the 4-hr. period. Each hydrolytic system was extracted with 5 cc. of chloroform and infrared curves were determined on the chloroform extract, after drying with a molecular sieve. No change in the infrared curves could be observed in any of the solutions except that from the action of hydrochloric acid in which a white precipitate had formed and absorption data here indicated the presence of the original naphthol as well as the silicon ether.

Trimethylchlorosilane and dimethyldichlorosilane were purchased from Dow Corning Corp. of Midland, Mich., and were always freshly distilled before using. Pyridine was obtained from Brothers Chemical Co., Orange, N. J., and made anhydrous by distilling and storing over potassium hydroxide pellets and a molecular sieve. Naphthalene derivatives were obtained through the courtesy of National Aniline Division, Allied Chemical and Dye Corp., Buffalo, N. Y.

Molecular weights were determined cryoscopically in benzene.

Molecular refractions were calculated from data supplied by Warrick.[4]

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[4] E. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Chlorination of Alkyl Disulfides and the Preparation of Thiolsulfonate Esters[1]

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Methyl methanethiolsulfonate has been prepared by the addition of 2 moles of chlorine to a cold mixture containing molar quantities of methyl disulfide and acetic acid, followed by the addition of 2 moles of water. During the chlorination reaction methanesulfenyl, acetyl and methanesulfinyl chlorides are formed. Hydrolysis of the latter forms methanesulfinic acid which combines immediately with methanesulfenyl chloride to form the thiolsulfonate ester. Mixed thiolsulfonate esters can be prepared by adding water to a reaction mixture containing sulfinyl and sulfenyl chlorides having different alkyl radicals.

The chlorination of mercaptans, disulfides, and other organosulfur compounds in the presence of water, or glacial or aqueous acetic acid has long been recognized as a superior method for the preparation of sulfonyl chlorides.[2–4] Occasionally, however, slight modifications in procedure have resulted in the formation of thiolsulfonate esters, RSO_2SR.[3–6]

Anhydrous chlorine acts on mercaptans and disulfides to form a variety of substances. The aromatic sulfenyl chlorides, RSCl, have been known for many years but only since World War II have the alkanesulfenyl chlorides been studied to any extent. The last decade has also seen the discovery of the organosulfur trichlorides, $RSCl_3$.[7,8] These latter compounds have been found to decompose into 1-chloroalkanesulfenyl chlorides, RCHClSCl, and to undergo solvolysis with the formation of sulfinyl chlorides, RSOCl,[9] and sulfinic acids, RSO_2H.

Disulfides, thus, can be transformed into sulfonyl chlorides, thiolsulfonate esters, sulfenyl chlorides, organosulfur trichlorides, 1-chloroalkanesulfenyl chlorides, sulfinyl chlorides, and sulfinic acids. The inter-relationships of these compounds and the reactions by which they are formed have been unfolding over the past few years but were not fully understood until recently when Stirling clearly established that thiolsulfonate esters are produced by the reaction of sulfenyl chlorides with sulfinic acids.[10,11]

The following diagram, modified from that of Stirling, represents the inter-relationships of the products from chlorinating alkyl disulfides. This chart emphasizes our finding that sulfinyl chlorides are intermediate solvolytic products between organosulfur trichlorides and sulfinic acids.[12] With few exceptions, the yields are nearly quantitative if the quantities of reactants are carefully controlled.

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[1] Presented before the Organic Division of the A.C.S. at the 134th Meeting in Chicago, Ill., September 11, 1958.

[2] Th. Zincke and W. Frohneberg, *Ber.*, **42**, 2721 (1909).

[3] I. B. Douglass and T. B. Johnson, *J. Am. Chem. Soc.*, **60**, 1486 (1938).

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

[5] D. Barnard, *J. Chem. Soc.*, **1957**, 4673.

[6] J. M. Stewart and H. P. Cordts, *J. Am. Chem. Soc.*, **74**, 5880 (1953).

[7] K. R. Brower and I. B. Douglass, *J. Am. Chem. Soc.*, **73**, 5787 (1951).

[8] I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Am. Chem. Soc.*, **74**, 5770 (1952).

[9] I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

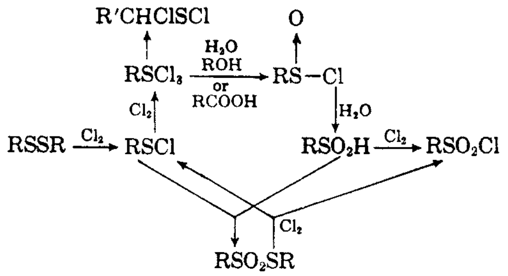
[10] C. J. M. Stirling, *J. Chem. Soc.*, **1957**, 3597.

[11] Shortly before the appearance of the paper by Stirling, D. Barnard told the senior author he had observed that sulfenyl chlorides combine with sulfinic acids to form thiolsulfonate esters. Barnard's comment suggested the work reported in this paper.

[12] It is interesting that Zincke and Frohneberg[2] suggested, without experimental proof, that the transformation of 1,4-benzenedithiol into the corresponding disulfonyl chloride by treatment with chlorine in glacial acetic acid takes place through the intermediate steps:

$$(SC_6H_4S)_n \longrightarrow C_6H_4(SCl_3)_2 \longrightarrow C_6H_4(SOCl)_2 \longrightarrow C_6H_4(SO_2Cl)_2$$

thus anticipating the formation of organosulfur trichlorides and their solvolysis to sulfinyl chlorides.



The present paper is concerned with an excellent method for obtaining thiolsulfonate esters, utilizing sulfinyl chlorides, and the improved procedure which makes them so readily available.[13] In its simplest form the new method consists of allowing a sulfenyl chloride to react with a sulfinic acid produced by the action of water on a sulfinyl chloride. As described in the experimental part, the reaction may be carried out in various ways. Water can be added to an equimolar mixture of an alkanesulfenyl chloride and an alkanesulfinyl chloride. If both compounds contain the same alkyl radical a simple thiolsulfonate ester results, but if the sulfenyl and sulfinyl chlorides contain different alkyl radicals, mixed thiolsulfonate esters are formed. The products obtained by this method are practically colorless.

It is not necessary that the sulfenyl and sulfinyl chlorides be prepared separately before carrying out the reaction. If exactly 2 moles of chlorine is passed into a cold mixture containing 1 mole of disulfide and 1 mole of glacial acetic acid, the resulting reaction mixture contains both the sulfinyl and sulfenyl chlorides necessary for the subsequent hydrolysis and metathetical reactions:

$$CH_3SSCH_3 + CH_3COOH + 2Cl_2 \longrightarrow CH_3SOCl + CH_3SCl + CH_3COCl + HCl$$

$$CH_3SOCl + CH_3SCl + CH_3COCl + 2H_2O \longrightarrow CH_3SO_2SCH_3 + CH_3COOH + 3HCl$$

Such a procedure can be carried out rapidly and conveniently but the resulting product must be separated from acetic acid and is apt to be colored by unidentified yellow impurities which boil only slightly lower than the desired thiolsulfonate esters.

To prepare an unsymmetrical thiolsulfonate ester, the above procedure is modified by using three moles of chlorine to convert 1 mole of disulfide to the sulfinyl chloride. Then 1 mole of a different disulfide is added and chlorinated with one mole of chlorine to the sulfenyl chloride stage. Finally, addition of water hydrolyzes the sulfinyl chloride and forms the mixed thiolsulfonate ester.

The constitutions of the mixed thiolsulfonate esters, methyl ethanethiolsulfonate, $C_2H_5SO_2SCH_3$, and ethyl methanethiolsulfonate, $CH_3SO_2SC_2H_5$, were established by the use of a reaction reported by Douglass and Osborne.[14] The thiolsulfonate ester was chlorinated in inert solvent, forming a sulfonyl chloride and an organosulfur trichloride. The organosulfur trichloride was hydrolyzed, neutralized, and the resulting sodium alkanesulfinate caused to react with α-chlorotoluene to form an alkyl benzyl sulfone. The sulfonyl chloride, in turn, was treated with *p*-toluidine and identified through the resulting sulfon-*p*-toluidide.

EXPERIMENTAL

Preparation of methyl methanethiolsulfonate. In a three-neck flask, fitted with a stirrer and an outlet tube leading to a hydrogen chloride absorption trap were placed 47.1 g. of methyl disulfide (0.5 mole) and 30.0 g. of glacial acetic acid (0.5 mole) and the mixture was cooled to −10° by an acetone-solid carbon dioxide bath. Exactly 71.0 g. of chlorine (1.0 mole) was condensed in a large test tube cooled to the temperature of Dry Ice, and the tube then connected to the inlet tube of the reaction flask. The liquid chlorine was allowed to boil spontaneously as it absorbed heat from the atmosphere or from the hand and the gas was introduced into the space above the surface of the reaction mixture.

When all of the liquid chlorine had evaporated the reaction mixture was reddish in color from the presence of methanesulfenyl chloride. At this time 19 ml. of water was slowly introduced into the cold reaction mixture while vigorous stirring was maintained. Immediate reaction ensued with the evolution of a large volume of hydrogen chloride. When the last of the water had been added, the color of the reaction mixture was only faintly yellow and, as stirring continued, faded to colorless. The cold bath was removed and stirring was continued while the reaction mixture warmed to room temperature.

The mixture was finally distilled under reduced pressure through a 12-in. Vigreux column and, after removal of acetic acid, yielded 55 g. (87%) of yellow product boiling 116–118° (16 mm.). Redistillation gave a colorless product boiling 114° (13 mm.) and having n_D^{25} 1.5112, d_4^{25} 1.3311, d_4^0 1.3567 and strong infrared absorption at about 1310, 1130, 955, and 750 cm.$^{-1}$

Anal. Calcd. for $C_2H_6O_2S_2$: C, 19.04; H, 4.68; S, 50.82. Found: C, 19.4, 19.64; H, 4.8, 4.7; S, 50.3, 50.5.

Preparation of ethyl methanethiosulfonate. Into the reaction flask previously described were introduced 23.5 g. methyl disulfide (0.25 mole) and 30.0 g. glacial acetic acid (0.5 mole), and the mixture was cooled to about −10°. In the same manner as previously described, 53.3 g. (0.75 mole) of chlorine was condensed in a large test tube and then allowed to evaporate into the reaction flask. When all the chlorine had been added the reaction mixture was only faintly yellow and consisted of methanesulfinyl and acetyl chloride together with dissolved hydrogen chloride.

Without disturbing the flask 30.6 g. of ethyl disulfide (0.25 mole) was added to the reaction mixture and an additional 17.8 g. of chlorine (0.25 mole), condensed as previously described, was allowed to evaporate into the flask. When all the chlorine had been added, 19 ml. of water (1.05 mole) was added slowly and the reaction mixture treated as previously described. Distillation under reduced pressure gave 57.6 g. (82%) of yellow liquid boiling 119–121° (16 mm.). Repeated redistillation gave a colorless product boiling at 115° (11 mm.) and having n_D^{25} 1.5018, d_4^{25} 1.2469, D_4^0 1.2721 and showing strong infrared absorption at about 1310, 1130, 955, and 750 cm.$^{-1}$

Anal. Calcd. for $C_3H_8O_2S_2$: S, 45.73. Found: S, 45.3, 45.7.

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[13] I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 330 (1958).

[14] I. B. Douglass and C. E. Osborne, *J. Am. Chem. Soc.*, **75**, 4582 (1953).

The structure of this liquid was established by chlorinolysis. Into two large test tubes, both cooled to the temperature of solid carbon dioxide, were weighed, respectively, 6.2 g. of the liquid believed to be ethyl methanethiolsulfonate and 5.7 g. of liquid chlorine. To each tube was added 15 ml. of previously chilled methylene chloride, and then the chlorine solution was quickly added to the solution of thiol ester. At first there was no evidence of reaction but slowly crystals began to form and in 20 min. the reaction appeared to be complete.

The resulting slurry of white crystals was quickly filtered by suction through a sintered glass crucible which had been chilled to the temperature of Dry Ice. The crystals were dissolved in glacial acetic acid, the solution was neutralized with aqueous sodium bicarbonate, and the alkaline solution refluxed for several hours with 4 ml. of benzyl chloride. On cooling, a solid separated, which, after recrystallizing from water, melted at 83–84° and at 84° when mixed with authentic ethyl benzyl sulfone.

The filtrate from the chlorination step was diluted with ether and treated with *p*-toluidine in presence of sodium bicarbonate solution. Alkaline extraction and acidification of the extract yielded methanesulfon-*p*-toluidide, melting at 103–104° and unchanging when mixed with an authentic sample.

Preparation of methyl ethanethiolsulfonate. The same procedure was followed as that described above for preparing ethyl methanethiolsulfonate except that the order of adding the disulfides was reversed. Ethyl disulfide (0.25 mole) was converted to ethanesulfinyl chloride and then methyl disulfide (0.25 mole) was added and chlorinated to methanesulfenyl chloride. Addition of water allowed the reaction to go to completion as already described. Distillation of the reaction mixture gave 58.6 g. (84% yield) of yellow product boiling at 120–122° (14 mm.). Repeated redistillation gave a colorless liquid boiling at 119° (13 mm.) and having n_{D}^{25} 1.5054, D_4^{25} 1.2593, D_4^{0} 1.2840 and showing strong infrared absorption at about 1310, 1125, 775, and 700 cm.$^{-1}$

Anal. Calcd. for $C_3H_8O_2S_2$: C, 25.70; H, 5.75; S, 45.73. Found: C, 25.5, 25.65; H, 5.94, 5.62; S, 45.7, 46.0.

The liquid thus obtained was shown to be methyl ethanethiolsulfonate by chlorinolysis as described above and by conversion of the chlorination products to ethanesulfon-*p*-toluidide, melting at 80–81° and methyl benzyl sulfone, melting at 125–126°. Both derivatives melted unchanged when mixed with authentic samples.

Preparation of methanesulfenyl chloride. Chlorine gas was led from a test tube, in which liquid chlorine (42.5 g., 0.6 mole) had been condensed, into 56.5 g. (0.6 mole) of well stirred methyl disulfide contained in a 500-ml. three-neck flask and held at −20° or lower. The chlorine inlet tube terminated well above the surface of the disulfide so that it would not become clogged with methylsulfur trichloride. When the last of the liquid chlorine had evaporated, the cold reaction vessel was shaken to bring unreacted methyl disulfide in contact with solid methylsulfur trichloride in order to convert both to methanesulfenyl chloride. Disappearance of solid indicated that the reaction was complete.

The product was not distilled but was kept at the temperature of solid carbon dioxide until used. The yield was nearly quantitative.

Preparation of methyl ethanethiolsulfonate (alternative methods). Ethanesulfinyl chloride[13] (22.5 g., 0.2 mole) and methanesulfenyl chloride (16.6 g., 0.2 mole) were mixed in the reaction flask already described and cooled to −10°. Exactly 3.6 g. of water (0.2 mole) was then added slowly from a medicine dropper and caused the reaction mixture to lose its color.

The mixture was warmed with stirring to room temperature and distilled through a 12-in. Vigreux column under reduced pressure. After 1.1 g. of slightly colored forerun there was obtained 21.4 g. (76.4%) of nearly colorless methyl ethanethiolsulfonate boiling at 125° (18 mm.).

Variations in procedure in which (1) the sulfenyl chloride was added dropwise to the hydrolyzed sulfinyl chloride and (2) the hydrolyzed sulfinyl chloride was added to the sulfenyl chloride made no significant difference in either yield or quality of product.

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