Bis[perfluoro(1,1-dimethylbutyl)] Trisulfide from the Cesium Fluoride-Assisted Reaction of Hexafluoropropene Dimers with Disulfur Dichloride

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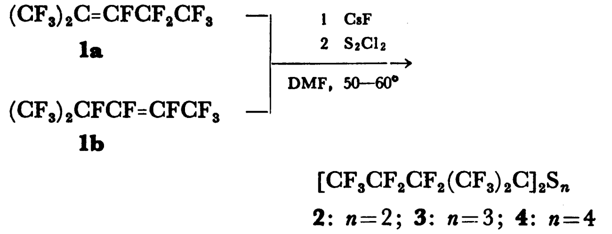
Synopsis. Perfluoro(1,1-dimethylbutanide) anion generated from hexafluoropropene dimers and cesium fluoride in *N,N*-dimethylformamide, reacts with disulfur dichloride to give the title trisulfide as the predominant product.

Compounds derived from perfluorinated hydrocarbons are characterized by chemical inertness and thermal stability, which justify their wide applications as hydraulic liquids, heat-transfer mediums, lubricants, sealants, protective coatings, etc. As part of our programme to seek perfluoroalkyl compounds of potential uses as dielectric fluids, we attempted to prepare bis[perfluoro(1,1-dimethylbutyl)] disulfide (**2**) by reacting disulfur dichloride with the anion generated from perfluorinated 2-methyl-2-pentene (**1a**) and cesium fluoride in *N,N*-dimethylformamide (*DMF*). Rather surprisingly, the main product was not the expected disulfide but bis[perfluoro(1,1-dimethylbutyl)] trisulfide (**3**) accompanied by small amounts of disulfide **2** and tetrasulfide **4**.



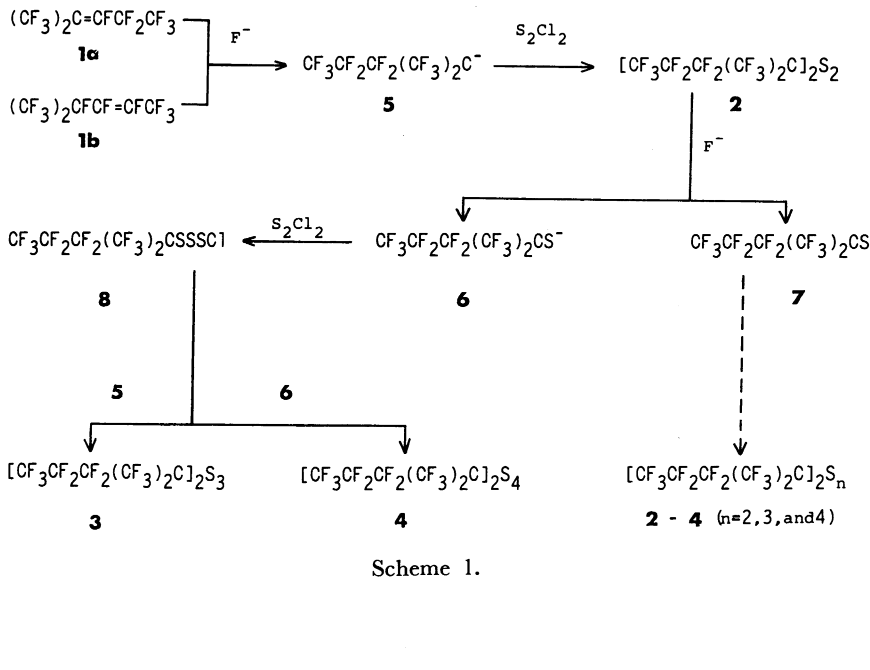
$(CF_3)_2C{=}CFCF_2CF_3$ **1a**, $(CF_3)_2CFCF{=}CFCF_3$ **1b** $\xrightarrow[\text{DMF, 50—60°}]{1\ CsF\quad 2\ S_2Cl_2}$ $[CF_3CF_2CF_2(CF_3)_2C]_2S_n$

2: $n=2$; **3**: $n=3$; **4**: $n=4$

Trisulfide **3** was identified by elemental analysis, ^{19}F NMR and high resolution mass spectra. It is a colorless liquid of low viscosity, which can be distilled without decomposition under reduced pressure and lacks unpleasant odor characteristic of organic sulfides. Compound **3** resists oxidation by hydrogen peroxide, potassium permanganate, and sodium periodate, but readily decomposes by the action of hydride reagents to form a complex product mixture. In spite of the difference in structure, perfluoro(4-methyl-2-pentene) (**1b**) afforded the same product, although perfluoro-olefin **1a** reacted more easily to produce **3** in a better yield. Hexafluoropropene dimer **1b** is known to isomerize into the thermodynamically more stable isomer **1a** in the presence of fluoride ion.[1] The reaction should be conducted in the presence of an excess of perfluoro(1,1-dimethylbutanide) anion **5**; otherwise an extensive liberation of sulfur occurs on addition of disulfur dichloride, leading to a poor yield of perfluoroalkyl polysulfides. Sulfur dichloride was not effective as a sulfurizing agent and led to a low yield of trisulfide as the main sulfur-containing product (≈10%). Mass spectral inspection revealed a slight incorporation of chlorine into the product.

Although the reason for preferential formation of trisulfide is not clear at present, a possible reaction passway is shown in Scheme 1.

Cleavage of a disulfide bond of **2** with fluoride ion followed by capture of the anion **6** with disulfur



Scheme 1.

dichloride affords **8**, which undergoes nucleophilic attack of anions **5** or **6** on the sulfur atom to yield oligosulfides **3** and **4**. Further fission of a sulfur-sulfur bond of **3** or **4** and subsequent trap of the resulting anionic species with sulfenyl fluoride **7** would lead to the polysulfides **2**—**4**.

Only a few descriptions of the formation of perfluoroalkyl tri- and tetrasulfides have been reported so far. They may be obtained as a by-product when perfluoroalkyl iodides of short chain length are heated with sulfur at 220—310 °C in a sealed tube or when carbon disulfide is treated with iodine pentafluoride at 195 °C in an autoclave.[2,3] Reaction of perfluoro-2-butene with potassium fluoride and elementary sulfur in sulfolane at 180 °C gives a low yield of trisulfide among other products.[4] Decomposition of azoperfluoroalkane or hexafluoroethane in the presence of sulfur vapor also forms trisulfides.[5,6] Reactions of perfluoro-olefins **1a** and **1b** with thiols or thiolate ions are known to lead to a mixture of several vinylic sulfides[7] which, of course, lack chemical inertness necessary for our purposes. Thus, our results present the first example of the preparation of perfluoroalkyl trisulfide from fluoro-olefins under mild liquid phase conditions.

Experimental

Perfluoro(2-methyl-2-pentene) (**1a**) and perfluoro(4-methyl-2-pentene) (**1b**) are commercial products available from NEOS Co. Ltd (Kano-cho, Chuo-ku, Kobe, Japan). Disulfur dichloride was purified by fractional distillation prior to use. Cesium fluoride was used as received.

Reaction of Perfluoro(2-methyl-2-pentene) with Disulfur Dichloride. A mixture of cesium fluoride (3.03 g, 20 mmol), perfluoro(2-methyl-2-pentene) (**1a**; 7.80 g, 26 mmol), and dry *DMF* (4 ml) was stirred at 50—60 °C for 1 h under nitrogen. Color gradually turned deep red. Then disulfur dichloride (1.35 g, 10 mmol; redistilled prior to use) in the same solvent (2 ml) was added dropwise during the course of 0.5 h. After addition, the mixture was kept with stirring at this temperature for 12 h and then diluted with water (15 ml). The resulting cloudy solution was filtered through a thin layer of Celite to remove free sulfur. Insoluble substance was washed with ether and the filtrate was extracted with the same solvent. The extract and washings were combined, dried with sodium sulfate, and evaporated. The residue was distilled in vacuo by Kugelrohr to give crude **3** containing about ten percent of disulfide (*m/z* 702 (M^+), 383 ($M^+-C_6F_{13}$)) and tetrasulfide (*m/z* 766 (M^+), 447 ($M^+-C_6F_{13}$)). Although these impurities tenaciously clung to **3**, they could be mostly removed by repeated chromatography on silica gel (Wako Gel C-200) using hexane as eluent. Further purification of **3** was made on a preparative liquid chromatograph (LC-08 Model, Japan Analytical Industry Co., Ltd). Isolated yield, 3.66 g (50% based on CsF). Bp 42—43 °C/0.08 mmHg (Kugelrohr) (1 mmHg=133.322 Pa). MS (20 eV) *m/z* (rel intensity) 734 (M^+; 40), 415 (100), and 181 (24); ^{19}F NMR ($CFCl_3$) δ=60.1 (12F, quint, CF_3), 80.3 (6F, t, CF_3), 103.7 (4F, m, CF_2), and 121.4 (4F, m, CF_2); IR (neat) 1335, 1200—1260 (vs), 1115, 965, 820, 735, and 710 cm^{-1}. Found: C, 19.66; F, 67.00%. Calcd for $C_{12}F_{26}S_3$: C, 19.63; F, 67.27%.

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