

**3,4-Dihydro-3,3-dimethyl-7-sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-Dioxide (X).**—Compound VI (5 g., 0.0157 mole) and 45 ml. of 2,2-dimethoxypropane (Dow) were refluxed for 24 hours. The excess 2,2-dimethoxypropane was removed at reduced pressure and the residue recrystallized from methanol-water; yield 1.6 g. (28%), m.p. 216–221°.

*Anal.* Calcd. for  $C_{10}H_{12}F_3N_2O_4S_2$ : C, 33.4; H, 3.34. Found: C, 33.1; H, 3.49.

**Compounds of Table I. General Method A.**—Compound VI (5 g., 0.0157 mole), 0.0173 mole of the appropriate aldehyde, one drop of concentrated sulfuric acid and 30 ml. of water were heated at reflux. The product was collected by filtration from the cooled reaction mixture and recrystallized from either methanol-water or acetone-water.

**General Method B.**—Compound VI (5 g., 0.0157 mole), 0.0173 mole of the appropriate aldehyde and 30 ml. of glacial acetic acid were heated at reflux. The solvent was removed at reduced pressure and the product recrystallized from methanol-water.

**General Method C.**—Compound VI (5 g., 0.0157 mole), 0.0173 mole of the ethylene ketal of cyclohexanone<sup>17</sup> (or cyclopentanone<sup>18</sup>), two drops of concentrated sulfuric acid, and 50 ml. of 1-butanol were heated at reflux. The solvent was removed at reduced pressure and the residue recrystallized from methanol-water.

(17) M. Salzbacher, E. Bergmann and E. R. Pariser, *THIS JOURNAL*, **70**, 2827 (1948).

(18) E. J. Salmi, *Ber.*, **71**, 1806 (1938).

SYRACUSE 1, N. Y.

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

## A New Class of Sulfenyl Derivatives; Perhalogenated Aliphatic Sulfenyl Fluorides<sup>1</sup>

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The first two representatives of the hitherto unknown class of sulfenyl fluorides, namely, trichloromethanesulfenyl fluoride and heptafluoro-*n*-propanesulfenyl fluoride, have been prepared. The synthesis of aromatic sulfenyl fluorides could not be achieved by the methods successfully applied for the perhalogenated aliphatic sulfenyl fluorides.

All recorded attempts to synthesize sulfenyl fluorides have failed,<sup>2–6</sup> while a number of more or less stable sulfenyl chlorides is known. On the assumption that the sulfenyl fluorides would have the same order of stability as the sulfenyl chlorides, we thought it would be most promising to employ the most stable sulfenyl chlorides for fluorination experiments in order to obtain the corresponding sulfenyl fluorides.

The most stable representative of this class appears to be the trichloromethanesulfenyl chloride (I).<sup>7</sup> Other rather stable compounds are the recently described perfluorinated aliphatic sulfenyl chlorides.<sup>8,9</sup> As a new representative of this class, heptafluoro-*n*-propanesulfenyl chloride (II) has been prepared in this Laboratory. All these compounds have one common characteristic: the SCl group is attached to a strongly electronegative group which might be responsible for the stability of the aforementioned perhalogenated aliphatic sulfenyl chlorides.

Therefore, compound I which is commercially available and compound II which was obtained in good yields by ultraviolet light-catalyzed chlorination of the corresponding perfluorinated polysulfides were selected as starting materials.

Trichloromethanesulfenyl chloride (I) was used in the first reported attempt to synthesize a sulfenyl

fluoride.<sup>2</sup> The authors used zinc fluoride as a fluorinating agent, but isolated only carbon tetrachloride. In a similar experiment, using a mixture of antimony fluorides, the so-called Swarts reagent,<sup>10</sup> we obtained a mixture of perhalogenated fluorochloromethanes and ethanes, indicating complete cleavage of the original sulfenyl moiety under the rather severe reaction conditions.

Mercuric fluoride is reported to be a relatively mild fluorination agent.<sup>11</sup> Therefore, a solution of I in dichloromethane was refluxed over mercuric fluoride to give the desired trichloromethanesulfenyl fluoride (III) in good yield. The same reaction product was obtained when (I) was heated over silver fluoride. In both cases small amounts of by-products, such as trichloromethyl sulfur difluoride (VII), bis-(trichloromethyl) disulfide (VIII), and bis-(trichloromethyl) trisulfide (IX) were isolated and identified.

Trichloromethane sulfenyl fluoride is a yellow liquid, having an odor similar to that of the corresponding sulfenyl chloride. This compound is relatively stable against hydrolysis; it does not react with water upon shaking at room temperature. That the fluorine atom of the product III is attached to the sulfur atom was proved by the reaction of III with potassium phthalimide. The reaction product was identical with the known *N*-trichloromethanesulfenylphthalimide (IV)<sup>12</sup> obtained by the reaction of trichloromethanesulfenyl chloride (I) and potassium phthalimide.

Although heptafluoro-*n*-propanesulfenyl chloride (II) was recovered nearly quantitatively after refluxing over mercuric fluoride or silver fluoride, the desired heptafluoro-*n*-propanesulfenyl fluoride (V) could be obtained when II was heated with silver

(1) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.

(2) O. B. Heffrich and E. E. Reid, *THIS JOURNAL*, **43**, 591 (1921).

(3) H. J. Emelius and H. G. Heal, *J. Chem. Soc.*, 1126 (1946).

(4) D. L. Chamberlain and N. Kharasch, *THIS JOURNAL*, **77**, 1041 (1955).

(5) D. L. Chamberlain, D. Peters and N. Kharasch, *J. Org. Chem.*, **23**, 381 (1958).

(6) A product cited as  $CF_2(CF_2)_2SF$  is claimed in U. S. Patent 2,519,983, but no details or structure proof are given.

(7) N. Kharasch, *Chem. Revs.*, **39**, 269 (1946).

(8) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

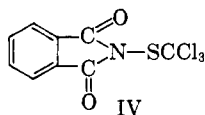
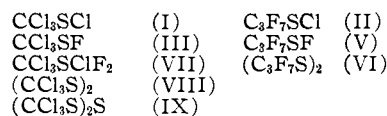
(9) M. Hauptschein and M. Braid, 132nd Meeting of the American Chemical Society, Sept. 8–13, 1957, New York, N. Y.

(10) A. Henne, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 49.

(11) A. L. Henne and Th. Midgley, *THIS JOURNAL*, **58**, 884 (1936).

(12) A. R. Kittleson, *Science*, **115**, 85 (1952).

fluoride in a stainless steel autoclave. Heptafluoro-*n*-propanesulfonyl fluoride (V) is a very volatile compound, boiling below 0°. Kept in a sealed glass ampule, the colorless liquid becomes yellow on exposure to the diffuse day-light. The principal product of the reaction is bis-(heptafluoro-*n*-propyl) disulfide (VI).



We believe that the procedures described can also be applied to the preparation of other perhalogenated aliphatic sulfonyl fluorides.

The application of these methods to the preparation of aromatic sulfonyl fluorides was not successful. In a variation of the experiments reported by Emeleus and Heal<sup>3</sup> we attempted the conversion of benzenesulfonyl chloride (X) and of *p*-nitrobenzenesulfonyl chloride (XI) to the corresponding sulfonyl fluorides by means of mercuric fluoride with dichloromethane as diluent. While these authors<sup>3</sup> obtained only diphenyl disulfide and a resinous material from X, we also isolated thiophenylmercuric chloride (C<sub>6</sub>H<sub>5</sub>SHgCl). From XI we obtained the bis-(*p*-nitrophenyl) disulfide and a compound of the composition O<sub>2</sub>N - C<sub>6</sub>H<sub>4</sub> - SO<sub>2</sub>Cl/O<sub>2</sub>N - C<sub>6</sub>H<sub>4</sub> - SO<sub>2</sub>F (XII).<sup>13</sup> The formation of XII seems to indicate that an intermolecular disproportionation takes place in the course of the reaction, the nitro group serving as oxygen donor and oxidizing sulfonyl to sulfonyl groups. This assumption is supported by the deep blue color of the reaction mixture and also by the observation of Chamberlain, Peters and Kharasch,<sup>5</sup> who reported the formation of bis-(2,2'-fluorosulfonyl)-azobenzene from *o*-nitrobenzene sulfonyl chloride and hydrofluoric acid.

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#### Experimental<sup>14</sup>

**Trichloromethanesulfonyl Chloride (I) and Antimony Fluoride.**—Trichloromethanesulfonyl chloride (100 g.) was added during one hour to a fluorination mixture, consisting of 165 g. of antimony trifluoride, 22 g. of antimony trichloride and 20 g. of chlorine at 160°. The reaction vessel was equipped with a condenser whose outlet was connected to a Dry Ice trap. After the addition of I was completed, the reaction mixture was kept at 160° for an additional hour. After this time more than 70 g. of material, boiling between -35 and +25° was collected in the trap. This distillate consisted of a mixture of chlorofluoromethanes and ethanes. More than 90% of the sulfur contained in the starting material was recovered as free sulfur when the distillation residue was dissolved in concd. hydrochloric acid.

(13) The formation of mixed crystals has also been reported in the attempted replacement of the chlorine atom of XI by fluorine by means of hydrogen fluoride.<sup>3</sup>

(14) Melting points are uncorrected (Fisher-Johns); analyses are by Spang Microanalytical Laboratory, Ann Arbor, Mich.

**Trichloromethanesulfonyl Fluoride (III).**—Mercuric fluoride (100 g.) was added portionwise, with stirring, to 90 g. of trichloromethanesulfonyl chloride (I) in 200 ml. of dichloromethane at room temperature. The addition required about 10 minutes and was slightly exothermic. The reaction mixture was refluxed for three hours and, after cooling, filtered by suction. Fractional distillation of the filtrate through a Widmer column gave, after removal of the unreacted dichloromethane, a first fraction, b.p. 96–101 (760 mm.), which consisted of 42.2 g. (51.5% of the theory) of trichloromethanesulfonyl fluoride (III). A second cut distilled between 65° (50 mm.) and 127° (7 mm.) (22.05 g.) and, finally, a third fraction was obtained at 128–133° (7 mm.). Redistillation of the first cut gave analytically pure trichloromethanesulfonyl fluoride (III), b.p. 97–99°, *n*<sub>D</sub> 1.4851.

*Anal.* Calcd. for CCl<sub>3</sub>FS: C, 7.09; Cl, 62.78; F, 11.21; S, 18.92. Found: C, 7.29; Cl, 62.71; F, 10.84; S, 18.70.

Fractional distillation of the second cut yielded trichloromethyl sulfur difluoro chloride (VII), b.p. 151.5–153.5° (760 mm.), *n*<sub>D</sub> 1.5675. *Anal.* Calcd. for CCl<sub>2</sub>F<sub>2</sub>S: C, 5.37; Cl, 63.33; F, 16.97; S, 14.32. Found: C, 5.39; Cl, 63.51; F, 16.41; S, 14.13, and bis-(trichloromethyl) disulfide (VIII), b.p. 156–157° (10 mm.). *Anal.* Calcd. for C<sub>2</sub>Cl<sub>6</sub>S<sub>2</sub>: C, 7.98; Cl, 70.71; S, 21.31. Found: C, 7.49; Cl, 70.83; S, 20.31.

The third fraction solidified on standing at room temperature. The solid was freed from oily by-products by pressing on a clay plate. Recrystallization from ethanol gave bis-(trichloromethyl) trisulfide (IX), white needles, m.p. 54.5° (lit.<sup>15</sup> 57.4°).

*Anal.* Calcd. for C<sub>2</sub>Cl<sub>6</sub>S<sub>3</sub>: C, 7.22; Cl, 63.89; S, 28.89. Found: C, 7.44; Cl, 63.55; S, 28.75.

No efforts were made to isolate and identify other by-products.

In another experiment, trichloromethanesulfonyl chloride (45 g.) was heated with 40 g. of silver fluoride between 125 and 145° for six hours. After cooling, the reaction mixture was filtered by suction. The filtrate was fractionated through a Widmer column to give trichloromethanesulfonyl fluoride (III) (11.7 g. or 28.6% of the theory), unreacted trichloromethanesulfonyl chloride (I) (7.9 g.), and bis-(trichloromethyl) disulfide (VIII) (6.7 g.).

**N-Trichloromethanesulfonylphthalimide (IV) Trichloromethanesulfonyl Fluoride (III).**—According to the procedure described by Kittleson<sup>12</sup> for the preparation of IV from trichloromethanesulfonyl chloride, trichloromethanesulfonyl fluoride was stirred with an aqueous solution of potassium phthalimide at 0° for one hour. The precipitate was collected, washed with ice-water, and recrystallized from acetic acid, yielding colorless crystals. A mixed melting point with an authentic sample of N-trichloromethanesulfonylphthalimide (IV) gave no depression.

**Preparation of Heptafluoro-*n*-propyl Sulfides.**—Perfluoro-*n*-propyl iodide (580 g.) was heated at 250° with 400 g. of sulfur in an 1800-ml. stainless steel autoclave. Contrary to the report of Haszeldine and Kidd<sup>16</sup> only a small amount of perfluoropropyl iodide was recovered in our experiment and excellent yields of the various perfluorinated *n*-propyl sulfides were obtained, the disulfide VI being the principal product. In addition to the known polysulfides, we also isolated a considerable amount of lower boiling material, which was refractionated through a small Raschig column. The fraction, boiling at 87–90° (760 mm.), *n*<sub>D</sub> 1.2890, proved to be the hitherto unknown bis-(heptafluoro-*n*-propyl) monosulfide.<sup>17</sup>

*Anal.* Calcd. for C<sub>6</sub>F<sub>14</sub>S: C, 19.47; F, 71.87; S, 8.66. Found: C, 19.50; F, 71.87; S, 8.53.

**Heptafluoro-*n*-propanesulfonyl Chloride (II).**—The apparatus consisted of a flask (2000 ml.) connected with a chlorine cylinder and through a condenser with a Dry Ice cooled trap. Bis-(perfluoro-*n*-propyl) disulfide (VI) was placed in

(15) B. Rathke, *Ann.*, **167**, 210 (1873).

(16) The authors state that reaction occurs under these conditions only to a small extent at temperatures up to 350° and that a temperature of 450° would be required for the reaction; *J. Chem. Soc.*, 3871 (1955).

(17) The possible formation of this compound has been reported by M. Hauptschein and A. V. Grosse, but no identification has been given; *THIS JOURNAL*, **73**, 5461 (1951).

the flask and irradiated with ultraviolet light, while chlorine was passed over the disulfide VI in intervals or continuously. At the end of the reaction the contents of the flask and the Dry Ice trap were fractionated through a small Raschig column. By variation of the chlorine stream, the reaction time, and the temperature the yield of II could be improved to 67.8% as illustrated by the following table.

Run	(C <sub>3</sub> F <sub>7</sub> S) <sub>2</sub> , g.	Temp., °C.	Reaction time, days	C <sub>3</sub> F <sub>7</sub> SCl		B. p. (760 mm.), °C.
				Yield, G.	%	
1 <sup>a</sup>	54.3	125	1.25	3.14	4.9	50.5-55
2 <sup>a</sup>	26.3	25-30	6	8.13	26.3	51.5-53.8
3 <sup>a</sup>	69.0	25-30	16	42.85	53.0	50.5-54
4 <sup>b</sup>	90.0	115-130	2	58.16	67.8 <sup>c</sup>	49-56

<sup>a</sup> Chlorine charged in intervals of 3-8 hours. <sup>b</sup> Continuous slow stream of chlorine. <sup>c</sup> 17.1 g. of (C<sub>3</sub>F<sub>7</sub>S)<sub>2</sub> was recovered; conversion 81%.

The perfluoro-*n*-propanesulfonyl chloride (II) is an orange-colored liquid with a pungent odor, b.p. 51-51.5°, *n*<sub>D</sub><sup>20</sup> 1.3239.

*Anal.* Calcd. for C<sub>3</sub>ClF<sub>7</sub>S: C, 15.23; Cl, 14.99; F, 56.23; S, 13.55. Found: C, 14.91; Cl, 14.93; F, 56.29; S, 13.34.

Since the separation of the disulfide VI from the other polysulfides by fractional distillation involves considerable loss, the crude mixture of the perfluorinated *n*-propyl sulfides was subjected to the above chlorination. This resulted in a very good yield of the sulfonyl chloride II, thus further improving the efficiency of the process. Sulfur dichloride was formed as a by-product in the latter experiment.

**Heptafluoro-*n*-propanesulfonyl Fluoride (V).**—The sulfonyl chloride II was refluxed over mercuric fluoride or silver fluoride for several hours, but only traces of a lower boiling material were collected in a Dry Ice cooled trap connected with the outlet of the reflux condenser; II was recovered in both experiments nearly quantitatively. Therefore, the experiment was carried out in a 300-ml. stainless steel autoclave by shaking a mixture of 33 g. of II and 29.5 g. of silver fluoride between 125 and 160° for six hours. After the autoclave had been cooled to -30°, it was unsealed and connected with a Dry Ice cooled trap. The autoclave was then slowly heated to 50-60° and kept at this temperature for 8 hours. About 1.5 g. (4.8% of the theory) of crude heptafluoro-*n*-propanesulfonyl fluoride (V) was collected in the trap. The crude V was purified by fractionation. The sulfonyl fluoride V distilled between -15 and 0°. This gas

has a very pungent odor. Because of its high volatility, only carbon, hydrogen and sulfur could be determined.

*Anal.* Calcd. for C<sub>3</sub>F<sub>7</sub>S: C, 16.37; H, 0.00; S, 14.56. Found: C, 16.45; H, 0.00; S, 14.30.

The remainder of the reaction mixture was distilled *in vacuo* to give the principal product, bis-(heptafluoro-*n*-propyl) disulfide (VI) (24.4 g. or 87% yield), b.p. 118-122° (lit.<sup>17</sup> 120-123°), *n*<sub>D</sub><sup>26</sup> 1.3226 (lit.<sup>16</sup> *nd* 1.3222).

**Benzenesulfonyl Chloride and Mercuric Fluoride in Dichloromethane.**—Mercuric fluoride (60 g.) was added to 40 g. of benzenesulfonyl chloride in 250 ml. of dichloromethane and the reaction mixture refluxed for 5 hours. After cooling, the solids were removed by filtration. Removal of the dichloromethane from the filtrate resulted in the precipitation of a solid which was filtered and identified as C<sub>6</sub>H<sub>5</sub>SHgCl, m.p. 190-192° (from benzene), lit.<sup>18</sup> 191.5°.

The oily filtrate was distilled yielding diphenyl disulfide which crystallized in the receiver; m.p. 57-59° (lit.<sup>19</sup> 60°). Another higher boiling compound was not identified, but was probably bis-(phenyl) trisulfide.

***p*-Nitrobenzenesulfonyl Chloride and Mercuric Fluoride in Dichloromethane.**—Mercuric fluoride (31.5 g.) was added to 20 g. of *p*-nitrobenzenesulfonyl chloride in 100 ml. of dichloromethane. Upon addition of the mercuric fluoride, the reaction mixture warmed and became deep violet. After refluxing for four hours, the mixture was cooled, filtered and the dichloromethane removed from the filtrate. The resulting residue was distilled *in vacuo*. An oil distilled between 96-101.5° (2 mm.). This compound (5.8 g.) solidified in the condenser and was recrystallized from Skellysolve C to give mixed crystals of *p*-nitrobenzenesulfonyl fluoride and *p*-nitrobenzenesulfonyl chloride (XII), colorless needles, m.p. 69-71°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>ClF<sub>6</sub>N<sub>2</sub>O<sub>6</sub>: C, 33.77; H, 1.89; Cl, 8.32; F, 4.45; N, 6.56; S, 15.02. Found: C, 34.03; H, 1.71; Cl, 10.94; F, 4.48; N, 6.43; S, 15.02.

Bis-(*p*-nitrophenyl)-disulfide, m.p. 177-179° (lit.<sup>20</sup> 181°), was isolated from the distillation residue as well as from the filtered mercuric salts.

***p*-Nitrobenzenesulfonyl Chloride and Silver Fluoride.**—When *p*-nitrobenzenesulfonyl chloride and silver fluoride were heated between 100 and 110° without a solvent for three hours, the only product identified was bis-(*p*-nitrophenyl)-disulfide.

(18) H. Lecher, *Ber.*, **53**, 571 (1920).

(19) C. Vogt, *Ann.*, **119**, 150 (1861).

(20) Th. Zincke and S. Leonhardt, *ibid.*, **400**, 7 (1913).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Cleavage Reactions of Some Organopolysilanes

BY DIETMAR WITTENBERG, M. V. GEORGE AND HENRY GILMAN

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Lithium cleavage of octaphenyltrisilane in tetrahydrofuran gave a mixture of triphenylsilyllithium and pentaphenyldisilyllithium. The latter reagent, along with triphenylsilyllithium and heptaphenyltrisilyllithium, was also obtained when decaphenyltetrasilane was cleaved by lithium in tetrahydrofuran. Hexaphenyldisilane was isolated from the reactions of triphenylsilyllithium with silicon tetrachloride, ethyl silicate, dichlorodiphenylsilane, pentaphenyldisilane, chloropentaphenyldisilane and diphenyl-(diphenylmethoxy)-silane. Reaction of trichlorosilane with triphenylsilyllithium gave a small yield of tris-(triphenylsilyl)-silane, which is apparently the first branched chain organosilane of this type. The formation of diphenylsilyllithium and related reactive intermediates is discussed.

The silicon-silicon bond in hexaaryldisilanes has been cleaved by sodium-potassium alloy in ether<sup>1,2</sup>; by potassium in *n*-butyl ether<sup>2</sup>; by lithium, sodium and sodium-potassium alloy in 1,2-dimethoxyethane<sup>3</sup>; by lithium in tetrahydro-

furan,<sup>4</sup> tetrahydropyran,<sup>5</sup> dioxane<sup>5</sup> and pyridine<sup>6</sup>; as well as by sodium in liquid ammonia.<sup>7</sup> Similarly, alkyldiarylsilyllithium and dialkylarylsilyllithium compounds were prepared by lithium cleavage of the corresponding disilanes in tetrahydrofuran.<sup>4</sup>

(1) R. A. Benkeser and R. G. Severson, *THIS JOURNAL*, **73**, 1424 (1951).

(2) H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951); *J. Org. Chem.*, **18**, 753 (1953).

(3) A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

(4) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 608 (1958).

(5) D. Wittenberg, D. Aoki and H. Gilman, *ibid.*, **0**, 5933 (1958).

(6) D. Wittenberg and H. Gilman, *Chemistry & Industry*, 390 (1958).

(7) T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, 913 (1958).