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

SULFENYL CHLORIDE STUDIES. I. THE ANHYDROUS CHLORINATION OF CERTAIN *s*-TRITHIANES[1]

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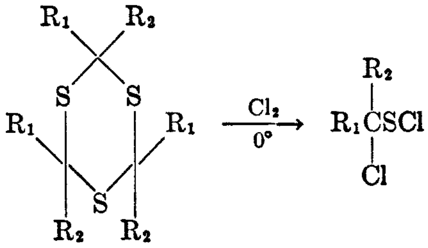
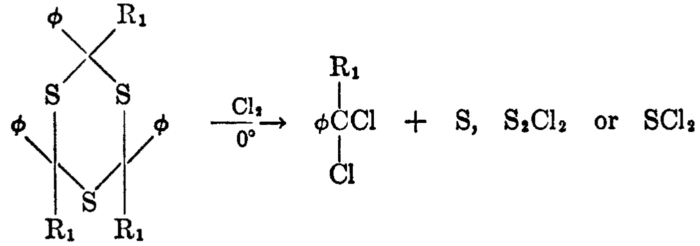
Earlier work in this laboratory (1) has shown that anhydrous chlorine reacts with *s*-trithiane to form chloromethanesulfenyl chloride, $ClCH_2SCl$. The present paper is concerned with a further study of this reaction and its extension to other trimeric thioaldehydes and thioketones.

It has been found that the 2,4,6-trialkyl-*s*-trithianes and 2,2,4,4,6,6-hexamethyl-*s*-trithiane react smoothly with chlorine at low temperatures to form 1-chloroalkanesulfenyl chlorides. It appears, however, that when the substituted *s*-trithiane has phenyl groups in the 2,4,6-positions the action of chlorine is to eliminate sulfur completely and form 1,1-dichloro compounds.



(a) $R_1 = H$, $R_2 = H$, CH_3, C_2H_5 or $n-C_3H_7$
(b) $R_1 = R_2 = CH_3$



$R_1 = H$, CH_3

The 1-chloroalkanesulfenyl chlorides are yellow, highly refractive and unstable liquids with unpleasant odors. Their instability appears to be associated with the presence of hydrogen atoms on the *alpha*-carbon atoms. Great difficulty was encountered, for example, in avoiding the over-chlorination of chloromethanesulfenyl chloride, $ClCH_2SCl$, but dimethylchloromethanesulfenyl chloride, $(CH_3)_2CClSCl$, was prepared and distilled with comparative ease. Wood, in a recent patent (2), has described the preparation of dichloromethanesulfenyl

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chloride, Cl_2CHSCl, by the reaction of chlorine with *s*-trithiane at higher temperatures than those employed in this study and has provided an explanation for some of the difficulties encountered in the preparation of chloromethanesulfenyl chloride. The instability of the compounds is reflected in the number of significant figures used in reporting their densities and refractive indices. We have found that the density in particular varies markedly with small changes in chlorine content.

The reactions of the 1-chloroalkanesulfenyl chlorides have not been thoroughly investigated but preliminary tests indicate that they are similar to those of other sulfenyl chlorides (10, 11). Chloromethanesulfenyl chloride reacts readily with acetone, olefins, mercaptans, phenols, secondary amines, potassium iodide and alcohol. The products formed, however, are themselves highly reactive in some cases and tend to decompose during the process of purification. It is planned to report later on further studies of the derivatives of the 1-chloroalkanesulfenyl chlorides.

EXPERIMENTAL PART

Chlorination procedure. A one-liter, three-necked flask fitted with stirrer, chlorine inlet tube, outlet tube, and thermometer was surrounded by ice and salt. In the more successful experiments the temperature of the reaction mixture was maintained constantly below 0°.

Method A. In some trials the solid *s*-trithiane was introduced in successive 2–5 g.-portions to the dry flask. The solid rapidly became liquefied and the accumulating liquid acted as a suspending medium for later portions of the solid. This method had the disadvantage that until a quantity of liquid had accumulated, the exothermic nature of the reaction and the low thermal conductivity of the dry solid made it difficult to control the temperature of the reaction at the solid-gas interface.

Method B. Another procedure which made more efficient cooling possible was to introduce 25–50 cc. of inert solvent, such as carbon tetrachloride or methylene chloride, along with 20–25 g. of the substance being chlorinated.

In all cases the flask with its contents was weighed before chlorinating and at intervals during the reaction. Chlorination was terminated when three moles of chlorine per mole of trithiane had been taken up.

Other experimental procedures. It was originally intended to carry out the purification of the new sulfenyl chlorides in a Todd Fractionation Assembly (3) in order to make possible the determination of precise physical constants. It was found, however, that the compounds were too unstable to withstand the prolonged refluxing of such close fractionation. A ten-inch wrapped Vigreux column was finally adopted as a compromise which would give reasonably good fractionation and still permit distillation in a minimum of time.

After distillation, the determination of refractive index, density, molecular weight, and chlorine content of the sulfenyl chlorides had to be made immediately, for standing overnight, even in the ice-chest, allowed decomposition to begin. Density determinations were carried out with the pycnometer described by Lipkin, Davison, Harvey, and Kurtz (4). All molecular weights were determined cryoscopically in benzene.

s-Trithiane. s-Trithiane was prepared by a more rapid method than that generally employed (5). The mixture of formalin and concentrated hydrochloric acid was placed in a flask fitted with a stirring device and hydrogen sulfide was passed in from a Kipp generator as rapidly as it could be generated. Heat was liberated but no attempt was made to cool the reaction mixture. When solid *s*-trithiane had formed to such an extent as to interfere with the stirring, the mixture was filtered, the filtrate returned to the flask and the passage of hydrogen sulfide continued. The solid was washed repeatedly with water and after drying was used for chlorination without further purification.

Chloromethanesulfenyl chloride, $ClCH_2SCl$. The chlorination of *s*-trithiane was repeated many times by both methods A and B with yields of 10–20%. The following properties of chloromethanesulfenyl chloride are probably more accurate than those previously reported (1) although it is doubtful if the compound has yet been prepared in a chemically pure condition: b.p. 33°/18 mm., n_D^{20} 1.542, d_4^{20} 1.52, d_4^{0} 1.55.

Anal. Calc'd for CH_2Cl_2S: Cl, 60.61; Mol. wt., 117.0.
Found: Cl, 60.5, 61.2; Mol. wt., 121, 122.

1-Chloroethanesulfenyl chloride, $CH_3CHClSCl$. When 20 g. of trithioacetaldehyde prepared by the method of Baumann and Fromm (6) was chlorinated by method A, 7 g. (16% yield) of a golden yellow liquid was obtained having the following properties: b.p. 47–50°/40 mm., n_D^{20} 1.5102, d_4^{20} 1.347, d_4^{0} 1.363.

Anal. Calc'd for $C_2H_4Cl_2S$: Cl, 54.12; Mol. wt., 131.
Found: Cl, 54.0, 54.3; Mol. wt., 136.

Trithiopropionaldehyde, 2,4,6-Triethyl-s-trithiane. Freshly distilled propionaldehyde (174 g.) was added to 500 cc. of cold ethanol into which previously 95 g. of hydrogen chloride had been absorbed. The mixture was then held at 5° or lower while hydrogen sulfide was passed in for three hours and there had been an increase in weight of 75 g. After standing overnight in the ice-chest the mixture separated into two layers. The lower layer was washed well with water and then with sodium bicarbonate solution, dried over calcium chloride, and subjected to vacuum-distillation. There was no sharp separation into fractions but a steady rise in temperature from 25°/23 mm. to 185°/13 mm. The principal fractions (53.4 g.) were collected between 135–160°/13 mm. After stopping the distillation at 185°/13 mm. there was 47 g. of residue undistilled.

Several of the fractions yielded white crystals on standing at room temperature or in the ice-chest. One fraction had b.p. 143°/10 mm., n_D^{25} 1.5472.

Anal. Calc'd for $C_9H_{18}S_3$: Mol. wt., 222. Found: Mol. wt., 228.

It solidified almost completely to a white solid which melted over a range of several degrees near 54°. This solid was resolved into two components by recrystallization from alcohol, one melting at 36° and the other at 76°.

The component melting at 36° was also obtained in pure condition by the partial crystallization of a liquid fraction, b.p. 135–143°/10 mm., n_D^{25} 1.5461. The solid was analyzed.

Anal. Calc'd for $C_9H_{18}S_3$: S, 43.24. Found: S, 42.6, 42.2.

The component melting at 76° was also obtained by the partial crystallization of a fraction b.p. 150-155°/10 mm., n_D^{25} 1.5478.

Anal. Calc'd for $C_9H_{18}S_3$: S, 43.24. Found: S, 44.0, 43.5.

Less than 15 g. of solid was obtained from all fractions.

It seems probable that the solids melting at 36° and 76° respectively are the *alpha* and *beta* isomers of 2,4,6-triethyl-s-trithiane which structural theory leads one to expect. The failure of the entire preparation to boil over a narrow temperature range may be due to the presence of a relatively large proportion of the dehydration and condensation products of propionaldehyde or thiopropionaldehyde in addition to linear polymers of the latter.

A dramatic description of the malodorous volatile by-products accompanying the preparation of trithioacetone has been recorded (7). The odors of certain compounds formed in the reaction of propionaldehyde with hydrogen sulfide and hydrogen chloride are fully as bad. Both the crude reaction mixture and the more volatile products of distillation have an exceedingly offensive smell somewhat resembling onions, hence the preparation of trithiopropionaldehyde should not be attempted without taking due precautions for the complete disposal of the waste liquids and the efficient trapping of all uncondensed vapors during distillation.

1-Choropropane-1-sulfenyl chloride, $C_2H_5CHClSCl$. A 28.2 g.-portion of liquid trithiopropionaldehyde, b.p. 143–160°/8 mm., was chlorinated until 26.8 g. of chlorine had been absorbed. Upon distillation 19.6 g. of yellow liquid boiling over the range 58°/29 mm. to 80°/39 mm. was collected. Upon redistillation there was obtained as the principal fraction 8.1 g. (14% yield) of a yellow liquid, b. p. 62–64°/27 mm.; n_D^{20} 1.501, d_4^{20} 1.276, d_4^{0} 1.301.

Anal. Calc'd for $C_3H_6Cl_2S$: Cl, 48.89; Mol. wt., 145.
Found: Cl, 48.2, 48.8; Mol. wt., 145.

Trithiobutyraldehyde. The preparation of trithiobutyraldehyde was attempted by essentially the same method as that used in the preparation of trithiopropionaldehyde but no pure compound was isolated. Four fractions collected within the range 120-200°/8 mm. had molecular weights of 234, 252, 261, and 320 respectively. Calc'd for $(C_3H_7CHS)_3$, 264. The fraction with molecular weight 261 and b.p. 155–180°/8 mm. was analyzed for sulfur.

Anal. Calc'd for $C_{12}H_{24}S_3$, S, 36.36. Found: S, 29.0, 28.7.

The fractions with molecular weights of 252, 261, and 320 were assumed to contain some trithiobutyraldehyde or closely related compounds, and were combined for chlorination without further attempts at fractionation.

1-Chlorobutane-1-sulfenyl chloride, $C_3H_7CHClSCl$. The combined liquid fractions of trithiobutyraldehyde referred to above (20 g.) were chlorinated in the absence of inert solvent. After 16 g. of chlorine had been absorbed the mixture was distilled. Three small fractions boiling in the range 67–73°/20 mm. were collected and immediately recombined. Redistillation yielded 4.9 g. of a yellow, sour-smelling, lacrymatory liquid with the following properties: b.p. 62–65°/15 mm., n_D^{20} 1.490, d_4^{20} 1.202.

Anal. Calc'd for $C_4H_8Cl_2S$: Cl, 44.58; Mol. wt., 159.
Found: Cl, 43.5, 43.8, 43.9; Mol. wt., 155.

Trithioacetone, 2,2,4,4,6,6-Hexamethyl-s-trithiane. By employing the method of Baumann and Fromm (7), except that steam-distillation was omitted, 81 g. (36% yield) of trithioacetone was obtained from 174 g. of acetone. The product had the properties: b.p. 105-107°/10 mm., n_D^{24} 1.5400.

Anal. Calc'd for $C_9H_{18}S_3$: Mol. wt., 222. Found: Mol.. wt., 218.

2-Chloropropane-2-sulfenyl chloride, $(CH_3)_2CClSCl$. Purified trithioacetone (18.5 g.) was chlorinated in the usual manner and distilled when the theoretical amount of chlorine had been absorbed. A total of 23.8 g. (67% yield) of yellow liquid was collected at 37–43°/27 mm. A principal fraction of 13.9 g. (38% yield) had b.p. 40°/26 mm.; n_D^{20} 1.493, d_4^{20} 1.249, d_4^{0} 1.273.

Anal. Calc'd for $C_3H_6Cl_2S$: Cl, 48.89; Mol. wt., 145.
Found: Cl, 48.9, 49.3; Mol. wt., 150.

Chlorination of trithiobenzaldehyde, 2,4,6-triphenyltrithiane. Twenty grams of trithiobenzaldehyde, in the presence of 25 cc. of methylene chloride, was chlorinated until 12.6 g. of chlorine (3.6 moles/mole trithiane) had been absorbed. Distillation of the product gave 24 g. (90%) of crude benzal chloride boiling at 77–82°/10 mm. Redistillation gave a purified product, b.p. 82°/10 mm.; n_D^{20} 1.5507, d_4^{20} 1.2485, d_4^{0} 1.2691.

Anal. Calc'd for $C_7H_6Cl_2$: Cl, 43.74; Mol. wt., 161; MR_D, 41.01 (8).
Found: Cl, 44.3, 44.1, 44.3; Mol. wt., 161; MR_D, 41.12.

Chlorination of trithioacetophenone, 2,4,6-trimethyl-2,4,6-triphenyl-s-trithiane. Twenty grams of trithioacetophenone, prepared by the method of Reid (9), was mixed with 25 cc. of methylene chloride and chlorinated as described. The prinicpal product was 1,1-dichloroethylbenzene, $C_6H_5CCl_2CH_3$, which was obtained in 57% yield. Although 1,1-dichloroethylbenzene has been prepared by several previous workers no physical properties have been reported because the compound could not be prepared in a pure condition. The reaction given here, however, takes place readily and no special difficulty was encountered in obtaining a purified product; b.p. 87–88°/11 mm., n_D^{20} 1.5432, d_4^{20} 1.2173, d_4^{0} 1.2339.

Anal. Calc'd for $C_8H_8Cl_2$; Cl, 40.51; Mol. wt., 175; MR_D, 45.66 (8).
Found: Cl, 40.54, 40.28, 40.68; Mol. wt., 175; MR_D, 45.33.

On standing several weeks this purified sample of 1,1-dichloroethylbenzene changed from colorless to dark green and fumed when the moist breath was blown across the opened container.

SUMMARY

1. The trimers of thioformaldehyde, thioacetaldehyde, thiopropionaldehyde, thiobutyraldehyde, and thioacetone yield upon chlorination under anhydrous conditions 1-chloroalkanesulfenyl chlorides.

2. The action of chlorine upon trithiobenzaldehyde and trithiobenzophenone is to eliminate sulfur and replace it with two chlorine atoms on the same carbon.
3. The *alpha* and *beta* forms of 2,4,6-triethyl-*s*-trithiane have been isolated.

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