

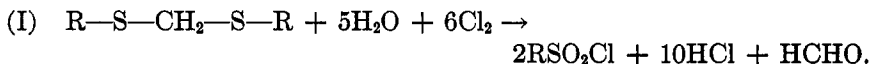
PROPERTIES OF THE THIOMETHYLENE RADICAL. II.
THE BEHAVIOR WITH CHLORINE AND WATER

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There are a number of references in the literature to the use of chlorine in the presence of water as an oxidizing agent for organic sulfur compounds. For example, alkyl sulfides have been oxidized to sulfoxides and sulfones (1); aryl mercaptans have been converted to sulfonyl chlorides (2); sulfonyl chlorides have also been obtained from S-alkyl isothioureas (3), mercaptans, disulfides, thiol esters, and other types of sulfur compounds (4). Kostsova (5) reported that chloromethane sulfonyl chloride is formed in 50% yield when chlorine is passed into a water suspension of trithiane (5).

This paper is mainly concerned with the action of chlorine on normal alkyl and benzyl mercaptals, and trithiane when the compounds are dissolved or suspended in a mixture of acetic acid and water. It was found that the formaldehyde mercaptals of ethyl, *n*-butyl, *n*-amyl, and benzyl mercaptans reacted to form the alkane sulfonyl chlorides in good yields. Formaldehyde was liberated in each case, and it was assumed that the reactions proceeded approximately as follows:

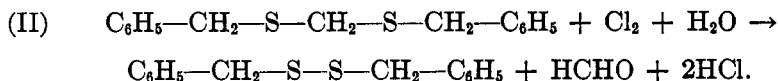


Acetone diethyl mercaptol behaved similarly, yielding ethane sulfonyl chloride and a mixture of the chlorination products of acetone. It was also found that the reagent, as used, acted upon both di-*n*-butyl and di-benzyl sulfides to give the corresponding sulfonyl chlorides.

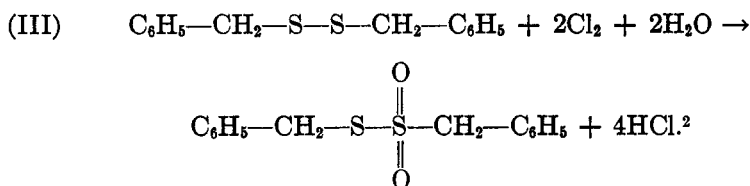
The question arose, at what stage in the above reactions scission of the sulfur-methylene bond occurred. In order to determine whether the oxidation proceeded first to the sulfone stage, sulfonal and di-*n*-butyl sulfone were treated in the manner mentioned above. Both compounds were obtained from this and even more drastic treatment unchanged. On the other hand, butane sulfonyl chloride was formed from dibutyl sulfide. Spring and Winssinger (6) obtained similar results with diethyl sulfoxide. Thus it may be said that the breaking of the sulfur-carbon

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bond occurs before the sulfone stage of oxidation is reached, but may take place after the formation of the sulfoxide. More positive information was obtained with the mercaptals by carrying out the reaction with an amount of chlorine insufficient to complete the process as indicated in equation (I). In particular, with formaldehyde dibenzyl mercaptal, dibenzyl disulfide, and dibenzyl "disulfoxide" were isolated in rather large amounts. Evidently the initial step is substantially as follows:



This is followed by:

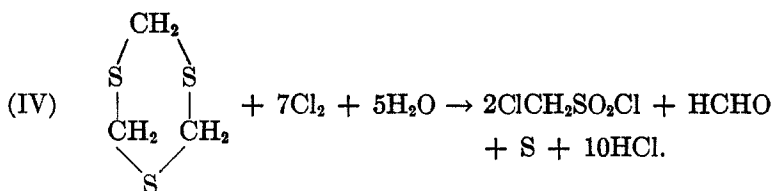


The oxidation continues at least to the "disulfoxide" stage before scission of the sulfur-sulfur bond occurs. No other intermediate oxidation products could be isolated, so that it cannot be said definitely at what stage of oxidation the actual breaking of the sulfur-sulfur bond takes place.

From equations (II) and (I), it is evident that the action of chlorine on alkyl disulfides dissolved in acetic acid and water should produce alkane sulfonyl chlorides in yields as high as those obtained from the mercaptals (70–95%). This is the fact with diethyl, di-*n*-amyl, and dibenzyl disulfides. As a method of preparation for normal or aryl substituted alkane sulfonyl chlorides, this process is probably superior to the more common procedures.

It was thought that Kostsova's (5) reaction involving trithiane might be similar to that which the mercaptals undergo. That is, trithiane may be considered to be a cyclic mercaptal, which would pass through the steps outlined for those compounds, *i.e.*, (a) loss of a methylene group as formaldehyde, and (b) conversion of the resulting cyclic disulfide to two molecules of chloromethane sulfonyl chloride. Also, according to this mechanism, one atom of sulfur would be liberated, either as free sulfur, or as an oxide or a chloride of sulfur. The overall reaction would be represented by the approximate equation:

² There is some question about the structure of "disulfoxides" of this kind. The other possible structure is $\text{C}_6\text{H}_5\text{—CH}_2\text{—SO—SO—CH}_2\text{—C}_6\text{H}_5$.



This equation accounts for all the products obtained when Kostsova's work was repeated. His low yields may be explained by his assumption that each molecule of trithiane is capable of forming three molecules of chloromethane sulfonyl chloride.

EXPERIMENTAL

The general procedure in the experiments reported was to dissolve the sulfur compound in acetic acid (two to five volumes) containing enough water to furnish the required amount of oxygen, and to pass chlorine gas into the solution at a slow rate until a permanent excess was present. The reactions were as a rule complete in a few minutes, and continued addition of the chlorine for several hours did not noticeably alter the yield of the desired products. The reaction-flask was cooled externally, and maintained at about room temperature. The acetic acid-water solution of the compound was sometimes saturated with gaseous hydrogen chloride previous to the addition of the chlorine; this gave a slightly higher yield of the alkane sulfonyl chlorides. At the end of the reaction, when liquid product was expected, two to three volumes of cold water was added to the reaction-mixture, whereupon the water-insoluble, dense alkane sulfonyl chloride formed a bottom layer. This layer was separated and washed once with cold water. The product was purified by distillation, at atmospheric or reduced pressure, and identified by boiling point, density, and refractive index determinations. In the compounds containing the benzylthio-radical, this separation and purification was not needed, for toluene-*alpha*-sulfonyl chloride, m.p. 92-93°, crystallized from the reaction-mixture. In some experiments, as previously noted, the starting materials were not changed under the conditions of the reactions.

The Action of Chlorine in Aqueous Acetic Acid (I) on Certain Sulfides and Disulfides

Di-n-butyl and dibenzyl sulfides. Eight grams of di-*n*-butyl sulfide gave 6.5 g. of *n*-butane sulfonyl chloride (about 80% of the theory), of boiling point 100-103°/27-8 mm., of d_4^{25} 1.215, and n_D^{20} 1.4548. These constants compare favorably with those reported by Douglass and Johnson (4).

Five grams of dibenzyl sulfide yielded 3 g. of toluene-*alpha*-sulfonyl chloride crystals, m.p. 92-93°. This was converted to the corresponding sulfonamide, m.p. 105-106°. Two grams of benzyl chloride was extracted from the filtrate with petroleum ether.

Diethyl, di-n-amyl, and dibenzyl disulfides. Twelve and two-tenths grams of diethyl disulfide yielded 22 g. of ethane sulfonyl chloride (b.p. 172-175°, d_4^{25} 1.351, and n_D^{20} 1.4518, all in accord with accepted values). This represented a yield of 90%.

Ten grams of di-*n*-amyl disulfide was converted to 7 g. of *n*-pentane sulfonyl chloride, b.p. 83-5°/5-6 mm., d_4^{25} 1.171, and n_D^{20} 1.4565. (Cf. values of Douglass and Johnson (4)).

Dibenzyl disulfide (5 g.) gave 7.4 g. of toluene-*alpha*-sulfonyl chloride, m.p. 92-93°. In experiments in which the amount of chlorine added was in slight excess of that required in equation III, benzyl toluene-*alpha*-thiosulfonate (dibenzyl "disulf-oxide") was isolated in good yields. (This parallels the experiment of Douglass and Johnson (4).) This "disulf-oxide" was best crystallized from absolute alcohol, and melted at 108°. Calc'd for $C_{14}H_{14}O_2S_2$: S, 23.0; Found: S, 22.9. This compound was quantitatively converted into toluene-*alpha*-sulfonyl chloride by treatment with a slight excess of chlorine. The reaction required only a few minutes for completion.

The Action of (I) on Certain Formaldehyde Mercaptals and on Acetone Mercaptol

Diethyl, di-n-amyl, and dibenzyl mercaptals of formaldehyde. Twenty-five grams of formaldehyde diethyl mercaptal (free from formaldehyde) gave 28 g. of ethane sulfonyl chloride, or 72% of the theory. The acetic acid-water layer from this reaction was about two-thirds neutralized with sodium hydroxide solution, and tested for formaldehyde with dimethyldihydroresorcinol. A copious precipitate was obtained, which melted at 189° after one crystallization from alcohol. A mixed melting point with the known product from formaldehyde and dimethyldihydroresorcinol showed no depression.

Seventeen and six-tenths grams of normal primary amyl mercaptan was converted into its formaldehyde mercaptal, by saturating the acetic acid solution of the mercaptan and formalin with hydrogen chloride gas. The mercaptal was not isolated, but was chlorinated directly. It yielded 26 g. of *n*-pentane sulfonyl chloride. This represents a yield of about 95%.

Formaldehyde dibenzyl mercaptal gave toluene-*alpha*-sulfonyl chloride in yields of 80-85%. The product was of high purity. In experiments in which the chlorine was added in small, measured amounts, it was possible to isolate appreciable quantities of dibenzyl disulfide, m.p. 69-70°. A mixed melting point with authentic disulfide likewise melted at 69-70°.

Acetone diethyl mercaptol. Sixteen and four-tenths grams of acetone diethyl mercaptol was converted into chlorination products of acetone, and 18 g. of ethane sulfonyl chloride. The properties of the sulfonyl chlorides obtained from the mercaptals and the mercaptol were the same as those noted in the preceding experiments.

The Action of (I) on Trithiane

Trithiane. Fourteen grams of formaldehyde-free trithiane gave 22.5 g. of chloromethane sulfonyl chloride, about 75% yield on the basis of equation IV. The compound had the following properties: B.p. 70-72° at 23 mm., d^{25}_4 1.600, n^{25}_D 1.4788, n^{25}_D 1.4771.

The acetic acid-water layer from this reaction contained at least one-third of the formaldehyde to be expected from the equation. The formaldehyde was estimated as in the above experiment. In some experiments, this layer gave a positive test for the sulfate ion; in others, the third sulfur atom appeared as a chloride of sulfur.

The Action of (I) on Di-n-butyl Sulfoxide

Di-n-butyl sulfoxide. Five grams of di-*n*-butyl sulfoxide gave 2 g. of *n*-butane sulfonyl chloride. No attempt was made to isolate the butyl chloride formed.

SUMMARY

1. The reactions of several types of organic sulfur compounds with chlorine and water, in acetic acid as a medium, have been studied.

2. Normal and aryl substituted alkyl sulfides are oxidized and converted by the reagent to alkane sulfonyl chlorides and alkyl chlorides. The splitting of the molecule may occur after oxidation to the sulfoxide stage; it must occur before oxidation to the sulfone stage is reached.

3. Several formaldehyde mercaptals and acetone mercaptol have been converted to alkane sulfonyl chlorides and their parent carbonyl compounds. This reaction probably proceeds stepwise from the mercaptal to the disulfide, the "disulfoxide," and finally by oxidation and splitting to the alkane sulfonyl chloride.

4. If one starts with the alkyl disulfide, this reaction offers an excellent method of preparing the corresponding alkane sulfonyl chloride.

5. This reaction of trithiane has been found to be similar to that of the structurally related mercaptals.

PRINCETON, N. J.

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