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

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

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

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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 tetra-chloro-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 α,α,β,β′- and α,β,β,β′-positions, respectively. They may be made by the addition of one molecule of chlorine to the respective unsaturated dichloro derivative. The α,α,β,β′-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).

one molar equivalent of chlorine and distilling the reaction product, there is obtained a good yield of β-chloro-ethyl-α,β-dichlorovinyl sulfide (from β-chloro-ethyl-α-chlorovinyl sulfide by addition of chlorine to form the unstable α,α,β,β′-tetrachlorodiethyl sulfide) and, in addition, a comparatively stable saturated tetrachloro derivative. This must have originated from β-chloro-ethyl-β-chlorovinyl sulfide and has, therefore, the structure α,β,β,β′-tetrachlorodiethyl sulfide. When heated under reflux instead of distilled, this compound decomposes into an unsaturated trichloro derivative, boiling at 90–91° (3.5 mm.) or 10° above its β-chloro-ethyl-α,β-dichlorovinyl isomer. Theoretically, α,β,β,β′-tetrachlorodiethyl sulfide should give two isomeric unsaturated trichloro compounds, but only the one was isolated, and this must have had the structure β-chloro-ethyl β,β-dichlorovinyl sulfide. Whether the other was formed in small amounts or was not formed at all we were not able to determine with the small amount of tetrachlorodiethyl sulfide on hand.

Pentachlorodiethyl Sulfide and its Decomposition Product

Mann and Pope[3] were unable to isolate a pentachlorodiethyl sulfide by chlorination of β,β-dichloro-ethyl sulfide and distillation of the reaction product, a fact which is in agreement with its postulated instability. Two pentachloro derivatives are theoretically possible, α,α,β,β,β′- and α,β,β,β,β′-. We obtained the former by adding exactly one molar equivalent of chlorine to pure β-chloro-ethyl-α,β-dichlorovinyl sulfide in carbon tetrachloride solution. The compound was isolated without distillation. Analysis of the product showed a pentachloro derivative. Because of the small amount of β-chloro-ethyl-β,β-dichlorovinyl sulfide on hand no effort was made to prepare the isomeric pentachloro sulfide.

When this addition product of chloro-ethyldichlorovinyl sulfide and chlorine was distilled, there was secured an unsaturated tetrachloro derivative in excellent yield, with no trace of a pentachloro compound. Pentachlorodiethyl sulfide decomposes slowly even at room temperature and on distillation gives an almost quantitative yield of β-chloro-ethyl-α,β,β-trichlorovinyl sulfide. No isomer of this compound is possible.

Hexachlorodiethyl Sulfide

When all the hydrogen atoms on the one ethyl group have been substituted by chlorine, formation of vinyl compounds becomes impossible and a stable saturated compound is first encountered. Mann and Pope[3] isolated α,α,β,β,β,β′-hexachlorodiethyl sulfide by chlorinating β,β-dichloro-ethyl sulfide. They were unable to secure any chlorination on the second ethyl group. Their findings have been confirmed by us.

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

Experimental Part

The same procedure was employed in the addition of chlorine to the higher chlorinated derivatives as was described in the previous paper on the chlorination of β,β-dichloro-ethyl sulfide. Chlorine was passed through an accurately calibrated flowmeter into a solution in carbon tetrachloride of the compound to be chlorinated. As an additional precaution beyond those previously observed, the exit tube from the reaction flask was immersed in potassium iodide solution and the escaping chlorine was titrated. This was found negligible in the case of reactions by which tetrachloro derivatives are formed. On completion of the reaction the solvent was distilled off and the residue was vacuum distilled twice from an ordinary distilling flask. The distillate was then fractionated with the aid of the modified Dufton column[4] until constant-boiling products were obtained. Boiling points were obtained by making a final distillation from an ordinary distilling flask so as to avoid any danger of superheating the vapor in the electrically heated Dufton column. Isolation of comparatively pure products was obtained much more readily than expected in view of the difficulty in separating the two chloro-ethylchlorovinyl isomers previously described. Analyses for both sulfur and chlorine were carried out by the Parr bomb method.[5]

α,β,β,β'-Tetrachlorodiethyl Sulfide.—A solution of a 100g. mixture of the two isomeric chloro-ethylchlorovinyl sulfides in 200 cc. of dry carbon tetrachloride was treated with one molar equivalent of chlorine (45.2 g.), the chlorine being added at the rate of 35.2 cc. per minute. After four distillations from an ordinary distilling flask and eight through the Dufton column, a fraction boiling at 118.5–119° (3 mm.) was obtained; yield, 17 g.

Anal. Calcd. for $C_4H_6SCl_4$: Cl, 62.22. Found: 61.99, 62.53.

Accompanying this fraction was another which had a boiling point and chlorine content closely approaching those for β-chloro-ethyl-α,β-dichlorovinyl sulfide.

α,α,β,β'-Tetrachlorodiethyl Sulfide.—This compound is too unstable to be isolated by distillation. On distillation its decomposition product, β-chloro-ethyl-α,β-dichlorovinyl sulfide, is always obtained.

β-Chloro-ethyl-α,β-dichlorovinyl Sulfide.—A sample of 100 g. of β,β-dichloro-ethyl sulfide dissolved in 200 cc. of dry carbon tetrachloride was treated with 89.25 g. of chlorine (2 molar equivalents) through a period of fourteen and one-half hours. After two distillations from an ordinary distilling flask and one through the Dufton column, a large fraction boiling at 79.7–80.5° (4 mm.) was secured; yield, 63 g.

A boiling point of 108.5–109° (15 mm.) was observed. Mann and Pope give 106.5–108° (15 mm.) for the compound they termed α,β,β'-trichlorodiethyl sulfide.

Anal. Calcd. for $C_4H_5SCl_3$: Cl, 55.55; S, 16.74. Found: Cl, 55.59, 55.51; S, 16.48, 16.63.

The compound was also formed by the addition of one molar equivalent of chlorine to a mixture of the two isomeric chloro-ethylchlorovinyl sulfides; b. p. 80–81° (4 mm.).

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

[5] All analyses were made by the Analytical Department, Chemical Division.

After oxidation with dilute nitric acid, ammonium β-chloro-ethane sulfonate was isolated and identified, following the procedure described in the previous paper.

β-Chloro-ethyl-β,β-dichlorovinyl Sulfide.—A sample of 14 g. of α,β,β,β'-tetrachlorodiethyl sulfide was refluxed in an oil-bath at 150–160° for fourteen hours. On distillation there was readily obtained an unsaturated trichloro derivative boiling at 90–91° (3.5 mm.) as compared with 79.5–80.5° (4 mm.) for β-chloro-ethyl-α,β-dichlorovinyl sulfide. The only unsaturated isomer for the latter compound would have the structure corresponding to the formula given above, and such a compound would be expected from its synthesis; yield, 9 g.

Anal. Calcd. for $C_4H_5SCl_3$: Cl, 55.55; S, 16.74. Found: Cl, 56.01, 56.30; S, 16.12, 15.32.

β-Chloro-ethyl-α,β,β-trichlorovinyl Sulfide.—To a sample of 100 g. of β-chloro-ethyl-α,β-dichlorovinyl sulfide dissolved in 200 cc. of dry carbon tetrachloride was added one molar equivalent of chlorine (37.05 g.), at a reaction temperature of 50–60°. No hydrogen chloride was evolved during the entire run and all but 0.035 g. of the chlorine was absorbed. After but two distillations, once from an ordinary distilling flask and once through the Dufton column, a large fraction boiling at 97–98° (4 mm.) was secured; yield, 68 g. A boiling point of 123.5–124.5° (15 mm.) was observed. Mann and Pope give 123–125° (15 mm.) for the compound they termed α,β,β,β'-tetrachlorodiethyl sulfide.

Anal. Calcd. for $C_4H_4SCl_4$: Cl, 62.77; S, 14.19. Found: Cl, 62.68, 62.54; S, 13.84, 14.06.

Since no hydrogen chloride came off during the chlorination, a pentachlorodiethyl sulfide must have been formed and subsequently decomposed during distillation into the unsaturated tetrachloro compound.

α,α,β,β,β'-Pentachlorodiethyl Sulfide.—A sample of pure β-chloro-ethyl-α,β-dichlorovinyl sulfide weighing 13 g. was dissolved in 100 cc. of carbon tetrachloride and 5.0 g. of chlorine (equivalent to one gram mole) was added. Absorption was almost complete. No hydrogen chloride was evolved. The bath in which the reaction flask was immersed was maintained at 60 to 70°. After the completion of the reaction, the solvent was removed under reduced pressure and the oil washed three times with a dilute aqueous solution of sodium bisulfite, then three times with a dilute solution of sodium carbonate, and finally shaken with water. The oil was extracted with ether, the ether solution dried with fused sodium sulfate, and the ether distilled off under vacuum. During this last operation some hydrogen chloride was evolved.

Anal. Calcd. for $C_4H_5SCl_5$: Cl, 67.55; S, 12.22. Found: Cl, 66.2, 67.3; S, 12.56, 12.55.

This compound breaks down completely on distillation to give the unsaturated β-chloro-ethyl-α,β,β-trichlorovinyl sulfide.

α,α,β,β,β,β'-Hexachlorodiethyl Sulfide.—A sample of completely chlorinated β,β-dichloro-ethyl sulfide[6] which had been made by treatment with an excess of chlorine at room temperature was separated into three main fractions by distillation through the Dufton column: (1) a mixture of low-boiling chlorinated hydrocarbons; (2) the unsaturated tetrachloro compound, β-chloro-ethyl-α,β,β-trichlorovinyl sulfide; (3) hexachlorodiethyl sulfide.

The hydrocarbons were not pure, analyzing 0.66% of sulfur and 81.26% of chlorine. The tetrachloro compound had the same boiling point as the one obtained by adding one gram mole equivalent of chlorine to β-chloro-ethyl-α,β-dichlorovinyl sulfide and

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[6] Furnished us through the courtesy of Dr. J. S. Reichert, Anti-Gas Department, Chemical Division.

distilling. It analyzed 62.52, 62.08% of chlorine and 13.39, 13.51% of sulfur, as compared with theoretical values of 62.77 and 14.19, respectively. $\alpha,\alpha,\beta,\beta,\beta,\beta'$-Hexachlorodiethyl sulfide boils at 131–132° (4.5 mm.) or 159.5–160° (15 mm.). Mann and Pope[3] give 160–161° (15 mm.) for the same compound.

Anal. Calcd. for $C_4H_4SCl_6$: Cl, 71.67; S, 10.80. Found: Cl, 70.88, 70.85; S, 11.05, 10.93.

This compound, since it contains no hydrogen in the chlorinated ethyl group, is stable and distils unchanged. Further chlorination under the conditions employed by us leads to a complete breaking up of the molecule with the formation of chlorinated hydrocarbons. This was also observed by Mann and Pope.

Summary

1. Practically all of the compounds theoretically possible on treating β,β-dichloro-ethyl sulfide with chlorine have been isolated and identified.

2. With one exception, all chlorinated derivatives below the hexachloro are unstable, splitting out hydrogen chloride on distillation with formation of unsaturated compounds. The exception, $\alpha,\beta,\beta,\beta'$-tetrachlorodiethyl sulfide, may be distilled, but breaks up like the others on refluxing.

3. None of these compounds is vesicant.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. III

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Previous work published from this Laboratory[1] has shown that, "when *o*-aminophenol is acylated with the structural isomers, *n*-carbopropoxy and *iso*carbopropoxy groups, irrespective of their original positions, a partial rearrangement occurs. When the corresponding compounds with the *n*- and *iso*butoxy groups are made, their behavior is somewhat different. While the butyl carbonate of *iso*butyl-*o*-hydroxycarbanilate rearranges partially, giving a mixture of the two isomers, *iso*butyl carbonate of butyl *o*-hydroxycarbanilate was not found to change." In view of the behavior of these isomers against each other in the acylating of *o*-aminophenol it became of interest to us to investigate the behavior of such structural isomers against an aliphatic group and also against an aromatic group. The following pairs of groups were used:

$—CO_2C_4H_9(n)$ and $—CO_2C_5H_{11}(iso)$; $—CO_2C_4H_9(iso)$ and $—CO_2C_5H_{11}(iso)$;
$—CO_2C_3H_7(n)$ and $—COC_6H_5$; $—CO_2C_3H_7(iso)$ and $—COC_6H_5$

Iso-amyl-*o*-hydroxycarbanilate was acylated with *n*-butylchloro-carbonate and a stable diacyl obtained which yielded *iso*-amyl-*o*-hydroxycarbanilate on saponification. When *n*-butyl-*o*-hydroxycarbanilate was

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[1] Nelson and Aitkenhead, THIS JOURNAL, **48**, 1680 (1926).