increased with rapidity and was complete in about two more minutes, leaving a colorless liquid. Hydrogen chloride was evolved in great quantity during the decomposition but was not evident before. The reaction was slightly endothermic. This decomposition does not take place when a thin layer is placed in a desiccator or spread out on filter paper in the open air. Instead, the chloride was found to be slowly converted to the sulfoxide. This suggests that the chlorination reaction may be catalyzed by hydrogen chloride. Alcohol increases sulfoxide formation, for pure sulfoxide was obtained by dissolving the sulfonium chloride in 95% alcohol.

Samples of the solid addition product were weighed into dry tared flasks and connected with bubblers containing sodium hydroxide solution. Dry air was used to sweep the liberated hydrogen chloride into the standard alkali solution. Only 64 to 73% of the theoretical amount of hydrogen chloride was collected, showing that considerable decomposition had taken place during the isolation and weighing of the material. This was confirmed by immersing the addition product in sodium hydroxide solution. After standing for ten days so as to insure complete hydrolysis of the chlorine, but 62.5% was accounted for.

Preparation of Chlorinated Sulfides

A modified Dufton column[9] of Pyrex glass was constructed, 57 cm. in length from constriction to side outlet and with an internal diameter of 18 mm. The column was well lagged with asbestos paper and provided with a nichrome wire heating element. The distilling flask was immersed in a Wood's metal bath.

β,β-Dichloro-ethyl sulfide was chlorinated in four lots of 100 g. each diluted with 300 cc. of dry carbon tetrachloride. Chlorine gas was passed in at about 35 cc. per minute, the solution being stirred vigorously throughout the period of addition and maintained at a temperature below 35°. The reaction products from the four runs were combined, freed from carbon tetrachloride by distilling under reduced pressure, then distilled twice at 5 to 6 mm. pressure; yield, 358 g.

This product was then distilled through the Dufton column at the rate of one drop every three to four seconds; yield, 284 g. After seven more distillations through the column, collecting separate fractions every two or three degrees, the isomers were finally separated in a comparatively pure state: β-chloro-ethyl-β-chlorovinyl sulfide, b. p. 73.5–74.5° (4 mm.), yield 130 g.; β-chloro-ethyl-α-chlorovinyl sulfide, b. p. 69.5–70.5° (4 mm.), yield 60 g.

The greater stability of the β-halogen, indicated above by the respective yields of the two isomers, was also shown by an analysis of the exit gases from the decomposition of α-bromo-β,β'-dichlorodiethyl sulfide. This showed 74% of hydrogen bromide and 26% of hydrogen chloride.

The following new compounds were prepared and identified in connection with this study.

β,β-Dichloro-ethylsulfonium Chloride.—Formed by the addition of chlorine to β,β-dichloro-ethyl sulfide at about 0°. Colorless needles; insoluble in carbon tetrachloride; decomposes at room temperature to form α,β,β'-trichlorodiethyl sulfide and hydrogen chloride, the hydrogen chloride apparently acting as a catalyst to speed up the reaction. In the presence of water or water vapor another reaction takes place, giving β,β-dichloro-ethyl sulfoxide and hydrogen chloride.

α,β,β'-Trichlorodiethyl Sulfide.—Colorless liquid formed by the decomposition of β,β-dichloro-ethyl sulfonium chloride. It decomposes slowly at room temperature with evolution of hydrogen chloride and cannot be distilled at a pressure as low as 3.5 mm.; $d_4^{20} = 1.4038$; $n_D^{22.5} = 1.5309$.

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[9] Dufton, *J. Soc. Chem. Ind.*, **38**, 45 (1919).

β-Chloro-ethyl-β-chlorovinyl Sulfide.—Colorless oil obtained by repeated fractionation of the distillation product of α,β,β′-trichlorodiethyl sulfide; b. p. 73.5–74.5° (4 mm.); d_4^{20} = 1.3280, $n^{22.5}_{D}$ = 1.5483.

Anal. Calcd., S, 20.42. Found: 20.03, 19.80. Calcd., Cl, 45.16. Found: 46.11, 46.27.

It was also obtained by repeated distillation of α-bromo-β,β′-dichlorodiethyl sulfide, but the purification was more difficult; b. p. 77.0–77.7° (4 mm.).

Anal. Calcd., S, 20.42. Found: 20.46, 20.35. Calcd., Cl, 45.16. Found: 43.87, 43.91; Br, none.

β-Chloro-ethyl-α-chlorovinyl Sulfide.—Colorless liquid obtained with the β-chlorovinyl compound by repeated fractionation of the distillation product of α,β,β′-trichlorodiethyl sulfide, b. p. 69.5–70.5° (4 mm.); d_4^{20} = 1.3193; $n^{22.5}_{D}$ = 1.550. It is produced in only about one-half the quantity of its β-chlorovinyl isomer.

Anal. Calcd., S, 20.42. Found: 20.19, 20.27. Calcd., Cl, 45.16. Found: 45.10, 44.99.

α-Bromo-β,β′-dichlorodiethyl Sulfide.—Yellow oil obtained from β,β-dichloroethyl sulfonium bromide by allowing it to stand for several days in a flask. When kept in a desiccator this decomposition was found not to take place. The compound is unstable even at room temperature and shortly decomposes into a black, tarry mass. When distilled it decomposes to give a variety of products of which only β-chloro-ethyl-β-chlorovinyl sulfide has been isolated.

***Bis*(β-naphthoxy-)-ethylvinyl Sulfide.**—Crystals, tiny, diamond-shaped plates, obtained by refluxing a solution of β-chloro-ethyl-β-chlorovinyl sulfide in absolute alcohol with sodium naphthionate for twelve hours on the water-bath and recrystallizing the product from hot absolute alcohol; m. p. 129.5° (corr.).

Anal. Calcd., S, 9.40. Found: 8.51. Cl, none. Found: none by qualitative test.

β-Naphthoxy-ethyl-α-chlorovinyl Sulfide.—Secured by treatment of β-chloro-ethyl-α-chlorovinyl sulfide with sodium naphthionate in the same manner as described above. The oil at first obtained gives crystals on treatment with petroleum ether; m. p. 56–57° (corr.).

Anal. Calcd., S, 12.90. Cl present by qualitative test (not enough sample for both Cl and S analyses).

Summary

1. It has been shown that β,β-dichloro-ethyl sulfonium chloride is the intermediate addition product in the chlorination of β,β-dichloroethyl sulfide and that it decomposes to give α,β,β′-trichlorodiethyl sulfide.

2. Distillation of α,β,β′-trichlorodiethyl sulfide gives two isomeric vinyl compounds, β-chloro-ethyl-β-chlorovinyl and β-chloro-ethyl-α-chlorovinyl sulfide. These have been isolated and proof of their structure has been obtained.

3. On the basis of the splitting out of hydrogen chloride to give the corresponding vinyl compound, there has been formulated a theory to account for the absence of pentachlorodiethyl sulfide from the chlorination product of β,β-dichloro-ethyl sulfide obtained by Mann and Pope. In accordance with this theory, the two lower chlorinated products obtained by them were chloro-ethylchlorovinyl sulfides. Their analyses check such formulas very closely.

4. A number of the chlorinated and brominated products from β,β-dichloro-ethyl sulfide together with some of their derivatives have been prepared.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE MEDICAL RESEARCH DIVISION, CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]

CHLORINATION OF β,β-DICHLORO-ETHYL SULFIDE. II[1]

BY T. P. DAWSON AND W. E. LAWSON

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In a previous article[2] there was given a table showing the total number of compounds theoretically possible on treatment of β,β-dichloro-ethyl sulfide with chlorine. The hypothesis on which this table was based is, in brief, that β,β-dichloro-ethyl sulfide will react with one, two, three, or four molecules of chlorine to give the corresponding tri-, tetra-, penta-, and hexachloro derivatives, in each of which only one ethyl group takes part in the reaction. On distillation of the three lower chlorinated compounds one molecule of hydrogen chloride splits out to give a chloro-ethyl mono-, di-, or tri-chlorovinyl sulfide. The chlorine may split out from either the alpha or beta position. The hexachloro product, having no hydrogen in the chlorinated ethyl group, distils unchanged.

This article describes the preparation of practically all of the compounds theoretically possible which were not given in the first paper, that is, the tetra-, penta-, and hexachlorodiethyl sulfides and the tri- and tetrachloro-ethylvinyl sulfides. None of the compounds is vesicant, that is, has skin-blistering properties.

Tetrachlorodiethyl Sulfide and its Decomposition Products

According to the above hypothesis, two tetrachloro isomers are possible, with the chlorine in the $\alpha,\alpha,\beta,\beta'$- and $\alpha,\beta,\beta,\beta'$-positions, respectively. They may be made by the addition of one molecule of chlorine to the respective unsaturated dichloro derivative. The $\alpha,\alpha,\beta,\beta'$-isomer may also be prepared by treatment of β,β-dichloro-ethyl sulfide with two equivalents of chlorine, both chlorine atoms substituting in the alpha position. This isomer is so unstable that when distilled it breaks down completely into β-chloro-ethyl-α,β-dichlorovinyl sulfide. No isomer of this vinyl compound is possible since hydrogen atoms are present only on the beta carbon of the saturated parent compound. A high yield is secured.

On treating a mixture of the two chloro-ethylchlorovinyl isomers with

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[1] Published by permission of the Chief of the Chemical Warfare Service.

[2] Lawson and Dawson, THIS JOURNAL, **49**, 3119 (1927).