[Contribution from the Department of Chemistry of the University of Maine]

SULFENYL CHLORIDE STUDIES. II. MONO-, DI-, AND TRI-CHLOROMETHANESULFENYL CHLORIDES AND CERTAIN OF THEIR DERIVATIVES[1,2]

IRWIN B. DOUGLASS, FREDERIC T. MARTIN, AND ROGER ADDOR

Received May 1, 1951

In the first paper of this series (1) reference was made to the difficulty encountered in the preparation of pure chloromethanesulfenyl chloride, $ClCH_2SCl$ (I), and some of its derivatives. The fact that dichloromethanesulfenyl chloride, Cl_2CHSCl (II), has been prepared by Wood (2) under conditions only slightly different than those employed in the preparation of I and the fact that the two compounds have boiling points not far apart at reduced pressure suggested that each might be contaminated by the other in ordinary preparations. Although II is sufficiently stable to withstand the long refluxing of close fractionation and can be prepared in a pure condition, I is much less stable and, at least in this laboratory, has never been prepared completely free from II.

In order to determine the properties of pure I, pure II and pure trichloromethanesulfenyl chloride, Cl_3CSCl (III), were prepared so that their refractive indices and densities might be plotted against chlorine content along with the similar properties of preparations of I (Figure 1). Since the density points fall on a curve which deviates only slightly from a straight line, the approximate density of pure I can be extrapolated.

The refractive index-chlorine content curve for the same three compounds (Fig. 2) assumed an unexpected shape and is essentially flat over a considerable range of composition. This fact helped to explain experimental difficulties encountered earlier when it was found that refractive index could not be satisfactorily employed to distinguish between distilled fractions of these sulfenyl chlorides which might have widely differing chlorine contents. In the latter part of this study it became evident that the density, as determined by the method of Lipkin (3), was of great value in identifying the composition of distilled fractions.

Attempts have been made to react I with various mercaptans in order to obtain representatives of a new series of chloromethyl disulfides. In spite of all efforts to purify them by fractionation through a four-foot packed column, these sulfides have not been prepared pure. No such difficulty was encountered in the isolation of dichloromethyl ethyl disulfide and it is not clear whether the disulfides derived from I are contaminated by the analogous disulfides derived from II or whether the contaminant of higher chlorine content is some compound such as bis(chloromethyl) disulfide, $ClCH_2SSCH_2Cl$, formed by disproportiona-

---

[1] This paper reports a portion of the work done on project NR 055 165 under contract N8onr77,000 with the Office of Naval Research, United States Navy.

[2] Presented before the Organic Division of the American Chemical Society, Boston, Massachusetts, April 4, 1951.

tion during the distillation. The latter view is supported by the fact that when fractions of chloromethyl phenyl disulfide boiling over a narrow temperature range were redistilled they yielded bis(chloromethyl) disulfide and left a residue of diphenyl disulfide.

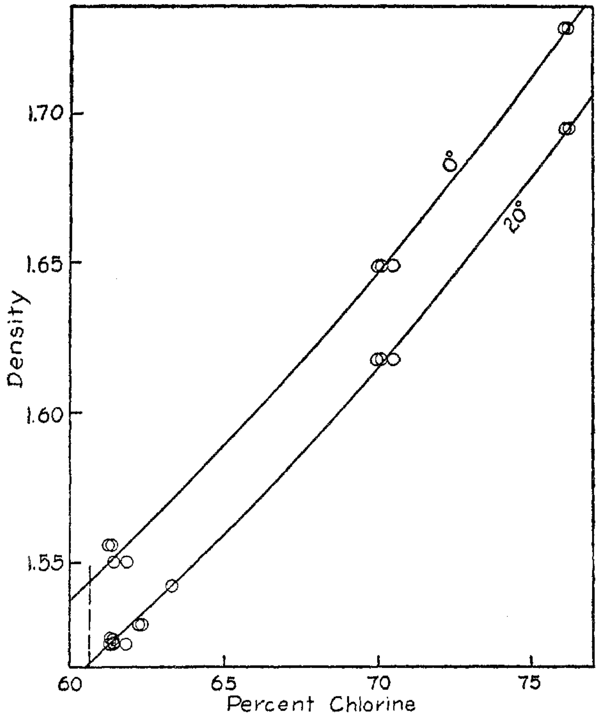

FIGURE 1. REPRESENTATIVE PREPARATIONS OF MONO-, DI-, AND TRI-CHLOROMETHANESULFENYL CHLORIDES

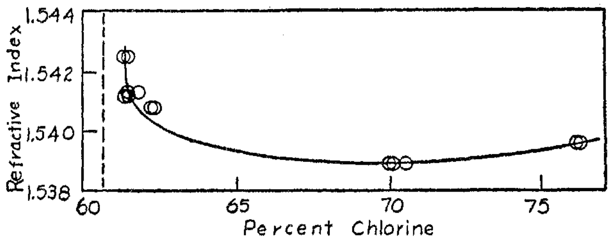

FIGURE 2. REPRESENTATIVE PREPARATIONS OF MONO-, DI-, AND TRI-CHLOROMETHANESULFENYL CHLORIDES

$$2\ ClCH_2SSC_6H_5 \rightarrow ClCH_2SSCH_2Cl + C_6H_5SSC_6H_5$$

By preparing the ethyl disulfide derivatives of II and III, $Cl_2CHSSC_2H_5$ and $Cl_3CSSC_2H_5$, and plotting their properties against chlorine content along with

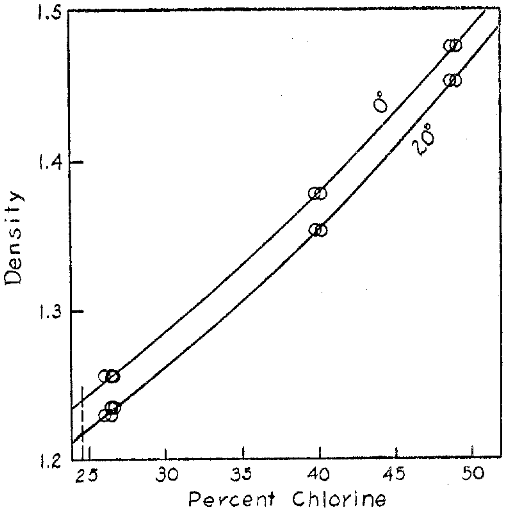

FIGURE 3. REPRESENTATIVE PREPARATIONS OF CHLORO-, DICHLORO- AND TRICHLOROMETHYL ETHYL DISULFIDES

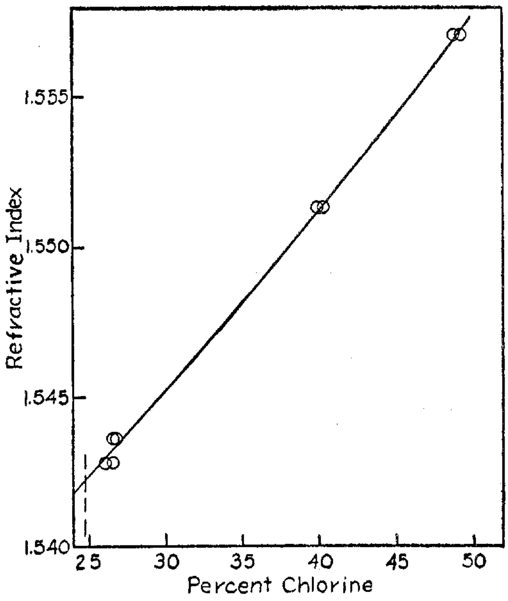

FIGURE 4. REPRESENTATIVE PREPARATIONS OF CHLORO-, DICHLORO- AND TRICHLOROMETHYL ETHYL DISULFIDES

the properties of the impure ethyl disulfide derivative of I, $ClCH_2SSC_2H_5$, it has been possible to extrapolate to the approximate properties of pure $ClCH_2SSC_2H_5$ (Figures 3 and 4).

The only derivative of I of reasonable purity thus far prepared is chloromethyl 2-chloroethyl sulfide, $ClCH_2SCH_2CH_2Cl$, which resulted from passing a stream of ethylene into a solution of I in methylene chloride. The 2-chloroethyl derivative of II, $Cl_2CHSCH_2CH_2Cl$, was prepared in a similar manner. Under the same conditions, however, it was not possible to bring about reaction between III and ethylene. Since the reaction of sulfenyl chlorides with olefins is a characteristic reaction of this class of compounds, the failure of III to react in this manner is another example of its unusual properties, the most outstanding being its ability to withstand hydrolysis during steam-distillation (4).

In all cases the calculated molar refractions were determined by using the values of Vogel (5).

EXPERIMENTAL PART

Chloromethanesulfenyl chloride, $ClCH_2SCl$ (I). The preparation of this compound was carried out by the methods already described (1) and also by the chlorination of *s*-trithiane in methylene chloride at −20 to −25°. The physical properties and analyses of representative preparations of I are shown in Table I.

TABLE I

REPRESENTATIVE PREPARATIONS OF CHLOROMETHANESULFENYL CHLORIDE

n_D^{20}	d_4^{20}	d_4^0	CHLORINE, % Calc'd for CH_2Cl_2S, 60.61
1.5413	1.5226	1.5501	61.8, 61.4
1.5408	1.5293	1.5558	62.3, 62.2
1.5412	1.5242		61.4, 61.3
1.5425	1.5229		61.3, 61.4
	1.542		63.3

It would appear from Figure 1 that the approximate density of pure chloromethanesulfenyl chloride is d_4^{20} 1.515, d_4^0 1.538.

Dichloromethanesulfenyl chloride, Cl_2CHSCl (II). The following modification of the method of Wood (2) was employed: *s*-Trithiane (25 g.) was placed in a dry flask fitted with a stirrer and surrounded by a bath of ice-water. Dry chlorine was passed in at a slow rate and as soon as the solid had liquefied, the mixture was maintained at 10° to 20° until approximately 57 g. of chlorine had been absorbed. The mixture was then distilled through a ten-inch Vigreux column at reduced pressure. In five preparations the yield of II was 46–60% based on the total carbon available in the *s*-trithiane used.

Careful fractionation of the accumulation of II from several preparations through a four-foot packed column gave a pure product with b.p. 30°/10 mm., n_D^{20} 1.5389, d_4^{20} 1.6176 d_4^0 1.6486.

Anal. Calc'd for $CHCl_3S$: Cl, 70.23; M.W., 151.45.
Found: Cl, 70.5, 70.1, 70.0; M.W., 152.

Bis(dichloromethyl) sulfide, $Cl_2CHSCHCl_2$. In the fractionation of preparations of II there was always a higher-boiling fraction corresponding in chlorine content and molar refraction to bis(dichloromethyl) sulfide. In five preparations the yield of this sulfide varied from 25–35% based on the carbon available in the original *s*-trithiane. The product from several preparations was fractionated through a four-foot packed column. The principal fraction had b.p. 103–104°/48 mm. (72°/6 mm.), n_D^{20} 1.5464; d_4^{20} 1.6273; d_4^0 1.6560.

Anal. Calc'd for $C_2H_2Cl_4S$: Cl. 70.98; M.W., 199.9; MR_D 39.219.
Found: Cl, 70.7; M.W., 199; MR_D 38.9.

Trichloromethanesulfenyl chloride, Cl_3CSCl (III). This compound was prepared by the method of Helfrich and Reid (4) and was carefully fractionated through a four-foot packed column. The major portion had b.p. 51°/25 mm.; n_D^{20} 1.5395; d_4^{20} 1.6947; d_4^0 1.7278.

Anal. Calc'd for CCl_4S: Cl, 76.30. Found: Cl, 76.1, 76.2.

Chloromethyl ethyl disulfide, $ClCH_2SSC_2H_5$. Ethyl mercaptan was added dropwise to a cooled solution of I in methylene chloride. When the yellow color had largely disappeared the reaction mixture was evacuated to remove excess ethyl mercaptan, methylene chloride, and gaseous HCl, and was then distilled through a four-foot packed column under a reflux ratio of approximately 10–1. Those fractions having identical refractive indices were refractionated. The middle portion had b.p. 73–74°/15 mm. (56°/8 mm.), n_D^{20} 1.5436, d_4^{20} 1.2349, d_4^0 1.2573.

Anal. Calc'd for $C_3H_7ClS_2$: Cl, 24.85; M.W., 142.7; MR_D 36.845.

Found: Cl, 26.6, 26.8; M.W., 146; MR_D 36.4.

The experiment was repeated a second time with greater care and the fraction isolated had n_D^{20} 1.5428, d_4^{20} 1.230, d_4^0 1.258.

Anal. Found: Cl, 26.1, 26.1, 26.6; MR_D 36.6.

The identity of the impurity with the high chlorine content was not established. The liquid product could not be purified by crystallization even at the temperature of Dry Ice.

By extrapolation of the properties–composition curves of Figures 3 and 4 it would appear that pure chloromethyl ethyl disulfide must have n_D^{20} 1.542, d_4^{20} 1.217, d_4^0 1.241.

Chloromethyl phenyl disulfide, $ClCH_2SSC_6H_5$. A freshly prepared sample of I was diluted with methylene chloride and treated with thiophenol until decolorized. The reaction mixture was fractionated through an 18-inch Vigreux column; it yielded three components, a low-boiling fraction A (11%, $ClCH_2SSCH_2Cl$), an intermediate boiling fraction B (17%, $ClCH_2SSC_6H_5$), and a solid residue C [27%, $(C_6H_5S)_2$]. The remaining 45% included fractions between the principal components.

The solid residue, C, after recrystallizing from alcohol melted at 61° and the mixture melting point with pure diphenyl disulfide was unchanged.

The intermediate fraction B, with b.p. 127–129°/6 mm., n_D^{20} 1.6290, d_4^{20} 1.323, d_4^0 1.342, is believed to be chloromethyl phenyl disulfide contaminated with some impurity having a higher chlorine content.

Anal. Calc'd for $C_2H_7ClS_2$: Cl, 18.59; MR_D 51.904.

Found: Cl, 22.7, 22.6; MR_D 51.2.

Although the reaction between I and thiophenol was carried out several times, no fraction corresponding to B was ever obtained containing less than 22% chlorine.

When the intermediate fraction B was redistilled it was resolved into the same fractions A, B, and C described above.

Bis(chloromethyl) disulfide, $ClCH_2SSCH_2Cl$. The low-boiling component A obtained above, b.p. 75–77°/6 mm., n_D^{20} 1.5863, d_4^{20} 1.470, d_4^0 1.495, is believed to be bis(chloromethyl) disulfide, $ClCH_2SSCH_2Cl$, recently reported by Brintzinger and others (6).

Anal. Calc'd for $C_2H_4Cl_2S_2$: Cl, 43.48; MR_D 37.036. Found: Cl, 42.8, 42.9.

Dichloromethyl ethyl disulfide, $Cl_2CHSSC_2H_5$. The sulfenyl chloride II (20 g.) was treated with ethyl mercaptan and the reaction mixture was distilled through a 10-inch Vigreux column. Redistillation of the crude product (80% yield) through a packed column gave a middle fraction with b.p. 87°/13 mm., d_4^{20} 1.353, d_4^0 1.377, n_D^{20} 1.5513.

Anal. Calc'd for $C_3H_6Cl_2S$: Cl, 40.04; MR_D 42.03.

Found: Cl, 39.9, 40.3; MR_D 41.77.

Trichloromethyl ethyl disulfide, $Cl_3CSSC_2H_5$. Carefully purified III (28 g.) treated with ethyl mercaptan gave 24 g. of product (76% yield), b.p. 100°/20 mm. Redistillation through a four-foot packed column, utilizing methyl phthalate as a "booster," gave a middle fraction with b.p. 82°/5 mm., n_D^{20} 1.5571, d_4^{20} 1.452, d_4^0 1.475.

Anal. Calc'd for $C_3H_5Cl_3S_2$: Cl, 50.28; MR_D 47.023.

Found: Cl, 48.8, 49.2, 50.3; MR_D 46.9.

Chloromethyl 2-chloroethyl sulfide, $ClCH_2SCH_2CH_2Cl$. The sulfenyl chloride I (19 g.) was diluted with 20 ml. of methylene chloride and stirred in a flask surrounded by an ice-bath. Ethylene was passed in while the temperature was maintained below 20° until the yellow color disappeared. The reaction mixture was distilled through a 10-inch Vigreux column and yielded 12 g. of product (52%), b.p. 83°/14 mm. to 84°/10 mm. A middle fraction had b.p. 82°/12 mm., n_D^{20} 1.5311, d_4^{20} 1.338, d_4^0 1.359.

Anal. Calc'd for $C_3H_6Cl_2S$: Cl, 50.03; MR_D 33.55.
Found: Cl, 49.3, 49.1, 49.2; MR_D 33.55.

This compound has been reported recently as having a slightly higher density (6). The low chlorine content of our sample suggests that some dehydrohalogenation has occurred.

Dichloromethyl 2-chloroethyl sulfide, $Cl_2CHSCH_2CH_2Cl$. Reaction between II (28 g.) and ethylene and fractionation through a ten-inch Vigreux column yielded 20 g. (60%) of colorless liquid, b.p. 100°/20 mm. A middle fraction had n_D^{20} 1.5390, d_4^{20} 1.461, d_4^0 1.485.

Anal. Calc'd for $C_3H_5Cl_3S$: Cl, 59.26; MR_D 38.708.
Found: Cl, 59.3, 59.3; MR_D 38.50.

Attempted reaction of trichloromethanesulfenyl chloride with ethylene. Carefully purified III (30 g.) was diluted with 25 ml. of methylene chloride and treated with ethylene gas as previously described. The yellow color did not diminish as in the reactions of ethylene with I and II. After passing ethylene slowly through the solution for 30 minutes, the mixture was fractionally distilled. After removing the methylene chloride 22 g. of a yellow product boiling at 45–46°/20 mm. was recovered and was identified by its density as unchanged starting material.

SUMMARY

1. When $ClCH_2SCl$ is prepared by the chlorination of *s*-trithiane it is always contaminated with small amounts of more highly chlorinated material, presumably Cl_2CHSCl.

2. The densities of carefully purified Cl_3CHSCl and Cl_2CSCl have been determined and have been utilized to determine by extrapolation the probable density of pure $ClCH_2SCl$.

3. The refractive index is a much less satisfactory criterion of purity among sulfenyl chlorides of this type than the density.

4. The ethyl and phenyl disulfide derivatives of $ClCH_2SCl$ have been formed but have proven to be resistant to purification. The probable properties of pure $ClCH_2SSC_2H_5$ have been determined by extrapolation from the properties of the corresponding dichloro- and trichloro-compounds.

5. By-products of the preparation and distillation of $ClCH_2SSC_6H_5$ are bis-(chloromethyl) disulfide and diphenyl disulfide suggesting that this compound undergoes disproportionation during distillation.

6. The formation of $Cl_2CHSCHCl_2$ during the preparation of Cl_2CHSCl has been described.

7. The 2-chloroethyl sulfide derivatives of mono- and di-chloromethanesulfenyl chlorides have been prepared but under the same conditions Cl_3CSCl fails to react with ethylene.

Orono, Maine

REFERENCES

(1) Douglass and Martin, *J. Org. Chem.*, **15**, 795 (1950).
(2) Wood, U. S. Patent 2,484,061 (1949).
(3) Lipkin, Davison, Harvey, and Kurtz, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 55 (1944).
(4) Helfrich and Reid, *J. Am. Chem. Soc.*, **43**, 591 (1921).
(5) Vogel, *J. Chem. Soc.*, 1833 (1948).
(6) Brintzinger, Pfannstiel, Koddebusch, and Kling, *Chem. Ber.*, **83**, 87 (1950).