The distillation data and the infrared spectra of the fractions indicated that the product consisted of 16.5 g. (0.18 mole) of *t*-butyl chloride, 23 g. (0.17 mole) of *t*-butyl bromide, 19 g. (0.18 mole) of *t*-pentyl chloride and 37.5 g. (0.25 mole) of *t*-pentyl bromide.

Under similar conditions, the reaction of 0.33 mole each of *t*-butyl chloride and *t*-pentyl bromide resulted in the formation of 0.11 mole of *t*-butyl bromide and 0.10 mole of *t*-pentyl chloride.

Attempted Halogen Exchange between *t*-Butyl Halides and 1-Halo-3,3-dimethylbutanes.—Very little reaction occurred when 68 g. (0.5 mole) of *t*-butyl bromide was added during 40 minutes to a stirred mixture of 3.0 g. of aluminum chloride and 60 g. (0.5 mole) of 1-chloro-3,3-dimethylbutane dissolved in 62 g. of *n*-pentane at −45 to −40° or at −5 to 0°. Attempts to cause the halogen exchange by carrying out the reaction in the presence of larger quantities of aluminum chloride (22 g.) at −45 to −40° or at −20 to −10° were also unsuccessful. The catalyst was converted to red-brown sludge (32 and 70 g., respectively); distillation of the washed upper layer in each case yielded only the unreacted alkyl halides.

Similarly, no 1-chloro-3,3-dimethylbutane was isolated from the product obtained by the addition of 0.2 mole of *t*-butyl chloride to 0.2 mole of 1-bromo-3,3-dimethylbutane and 5.0 g. of aluminum bromide in 60 g. of *n*-pentane at −20 to −10°.

RIVERSIDE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Chlorination of Dimethyl Sulfide and Some of Its Derivatives with Sulfuryl Chloride and Thionyl Chloride[1]

BY WILLIAM E. TRUCE, G. H. BIRUM AND E. T. MCBEE

RECEIVED JANUARY 2, 1952

Sulfuryl chloride and thionyl chloride have been found to be new chlorinating agents for alkyl sulfides. All nine of the possible chlorinated dimethyl sulfides have been prepared by chlorination of dimethyl sulfide and trithiane with sulfuryl chloride. Thionyl chloride is a less vigorous chlorinating agent than sulfuryl chloride, but it affords good yields of mono-, di- and trichlorodimethyl sulfides from dimethyl sulfide, and almost a quantitative yield of α,α'-dichlorodimethyl sulfide from trithiane. In the chlorination of dimethyl sulfide, it has been found that all three hydrogens of one carbon atom are replaced by chlorine before the second methyl group is chlorinated. Thionyl chloride has been used to introduce one, two and three chlorine atoms on the methyl group of *t*-butyl methyl sulfide. Evidence is provided to support an ionic mechanism for the chlorination of sulfides. Chromic anhydride has been employed for the oxidation of α-chlorosulfides, and all nine of the chlorodimethyl sulfones have been thus prepared. The chlorine in several of the chlorodimethyl sulfides, having three chlorine atoms on at least one carbon atom, has been replaced by fluorine. The sulfones of some of these fluorodimethyl sulfides have been prepared.

The present investigation has been principally concerned with the chlorination of dimethyl sulfide and its chloro-derivatives with sulfuryl chloride and thionyl chloride, two new chlorinating agents for organic sulfides.[2a] A few of the chlorodimethyl sulfides have been prepared previously by chlorination of dimethyl sulfide with chlorine. Riche[2b] was the first to report that dimethyl sulfide can be chlorinated with chlorine, but he gave no structures or physical properties for his products except a boiling point for a substance that analyzed for hexachlorodimethyl sulfide. James[2c] suggested that this boiling point was much too low for hexachlorodimethyl sulfide and that the product was probably perchloromethyl mercaptan; this suggestion has been confirmed by the present work. Feichtinger and Moos[3] reported that the same tetrachlorodimethyl sulfide was obtained by the reaction of chlorine with dimethyl sulfide as was obtained by the reaction of α,α'-dichlorodimethyl sulfide with chlorine, but they gave no structure for their product. Because of the nature of the decomposition products when tetrachlorodimethyl sulfide was chlorinated further, they believed that penta- and hexachlorodimethyl sulfide were formed, but they were unable to isolate these postulated more highly chlorinated sulfides. Bohme[4] prepared monochlorodimethyl sulfide from paraformaldehyde, methyl mercaptan, and hydrogen chloride, and, also, by the reaction of chlorine with dimethyl sulfide in carbon tetrachloride at −20°. He gave no yield by the latter method. α,α'-Dichlorodimethyl sulfide has been prepared by chlorination of trithiane with sulfur monochloride[5] and sulfur dichloride.[6]

The only chlorodimethyl sulfides that had been definitely isolated, identified, and characterized previous to the present work were monochlorodimethyl sulfide and α,α'-dichlorodimethyl sulfide. Nothing has been known of the order of replacement of the remaining hydrogen atoms upon further chlorination. This lack of knowledge of the chlorination of dimethyl sulfide has, no doubt, been due in large part to the difficulty of controlling the reaction with chlorine. The present investigation of the chlorination of dimethyl sulfide has been greatly facilitated by the use of sulfuryl chloride and thionyl chloride as the chlorinating agents. By the reaction of sulfuryl chloride with dimethyl sulfide and trithiane, all of the nine possible chlorodimethyl sulfides have been prepared. The identification of many of the products has been greatly aided by finding that chromic anhydride in glacial acetic acid is a convenient reagent for oxidizing α-chlorosulfides to sulfones.

Chlorination of Dimethyl Sulfide with Sulfuryl Chloride.—Sulfuryl chloride reacts vigorously with dimethyl sulfide according to the equation

$$CH_3SCH_3 + SO_2Cl_2 \longrightarrow CH_2ClSCH_3 + HCl + SO_2$$

---

[1] Taken from G. H. Birum's Ph.D. thesis. Presented at the Milwaukee Meeting of the American Chemical Society, April 2, 1952.

[2] (a) F. G. Bordwell and co-workers recently observed analogous results (private communication). (b) M. A. Riche, *Ann. chim. phys.*, [iii] **43**, 283 (1855). (c) J. W. James, *J. Chem. Soc.*, **51**, 273 (1887).

[3] H. Feichtinger and J. Moos, *Ber.*, **81**, 371 (1948).

[4] H. Bohme, H. Fisher and R. Frank, *Ann.*, **563**, 54 (1949).

[5] I. Bloch and F. Hohn, *Ber.*, **55B**, 53 (1922).

[6] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **123**, 1172 (1923).

The methyl group on which the first chlorine atom is substituted is completely chlorinated before there is any chlorination of the second methyl group.

$$CH_3SCH_3 + SO_2Cl_2 \longrightarrow CH_2ClSCH_3 \longrightarrow CHCl_2SCH_3 \longrightarrow CCl_3SCH_3 \longrightarrow CCl_3SCH_2Cl$$

No indication of the formation of any α,α'-dichlorodimethyl sulfide, α,α,α'-trichlorodimethyl sulfide or α,α,α',α'-tetrachlorodimethyl sulfide has been found when dimethyl sulfide is chlorinated.

Chlorination of dimethyl sulfide with sulfuryl chloride proceeds readily until α,α,α,α'-tetrachlorodimethyl sulfide is formed. Further chlorination then takes place only very slowly and is accompanied by cleavage of the sulfur–carbon bond to give perchloromethyl mercaptan as the principal product. Small quantities of pentachloro- and hexachlorodimethyl sulfide are produced when 3.5 moles or more of sulfuryl chloride are used per mole of dimethyl sulfide. Increase in the ratio of sulfuryl chloride to sulfide increases the yield of pentachlorodimethyl sulfide to a maximum of about 5% but the yield of hexachlorodimethyl sulfide never becomes greater than about 2%.

Six of the nine possible chlorodimethyl sulfides can be prepared by chlorination of dimethyl sulfide with sulfuryl chloride. Table I gives the percentage conversions to these six derivatives for various ratios of sulfuryl chloride and dimethyl sulfide.

TABLE I

Moles of SO_2Cl_2 per mole of $(CH_3)_2S$	CH_2-Cl-SCH_3, %	$CHCl_2$-SCH_3, %	CCl_3-SCH_3, %	CCl_3-SCH_2-Cl, %	CCl_3-$SCHCl_2$, %	CCl_3-$SCCl_3$, %
1.2	45	19	3	0	0	0
1.5	26	34	5	0	0	0
2.25	26	25	42	0	0	0
3.5	0	0	77	18	0.5–1	0.5–1
4.0	0	0	33	58	1.5–2	1.5–2
4.5	0	0	23	72	2–3	1–2
6.0	0	0	0	76	4	1–2
10.0	0	0	0	48	5	2

Chlorination of Dimethyl Sulfide with Thionyl Chloride.—The use of thionyl chloride for chlorinating sulfides is a new application of thionyl chloride. Whereas sulfuryl chloride reacts vigorously with dimethyl sulfide at 0°, thionyl chloride does not react perceptibly at this temperature. Reaction appears to begin at about 12° and proceeds smoothly at room temperature. This decreased reactivity of thionyl chloride under that of sulfuryl chloride is helpful in the preparation of monochlorodimethyl sulfide and α,α-dichlorodimethyl sulfide. An excellent yield of α,α,α-trichlorodimethyl sulfide can also be obtained by using an excess of thionyl chloride.

The difference in reactivity of sulfuryl chloride and thionyl chloride in chlorinating sulfides is illustrated by the limits of progressive chlorination of dimethyl sulfide by these reagents. Sulfuryl chloride chlorinates dimethyl sulfide readily to tetrachlorodimethyl sulfide and, with more difficulty, to pentachloro- and hexachlorodimethyl sulfides. However, refluxing dimethyl sulfide with a large excess of thionyl chloride for 100 hours gave no detectable quantity of more highly chlorinated products than α,α,α-trichlorodimethyl sulfide. Likewise, refluxing α,α'-dichlorodimethyl sulfide or α,α,α'-trichlorodimethyl sulfide with thionyl chloride for a long period of time gave no indication of reaction. Sulfuryl chloride warmed at reflux with these sulfides produced more highly chlorinated products.

In the reaction of dimethyl sulfide with sulfuryl chloride the by-products are hydrogen chloride and sulfur dioxide. When one or two moles of thionyl chloride are used per mole of dimethyl sulfide, the by-products are hydrogen chloride, sulfur dioxide and sulfur. Measurement of the sulfur dioxide and sulfur revealed that equimolar quantities of these two substances are produced according to the equation

$$2CH_3SCH_3 + 2SOCl_2 \longrightarrow 2CH_2ClSCH_3 + 2HCl + SO_2 + S$$

This suggests the probability that sulfur monoxide is formed as an intermediate and disproportionates to sulfur and sulfur dioxide, $2SO \rightarrow S + SO_2$. Sulfur monoxide has been produced by reaction of thionyl chloride with stannous chloride and with metals such as tin, sodium and antimony. It is soluble in thionyl chloride and undergoes decomposition to sulfur dioxide and sulfur in a 1:1 ratio.[7,8] When an excess of thionyl chloride is treated with dimethyl sulfide, no appreciable quantity of sulfur is obtained, but sulfur monochloride is isolated instead. The excess thionyl chloride apparently chlorinates sulfur to sulfur monochloride. Chlorination of sulfur to sulfur monochloride with thionyl chloride is known to occur,[9,10] but at a higher temperature than is used in the chlorination of dimethyl sulfide.

Chlorination of Dimethyl Sulfide with Chlorine.—Feichtinger and Moos[3] obtained a tetrachlorodimethyl sulfide by chlorination of dimethyl sulfide with chlorine, but they proposed no structure for their product. Using their method of chlorination, it has been found that α,α,α,α'-tetrachlorodimethyl sulfide is the principal product obtained. No α,α,α',α'-tetrachlorodimethyl sulfide could be isolated, but small quantities of pentachloro- and hexachlorodimethyl sulfide were obtained. Hence, chlorination of dimethyl sulfide with chlorine and with sulfuryl chloride gave similar results.

Chlorination of Trithiane with Sulfuryl Chloride and Thionyl Chloride.—Both sulfuryl chloride and thionyl chloride react with trithiane to give α,α'-dichlorodimethyl sulfide which has been previously prepared by reaction of trithiane with sulfur monochloride[5] and sulfur dichloride.[6] Almost a quantitative yield is obtained with thionyl chloride, but sulfuryl chloride gives some decomposition products and higher chlorinated sulfides. Thionyl chloride does not further chlorinate α,α'-dichlorodimethyl sulfide.

Sulfuryl chloride reacts readily with α,α'-dichlorodimethyl sulfide to give α,α,α'-trichlorodimethyl sulfide which is further chlorinated with

---

(7) P. W. Schenk, *Z. anorg. Chem.*, **211**, 150 (1933).

(8) P. W. Schenk and H. Platz, *ibid.*, **215**, 113 (1933).

(9) H. Prinz, *Ann.*, **223**, 355 (1884).

(10) H. B. North and C. B. Conover, THIS JOURNAL, **37**, 2486 (1915).

sulfuryl chloride to give an 81% yield of unsymmetrical tetrachlorodimethyl sulfide and a 3% yield of symmetrical tetrachlorodimethyl sulfide. Feichtinger and Moos reported that chlorination of α,α'-dichlorodimethyl sulfide with chlorine gave the same product as chlorination of dimethyl sulfide with chlorine. However, the refractive index of their product is between the refractive indices of the two tetrachlorodimethyl sulfides, and it is probable that they had a mixture of the two compounds. The boiling points of the two isomers are very close, and repeated rectification in a good column is necessary for separation. Formation of the unsymmetrical isomer in much the largest yield is another indication of the tendency for complete chlorination of one of the carbon atoms before the other carbon is chlorinated.

Chlorination of trithiane with sulfuryl chloride provides a means for the preparation of six of the nine possible chlorodimethyl sulfides. Three of these, α,α'-dichlorodimethyl sulfide, α,α,α'-trichlorodimethyl sulfide, and α,α,α',α'-tetrachlorodimethyl sulfide, are the three that could not be obtained from dimethyl sulfide. Hence, chlorination of trithiane and dimethyl sulfide with sulfuryl chloride and thionyl chloride provides a convenient means for the preparation of all nine of the possible chlorodimethyl sulfides as illustrated in Fig. 1.

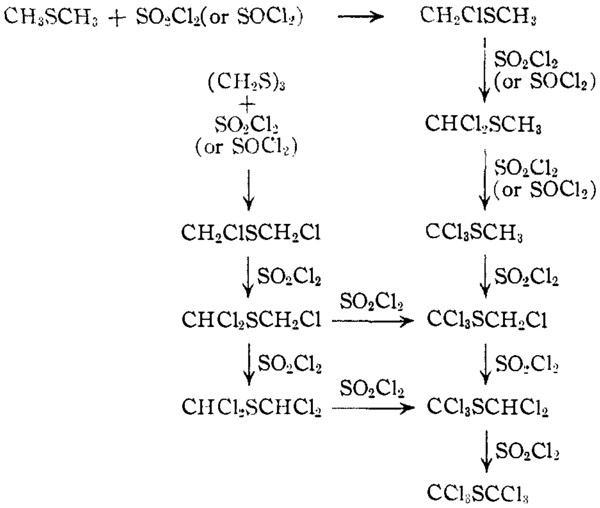


Fig. 1.

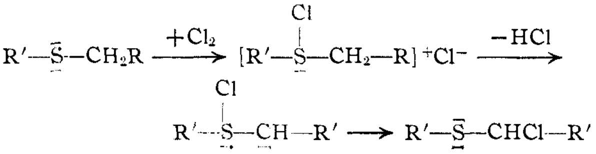
All of the chlorodimethyl sulfides are clear, colorless liquids varying in odor from very unpleasant for monochlorodimethyl sulfide to a mild, camphor-like odor for the highly chlorinated ones. All of them can be refluxed at atmospheric pressure with only very slow decomposition.

Chlorination of *t*-Butyl Methyl Sulfide with Thionyl Chloride and Sulfuryl Chloride.—Thionyl chloride reacts with *t*-butyl methyl sulfide to place one, two and three chlorine atoms on the methyl group.

$$(CH_3)_3CSCH_3 + SOCl_2 \longrightarrow (CH_3)_3CSCH_2Cl \longrightarrow (CH_3)_3CSCHCl_2 \longrightarrow (CH_3)_3CSCCl_3$$

Further chlorination does not take place when an excess of thionyl chloride is used. Reaction of *t*-butyl trichloromethyl sulfide with sulfuryl chloride gives *t*-butyl chloride and perchloromethyl mercaptan. The three *t*-butyl chloromethyl sulfides are somewhat unstable and slowly decompose on standing.

Mechanism of Chlorination of Sulfides.—Bohme[4] has proposed an ionic mechanism for the chlorination of sulfides with chlorine.



$$R'\text{—}\bar{\underset{-}{S}}\text{—}CH_2R \xrightarrow{+Cl_2} [R'\text{—}\overset{\overset{Cl}{|}}{\underset{-}{S}}\text{—}CH_2\text{—}R]^+Cl^- \xrightarrow{-HCl}$$

$$R'\text{—}\overset{\overset{Cl}{|}}{\underset{..}{S}}\text{—}\underset{..}{C}H\text{—}R' \longrightarrow R'\text{—}\bar{\underset{-}{S}}\text{—}CHCl\text{—}R'$$

The results of chlorination of dimethyl sulfide in the present work support this mechanism. The mechanism accounts for the complete chlorination of one methyl group before the second methyl group is chlorinated because the presence of chlorine on one of the carbon atoms facilitates removal of the remaining hydrogen atoms on the same carbon atom. As the number of chlorine atoms in the molecule increases, difficulty of further chlorination increases. This may be explained on the basis that the increasing inductive effect of increasing numbers of chlorine atoms would decrease the tendency for sulfur–chlorine bond formation, and therefore, slow the reaction. When α,α-dichlorodimethyl sulfide was treated with sulfuryl chloride in the presence of a high concentration of bromine, α,α,α-trichlorodimethyl sulfide was the only product isolated. The failure to obtain any brominated sulfide indicates rearrangement of the chlorine atom from the sulfur to the α-carbon may be taking place as the proton is being removed. If an intermediate ion existed with an unshared pair of electrons on the carbon atom, some reaction with bromine would be expected. Since chlorination with chlorine, sulfuryl chloride and thionyl chloride give similar results, inasfar as each agent is capable of chlorinating, it appears that the mechanisms for chlorination by all three are the same except for the separation of sulfur dioxide from sulfuryl chloride and sulfur monoxide from thionyl chloride, either as the sulfonium molecule is being formed or as the proton is being removed.

Oxidation of Chlorosulfides to Sulfones.—Because of ease of hydrolysis, α-chlorosulfides cannot be satisfactorily oxidized to sulfones in aqueous solutions. This eliminates the use of most of the common oxidizing agents. Perbenzoic acid,[11–14] perphthalic acid[15,16] and peracetic acid[16a] have been previously used for oxidizing α-chlorosulfides. However, chromic anhydride in glacial acetic acid has been found to be more convenient for the oxidation of α-chlorosulfides, and it has been used to oxidize all nine of the chlorodimethyl sulfides to sulfones.

The chlorodimethyl sulfones are all white, crystalline solids except α,α,α'-trichlorodimethyl sulfone which freezes at −35°. The more highly

---

(11) L. N. Levin, *J. prakt. Chem.*, **118**, 282 (1928).

(12) L. N. Levin, *ibid.*, **119**, 211 (1928).

(13) L. N. Levin, *ibid.*, **127**, 77 (1930).

(14) H. Bohme, *Ber.*, **69B**, 1610 (1936).

(15) H. Bohme, *ibid.*, **70B**, 379 (1937).

(16) L. Ramberg and B. Backlund, *Arkiv Kemi, Mineral. Geol.*, **13A**, No. 27, 50 (1940).

(16a) F. G. Bordwell and C. D. Cooper, THIS JOURNAL, **73**, 5187 (1951).

chlorinated ones have a weak camphor-like odor. Solubility in polar solvents decreases and in nonpolar solvents increases as the chlorine content increases. Furthermore, oxidation to sulfones becomes more difficult as the degree of chlorination increases.

Preparation of Fluorodimethyl Sulfides from Chlorodimethyl Sulfides.—Attempts to replace the chlorine in the chlorodimethyl sulfides with fluorine have been successful in some cases, but in those cases where neither one of the carbon atoms is bonded to three chlorine atoms, no appreciable quantities of fluorodimethyl sulfides have been obtained. The failure to obtain some of these sulfides is apparently due to their instability. Similar instability of α-fluoroethers has been cited by Henne.[17] The only fluorodimethyl ether that has been definitely isolated and identified is perfluorodimethyl ether prepared by the Minnesota Mining and Manufacturing Company. A trifluorodimethyl ether was reported[18] but not structurally identified.

Addition of α,α,α-trichlorodimethyl sulfide to antimony trifluoride in the presence of antimony pentachloride readily gives α,α,α-trifluorodimethyl sulfide and α-monochloro-α,α-difluorodimethyl sulfide. Similar treatment of α,α,α,α′-tetrachlorodimethyl sulfide gives α-chloro-α′,α′,α′-trifluorodimethyl sulfide and α,α′-dichloro-α′,α′-difluorodimethyl sulfide. Pentafluorodimethyl sulfide was obtained from pentachlorodimethyl sulfide. The treatment of hexachlorodimethyl sulfide with antimony trifluoride and antimony pentachloride gave no hexafluorodimethyl sulfide. Trichlorofluoromethane and dichlorodifluoromethane were isolated instead. This decomposition of hexachlorodimethyl sulfide with antimony trifluoride recalls the decomposition of the same substance by sulfuryl chloride.

α,α,α-Trifluorodimethyl sulfide, α-monochloro-α,α-difluorodimethyl sulfide and α-monochloro-α′,α′,α′-trifluorodimethyl sulfide were successfully oxidized to the corresponding sulfones by long refluxing with chromic anhydride in glacial acetic acid. However, pentafluorodimethyl sulfide could not be oxidized with chromic anhydride.

Experimental

Monochlorodimethyl Sulfide.—A 500-ml., 3-neck flask was equipped with a sealed stirrer, a dropping funnel and a condenser protected with a calcium chloride drying tube. Dimethyl sulfide (Eastman Kodak 1106, 50 g., 0.81 mole), was placed in the flask, which was cooled in a water-bath at 20°, and thionyl chloride, 115 g. (0.97 mole), was added over a period of 1.5 hours. The temperature was then increased to 95° and maintained there until the evolution of hydrogen chloride and sulfur dioxide ceased (about 2 hours). The reaction mixture was cooled to 0° and the liquid product was removed from the sulfur by decantation. Rectification in a 3-foot, helix-packed column gave 58.4 g. (75% yield) of monochlorodimethyl sulfide, b.p. 50–52° at 100 mm., and 13.0 g. (12.3% yield) of α,α-dichlorodimethyl sulfide, b.p. 57–60° at 50 mm. Monochlorodimethyl sulfide was also prepared in 45% yield by adding 1.2 moles of sulfuryl chloride to 1.0 mole of dimethyl sulfide cooled at −75° and warming the mixture until the evolution of hydrogen chloride and sulfur dioxide ceased. Monochlorodimethyl sulfide, carefully purified by rectification, has a boiling point of 107.1° at 750 mm., $n^{20}{}_{\mathrm{D}}$ 1.4967. Boiling points reported in the literature[4,19] are 110–112° and 105–107°.

α,α′-Dichlorodimethyl Sulfide.—A 1-liter, 3-neck flask was equipped with a sealed stirrer and a condenser protected with a calcium chloride drying tube. Trithiane, 200 g. (1.45 moles), and thionyl chloride, 517.5 g. (4.35 moles), were added at room temperature, and the mixture was warmed at reflux for 32 hours. Rectification to separate the product from sulfur monochloride and sulfur gave 200 g. of crude α,α′-dichlorodimethyl sulfide, b.p. 68–74°. Careful rectification of the crude product in a 3-foot, helix-packed column gave 185 g. (97.5% yield) of α,α′-dichlorodimethyl sulfide, b.p. 156–156.5° (747 mm.), b.p. 46.2° (10 mm.), $n^{20}{}_{\mathrm{D}}$ 1.5322, $d^{20}{}_{4}$ 1.4103, f.p. −37.5° (lit.[3] b.p. 156.5° at 760 mm., $n^{20}{}_{\mathrm{D}}$ 1.5313, $d^{20}{}_{4}$ 1.4116, f.p. −54°).

Anal. Calcd. for $C_2H_4Cl_2S$: C, 18.33; H, 3.08. Found: C, 18.52; H, 3.10.

α,α-Dichlorodimethyl Sulfide.—Dimethyl sulfide, 53 g. (0.86 mole), was placed in a 500-ml., 3-neck flask equipped with a sealed stirrer, a dropping funnel and a condenser protected with a calcium chloride drying tube. The flask was cooled in an ice-bath, and 224 g. (1.88 moles) of thionyl chloride was added over a period of 1.5 hours. The temperature was slowly increased to 95° (4 hours) and maintained there until the evolution of hydrogen chloride and sulfur dioxide ceased. After cooling, the liquid product was separated from sulfur by decantation. Rectification in a 3-foot, helix-packed column gave 3.6 g. (4% yield) of monochlorodimethyl sulfide, 86.4 g. (77% yield) of α,α-dichlorodimethyl sulfide, b.p. 75.9–76.8° (100 mm.), and 9.1 g. of higher boiling products. The properties of carefully rectified α,α-dichlorodimethyl sulfide are: b.p. 137.0° (742 mm.), b.p. 60.1° (50 mm.), $n^{20}{}_{\mathrm{D}}$ 1.5159, $d^{20}{}_{4}$ 1.3702, f.p. −36°.

Anal. Calcd. for $C_2H_4Cl_2S$: C, 18.33; H, 3.08. Found: C, 18.33; H, 2.98.

α,α-Dichlorodimethyl sulfide can also be prepared in about 30% yield by chlorination of dimethyl sulfide with sulfuryl chloride. The sulfide has been identified as α,α-dichlorodimethyl sulfide because of the marked differences in properties between it and α,α′-dichlorodimethyl sulfide, which has been identified.[5] The mixed melting point of the sulfones of the two dichlorodimethyl sulfides has a marked depression.

α,α,α′-Trichlorodimethyl Sulfide.—α,α′-Dichlorodimethyl sulfide, 41 g. (0.31 mole), was placed in a 500-ml., 3-neck flask equipped with a sealed stirrer, a dropping funnel and a condenser protected with a calcium chloride drying tube. The flask was cooled in an ice-bath, and 50 g. (0.37 mole) of sulfuryl chloride was added over a period of one hour. The temperature was then slowly increased to 95° and maintained there until the evolution of hydrogen chloride and sulfur dioxide ceased (6 hours). Rectification gave 40.5 g. (78% yield) of α,α,α′-trichlorodimethyl sulfide, b.p. 58.2–61.5° (10 mm.). The properties of carefully rectified α,α,α′-trichlorodimethyl sulfide are: b.p. 177.2° (753 mm.), b.p. 41.5° (5 mm.), $n^{20}{}_{\mathrm{D}}$ 1.5395, $d^{20}{}_{4}$ 1.5258, f.p. (below −110°).

Anal. Calcd. for $C_2H_3Cl_3S$: C, 14.51; H, 1.83. Found: C, 14.50; H, 1.79..

α,α,α-Trichlorodimethyl Sulfide.—Dimethyl sulfide, 100 g. (1.61 moles), was placed in a 1-liter, 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a Dry Ice condenser. The flask was cooled in an ice-bath, and 762 g. (5.65 moles) of sulfuryl chloride was added over a period of two hours. The ice-bath was removed soon after the addition of sulfuryl chloride was begun. After the addition of sulfuryl chloride was complete, the Dry Ice condenser was replaced with a tap water condenser so that sulfur dioxide could escape. After standing overnight at room temperature, the reaction mixture was slowly warmed to 95° and maintained at that temperature for five hours. Rectification gave 204 g. (76.5% yield) of α,α,α-trichlorodimethyl sulfide, b.p. 146.0° (750 mm.), b.p. 67.7° (50 mm.), $n^{20}{}_{\mathrm{D}}$ 1.5219, $d^{20}{}_{4}$ 1.4907, f.p. −5°; and 59 g. (18.2% yield) of α,α,α,α′-tetrachlorodimethyl sulfide.

Anal. Calcd. for $C_2H_3Cl_3S$: C, 14.51; H, 1.83. Found: C, 14.51; H, 1.71.

Reaction of one mole of dimethyl sulfide with six moles of

---

[17] A. L. Henne and M. A. Smock, This Journal, **72**, 4378 (1950).

[18] H. S. Booth and P. E. Burchfield, *ibid.*, **57**, 2070 (1935).

[19] L. A. Walter, *et al.*, *ibid.*, **67**, 655 (1945).

thionyl chloride at reflux temperature for 100 hours gave an 89% yield of α,α,α-trichlorodimethyl sulfide, but this product was difficult to separate from sulfur monochloride which was also produced.

Proof of the structure of α,α,α-trichlorodimethyl sulfide is afforded by the marked difference between its physical properties and those of α,α,α′-trichlorodimethyl sulfide and, also, by the difference in their respective sulfones: $CCl_3SO_2CH_3$, m.p. 173.8–174.2°; $CHCl_2SO_2CH_2Cl$, m.p. −35°.

α,α,α,α′-**Tetrachlorodimethyl Sulfide**.—This compound was prepared in a manner similar to that described for α,α,α-trichlorodimethyl sulfide except that 960 g. (7.1 moles) of sulfuryl chloride was treated with 100 g. (1.61 moles) of dimethyl sulfide. Rectification in a 3-foot, helix-packed column gave 233.3 g. (72.4% yield) of α,α,α,α′-tetrachlorodimethyl sulfide, 60.9 g. (22.8% yield) of α,α,α-trichlorodimethyl sulfide, and 11.9 g. of a mixture of pentachloro- and hexachlorodimethyl sulfides. The properties of carefully rectified α,α,α,α′-tetrachlorodimethyl sulfide are: b.p. 188.7° (744 mm.), b.p. 55.4° (4 mm.), $n^{20}\mathrm{D}$ 1.5457, d^{20}_{4} 1.6322, f.p. −15°.

Anal. Calcd. for $C_2H_2Cl_4S$: C, 12.01; H, 1.01. Found: C, 12.11; H, 1.19.

Proof of structure of α,α,α,α′-tetrachlorodimethyl sulfide is afforded by its preparation from α,α,α-trichlorodimethyl sulfide and by the isolation of some trichlorofluoromethane when α,α,α,α′-tetrachlorodimethyl sulfide is treated with antimony trifluoride and antimony pentachloride. The chlorination of one mole of α,α′-dichlorodimethyl sulfide with 3.2 moles of sulfuryl chloride gave an 81% yield of α,α,α,α′-tetrachlorodimethyl sulfide. It can also be prepared by chlorination of dimethyl sulfide and α,α′-dichlorodimethyl sulfide with chlorine.[3]

α,α,α′,α′-**Tetrachlorodimethyl Sulfide**.—This substance is produced in about 3% yield when one mole of α,α′-dichlorodimethyl sulfide is treated with two to three moles of sulfuryl chloride. The sample isolated in the present work was obtained by combining fractions that boiled between the boiling points of α,α,α′-trichlorodimethyl sulfide and α,α,α,α′-tetrachlorodimethyl sulfide from four reactions of α,α′-dichlorodimethyl sulfide with sulfuryl chloride, and carefully rectifying the combined fractions three times. Its properties are: b.p. 62–64° (10 mm.), b.p. 187–188° (746 mm.), $n^{20}\mathrm{D}$ 1.5368, d^{20}_{4} 1.5906.

Anal. Calcd. for $C_2H_2Cl_4S$: C, 12.01; H, 1.01. Found: C, 12.03; H, 1.04.

Pentachlorodimethyl Sulfide and Hexachlorodimethyl Sulfide.—These compounds are produced in small quantities when dimethyl sulfide and α,α′-dichlorodimethyl sulfide are treated with three and one-half moles or more of sulfuryl chloride per mole of sulfide. The pentachloro- and hexachlorodimethyl sulfides isolated in the present work were obtained by accumulating high-boiling fractions from several chlorinations of dimethyl sulfide and α,α′-dichlorodimethyl sulfide with sulfuryl chloride. The best yields, 5% of pentachlorodimethyl sulfide and 2% of hexachlorodimethyl sulfide, were obtained when one mole of dimethyl sulfide was treated with ten moles of sulfuryl chloride at 95° for seven days. The properties of pentachlorodimethyl sulfide are: b.p. 203.5° (751 mm.), b.p. 57.8° (4 mm.), $n^{20}\mathrm{D}$ 1.5434, d^{20}_{4} 1.6733, f.p. −36°. The properties of hexachlorodimethyl sulfide are: b.p. 219–220° (732 mm.), b.p. 60.8° (1.5 mm.), $n^{20}\mathrm{D}$ 1.5560, d^{20}_{4} 1.7433, f.p. 10°.

Anal. Calcd. for C_2HCl_5S: C, 10.25; H, 0.43. Found: C, 10.18; H, 0.37. Calcd. for C_2Cl_6S: C, 8.94; H, 0.00. Found: C, 9.04; H, 0.02.

***t*-Butyl Monochloromethyl Sulfide and *t*-Butyl Dichloromethyl Sulfide**.—*t*-Butyl methyl sulfide, 50 g. (0.48 mole), b.p. 98.8° (757 mm.), $n^{20}\mathrm{D}$ 1.4397, prepared in 97.6% yield by the method of Rheinboldt,[20] was placed in a 500-ml., 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a condenser protected with a calcium chloride drying tube. The flask was cooled in an ice-bath, and 69 g. (0.58 mole) of thionyl chloride was added over a period of 1.5 hours. After standing overnight at room temperature, the reaction mixture was slowly warmed to 80° and maintained at that temperature until the evolution of hydrogen chloride and sulfur dioxide ceased. Rectification gave 10.9 g. (16% yield) of *t*-butyl monochloromethyl sulfide, b.p. 48–49° (18 mm.), $n^{20}\mathrm{D}$ 1.4816; and 27.4 g. (33% yield) of *t*-butyl dichloromethyl sulfide, b.p. 46–47° (2 mm.), $n^{20}\mathrm{D}$ 1.5056, d^{20}_{4} 1.2132. Treatment of both products with thionyl chloride gave *t*-butyl trichloromethyl sulfide.

Anal. Calcd. for $C_5H_{10}Cl_2S$: C, 34.69; H, 5.82. Found: C, 34.60; H, 5.92. Calcd. for $C_5H_{11}ClS$: C, 43.31; H, 8.00. Found: C, 43.33; H, 7.97.

***t*-Butyl Trichloromethyl Sulfide**.—*t*-Butyl methyl sulfide, 100 g. (0.96 mole), was placed in a 1-liter, 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a condenser protected with a calcium chloride drying tube. The flask was cooled in an ice-bath, and 402 g. (3.38 moles), of thionyl chloride was added over a period of 45 minutes. The temperature was increased to 60° and maintained there for two hours, and then increased again to 95° until the evolution of hydrogen chloride and sulfur dioxide ceased (about 8 hours). After removal of sulfur monochloride and excess thionyl chloride, rectification in a 3-foot helix-packed column gave 91.5 g. (46% yield) of *t*-butyl trichloromethyl sulfide, b.p. 72.5–75° (4 mm.). The product was a solid and was melted from the receiving system with an infrared lamp. Rectification of the product again gave *t*-butyl trichloromethyl sulfide, b.p. 90.2° (11 mm.), m.p. 53.5–54.5°.

Anal. Calcd. for $C_5H_9Cl_3S$: C, 28.93; H, 4.37. Found: C, 28.97; H, 4.48.

α,α,α-**Trifluorodimethyl Sulfide**.—Finely pulverized antimony trifluoride, 150 g. (0.84 mole), and 2 g. of antimony pentachloride were placed in a 500-ml., 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a condenser connected to a Dry Ice trap. Forty-six grams (0.28 mole) of α,α,α-trichlorodimethyl sulfide, b.p. 146.0° (750 mm.), $n^{20}\mathrm{D}$ 1.5219, was added over a period of 15 minutes. The flask was warmed in a water bath at 95° until refluxing stopped (about 1 hour). Twenty-eight grams of liquid was collected in the Dry Ice trap. Rectification in a low-temperature column gave 24.3 g. (73% yield) of α,α,α-trifluorodimethyl sulfide, b.p. 11.5–11.7° (750 mm.); molecular weight by the vapor density method, 115.8 and 115.1; calculated molecular weight, 116.1.

α-**Chloro**-α,α-**difluorodimethyl Sulfide**.—Finely pulverized antimony trifluoride, 320 g. (1.79 moles), was placed in a 500-ml., 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a glass delivery tube connected to a receiver cooled in Dry Ice. The flask was heated in an oil-bath at 140°, and 98 g. (0.59 mole) of α,α,α-trichlorodimethyl sulfide was added over a period of 15 minutes. The low-boiling product was rectified in a low-temperature column, and 26.5 g. (37.8% yield) of α,α,α-trifluorodimethyl sulfide, b.p. 11.7–12.0° (750 mm.), was obtained. Rectification of the higher boiling product in a 2-foot, helix-packed column gave 26.5 g. (32.4% yield) of α-chloro-α,α-difluorodimethyl sulfide, b.p. 56.3° (755 mm.), $n^{20}\mathrm{D}$ 1.3926, d^{20}_{4} 1.298, f.p. −100.2°.

Anal. Calcd. for $C_2H_3ClF_2S$: C, 18.12; H, 2.28. Found: C, 18.07; H, 2.27.

α′-**Chloro**-α,α,α-**trifluorodimethyl Sulfide and** α,α′-**Dichloro**-α,α-**difluorodimethyl Sulfide**.—Finely pulverized antimony trifluoride, 850 g. (4.76 moles), and 25 g. of antimony pentachloride were placed in a 1-liter, 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a glass delivery tube extending into a receiver cooled in ice-water and, in turn, connected to a Dry Ice trap. The flask was cooled in a water-bath at 20°, and 478 g. (2.38 moles), of α,α,α,α′-tetrachlorodimethyl sulfide, b.p. 188.7° (744 mm.), $n^{20}\mathrm{D}$ 1.5457, was added over a period of 15 minutes. The temperature of the bath was increased to 80° and maintained there until distillation stopped. Rectification of the product in a 3-foot, helix-packed column gave 236.5 g. (66% yield) of α′-chloro-α,α,α-trifluorodimethyl sulfide, b.p. 63.5° (740 mm.), $n^{20}\mathrm{D}$ 1.3818, d^{20}_{4} 1.4122; and 36.0 g. (9% yield) of α,α′-dichloro-α,α-difluorodimethyl sulfide, b.p. 105.7° (740 mm.), $n^{20}\mathrm{D}$ 1.4408, d^{20}_{4} 1.510. Treatment of α,α′-dichloro-α,α-difluorodimethyl sulfide with more antimony trifluoride and antimony pentachloride gave α′-chloro-α,α,α-trifluorodimethyl sulfide, which was also prepared by treating α,α,α-trifluorodimethyl sulfide with chlorine in a Carius tube at 190°.

Anal. Calcd. for $C_2H_2ClF_3S$: C, 15.95; H, 1.34. Found: C, 15.95; H, 1.35. Calcd. for $C_2H_2Cl_2F_2S$: C, 14.38; H, 1.21. Found: C, 14.50; H, 1.16.

Pentafluorodimethyl Sulfide.—Finely pulverized antimony trifluoride, 250 g. (1.12 moles), and 20 g. of antimony pentachloride were placed in a 500-ml., 3-neck flask equipped with a sealed stirrer, a dropping funnel, and a condenser

---

[20] H. Rheinboldt, *et al.*, *J. prakt. Chem.*, **134**, 272 (1932).

TABLE II

Sulfone	Yield, %	M.p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$CH_3SO_2CH_2Cl$	37	57.2–58.2[a]				
$CH_3SO_2CHCl_2$	56	72.0–73.3	14.73	2.47	14.83	2.38
$CH_2ClSO_2CH_2Cl$	36	69.4–70.5[b]	14.73	2.47	14.84	2.54
$CH_2ClSO_2CHCl_2$	67	Clear, colorless liquid[c]	12.16	1.53	12.11	1.53
$CH_3SO_2CCl_3$	62	173.8–174.2	12.16	1.53	12.35	1.77
$CH_2ClSO_2CCl_3$	66	49.8–50.0	10.36	0.87	10.37	0.83
				Cl, 61.11		Cl, 61.1
$CHCl_2SO_2CHCl_2$	[d]	103.8–104.5	10.36	0.87	10.30	0.91
				Cl, 61.11		Cl, 61.1
$CHCl_2SO_2CCl_3$	13	36.2–36.4[e]	9.02	0.38	9.06	0.40
$CCl_3SO_2CCl_3$	36	35.7–36.0[e]	7.98	0.00	8.04	0.06
$(CH_3)_3CSO_2CCl_3$	17	130.2–130.8	25.07	3.79	25.05	3.82
$CH_3SO_2CF_3$	40	Clear, colorless, odorless liquid[f]	16.22	2.04	15.94	2.01
$CH_3SO_2CClF_2$	62	21.0–21.6[g]	14.60	1.84	14.71	1.79
$CH_2ClSO_2CF_3$	46	[h]	13.16	1.10	13.13	1.09

[a] Literature value, 56°.[4] [b] Literature value, 70.5–72°[13]; mixed m.p. with $CH_3SO_2CHCl_2$. 44–64°. [c] B.p. 96° (2 mm.). n^{20}_4 1.5303, d^{20}_4 1.7010, f.p. −35°. [d] Obtained by oxidation of a mixture of $CH_2ClSCCl_3$ and $CHCl_2SCHCl_2$ followed by fractional crystallization from petroleum ether (b.p. 60–70°). [e] Mixed m.p. of these two compounds was below room temperature. [f] B.p. 128.9° (737 mm.), n^{20}_D 1.3486, d^{20}_4 1.5141, f.p. 14.0°. [g] B.p. 165.1° (760 mm.), n^{20}_D 1.4050, d^{20}_4 1.5685. [h] B.p. 139.9° (751 mm.), n^{20}_D 1.3859, d^{20}_4 1.6533, f.p. −90°.

connected to a Dry Ice trap. One hundred and six grams of products (about 30 g. of pentachlorodimethyl sulfide and 76 g. of α,α,α,α′-tetrachlorodimethyl sulfide), b.p. 55–60° (4 mm.), obtained in several chlorinations of dimethyl sulfide with sulfuryl chloride were combined and added to the flask over a period of 10 minutes. The flask was warmed in a water-bath at 95° for 30 minutes, and then the condenser was replaced with a delivery tube extending into a receiver cooled in ice water. Warming at 95° was continued until distillation stopped. Rectification of the product boiling below room temperature in a Podbielniak Hyd-Robot low-temperature fractionation apparatus gave 9.3 g. (about 45% yield) of pentafluorodimethyl sulfide, b.p. 0.8–1.3° (760 mm.). Qualitative analysis showed that it contained sulfur and fluorine but no chlorine. The molecular weight found by the vapor density method was 152.7 and 153.3; calculated molecular weight, 152.1.

Oxidation to Sulfones.—A solution of the sulfide in glacial acetic acid was added with stirring and external cooling to a solution of chromic oxide in glacial acetic acid (approx. molar ratio, 2.5 CrO_3:1.0 sulfide). The reaction mixture was heated to 95° and kept there for 15 minutes to one hour. The solution was poured into ice water and neutralized with sodium hydroxide. The resulting sulfone was filtered off or extracted with chloroform and it was recrystallized usually from petroleum ether (b.p. 60–70°). Results in these oxidations are tabulated below.

Acknowledgment.—The authors are indebted to the Air Materiel Command, Wright Field, and to the Purdue Research Foundation for the financial assistance which made this work possible.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE PURDUE UNIVERSITY]

Alkylation of Certain Phenolic Compounds[1]

BY ED. F. DEGERING, HAROLD J. GRYTING AND P. A. TETRAULT

RECEIVED JANUARY 6, 1952

A series of alkylated cresols and chlorophenols has been prepared by the alkylation of *o*-cresol, *p*-cresol, *o*-chlorophenol and *p*-chlorophenol with capryl, cetyl and lauryl alcohols. *o*-Cresol was also alkylated with *n*-decyl alcohol and 1-octanol. The 4-capryl-2-methylphenol and 4-(2-decyl)-2-methylphenol were ring acylated with chloroacetyl chloride. Certain physical properties of these compounds are tabulated. The compounds described herein, some of which are of themselves good germicides,[2] were prepared as intermediates in the synthesis of phenolic-quaternary-ammonium type germicides.

Alkylation and alkylation of phenols have been discussed, respectively, by Shreve[3a] and Price.[3b]

It is also known that zinc chloride catalyzes alkylation of phenols with alcohols in the para-position and, where that is impossible, in the ortho-position without substantial rearrangements to meta-derivatives which are often obtained with aluminum chloride. Rearrangements of alkyl groups from primary to secondary generally occur, however, in zinc chloride-catalyzed alkylations of this type.[4]

Experimental

The alkylation of *o*-cresol with cetyl alcohol in the presence of zinc chloride for the preparation of a mixture of alkylphenol isomers, in which 4-(2-cetyl)-2-methylphenol predominates, is typical of the reactions we have utilized in the synthesis of the alkylcresols and alkylchlorophenols whose physical properties are recorded in the accompanying table.

---

(1) Abstract of a portion of a thesis submitted to the Faculty of Purdue University by Harold J. Gryting in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947. This project was sponsored by the Alrose Chemical Company, Providence, Rhode Island.

(2) Ed. F. Degering, H. J. Gryting and P. A. Tetrault, unpublished work.

(3) (a) P. H. Groggins, "Unit Processes in Organic Synthesis," Chapter by R. N. Shreve, pp. 485–532 (1938); (b) C. C. Price, *Chem. Revs.*, **29**, 37 (1941); also R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946.

(4) L. H. Flett, U. S. Patent 2,205,947 (June 25, 1940).