

## PERFLUOROTETRAMETHYLENESULFUR DIFLUORIDE AND ITS DERIVATIVES. PERFLUORO-1,3-DITHIETANE OCTAFLUORIDE AND PERFLUORO-1,4-DITHIANE OCTAFLUORIDE

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### SUMMARY

The fluorination of perfluorotetramethylene sulfide with chlorine monofluoride under controlled conditions results in the formation of both sulfur(IV) and sulfur(VI) compounds as main products. While perfluorotetramethylenesulfur tetrafluoride is very stable to thermolysis and to chemical attack, the hydrolysis of the novel perfluorotetramethylenesulfur difluoride affords perfluorotetramethylene sulfoxide, and its pyrolysis gives perfluoro(di-n-butyl)disulfide. Chlorine monofluoride converts perfluorotetramethylene sulfoxide to perfluorotetramethylenesulfur oxyfluoride, and perfluorotetramethylene sulfone is obtained quantitatively as a decomposition product in contact with Pyrex glass. Perfluoro-1,3-dithietane octafluoride and perfluoro-1,4-dithiane octafluoride are also formed by the reaction of corresponding perfluorocyclic sulfides with ClF at ambient temperature. Infrared, mass and  $^{19}\text{F}$  NMR spectroscopic as well as thermodynamic data are reported.

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### INTRODUCTION

Recently, it was reported that perfluoroalkyl sulfides react smoothly with chlorine monofluoride at  $-78^\circ$  to give the corresponding perfluoroalkylsulfur difluorides in high yields<sup>1</sup>. The latter compounds were defluorinated with anhydrous hydrogen chloride in Pyrex glass vessels by passing through an unstable dichloride intermediate, to form perfluoroalkyl sulfoxides. Chlorine monofluoride oxidatively fluorinated the sulfoxides to perfluoroalkylsulfur oxydifluorides at  $-78^\circ$ <sup>2</sup>.

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Since there are no good routes for the production of perfluorocyclic sulfur compounds which contain sulfur(IV), it was of interest to investigate the fluorination of perfluorotetramethylene sulfide with chlorine monofluoride and to synthesize some of its derivatives in an analogous manner. We found that ClF not only fluorinated the cyclic sulfide to a sulfur(IV) compound, but some of the sulfur(VI) compound formed, also.

In the present work, the synthesis and properties of derivatives of perfluorotetramethylene sulfide—perfluorotetramethylenesulfur difluoride,  $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SF}_2$ , perfluorotetramethylene sulfoxide,  $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}=\text{O}$ , perfluorotetramethylenesulfur oxydifluoride,  $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}(\text{O})\text{F}_2$ , and perfluorotetramethylene sulfone,  $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2$ , are reported. In addition, the preparation and characterization of perfluorocyclic derivatives of sulfur hexafluoride, such as perfluorotetramethylenesulfur tetrafluoride,  $\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SF}_4$ , perfluoro-1,3-dithietane octafluoride,  $\text{SF}_4\text{CF}_2\text{SF}_4\text{CF}_2$ , and perfluoro-1,4-dithiane octafluoride,  $\text{F}_4\text{SCF}_2\text{CF}_2\text{SF}_4\text{CF}_2\text{CF}_2$ , are described.

## RESULTS AND DISCUSSION

Chlorine monofluoride, when reacted with perfluorotetramethylene sulfide (2:1 mole ratio) at low temperature ( $-40^\circ$ ) for 8–12 h, gave the cyclic sulfur(IV) difluoride analogous to its reactions with bis(perfluoroalkyl)sulfides to give the respective bis(perfluoroalkyl)sulfur difluorides<sup>1</sup>. In addition, it was found that by raising the reaction temperature to  $25^\circ$  and increasing the ClF: sulfide ratio to 4:1, the cyclic sulfur tetrafluoride, as well as the bis(perfluoroalkyl)sulfur tetrafluorides<sup>3</sup>, can also be synthesized in good yields. This provides a simple, new route to perfluorocyclic and bis(perfluoroalkyl) derivatives of sulfur tetrafluoride. Thus, in the work described here, perfluorotetramethylenesulfur difluoride and perfluorotetramethylenesulfur tetrafluoride were obtained as the major reaction products from the oxidative fluorination of perfluorotetramethylene sulfide *via* controlled reaction conditions.

Perfluorotetramethylenesulfur difluoride is a colorless solid at  $25^\circ$ . Whilst it does not react with water or mercury, it is slowly hydrolyzed by 10% aqueous NaOH solution and slowly forms the sulfoxide when in contact with glass. No reaction occurred with gaseous  $\text{NH}_3$  after 5 h at  $100^\circ$ . Pyrolysis of the non-cyclic perfluoroalkylsulfur difluorides at about  $200^\circ$  formed perfluoroalkylsulfur trifluorides,  $\text{R}_1\text{SF}_3$ , and perfluoroalkyl disulfides,  $\text{R}_1\text{SSR}_1$ <sup>1</sup>. Perfluorotetramethylenesulfur difluoride is significantly more stable, with thermal decomposition occurring at  $\sim 300^\circ$  to give perfluoro(di-n-butyl)disulfide in substantial yield.

The characterization of  $\overbrace{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SF}_2}$  was aided by the presence of a strong infrared absorption band at  $675\text{ cm}^{-1}$  which was assigned to a S-F stretching frequency. Small amounts of hydrogen chloride enhance the hydrolysis of the sulfur difluoride to the corresponding sulfoxide in a Pyrex bulb. Perfluorotetramethylene sulfide is invariably a by-product of this hydrolysis reaction.

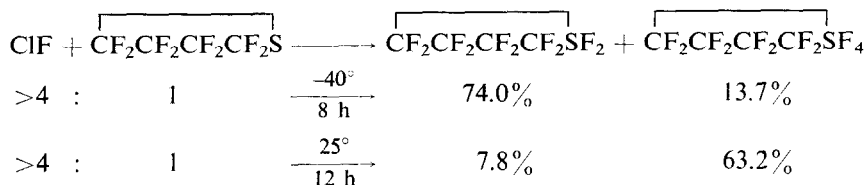
Perfluorotetramethylene sulfoxide is a colorless solid at  $25^\circ$  and freezes to a glass. Although it is stable towards water or mercury, it decomposed when in contact with a 10% aqueous NaOH solution. In the mass spectrum, a molecular ion was observed at an intensity of 15.7% base, as well as characteristic ions at  $m/e$  198 ( $\text{C}_3\text{F}_6\text{SO}^+$ ), 179 ( $\text{C}_3\text{F}_5\text{SO}^+$ ) and 48 ( $\text{SO}^+$ ). The latter species was observed invariably in the spectra of the non-cyclic perfluoroalkyl sulfoxides<sup>1</sup>.

Chlorine monofluoride oxidatively fluorinates  $\overbrace{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}=\text{O}}$  to perfluorotetramethylenesulfur oxydifluoride in excellent yields. This compound is a sublimable white solid which is stable in a Kel-F tube and in the presence of mercury, but is very reactive to glass and water unlike the non-cyclic perfluoroalkylsulfur oxydifluorides<sup>2</sup>. To illustrate the instability of the cyclic compound in glass, it was placed in an infrared cell of Pyrex glass at 10 Torr and its infrared spectrum was recorded at intervals. After 2 h, the intensity of the absorption band at  $717\text{ cm}^{-1}$  (S-F stretching frequency) was decreased by 50% accompanied by the concomitant appearance and growth of a band at  $1426\text{ cm}^{-1}$ . This new band was assigned as the asymmetric vibration of the  $\text{SO}_2$  group of perfluorotetramethylene sulfone. The aqueous hydrolysis of  $\overbrace{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{S}(\text{O})\text{F}_2}$  yielded the new perfluorotetramethylene sulfone essentially quantitatively. Electrochemical fluorination of tetramethylene sulfone<sup>4</sup> has been shown to yield only perfluoro-*n*-butylsulfonyl fluoride, which resulted from the scission of the C-S bond, as a main product.

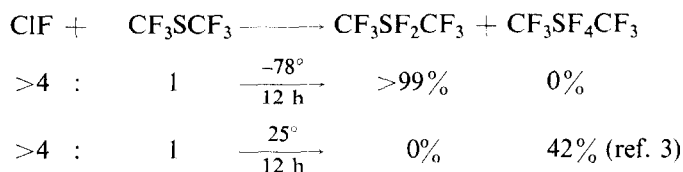
Although the electrochemical fluorination of perfluoro-1,3-dithietane, thiophosgene dimer<sup>5</sup> and *p*-dithiane<sup>6</sup> did not afford the expected perfluoro-1,3-dithietane octafluoride and perfluoro-1,4-dithiane octafluoride, respectively, these perfluorocyclic derivatives of sulfur hexafluoride were formed by the reaction of the corresponding perfluorocyclic sulfides, perfluoro-1,3-dithietane and perfluoro-1,4-dithiane, with chlorine monofluoride at  $25^\circ$  in yields of 40 and 32%, respectively. However, at  $25^\circ$ , ClF destructively fluorinated the thiophosgene dimer to give  $\text{CF}_4$ ,  $\text{CCl}_2\text{F}_2$ ,  $\text{CCl}_3\text{F}$ ,  $\text{SF}_4$  and  $\text{SF}_6$ .

Although perfluorotetramethylenesulfur tetrafluoride had been reported<sup>7</sup> as a product of the electrochemical fluorination of tetramethylene sulfide or di-*n*-butyl disulfide, it was identified by  $^{19}\text{F}$  NMR spectroscopy in a mixture with  $\text{C}_4\text{F}_9\text{SF}_5$ . No data are given. We report a simpler preparation of this derivative of sulfur hexafluoride in good yield. Purification *via* gas chromatography has now permitted full characterization of this thermally and hydrolytically stable compound.

The ability of chlorine monofluoride to oxidatively fluorinate sulfur compounds appears to be largely a function of temperature, *e.g.*,



and



These examples illustrate the ease with which it is possible to generate a majority of either the sulfur(IV) or sulfur(VI) compound from sulfur(II).

The  $^{19}\text{F}$  NMR spectra consist of resonances in the expected regions in all cases. However, only chemical shifts of the chemically non-equivalent nuclei and evident coupling constants are given in Table 3. The high resolution spectra of all except that of perfluoro-1,4-dithiane will be reported later. Apparently these perfluorocyclic compounds except the sulfoxide undergo rapid conformational interconversion, so, for example, the geminal fluorine atoms at the  $\alpha$ - and  $\beta$ -methylene become equivalent and show a single peak. On the other hand, the skeleton of the sulfoxide does not undergo such rapid interconversion of conformers which results in the magnetic non-equivalence of the geminal fluorine atoms of both the  $\alpha$ - and  $\beta$ -methylene. The coupling constants are  $J = 236$  and  $262$  Hz, respectively.

## EXPERIMENTAL

### Reagents

Perfluorotetramethylene sulfide and perfluoro-1,4-dithiane were prepared by the reaction of tetrafluoroethylene with sulfur as described in the literature<sup>8</sup>. Tetrafluoroethylene was obtained from Columbia Organic Chemicals and perfluoro-1,3-dithietane from PCR, Inc., and were used without further purification. Chlorine monofluoride was purchased from Ozark-Mahoning and hydrogen chloride was obtained from Matheson.

### Apparatus

Monel Hoke cylinders (75 ml) with stainless-steel valves were used for the fluorination reactions and a Pyrex vacuum line equipped with a Heise-Bourdon tube gauge was used for handling the volatile compounds.

Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrometer using a 5 cm gas cell with KBr windows and were calibrated against known absorption bands in polyethylene film.  $^{19}\text{F}$  NMR spectra were recorded with a Varian Model HA-100 spectrometer operating at 94.1 MHz with Freon 11 as an internal standard. Mass spectra were obtained using a Hitachi-Perkin-Elmer Model RMU-6E mass spectrometer. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Characterizing data for the compounds prepared in this study as well as for some of the starting materials are found in Table 1 (infrared spectra), Table 2 (mass spectra), Table 3 ( $^{19}\text{F}$  NMR spectra) and Table 4 (elemental analysis and thermodynamic data), respectively.

TABLE 1  
INFRARED SPECTRA ( $\text{cm}^{-1}$ )

c-C <sub>4</sub> F <sub>8</sub> S	1351 (m), 1292 (s), 1219 (vs), 1169 (s), 1144 (s), 991 (vs), 868 (w), 608 (w)
(C <sub>2</sub> F <sub>4</sub> S) <sub>2</sub>	1283 (w), 1236 (s), 1180 (vs), 1137 (m), 1015 (vs), 959 (ms), 510 (w)
c-C <sub>4</sub> F <sub>8</sub> SF <sub>2</sub>	1342 (m), 1289 (m), 1265 (vs), 1220 (m), 1192 (s), 1062 (m), 994 (s), 675 (s), 610 (w), 495 (m)
c-C <sub>4</sub> F <sub>8</sub> SO	1350 (m), 1300 (s), 1240 (vs), 1175 (s), 1158 (s), 1061 (m), 993-960, (s-ms) 607 (w), 514 (w)
c-C <sub>4</sub> F <sub>8</sub> S(O)F <sub>2</sub>	1306 (s), 1290-1264 (s-vs), 1222 (m), 1199 (s), 1035 (m), 976 (s), 935 (s), 712 (s), 582 (m), 483 (m)
c-C <sub>4</sub> F <sub>8</sub> SO <sub>2</sub>	1426 (vs), 1339 (m), 1303 (m), 1252 (vs), 1218 (w), 1196 (vs), 1055 (m), 989 (s), 954 (s), 883 (w), 663 (w), 561 (s), 514 (m), 488 (w)
c-C <sub>4</sub> F <sub>8</sub> SF <sub>4</sub>	1356 (m), 1318 (m), 1260 (vs), 1223 (w), 1202 (s), 1078 (m), 1006 (s), 908 (m), 882 (s), 835 (vs), 795 (s), 598 (w), 532 (m)
(CF <sub>2</sub> SF <sub>4</sub> ) <sub>2</sub>	1271 (s), 1226 (s), 999 (m), 903 (s), 844 (s), 796 (vs), 750 (w), 661 (w), 638 (w), 577 (ms), 533 (m)
(C <sub>2</sub> F <sub>4</sub> SF <sub>4</sub> ) <sub>2</sub>	1232 (s), 1203 (ms), 1160 (w), 1015 (w), 886 (s), 815-798 (s-vs), 590 (w), 540 (w)

TABLE 2  
MASS SPECTRA

c-C <sub>4</sub> F <sub>8</sub> S:	232 c-C <sub>4</sub> F <sub>8</sub> S <sup>+</sup> (37.3), 213 c-C <sub>4</sub> F <sub>7</sub> S <sup>+</sup> (13.0), 163 C <sub>3</sub> F <sub>5</sub> S <sup>+</sup> (8.1), 150 C <sub>3</sub> F <sub>8</sub> <sup>-</sup> (44.1), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (16.8), 113 C <sub>2</sub> F <sub>3</sub> S <sup>+</sup> (37.9), 101 CF <sub>3</sub> S <sup>+</sup> (3.7), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 94 C <sub>2</sub> F <sub>2</sub> S <sup>+</sup> (5.6), 93 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (4.3), 82 CF <sub>2</sub> S <sup>+</sup> (18.0), 81 C <sub>2</sub> F <sub>3</sub> <sup>+</sup> (3.1), 69 CF <sub>3</sub> <sup>+</sup> (19.9), 63 CFS <sup>+</sup> (60.8), 50 CF <sub>2</sub> <sup>+</sup> (6.2), 44 SC <sup>+</sup> (3.7), 32 S <sup>+</sup> (6.8), 31 CF <sup>+</sup> (16.1).
(C <sub>2</sub> F <sub>4</sub> S) <sub>2</sub> :	264 (C <sub>2</sub> F <sub>4</sub> S) <sub>2</sub> <sup>+</sup> (25.1), 245 M-F <sup>+</sup> (2.8), 195 C <sub>3</sub> F <sub>5</sub> S <sub>2</sub> <sup>+</sup> (6.1), 182 C <sub>2</sub> F <sub>4</sub> SCF <sub>2</sub> <sup>-</sup> (13.2), 164 C <sub>2</sub> F <sub>4</sub> S <sub>2</sub> <sup>+</sup> (5.3), 132 C <sub>2</sub> F <sub>4</sub> S <sup>+</sup> (1.6), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (2.6), 113 C <sub>2</sub> F <sub>3</sub> S <sup>+</sup> (30.0), 101 CF <sub>3</sub> S <sup>+</sup> (3.4), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 94 C <sub>2</sub> F <sub>2</sub> S <sup>+</sup> (2.8), 82 CF <sub>2</sub> S <sup>+</sup> (32.0), 69 CF <sub>3</sub> <sup>+</sup> (12.0), 64 S <sub>2</sub> <sup>+</sup> (15.0), 63 CSF <sup>-</sup> (44.1), 50 CF <sub>2</sub> <sup>+</sup> (5.8), 44 CS <sup>+</sup> (4.2), 32 S <sup>+</sup> (12.4), 31 CF <sup>-</sup> (17.3).
c-C <sub>4</sub> F <sub>8</sub> SF <sub>2</sub> :	270 c-C <sub>4</sub> F <sub>8</sub> SF <sub>2</sub> <sup>+</sup> (2.3), 251 c-C <sub>4</sub> F <sub>8</sub> SF <sup>+</sup> (15.4), 232 c-C <sub>4</sub> F <sub>8</sub> S <sup>+</sup> (2.5), 213 C <sub>4</sub> F <sub>7</sub> S <sup>+</sup> (2.0), 201 C <sub>3</sub> F <sub>7</sub> S <sup>+</sup> (8.8), 200 C <sub>4</sub> F <sub>8</sub> <sup>+</sup> (2.1), 182 C <sub>3</sub> F <sub>4</sub> S <sup>+</sup> (3.1), 181 C <sub>4</sub> F <sub>7</sub> <sup>-</sup> (2.1), 163 C <sub>3</sub> F <sub>5</sub> S <sup>+</sup> (10.4), 151 C <sub>2</sub> F <sub>5</sub> S <sup>+</sup> (8.8), 150 C <sub>3</sub> F <sub>6</sub> <sup>+</sup> (4.3), 132 C <sub>2</sub> F <sub>4</sub> S <sup>-</sup> (6.6), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (41.0), 120 CF <sub>3</sub> SF <sup>+</sup> , CF <sub>2</sub> SF <sub>2</sub> <sup>+</sup> (7.7), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (25.9), 113 C <sub>2</sub> F <sub>3</sub> S <sup>+</sup> (22.4), 101 CF <sub>3</sub> S <sup>+</sup> (54.2), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 94 C <sub>2</sub> F <sub>2</sub> S <sup>+</sup> (4.2), 93 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (10.6), 82 CF <sub>2</sub> S <sup>-</sup> (9.5), 81 C <sub>2</sub> F <sub>3</sub> <sup>+</sup> (5.0), 70 SF <sub>2</sub> <sup>+</sup> (20.9), 69 CF <sub>3</sub> <sup>-</sup> (96.7), 63 CSF <sup>+</sup> (27.2), 62 C <sub>2</sub> F <sub>2</sub> <sup>+</sup> (3.9), 51 SF <sup>+</sup> (12.7), 50 CF <sub>2</sub> <sup>+</sup> (11.3), 32 S <sup>+</sup> (8.4), 31 CF <sup>-</sup> (32.3).

Table 2 (continued)

c-C <sub>4</sub> F <sub>8</sub> SO:	248 c-C <sub>4</sub> F <sub>8</sub> SO <sup>+</sup> (15.7), 232 c-C <sub>4</sub> F <sub>8</sub> S <sup>-</sup> (1.7), 213 C <sub>4</sub> F <sub>7</sub> S <sup>+</sup> (1.3), 198 C <sub>3</sub> F <sub>6</sub> SO <sup>+</sup> (1.7), 181 C <sub>4</sub> F <sub>7</sub> <sup>+</sup> (4.7), 179 C <sub>3</sub> F <sub>5</sub> SO <sup>+</sup> (1.9), 169 C <sub>3</sub> F <sub>7</sub> <sup>-</sup> (1.9), 163 C <sub>3</sub> F <sub>5</sub> S <sup>+</sup> (2.3), 162 C <sub>4</sub> F <sub>6</sub> <sup>+</sup> (19.1), 150 C <sub>3</sub> F <sub>6</sub> <sup>+</sup> (5.8), 132 C <sub>2</sub> F <sub>4</sub> S <sup>+</sup> (3.0), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (53.6), 129 C <sub>2</sub> F <sub>3</sub> SO <sup>+</sup> (10.1), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (9.1), 117 CF <sub>3</sub> SO <sup>+</sup> (5.0), 113 C <sub>2</sub> F <sub>3</sub> S <sup>+</sup> (6.2), 101 CF <sub>3</sub> S <sup>+</sup> (5.8), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 98 CF <sub>2</sub> SO <sup>-</sup> (3.8), 94 C <sub>2</sub> F <sub>2</sub> S <sup>+</sup> (2.7), 93 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (10.5), 82 CF <sub>2</sub> S <sup>+</sup> (25.9), 81 C <sub>2</sub> F <sub>3</sub> <sup>+</sup> (5.0), 74 C <sub>3</sub> F <sub>2</sub> <sup>+</sup> (2.9), 69 CF <sub>3</sub> <sup>+</sup> (33.4), 67 SOF <sup>+</sup> (3.9), 63 CSF <sup>+</sup> (18.5), 62 C <sub>2</sub> F <sub>2</sub> <sup>+</sup> (2.6), 50 CF <sub>2</sub> <sup>+</sup> (9.1), 48 SO <sup>+</sup> (36.8), 47 CFO <sup>+</sup> (9.5), 44 SC <sup>+</sup> (2.9), 43 C <sub>2</sub> F <sup>+</sup> (2.2), 32 S <sup>+</sup> , O <sub>2</sub> <sup>+</sup> (65.7), 31 CF <sup>+</sup> (24.7).
c-C <sub>4</sub> F <sub>8</sub> S(O)F <sub>2</sub> :	169 C <sub>3</sub> F <sub>7</sub> <sup>+</sup> (3.0), 150 C <sub>3</sub> F <sub>6</sub> <sup>+</sup> (3.0), 132 C <sub>2</sub> F <sub>4</sub> S <sup>+</sup> (4.1), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (75.8), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (2.7), 112 C <sub>3</sub> F <sub>4</sub> <sup>+</sup> (3.2), 101 CF <sub>3</sub> S <sup>+</sup> (5.2), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 93 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (8.2), 86 SOF <sub>2</sub> <sup>+</sup> (20.7), 85 CF <sub>3</sub> O <sup>+</sup> (19.1), 82 CF <sub>2</sub> S <sup>+</sup> (3.3), 81 C <sub>2</sub> F <sub>3</sub> <sup>+</sup> (4.9), 74 C <sub>3</sub> F <sub>2</sub> <sup>+</sup> (5.0), 69 CF <sub>3</sub> <sup>-</sup> (29.6), 67 SOF <sup>+</sup> (29.8), 50 CF <sub>2</sub> (9.6), 48 SO <sup>+</sup> (10.0), 43 C <sub>2</sub> F <sup>-</sup> (7.7), 32 S <sup>+</sup> , O <sub>2</sub> <sup>+</sup> (7.7), 31 CF <sup>-</sup> (18.7).
c-C <sub>4</sub> F <sub>8</sub> SO <sub>2</sub> :	181 C <sub>4</sub> F <sub>7</sub> <sup>-</sup> (1.5), 169 C <sub>3</sub> F <sub>7</sub> <sup>+</sup> (3.8), 150 C <sub>3</sub> F <sub>6</sub> <sup>+</sup> (2.3), 132 C <sub>2</sub> F <sub>4</sub> S <sup>-</sup> (2.9), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (44.1), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (2.8), 112 C <sub>3</sub> F <sub>4</sub> <sup>+</sup> (2.3), 101 CF <sub>3</sub> S <sup>+</sup> (3.8), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 93 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (7.6), 82 CF <sub>2</sub> S <sup>+</sup> (3.2), 81 C <sub>2</sub> F <sub>3</sub> <sup>+</sup> (4.3), 69 CF <sub>3</sub> <sup>-</sup> (27.5), 67 SOF <sup>-</sup> (2.7), 64 SO <sub>2</sub> <sup>+</sup> (4.8), 63 CSF <sup>+</sup> (4.8), 50 CF <sub>2</sub> <sup>+</sup> (8.1), 48 SO <sup>+</sup> (9.8), 47 CFO <sup>+</sup> (2.6), 44 CO <sub>2</sub> <sup>+</sup> , SC <sup>+</sup> (27.1), 32 O <sub>2</sub> <sup>+</sup> , S <sup>+</sup> (5.2), 31 CF <sup>-</sup> (19.5).
c-C <sub>4</sub> F <sub>8</sub> SF <sub>4</sub> :	219 C <sub>4</sub> F <sub>9</sub> <sup>+</sup> (1.8), 181 C <sub>4</sub> F <sub>7</sub> <sup>+</sup> (2.8), 169 C <sub>3</sub> F <sub>7</sub> <sup>+</sup> (1.9), 150 C <sub>3</sub> F <sub>6</sub> <sup>+</sup> (2.8), 132 C <sub>2</sub> F <sub>4</sub> S <sup>+</sup> (3.9), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (54.8), 119 C <sub>2</sub> F <sub>5</sub> <sup>-</sup> (11.0), 113 C <sub>2</sub> F <sub>3</sub> S <sup>+</sup> (2.2), 112 C <sub>3</sub> F <sub>4</sub> <sup>+</sup> (2.9), 101 CF <sub>3</sub> S <sup>+</sup> (5.0), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (88.1), 93 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (6.0), 89 SF <sub>3</sub> <sup>+</sup> (31.5), 82 CF <sub>2</sub> S <sup>+</sup> (3.1), 81 C <sub>3</sub> F <sub>3</sub> <sup>+</sup> (3.9), 70 SF <sub>2</sub> <sup>-</sup> (7.9), 69 CF <sub>3</sub> <sup>+</sup> (84.9), 63 CFS <sup>-</sup> (5.3), 51 SF <sup>-</sup> (2.9), 50 CF <sub>2</sub> <sup>+</sup> (5.8), 32 S <sup>-</sup> (100), 31 CF <sup>-</sup> (11.5).
(CF <sub>2</sub> SF <sub>4</sub> ) <sub>2</sub> :	158 CF <sub>2</sub> SF <sub>4</sub> <sup>+</sup> (1.6), 139 CF <sub>2</sub> SF <sub>3</sub> <sup>+</sup> (4.6), 120 CF <sub>2</sub> SF <sub>2</sub> <sup>-</sup> (2.3), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (3.2), 101 CF <sub>2</sub> SF <sup>+</sup> (6.8), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (20.6), 89 SF <sub>3</sub> <sup>+</sup> (100), 82 CF <sub>2</sub> S <sup>-</sup> (4.3), 70 SF <sub>2</sub> <sup>+</sup> (21.4), 69 CF <sub>3</sub> <sup>+</sup> (91.4), 63 CSF <sup>+</sup> (4.6), 51 SF <sup>-</sup> (8.1), 50 CF <sub>2</sub> <sup>-</sup> (14.5), 32 S <sup>+</sup> (11.9), 31 CF <sup>+</sup> (15.7).
(C <sub>2</sub> F <sub>4</sub> SF <sub>4</sub> ) <sub>2</sub> :	189 C <sub>2</sub> F <sub>4</sub> SF <sub>3</sub> <sup>+</sup> (3.4), 151 C <sub>2</sub> F <sub>4</sub> SF <sup>+</sup> (4.3), 132 C <sub>2</sub> F <sub>4</sub> S <sup>+</sup> (2.4), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (4.7), 119 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (83.2), 101 CF <sub>2</sub> SF <sup>-</sup> (9.1), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (100), 89 SF <sub>3</sub> <sup>+</sup> (66.7), 82 CF <sub>2</sub> S <sup>+</sup> (7.7), 81 C <sub>2</sub> F <sub>3</sub> <sup>+</sup> (6.2), 70 SF <sub>2</sub> <sup>+</sup> (14.5), 69 CF <sub>3</sub> <sup>+</sup> (35.8), 63 CSF <sup>+</sup> (10.5), 51 SF <sup>-</sup> (5.4), 50 CF <sub>2</sub> <sup>+</sup> (9.7), 32 S <sup>+</sup> (10.6), 31 CF <sup>-</sup> (29.2).
(n-C <sub>4</sub> F <sub>9</sub> S) <sub>2</sub> :	502 n-C <sub>4</sub> F <sub>9</sub> SSC <sub>4</sub> F <sub>9</sub> <sup>+</sup> (13.0), 483 n-C <sub>4</sub> F <sub>9</sub> SSC <sub>4</sub> F <sub>8</sub> <sup>-</sup> (8.3), 333 n-C <sub>4</sub> F <sub>9</sub> SSCF <sub>2</sub> <sup>+</sup> (5.2), 283 C <sub>4</sub> F <sub>9</sub> SS <sup>+</sup> (7.7), 264 C <sub>4</sub> F <sub>8</sub> S <sub>2</sub> <sup>+</sup> (5.0), 219 C <sub>4</sub> F <sub>9</sub> <sup>+</sup> (26.4), 169 C <sub>3</sub> F <sub>7</sub> <sup>-</sup> (4.3), 145 C <sub>2</sub> F <sub>3</sub> S <sub>2</sub> <sup>+</sup> (2.1), 131 C <sub>3</sub> F <sub>5</sub> <sup>+</sup> (22.3), 119 C <sub>2</sub> F <sub>5</sub> <sup>+</sup> (8.2), 114 CF <sub>2</sub> S <sub>2</sub> <sup>+</sup> (2.3), 113 C <sub>2</sub> F <sub>3</sub> S <sup>+</sup> (2.7), 101 CF <sub>3</sub> S <sup>+</sup> (2.1), 100 C <sub>2</sub> F <sub>4</sub> <sup>+</sup> (6.8), 82 CF <sub>2</sub> S <sup>-</sup> (8.1), 69 CF <sub>3</sub> <sup>+</sup> (100), 64 S <sub>2</sub> <sup>-</sup> (10.6), 63 CSF <sup>+</sup> (11.3), 50 CF <sub>2</sub> <sup>-</sup> (2.2), 32 S <sup>+</sup> (10.2), 31 CF <sup>+</sup> (4.2).

### Reaction of perfluorotetramethylene sulfide with ClF

Perfluorotetramethylenesulfur difluoride was formed as a main product by fluorination of the sulfide at low temperature. In a typical reaction, 5 mmole of perfluorotetramethylene sulfide was condensed into a 75 ml Monel Hoke bomb, and 10 mmole of ClF was added. The reaction was carried out at  $-40^{\circ}$  for 8 h. The products were purified by passing them through a trap at  $-40^{\circ}$ , then further

TABLE 3

 $^{19}\text{F}$  NMR SPECTRA† (MHz)

Compound	$\alpha\text{-CF}_2$	$\beta\text{-CF}_2$	$\text{SF}_2(\text{ax})$	$\text{SF}_2(\text{eq})$	Coupling constants (Hz)
c-C <sub>4</sub> F <sub>8</sub> S	87.2	132.1			
c-C <sub>4</sub> F <sub>8</sub> SF <sub>2</sub>	101.0	122.8	11.3		$J(\alpha\text{-CF}_2\text{-SF}_2(\text{ax})) = 24.6$
c-C <sub>4</sub> F <sub>8</sub> SF <sub>4</sub>	108.8	134.4	-13.8	-41.3	$J(\text{SF}_2(\text{ax})\text{-SF}_2(\text{eq})) = 95.3$
c-C <sub>4</sub> F <sub>8</sub> SO	114.7 ax*	128.1 ax			$J(\alpha\text{-CF}_2(\text{ax})\text{-}\alpha\text{-CF}_2(\text{eq})) = 236$
	118.3 eq*	131.8 eq			$J(\beta\text{-CF}_2(\text{ax})\text{-}\beta\text{-CF}_2(\text{eq})) = 262$
c-C <sub>4</sub> F <sub>8</sub> SO <sub>2</sub>	114.4	129.7			
(CF <sub>2</sub> S) <sub>2</sub>	52.2				
(CF <sub>2</sub> SF <sub>4</sub> ) <sub>2</sub>	90.9		-15.4	-44.2	$J(\text{SF}_2(\text{ax})\text{-SF}_2(\text{eq})) = 105.2$
(C <sub>2</sub> F <sub>4</sub> S) <sub>2</sub>	92.4				
(C <sub>2</sub> F <sub>4</sub> SF <sub>4</sub> ) <sub>2</sub>	92.1		-20.2	-48.8	$J(\text{SF}_2(\text{ax})\text{-SF}_2(\text{eq})) = 96.2$

\* ax = axial; eq = equatorial.

† CFC<sub>3</sub> used as internal reference.

purified by gas chromatography using a column of 15% Fluolube grease GR-90 on Chromosorb P. The yield of the solid perfluorotetramethylenesulfur difluoride was 74%. The production of a small amount of perfluorotetramethylenesulfur tetrafluoride was also observed.

When 3.1 mmole of perfluorotetramethylene sulfide was mixed with 12.5 mmole of ClF and held at 25° for 8 h, the yield of perfluorotetramethylenesulfur tetrafluoride was 63%.

#### *Reaction of perfluorotetramethylenesulfur difluoride with HCl*

In a 300 ml Pyrex bulb, 0.45 g (1.6 mmole) of perfluorotetramethylenesulfur difluoride and 1 mmole of HCl were kept at 25° for about 1 h until no solid remained. Gas chromatographic separation of the reaction mixture afforded perfluorotetramethylene sulfoxide (~67% yield) along with a small amount of perfluorotetramethylene sulfide.

#### *Pyrolysis of perfluorotetramethylenesulfur difluoride*

Perfluorotetramethylenesulfur difluoride (0.38 g, 1.4 mmoles) was placed in a 30 ml stainless-steel Hoke bomb and was heated at ~300° for 5 h. Purification was conducted by trap-to-trap distillation using consecutive U-traps immersed in -40, -78 and -196° cold baths, respectively. The transparent liquid (0.22 g, 63%) which was collected in the trap at -40° needed no further purification, and was assigned as perfluoro(di-n-butyl)disulfide based on NMR and mass spectral analysis, and elemental analysis. Small quantities of volatile compounds in the trap at -196° consisted of SOF<sub>2</sub> and n-C<sub>4</sub>F<sub>10</sub> along with SiF<sub>4</sub>.

TABLE 4  
ELEMENTAL ANALYSES AND THERMODYNAMIC DATA

	Elemental analysis (%)		B.p. (°C)	$\Delta H_v$ (kcal mole <sup>-1</sup> )	$\Delta S_v$ (e.u.)	$\log P$ (mmHg)	
	S					$X-(Y/T^\circ K)$	
	C	S				X	Y
	Exptl. Calcd.	Exptl. Calcd.					
c-C <sub>4</sub> F <sub>8</sub> S	20.52 (20.69)	13.86 (13.79)	39.5 <sup>n</sup>	6.43	20.6	7.38	1406
c-C <sub>4</sub> F <sub>8</sub> SF <sub>2</sub>			73.5	9.93	28.6	9.14	2171
c-C <sub>4</sub> F <sub>8</sub> SF <sub>4</sub>	15.60 (15.58)	10.36 (10.39)	61.8 <sup>b</sup>	7.52	22.5	7.79	1644
c-C <sub>4</sub> F <sub>8</sub> SO <sup>e</sup>	19.65 (19.36)	12.88 (12.90)	75.8	8.87	25.4	8.43	1939
c-C <sub>4</sub> F <sub>8</sub> S(O)F <sub>2</sub>							
c-C <sub>4</sub> F <sub>8</sub> SO <sub>2</sub> <sup>d</sup>	18.30 (18.18)	12.10 (12.12)	59.2	7.44	22.4	8.00	1626
(CF <sub>2</sub> S) <sub>2</sub>			46.9 <sup>e</sup>	6.97	21.8	7.64	1524
(CF <sub>2</sub> SF <sub>4</sub> ) <sub>2</sub>	7.79 (7.60)	20.32 (20.25)	69.6 <sup>b</sup>	8.50	24.8	8.29	1857
(C <sub>2</sub> F <sub>4</sub> S) <sub>2</sub>	18.31 (18.18)	24.39 (24.24)	70.4 <sup>f</sup>	7.89	23.0	7.90	1724
(C <sub>2</sub> F <sub>4</sub> SF <sub>4</sub> ) <sub>2</sub>	11.81 (11.54)	15.56 (15.39)	135 <sup>g</sup>	9.69	23.8	8.08	2117
(n-C <sub>4</sub> F <sub>9</sub> S) <sub>2</sub>	19.01 (19.12)	12.51 (12.75)	160	10.73	24.8	8.30	2345

<sup>a</sup> Reported b.p. 42–43°; See ref. 8; <sup>b</sup> Sublimes; <sup>c</sup> M.p. 42–43°; <sup>d</sup> M.p. 43–44°; <sup>e</sup> Reported b.p. 48°, W. J. MIDDLETON, E. G. HOWARD AND W. H. SHARKEY, *J. Org. Chem.*, **30** (1965) 1375; <sup>f</sup> Reported b.p. 81.5°, see ref. 8; <sup>g</sup> Glassy, m.p. 45–56°, reported b.p. 82°/61 mmHg, R. D. DRESDNER AND J. A. YOUNG, *J. Amer. Chem. Soc.*, **81** (1959) 574.



*Reaction of perfluorotetramethylene sulfoxide with ClF*

In a 75 ml Hoke bomb, 0.24 g (1.0 mmole) of perfluorotetramethylene sulfoxide and 2.2 mmole of ClF were held at  $-78^\circ$  for 3 h. Purification was successfully carried out by trap-to-trap distillation. A white solid (0.27 g, 94%) which was found in the trap at  $-40^\circ$  was assigned as perfluorotetramethylenesulfur oxydifluoride by infrared and mass spectral data, and fluorine analysis. The  $^{19}\text{F}$  NMR spectrum could not be obtained because of the strong reactivity of the compound with glass. Perfluorotetramethylenesulfur oxydifluoride thus obtained could be stored in a Kel-F tube at  $25^\circ$  for a week without decomposition.

*Reaction of perfluorotetramethylenesulfur oxydifluoride with water*

In a 5 ml Kel-F tube fitted with a stainless-steel valve which contained 0.1 ml  $\text{H}_2\text{O}$ , perfluorotetramethylenesulfur oxydifluoride (0.16 g, 0.56 mmole) was condensed. The Kel-F tube was then warmed to  $25^\circ$ , and held there for 3.5 h. The product was distilled out, passed over NaF to remove HF and then dried over 5A molecular sieves. Perfluorotetramethylene sulfone (0.5 g, 0.56 mmole) was obtained. The aqueous solution in the Kel-F tube was strongly acidic when tested with pH indicator paper.

*Reaction of perfluoro-1,3-dithietane with ClF*

A reaction mixture of 0.33 g (2.0 mmole) of perfluoro-1,3-dithietane and 22.0 mmole of ClF in a 75 ml Monel Hoke bomb was kept at  $25^\circ$  for 12 h. Initial separation was conducted by passing the mixture through a trap held at  $-40^\circ$ . Further purification by gas chromatography yielded 0.25 g (0.79 mmole) of perfluoro-1,3-dithietane octafluoride. This is the first example of a four-membered perfluorocyclic derivative of sulfur hexafluoride. Similar to other perfluorocyclic derivatives of sulfur hexafluoride, it was resistant to photolysis, thermolysis ( $300^\circ$ ) and chemical attack by 10% aqueous NaOH solution.

*Reaction of perfluoro-1,4-dithiane with ClF*

Perfluoro-1,4-dithiane (0.26 g, 1.0 mmole) was reacted with ClF (10 mmole) at  $25^\circ$  for 12 h. Trap-to-trap distillation resulted in the isolation of 0.13 g (32%) of the white solid perfluoro-1,4-dithiane octafluoride.

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