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

A New Method for the Preparation of Sulfinyl Chlorides[1-3]

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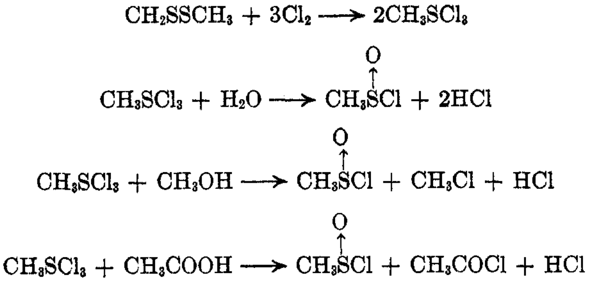
Organosulfur trichlorides, $RSCl_3$, react readily with water, alcohols, or carboxylic acids to form sulfinyl chlorides, $RS(O)Cl$. The reactions take place smoothly and the sulfinyl chlorides are produced in excellent yields.

The organosulfur trichlorides and their reactions have been studied in this laboratory for several years.[4,5] It has now been found that when these compounds are treated with equivalent amounts of water, alcohols, or organic acids, solvolysis occurs and the organosulfur trichloride is converted in high yield to the corresponding sulfinyl chloride. The reaction is particularly useful for preparing the lower alkanesulfinyl chlorides such as those containing methyl, ethyl, *n*-propyl, and *n*-butyl radicals. On the basis of chlorine analyses, sulfinyl chlorides prepared from isopropyl and *n*-amyl disulfides showed some signs of chain chlorination. The reaction proceeded in a normal manner with *n*-dodecyl- and phenylsulfur trichlorides but the products could not be purified by distillation.

Starting with methyl disulfide the reactions involved are:



$$CH_2SSCH_3 + 3Cl_2 \longrightarrow 2CH_3SCl_3$$

$$CH_3SCl_3 + H_2O \longrightarrow CH_3\overset{\overset{O}{\uparrow}}{S}Cl + 2HCl$$

$$CH_3SCl_3 + CH_3OH \longrightarrow CH_3\overset{\overset{O}{\uparrow}}{S}Cl + CH_3Cl + HCl$$

$$CH_3SCl_3 + CH_3COOH \longrightarrow CH_3\overset{\overset{O}{\uparrow}}{S}Cl + CH_3COCl + HCl$$

These reactions were discovered as a result of work intended to determine how methylsulfur trichloride would react with benzoic acid. In early experiments dry benzoic acid was added to a suspension of methylsulfur trichloride in a 2:1 molar ratio. The reaction mixture yielded, after extraction with cold sodium bicarbonate solution, sodium methanesulfinate, sodium benzoate, benzoyl chloride, and benzoic anhydride, suggesting that benzoic acid had been used in excess.

Titration of a cold suspension of methylsulfur trichloride with glacial acetic acid revealed that the reaction involves equimolecular quantities. From the reaction mixture were isolated acetyl chloride and the previously unexpected methanesulfinyl chloride. Repetition of the experiment using benzoic acid, with the reactants in 1:1 molar ratio, confirmed the formation of acyl and sulfinyl chlorides. This observation led to the investigation of alcohols and water as solvolytic agents with the results already indicated.

Since the new synthesis is readily carried out as a succession of steps in the same reaction vessel and does not require the isolation of intermediate products, it possesses many advantages over previous methods[6] available for preparing the lower aliphatic sulfinyl chlorides.

EXPERIMENTAL

General procedure for preparing sulfinyl chlorides. An organic disulfide (0.1 mole)[7] or mercaptan (0.2 mole) and 150 ml. dry methylene chloride were introduced into a 1-l. three-neck flask fitted with stirrer, gas inlet, and gas outlet tubes. The flask and contents were cooled in an acetone–solid carbon dioxide bath, while chlorine was passed in above the surface of the methylene chloride until the orange color of the sulfenyl chloride first formed had completely disappeared and the reaction mixture had changed to a thin paste of white organosulfur trichloride crystals.

A carefully measured quantity of water (0.2 mole) or methanol (0.2 mole) was introduced slowly to the cold mixture. At first there was no evidence of reaction, but on allowing the mixture to warm slowly to about −15° the solid gradually disappeared leaving a nearly colorless solution of sulfinyl chloride in methylene chloride. Most of the solvent was removed at atmospheric pressure and the sulfinyl chloride was distilled under vacuum.

Methylsulfur trichloride with carboxylic acids. In preliminary experiments, benzoic acid (0.2 mole), previously dried and dissolved in methylene chloride, was added with stirring to 0.1 mole of freshly prepared methylsulfur trichloride at such a rate that the temperature remained near the temperature of solid carbon dioxide. No reaction was evident at the low temperature but when the reaction mixture was allowed to warm, hydrogen chloride began to evolve at −15° and rapidly increased as the temperature rose.

The contents of the reaction flask were neutralized with cold sodium bicarbonate solution and separated. On acidifying the aqueous layer, benzoic acid was recovered (8–54% in different trials). After again making the aqueous layer

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(2) Taken from the Master's thesis of Donald R. Poole.

(3) Presented before the Organic Division of the AMERICAN CHEMICAL SOCIETY at Atlantic City, N. J., September 17, 1956.

(4) I. B. Douglass and others, *J. Am. Chem. Soc.*, **73,** 5787 (1951); **74,** 5770 (1952).

(5) F. J. Marascia, Master's Thesis, University of Maine, 1954.

(6) A. Meuwsen and H. Gebhardt, *Ber.*, **69B,** 937 (1936).

(7) In preparing 1.0 mole quantities of methylsulfur trichloride 500 ml. methylene chloride proved adequate to insure sufficient fluidity that the last traces of methanesulfenyl chloride in the reaction mixture could be brought in contact with the chlorine atmosphere above the liquid-solid phase.

TABLE I

SULFINYL CHLORIDES PREPARED

Sulfinyl Chloride $\overset{\text{O}}{\overset{\uparrow}{\text{RSCl}}}$	Per Cent Yield	Boiling Point, °C.	n_D^{25}	d_4^0	d_4^{25}	Analysis	
						Calcd. % Cl	Found % Cl
CH_3—	89	57 (32 mm.)	1.5038	1.4044	1.3706	35.98	36.14[a]
C_2H_5—	95	56 (15 mm.)	1.4954	1.2994	1.2685	31.51	31.57[a]
n-C_3H_7—	80	66 (12 mm.)	1.4864	1.2194	1.1912	28.02	27.94[a]
i-C_3H_7—	74	77 (36 mm.)	1.486	1.2473	1.2193	28.02	25.70[a] 32.59[b]
n-C_4H_9—	86	76 (7 mm.)	1.4849	1.1724	1.1466	25.23	25.16[a]
n-C_5H_{11}—	92	85 (7 mm.)	1.4829	1.1465	1.1220	22.94	21.32[a] 25.04[b]
C_6H_5—	92	111–114 (8 mm.)	1.577	1.373	1.347	22.08	20.90[a]

[a] Hydrolyzable chlorine. [b] Total chlorine by Parr Bomb method.

alkaline and boiling with benzyl chloride, methyl benzyl sulfone was obtained in 13–59% yields, indicating that the aqueous solution had contained sodium methanesulfinate.

The methylene chloride layer from the neutralized reaction mixture was distilled and yielded benzoyl chloride (7–36% yields based on benzoic acid used) and benzoic anhydride (33–50% yields). The nonreproducibility of the results suggested that the compounds were not reacting in the 2:1 molar ratio of acid to methylsulfur trichloride used and that the excess benzoic acid was reacting with the other reaction products.

Glacial acetic acid was added from a buret into a flask containing 0.4 mole of methylsulfur trichloride. After the first small addition the flask was allowed to warm until there was evidence of reaction and then the reaction was maintained at this temperature while addition was continued until all solid methylsulfur trichloride had disappeared, leaving a clear, pale yellow solution. The disappearance of solid was assumed to indicate completion of the reaction. Only 0.335 mole of acetic acid was used.

The hydrogen chloride evolved in the reaction was absorbed in a series of traps and titrated, requiring 0.353 mole of sodium hydroxide. Distillation of the reaction mixture yielded acetyl chloride which was caused to react with aniline and produced 0.245 mole of acetanilide.

After removing the methylene chloride and acetyl chloride from the reaction mixture, the remaining liquid was distilled at reduced pressure and yielded 32.3 g. of a pale yellow product boiling at 59° (38 mm.) and having d_4^{25} 1.3706 and n_D^{25} 1.5038. The liquid was identified as methanesulfinyl chloride (0.328 mole, 82% yield) by hydrolysis to methanesulfinic acid and subsequent transformation to methyl benzyl sulfone. It was further identified by hydrolyzing a known weight and titrating the chloride ion formed with standard silver nitrate solution.

After determining from the preceding experiment that the reacting molar ratio was 1:1, the reaction with benzoic acid was repeated. After adding 0.2 mole dried benzoic acid to 0.2 mole methylsulfur trichloride, the products found were 0.133 mole benzoyl chloride (66.5% yield), 0.178 mole methanesulfinyl chloride (89% yield), and 0.172 mole of hydrogen chloride.

Methylsulfur trichloride with methanol. Anhydrous methanol (0.5 mole) was run slowly into a reaction flask containing 0.5 mole freshly prepared methylsulfur trichloride and the flask was allowed to warm slowly. When gases began to evolve they were first led through a Dry Ice trap and then through a trap containing water. When the reaction appeared to be complete, the reaction mixture was gently heated to the boiling point of methylene chloride to drive out dissolved gases.

Distillation of the reaction mixture yielded 45.2 g. (92% yield) of methanesulfinyl chloride. The Dry Ice trap yielded 17.5 g. (69.3% yield) of methyl chloride which was identified by boiling point and molecular weight. Titration of the water from the traps indicated that 0.543 mole of acid had been carried over from the reaction flask.

Methylsulfur trichloride with water. Exactly one mole of water was run from a buret into a reaction flask containing 1.0 mole of methylsulfur trichloride. The mixture was stirred vigorously and, when the addition was complete, the flask was allowed to warm slowly to room temperature. A large volume of hydrogen chloride was evolved and absorbed in a water trap. After heating the reaction mixture to the boiling point of methylene chloride to drive off the dissolved hydrogen chloride, a total of 1.93 moles of acid was found in the water from the trap. Distillation of the clear methylene chloride solution from the reaction flask produced 87.7 g. of pale yellow methanesulfinyl chloride which boiled 57–58° (32 mm.).

Other preparations were carried out using various organosulfur trichlorides with the results shown in Table I. Ethanol and 1-butanol were also used in various preparations but they appeared to have no advantages over methanol or water.

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