to about 20 ml., cooling gave a solid product which, after washing with petroleum ether (30–60°), gave 2.0 g., m.p. 161–162° dec. (after two recrystallizations from benzene, 174–174.5° dec.), of light cream colored crystals which were soluble in diethyl ether and chloroform and insoluble in petroleum ether and carbon tetrachloride.

Anal. Calcd. for $C_{18}H_{16}BNO$ (273.1): C, 79.14; H, 5.90; N, 5.53. Found: C, 78.50; H, 5.64; N, 5.50.

Aqueous Chlorination of Dimethyl Sulfide

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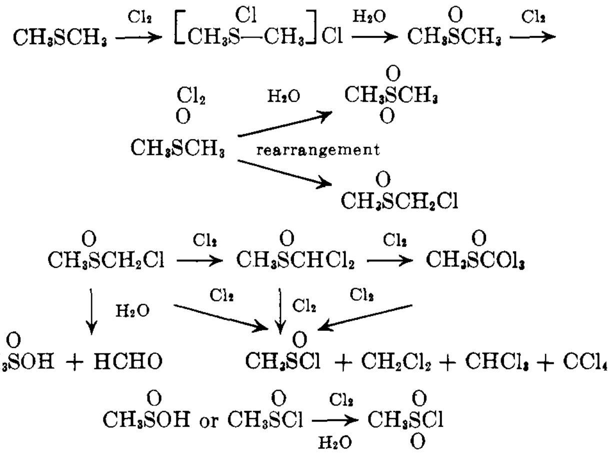
The products resulting from the reaction of chlorine with dimethyl sulfide are determined by the choice of reaction conditions, particularly by the presence or absence of water. The pattern is similar to that observed with other bivalent sulfur compounds.[1]

Under anhydrous conditions chlorination proceeds stepwise with replacement of all the halogens on one carbon atom before any attack at the second one.[2] The chlorination using chlorine proceeds well until four chlorine atoms have been introduced while the main reaction beyond that point is cleavage to carbon tetrachloride and other products. The cleavage pattern here is analogous to that of the triphenylmethyl sulfides.[3]

Chlorinating dimethyl sulfide in the presence of water leads to products that are consistent with the following scheme.



The first reaction step is the very rapid formation of the dimethyl sulfide–chlorine adduct. The adduct, which rapidly rearranges to chloromethyl methyl sulfide in the absence of water,[4] is hydrolyzed by water to give dimethyl sulfoxide in 80% yield.

Introduction of a second chlorine at −10° initially produced an adduct as evidenced by a decreased heat evolution and by the recovery of a 74% yield of dimethyl sulfide when a freshly prepared adduct solution in concentrated hydrochloric acid was reduced with methyl mercaptan at −10°.

When the dimethyl sulfoxide–chlorine adduct solution was allowed to warm to room temperature, it reacted partly to give dimethyl sulfone and partly by rearrangement and hydrolytic cleavage to give formaldehyde and acids. Although methanesulfinic acid was not positively identified its presence was indicated by the isolation of methyl methanethiosulfonate[5] from an experiment in which the temperature was allowed to rise to 45°. The presence of a large amount of water leads almost exclusively to sulfone formation. In common with dibutyl sulfone[6] and α-chlorobenzyl benzyl sulfone,[1d] dimethyl sulfone is inert to the chlorination conditions.

The cleaved carbon atom was isolated in different forms depending partly upon the extent of chlorination and the amount of water present as shown in Table I.

Table I

Products from Dimethyl Sulfide (DMS) Chlorination in Hydrochloric Acid

Mole ratio Cl_2/DMS	Mole ratio H_2O/DMS	Mole yield per mole DMS
1	8.3	0.8 DMSO
2	16.7[a]	0.7 $DMSO_2$
2	8.3	0.2 to 0.4 $DMSO_2$; 0.3 HCHO
3	8.3	0.2 $DMSO_2$; 0.1 HCHO; 0.2 mesyl chloride
3	3.0	0.3 $DMSO_2$; 0.2 mesyl chloride; 0.05 $CHCl_3$
4	8.3	0.2 $DMSO_2$; 0.14 mesyl chloride
5	2.5	0.1 $DMSO_2$; 0.47 mesyl chloride; 0.02 CH_2Cl_2; 0.13 $CHCl_3$; 0.12 CCl_4

[a] No hydrochloric acid present at start.

When the cleavage was accomplished by hydrolysis the carbon appeared as formaldehyde. Formic acid was found only in trace amounts. In chlorinations favorable for preparing mesyl chloride the carbon appeared as mixtures of methylene chloride, chloroform, and carbon tetrachloride. Methyl chloride was not found as a reaction product so the cleavage by chlorolysis occurred after the introduction of at least one α chlorine. In this respect the cleavage of the chlorinated sulfoxides is similar to that demonstrated for the benzyl, benzhydryl, and trityl sulfides by Schreiber and Fernandez.[1d]

The yield of mesyl chloride from chlorinating dimethyl sulfide in the presence of water is usually around 50% due largely to the formation of 15 to 30% of dimethyl sulfone. The yield can be increased to above 75% by chlorinating the sulfide to at least the monochloro level before introducing water. Hydrolysis of chloromethyl methyl sulfide to bis(methylthio)methane is not harmful since the latter gave an 83% yield of mesyl chloride under the reaction conditions.

Trichloromethyl chloromethyl sulfide is cleanly cleaved by excess chlorine at 20–30° in the presence of hydrochloric acid to give 83% of carbon tetrachloride and 81% of chloromethanesulfonyl chloride. The

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(2) H. Richtzenhain and B. Alfredsson, *Ber.*, **86**, 142 (1953).

(3) K. C. Schreiber and V. Fernandez, *J. Org. Chem.*, **26**, 2478 (1961).

(4) H. Bohme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949).

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(6) S. W. Lee and G. Dougherty, *J. Org. Chem.*, **5**, 81 (1940).

corresponding sulfone is inert to these reaction conditions.

Experimental

Typical Chlorination Conditions.—A 500-cc. three-neck flask was fitted with a sealed stirrer, thermometer, a fritted gas inlet tube extending as deep as possible into the flask, and a vent for exit gas. One mole of dimethyl sulfide and an amount of concentrated hydrochloric acid to provide the desired water were placed in the flask and cooled to −10° to −15°. This temperature was maintained while introducing chlorine (up to 2 moles). Subsequent amounts were introduced at +10° to +30° to obtain more complete absorption. When two phases were present at the end of the reaction, the heavy oil layer was fractionally distilled at atmospheric pressure to obtain a chlorinated hydrocarbon cut and mesyl chloride. Both cuts were analyzed by gas chromatography. The dimethyl sulfone was isolated from the still residue or, when no oil phase was present, was obtained by evaporating the acidic aqueous solution under reduced pressure. In either case the dimethyl sulfone was recrystallized from ethanol. The formaldehyde was isolated by treating the aqueous layer with methyl mercaptan and isolating the bis(methylthio)-methane. Some dimethyl disulfide and dimethyl sulfide also are produced at times due to oxidation of the mercaptan by dimethyl sulfoxide, so gas chromatographic assay was required.

Mesyl Chloride.—Two moles of dimethyl sulfide (147 cc.) was placed in the previously described apparatus and chlorine was introduced while maintaining the temperature at 0° to −20° until 3 moles of chlorine was introduced, and at +5° until 3.5 moles was introduced. Water (100 cc.) was then added dropwise and the chlorination continued at 20–28° until 12 moles of chlorine was introduced. The 274-g. lower layer was separated from the 42-g. aqueous layer and distilled in the manner described previously to obtain 174 g. (76%) of mesyl chloride boiling at 161–165° (760 mm).

Chloromethanesulfonyl Chloride.—An excess of chlorine was introduced over 3 hr. into tetrachlorodimethyl sulfide (200 g., 1.00 mole) and water (500 g., 27.8 moles) at 19° to 32°. Distillation of the organic layer at atmospheric pressure yielded 121.1 g. (0.81 mole, 81%) of chloromethanesulfonyl chloride (b.p. 165–175°; n^{25}D 1.4820) and 127.4 g. (0.83 mole, 83%) of carbon tetrachloride.

Dithiazanes or Methylenediisothiuronium Salts[1]

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During the course of research on isothiuronium salts and derivatives, as part of the doctoral thesis of one of us (C.H.G.), the anomalous behavior of methylene dihalides in the formation of methylenediisothiuronium salts was noted. Most of this work has been published.[3,4] However, details of the reaction of thiourea and N-substituted thioureas with methylene halides have not been published. In view of the continued erroneous references to methylenediisothiuronium salts appearing in the literature, it was felt that our investigations should be published in order to delineate the reactions involved and what actually is obtained.

Dixon and Taylor[5] first reported that they obtained methylenediisothiuronium dihydroiodide by the usual procedure of refluxing methylene iodide and thiourea in alcohol. They gave no melting point for the salt and stated that the base melted at 198°, and gave unreliable analytical data. Based on a sulfur determination on the hydroiodide salt (no melting point given) they assumed the obtention of the methylenediisothiuronium dihydroiodide. The use of isothiuronium picrates as identifying derivatives of alkyl and polymethylene halides is a useful and widely used procedure.[6-8] Jurecek and Vecera[8] prepared a number of such isothiuronium picrates, including the one from methylene iodide, as proposed identifying derivatives. They give a melting point for this picrate of 232° dec.; they state that it is methylenediisothiuronium picrate and give closely corresponding elemental analyses. They also claim to have prepared methylene diisothiuronium dihydroiodide and to have recrystallized it three times from water, giving no melting point, but closely corresponding elemental analyses for four elements therein.

Recently Parham, *et al.*,[9] prepared crude methylenediisothiuronium dihydroiodide (not characterized), which was converted into a picrate, m.p. 232–233° dec. This picrate was compared with the "authentic picrate" prepared according to Jurecek and Vecera and no depression of the melting point was noted.

Underwood and Dains[10] showed that the reaction of methylene dihalides and thiourea, monoarylthioureas and 1,5-diaryldithiobiurets gave rise to 1,3,5-dithiazanes, but that *s*-diarylthioureas gave ill-defined products. They repeated the work of Dixon and Taylor and obtained a base from thiourea and methylene iodide of rather indefinite melting point (202–209°) which gave inconclusive analyses. However, they state that the nitrogen analysis of the hydroiodide salt (no melting point given) corresponded to the 1,3,5-dithiazane structure. Recently Esayan and Oganesyan[11] repeated the work of Dixon and Taylor and obtained a hydroiodide from thiourea and methylene iodide, m.p. 245°, and a picrate, m.p. 228–230°, to which they correctly assigned the 1,3,5-dithiazane structure.

In view of the general confusion and contradiction in the chemical literature on this subject, we have presented conclusive experimental proof of the formation of dithiazanes from thiourea and methylene bromide and, particularly, methylene iodide. The "methylenediisothiuronium picrates" reported in the literature have been shown to be the picrate of 4,6-diimino-1,3,5-dithiazane. This has been confirmed by alternate synthetic routes, conclusive analytical data, and infrared spectra.

Most of the reactions reported in the literature were carried out in ethanol, or higher boiling solvents for pro-

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(1) Supported in part by The Geschickter Fund for Medical Research, Inc.

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