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

Studies in Organosilicon Chemistry. XXXVII. The Preparation of Dimethylsiloxy and Trimethylsiloxy Derivatives of Naphthalene

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By the action of trimethylchlorosilane and dimethyldichlorosilane, in the presence of pyridine, on 1-naphthol, 2-naphthol, and several dihydroxynaphthalenes, a series of ten methylsiloxynaphthalenes has been prepared in good yields.

By the interaction of trimethylchlorosilane, pyridine, and the appropriate naphthol or dinaphthol, the following compounds have been prepared and characterized: 1-trimethylsiloxynaphthalene (I), 2-trimethylsiloxynaphthalene (II), 5,8-dichloro-1-trimethylsiloxynaphthalene (III), bis-(1,5-trimethylsiloxy)naphthalene (IV), bis(1,6-trimethylsiloxy)naphthalene (V), bis(2,3-trimethylsiloxy)naphthalene (VI) and bis(2,7-trimethylsiloxy)naphthalene (VII). From dimethyldichlorosilane there have been prepared dimethylbis(1-naphthoxy)silane (VIII), dimethylbis(2-naphthoxy)silane (IX) and dimethylbis(5,8-dichloro-1-naphthoxy)silane (X). Infrared absorption curves have been determined for each of these products.

TABLE I

PHYSICAL PROPERTIES

	B.P.	Mm.	M.P.	n_D^{20}	d_4^t
I	98.0–102.3	3		1.5596	1.011 (24°)
	271.0–272.0	742 (1)		1.5590 (1)	1.000 (20°) (1)
II	98.2–101.0	8		1.5559	1.006 (24°)
III	174.8–177.5	4		1.5885	1.215 (25°)
IV			87		
V	167.2–169.0	5		1.5330	1.003 (25°)
VI	153.8–156.0	5	60–61		
VII			51–53		
VIII	155–160	11 (2)	55–57		
IX			60–61		
X			117–118		

Langer, Connell and Wender[1] have reported the formation of a number of trimethylsilyl ethers including 1-trimethylsiloxynaphthalene. Larsson[2] caused 1-naphthol to react with dimethyldiethoxysilane, obtaining dimethylbis(1-naphthoxy)silane.

In this work, three compounds have been prepared of the formula $ROSi(CH_3)_3$, four of the formula $R'(OSi(CH_3)_3)_2$ and three of the formula $(RO)_2Si(CH_3)_2$ where R is $C_{10}H_7$ or $C_{10}H_5Cl_2$ and R' is $C_{10}H_6$ or $C_{10}H_4Cl_2$. Anhydrous benzene or diethyl ether was used as the solvent and anhydrous pyridine as the proton acceptor. As outlined in the experimental part, hydrolytic tests on 1-trimethylsiloxynaphthalene and 2-trimethylsiloxynaphthalene with water and with sodium hydroxide demonstrated unexpected resistance and stability. Hydrochloric acid, however, caused hydrolysis to the original naphthol and an insoluble silicon compound which was not identified.

Infrared absorption curves were determined for all ten products. Bellamy[3] has assigned the region 900–700 cm.$^{-1}$ to silicon-carbon absorption, 1250, 841, 756–754 cm.$^{-1}$ to trimethylsilyl and 1259, 814–800 cm.$^{-1}$ to dimethylsilylene. These correspond to 11.8–14.3, 8.0, 11.8, 13.2, 7.9, and 12.2–12.5 microns, respectively. Prominent bands in all of these assigned regions have been observed and are reported herein wherever they are not masked by solvent effects.

EXPERIMENTAL

1-Trimethylsiloxynaphthalene. 1-Naphthol (30.0 g., 0.208 mole) in 300 cc. of anhydrous ethyl ether in a 500 cc. three necked flask equipped with mercury sealed stirrer, thermometer, condenser, and calcium chloride tube, was treated with 24.7 g. (0.313 mole) of anhydrous pyridine, then dropwise with 33.7 g. (0.313 mole) of trimethylchlorosilane, with stirring. An immediate reaction occurred with the formation of a heavy white precipitate accompanied by a rise in temperature. The mixture was refluxed for 2 hr., then allowed to stand overnight. The precipitate of pyridine hydrochloride was filtered off and ether distilled from the filtrate. Distillation at reduced pressure first removed unreacted pyridine, then 1-trimethylsiloxynaphthalene distilled over, b.p. (found) 98.0–102.3° (2 mm.), (lit.) (1) 271.0–272.0°; n_D^{20} (found) 1.5596, (lit.) (1) 1.5590; d_4^{25} (found) 1.011, d_4^{20} (lit.) (1) 1.000.

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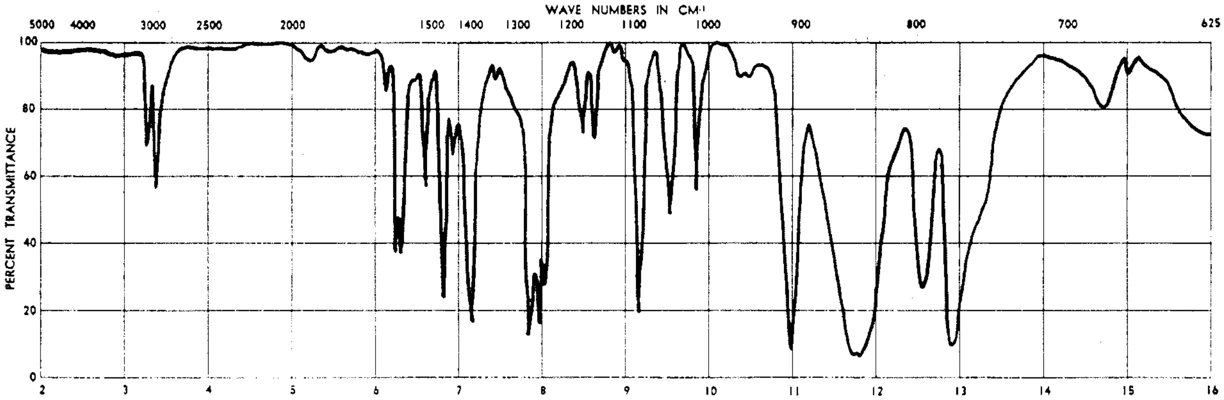
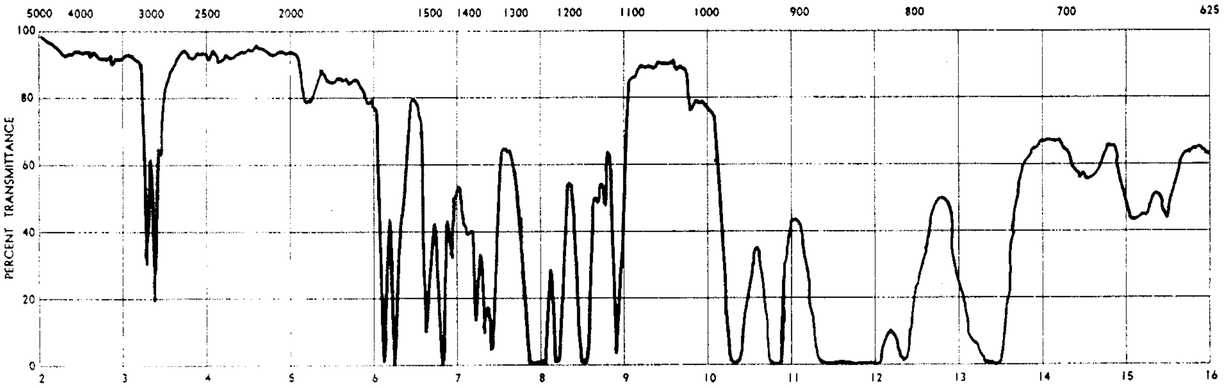
(1) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(2) E. Larsson, *Chem. Ber.*, **86**, 1382 (1953).

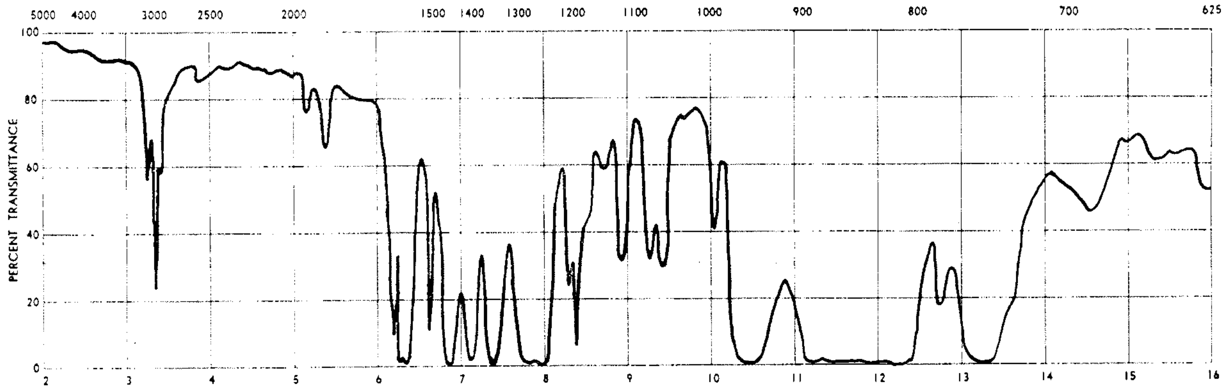
(3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc. (1954).



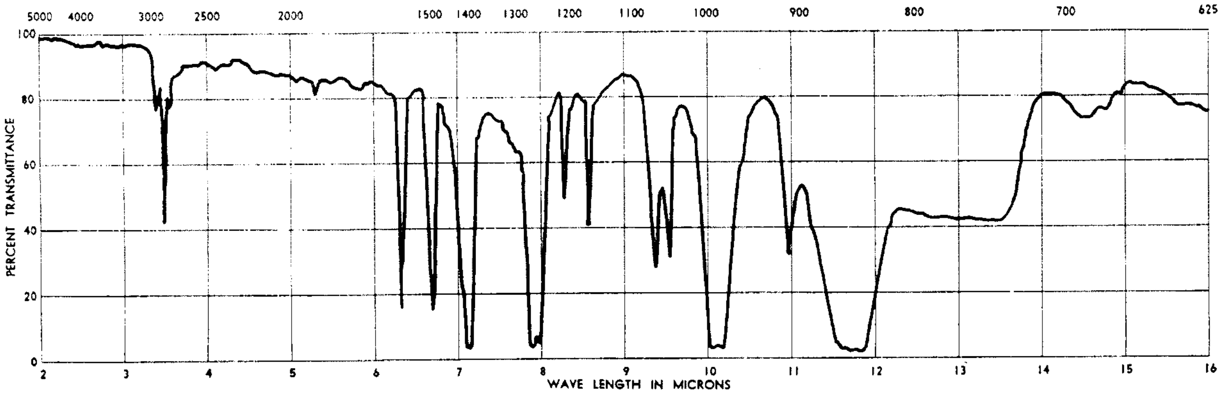
1-Trimethylsiloxynaphthalene. Capillary cell



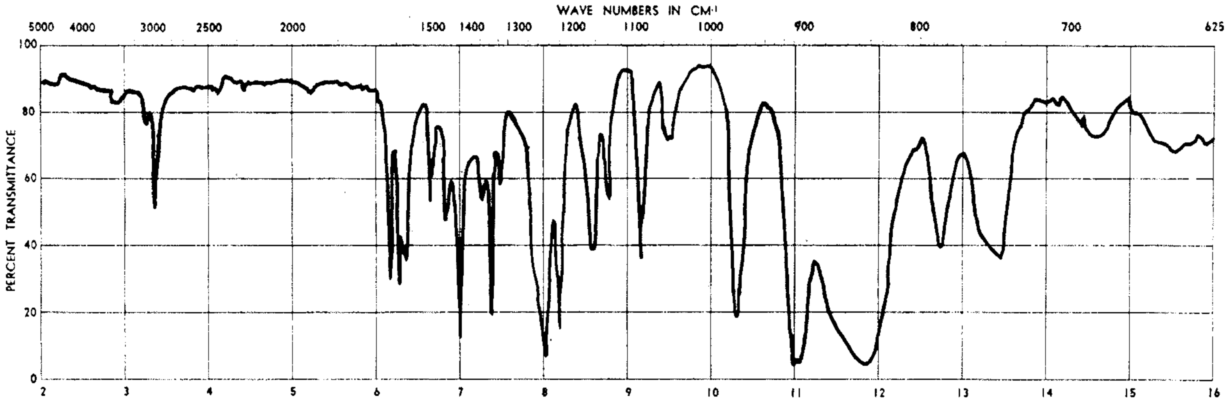
2-Trimethylsiloxynaphthalene. Capillary cell



5,8-Dichloro-1-trimethylsiloxynaphthalene. Capillary cell



Bis(1,5-trimethylsiloxy)naphthalene. 10% in CCl_4, 0.1-mm. cell



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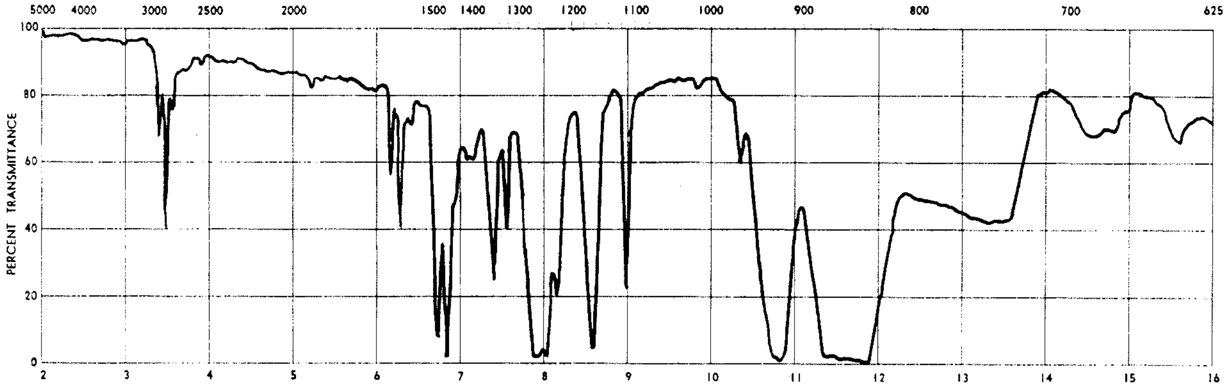
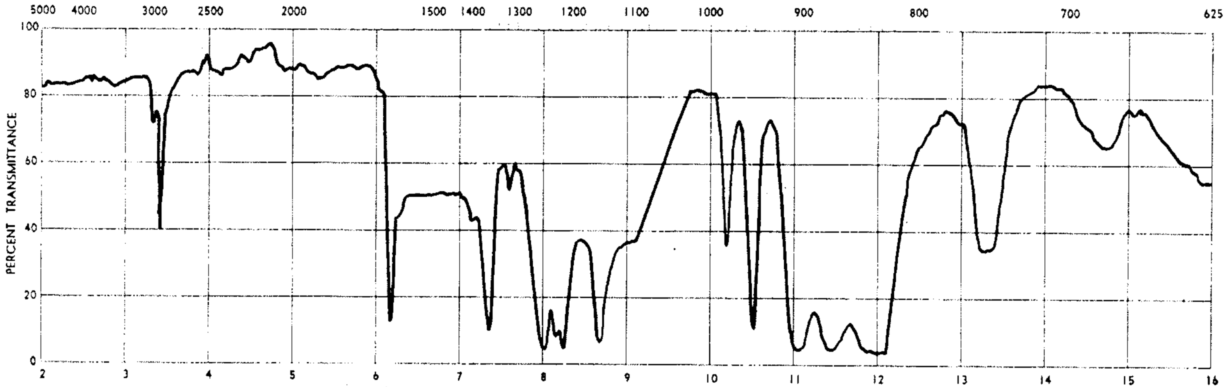
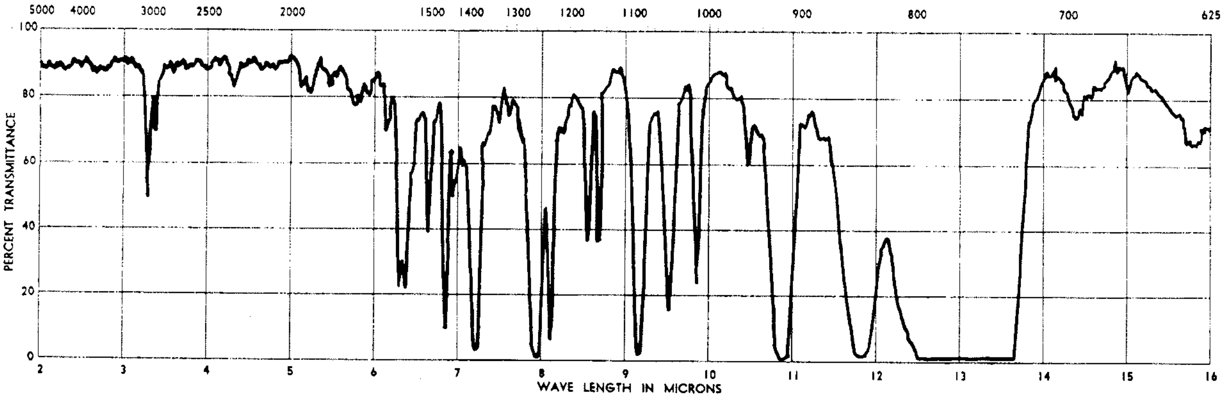


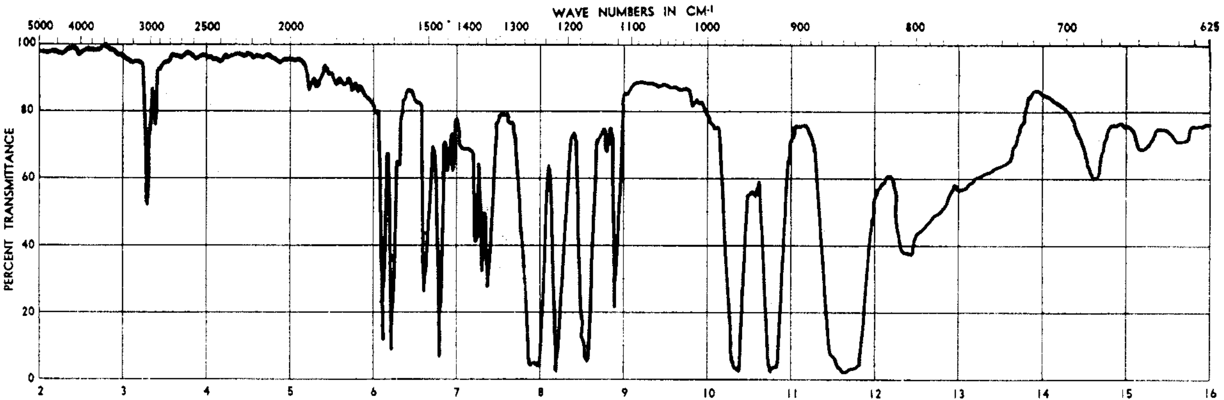
Bis(2,3-trimethylsiloxy)naphthalene. 10% in CCl_4, 0.1-mm. cell



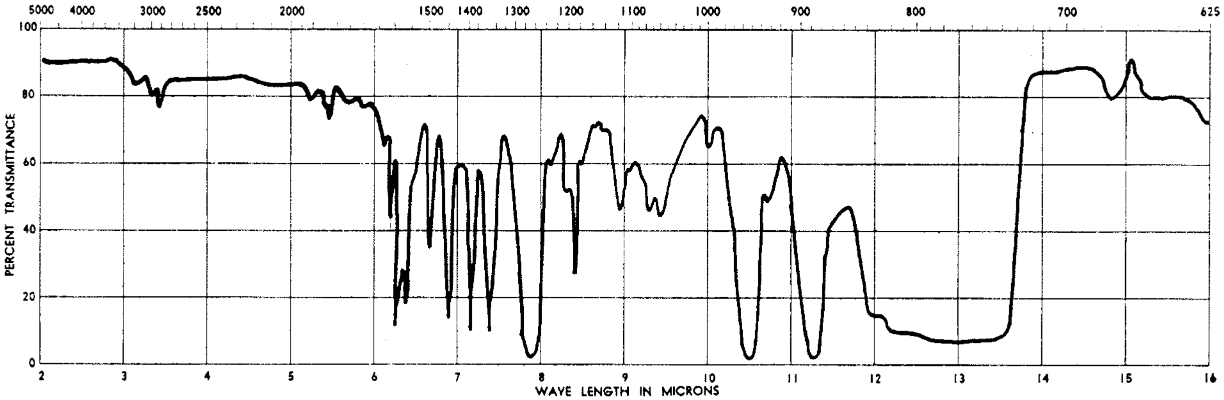
Bis(2,7-trimethylsiloxy)naphthalene. 5% in CS_2, 0.2-mm. cell



Dimethylbis(1-naphthoxy)silane. 10% in CCl_4, 0.1-mm. cell



Dimethylbis(2-naphthoxy)silane. 10% in CCl_4, 0.1-mm. cell



Dimethylbis(5,8-dichloro-1-naphthoxy)silane. 10% in CCl_4, 0.1-mm. cell

TABLE II

ANALYTICAL DATA

	Si		Mol. Wt.		M.R.		Yield,	Cl	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	%	Calcd.	Found
I	12.97	12.9 12.7	216	206	68.4	69.0	67		
II	12.97	12.6 12.7	216	203	68.4	68.9	71		
III	9.86	9.6 9.8	285	274	78.1	78.8	57	28.4	27.8 27.7
IV	18.42	18.4 18.5	304	297			5.4		
V	18.42	18.4 18.3	304	289	93.2	93.8	81		
VI	18.42	18.4 18.5	304	287			30		
VII	18.42	18.3 18.2	304	287			22		
VIII	8.14	8.1 8.2	344	330			35		
IX	8.14	8.1 8.2	344	326			30		
X	5.82	6.0 6.0	482	443			16	29.4	29.6 29.5

Anal. Calcd. for $C_{13}H_{16}OSi$: Si, 12.97; mol. wt., 216 M.R., 68.4. Found: Si, 12.9, 12.7; mol. wt., 206, M.R., 69.0.

The preparation of the other products followed the same general procedure. Benzene (300 cc.) was used as the solvent in the synthesis of compounds IV, V, and VI.

Hydrolytic tests. To 1-cc. portions of trimethylsiloxynaphthalene and its 2-isomer, was added respectively, 2 cc. of each of the following: distilled water, 0.08% sodium hydroxide (*p*H 13), 1% hydrochloric acid (c.p. 35%). Each was allowed to stand at room temperatures for 4 hr. One portion using water was kept at 110° in an oven for 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.