The Reaction of Sulfuryl Fluoride and Sulfonyl Fluorides with Fluoro Olefins

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Fluoro olefins react with sulfuryl fluoride, in the presence of alkali metal fluorides or tetramethylammonium bromide and polar aprotic solvents, to give perfluorodialkyl sulfones or perfluoroalkanesulfonyl fluorides. Sulfonyl fluorides react with fluoro olefins under the same conditions to give sulfones.

The fluoride-catalyzed reaction of inorganic acyl fluorides with fluoro olefins has been largely limited to carbonyl fluoride and carboxylic acid fluorides,[1,2] to nitrosyl fluoride,[3] and to sulfur tetrafluoride.[4] We now wish to report a fluoride-catalyzed reaction of fluoro olefins with sulfuryl fluoride to give fluoroalkyl sulfones and sulfonyl fluorides.

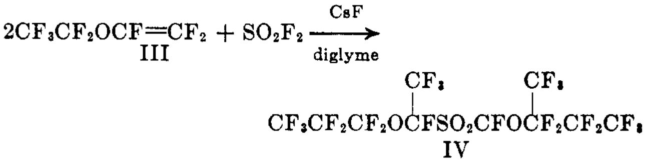
Such additions are presumed to proceed by initial formation of a perfluoroalkyl carbanion, *e.g.*, $F^- + C_2F_4 \rightleftharpoons C_2F_5^-$, which then attacks the acyl fluoride, displaying fluoride ion. Recent work by Graham, Weinmayr, and McCormack describing the synthesis of telomeric olefins from tetrafluoroethylene[5] and synthesis of perfluorinated tertiary carbinols[6] and of carboxylic acids[7] gives further support to the fluoro carbanion hypothesis.

Other synthesis of fluoroalkyl sulfones have employed oxidation[8] of sulfides or Grignard reactions of alkyl or aryl Grignard reagents upon perfluoroalkyl sulfonyl fluorides.[9] Bis(perfluoroalkyl) sulfones have not been prepared by these methods. Clark and Willis claim to have prepared bis(perfluoromethyl) sulfone by electrochemical fluorination of dimethyl sulfone.[10] Perfluoroalkane sulfonyl fluorides have been prepared by electrochemical fluorination of alkanesulfonyl fluorides.[11]

The reaction of tetrafluoroethylene with sulfuryl fluoride in the presence of cesium fluoride and diglyme gave perfluorodiethyl sulfone (I), bp 64°, pour point −93.6°, in 83% yield. In contrast, hexafluoropropene gave only the heptafluoro-2-propanesulfonyl fluoride (II). Attempts at preparation of the sulfone gave only the sulfonyl fluoride and hexafluoropropene dimers and trimers.

The attempted preparation of perfluoroethylisopropyl sulfone by stepwise addition of tetrafluoroethylene and hexafluoropropene to sulfuryl fluoride gave very low yields of the mixed sulfone; the major products were perfluorodiethyl sulfone, heptafluoro-2-propanesulfonyl fluoride, and hexafluoropropene dimers and trimers.

In contrast to the behavior of hexafluoropropene, perfluoro(propyl vinyl ether) (III) reacted with sulfuryl fluoride to form the sulfone (IV) in 23% yield.

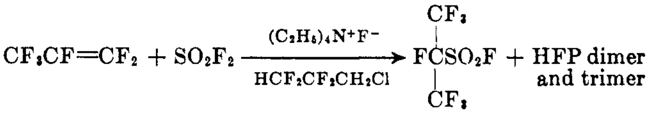


$$\underset{\text{III}}{2CF_3CF_2OCF{=}CF_2} + SO_2F_2 \xrightarrow[\text{diglyme}]{\text{CsF}} \underset{\text{IV}}{CF_3CF_2CF_2O\overset{\displaystyle CF_3}{\overset{|}{C}}FSO_2CFO\overset{\displaystyle CF_3}{\overset{|}{C}}F_2CF_2CF_3}$$

Similarly, benzenesulfonyl fluoride (V) gave phenyl perfluoroethyl sulfone (VI) in 75% yield and perfluoro-1,6-hexanedisulfonyl fluoride (VII), $FSO_2(CF_2)_6SO_2F$, gave the corresponding bis(sulfone), $C_2F_5SO_2(CF_2)_6SO_2C_2F_5$ (VIII).

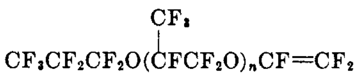
The addition of 1 mole of fluoro olefin to sulfuryl fluoride generally proceeded with ease. In one case tetraethylammonium bromide was used to catalyze the addition of hexafluoropropene to sulfuryl fluoride, presumably through formation of a small amount of tetraethylammonium fluoride *in situ.*

$$(C_2H_5)_4N^+Br^- + SO_2F_2 \rightleftharpoons (C_2H_5)_4N^+F^- + SO_2FBr$$



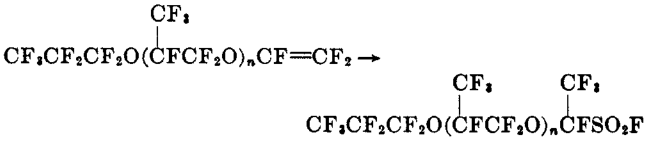
$$CF_3CF{=}CF_2 + SO_2F_2 \xrightarrow[\text{HCF}_2\text{CF}_2\text{CH}_2\text{Cl}]{(C_2H_5)_4N^+F^-} F\overset{\displaystyle CF_3}{\overset{|}{\underset{\displaystyle CF_3}{\underset{|}{C}}}}SO_2F + \text{HFP dimer and trimer}$$

In addition to hexafluoropropene, perfluoro(alkyl vinyl ethers) were added to sulfuryl fluoride to give sulfonyl fluorides in fair to good yields. This was applicable to perfluoro(propyl vinyl ether) and to members of the following series (see Table I).



$$CF_3CF_2CF_2O(\overset{\displaystyle CF_3}{\overset{|}{C}}FCF_2O)_nCF{=}CF_2$$

Table I



$$CF_3CF_2CF_2O(\overset{\displaystyle CF_3}{\overset{|}{C}}FCF_2O)_nCF{=}CF_2 \rightarrow CF_3CF_2CF_2O(\overset{\displaystyle CF_3}{\overset{|}{C}}FCF_2O)_n\overset{\displaystyle CF_3}{\overset{|}{C}}FSO_2F$$

R_fSO_2F $n + 2 =$	No.	Bp, °C (mm)	Calcd, % C	Calcd, % F	Calcd, % S	Found, % C	Found, % F	Found, % S	Yield, %
2	IX	38–39 (100)	16.3	61.7	8.7	16.5	61.5	8.5	83
3	X	80–81 (100)	18.0	64.0	6.0	16.6	63.7	6.5	46
4	XI	75–77 (10)	18.8	65.1	4.6	18.9	65.6	4.4	48
5	XII	103.9–104.8 (10)	19.4	65.9	3.7	18.4	65.3	3.1	30
6	XIII	107–108 (5)	18.0	66.8	3.0	19.6	65.5	3.1	68

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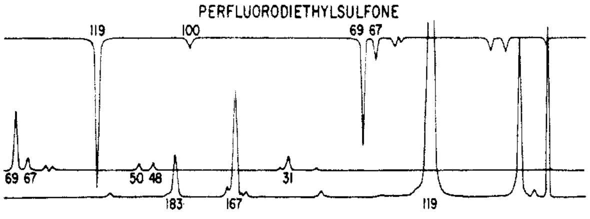


Figure 1.—Mass spectra of the addition product of SO_2F_2 to $CF_2{=}CF_2$.

Experimental Section

Infrared spectra were obtained on the neat liquids using NaCl optics and a Perkin-Elmer Model 221 or 621 spectrophotometer. Nmr spectra were run in a Varian A-56-60 at a frequency of 56.4 Mc with CCl_3F as the standard. All chemical shifts for C–F were toward the high-field side relative to the standard. Mass spectra were run by time-of-flight spectrometry on a Bendix time-of-flight spectrometer, Model 12.

In general, reactions were run under essentially anhydrous conditions in Hastalloy shaker tubes or Fischer–Porter aerosol bottles. In general, scouting runs made during investigation of the synthesis of perfluorodiethyl sulfone showed that dilution of the diglyme or acetonitrile with water resulted in less than 5% recovery of more perfluorodiethyl sulfone so further work-up of the solvent layer was not investigated.

Reactions with tetrafluoroethylene were conducted at temperatures below 130° to minimize reaction of the olefin with itself. In the presence of diglyme the rate of reaction of tetrafluoroethylene with SO_2F_2 seemed roughly proportional to the CsF concentration although no quantitative estimates were made. Purely thermal reaction between tetrafluoroethylene and TFE was not attempted although the reaction of HFP with SO_2F_2 in the presence of CsF but without diglyme was attempted and failed.

Perfluorodiethyl Sulfone.—Into a clean, dry Hastelloy C lined bomb, under nitrogen, were loaded 40 g of CsF (0.38 mole) and 150 ml of diglyme (Ansul Ether 141, distilled from $LiAlH_4$). The bomb was sealed, flushed with nitrogen three times, evacuated, cooled in Dry Ice-acetone, and loaded with 51 g (0.5 mole) of SO_2F_2 and 10 g of tetrafluoroethylene. The bomb was heated to 100° and 5 g of tetrafluoroethylene was added. An immediate pressure drop occurred. The temperature was lowered to 80° and tetrafluoroethylene was added in 10-g increments until 100 g (1 mole) was added. The reaction was held to 80° for 8 hr and cooled to room temperature. The reaction mixture appeared as two clear liquid layers plus a solid (CsF). The lower layer weighed 157 g and distilled at 64°. The product was redistilled on a spinning band and the cut distilling at 63–64° was collected, weighing 126 g (83%).

Anal. Calcd for $C_4F_{10}O_2S$: C, 16.0; F, 62.9; S, 10.6. Found: C, 15.7; F, 64.5; S, 10.1.

The infrared spectrum showed bands at 7.02 and 7.03 μ. The nmr spectrum shows two singlets at −81.2 and −113.8 ppm. The mass spectrum is given in Figure 1.

Reaction of Perfluoro-1,6-hexanedisulfonyl Fluoride with Tetrafluoroethylene.—Disulfonyl fluoride (28 g, bp 65° (20 mm), 10 ml of diglyme, and 2 g of CsF were placed in a 100-ml glass aerosol bottle (Fischer–Porter). The bottle was placed on a manifold and pressurized with tetrafluoroethylene and evacuated three times. The bottle was heated to 60–65° with stirring and tetrafluoroethylene (approximately 12 g) was added over 56 hr. The bottle was cooled and vented and the fluorocarbon layer separated and diluted with Freon® 113 fluorocarbon. The solution was washed with 10% aqueous K_2CO_3 and then with water until neutral. It was dried over $MgSO_4$, filtered, and distilled. The product (12 g) distilled at 105° (2 mm) and then solidified. The product, after purification by sublimation, gave colorless plates, mp 28–30°.

Anal. Calcd for $C_{10}F_{22}O_4S_2$: C, 18.0; F, 62.7; S, 9.6. Found: C, 17.6; F, 62.8; S, 9.3.

The infrared spectrum shows a single strong band at 7.02 μ. The nmr spectrum for

$$\overset{1}{CF_3}\overset{2}{CF_2}SO_2\overset{3}{CF_2}\overset{4}{CF_2}\overset{5}{CF_2}\overset{5}{CF_2}\overset{4}{CF_2}\overset{3}{CF_2}SO_2\overset{2}{CF_2}\overset{1}{CF_3}$$

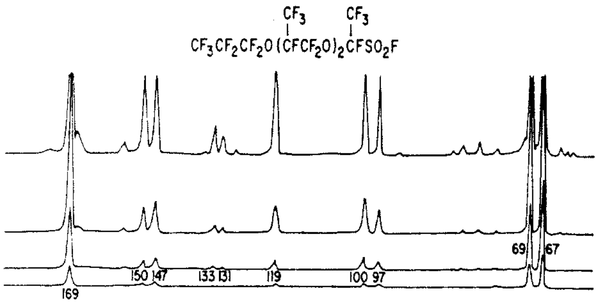


Figure 2.—Mass spectra of the addition product of SO_2F_2 to $CF_3CF_2CF_2O(CF(CF_3)CF_2O)_2CF{=}CF_2$.

shows the following: 1, −79.0 ppm, triplet; 2, −111.3 ppm, complex; 3, −106.6 ppm, broad; 4, −120.0 ppm, broad; 5, 121.7 ppm, broad.

Reaction of Benzenesulfonyl Fluoride with Tetrafluoroethylene.—Benzenesulfonyl fluoride (32 g), 7 g of CsF, and 50 ml of diglyme were placed in an aerosol bottle and caused to react with tetrafluoroethylene as in the previous experiment to give 39 g (75%) of product distilling at 125–127° (47–48 mm).

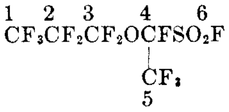
Anal. Calcd for $C_8H_5F_5O_2S$: C, 36.9; H, 1.9; F, 36.4; S, 12.5. Found: C, 37.3; H, 2.1; F, 34.7; S, 12.4.

The refractive index was $n^{25}D$ 1.4394. The infrared spectrum showed a maximum at 7.29 μ. The nmr spectrum showed a singlet at −29.1 ppm and one at −117.2 ppm. The aromatic multiplet is centered at 7.2 ppm, relative to tetramethylsilane.

Reaction of Perfluoro(propyl vinyl ether) with Sulfuryl Fluoride.—CsF (40 g) and 150 ml of diglyme were added to a Hastelloy bomb under nitrogen. The bomb was evacuated and cooled in Dry Ice-acetone and loaded with 133 g (0.5 mole) of perfluoro(propyl vinyl ether) and 51 g (0.5 mole) of sulfuryl fluoride. The bomb was heated to 60–65°. The pressure rose to 130 psig and then dropped to 0 psig in 8.5 hr. The bomb was cooled, vented, and discharged. Distillation of the fluorocarbon layer gave 151 g (83%) of the sulfonyl fluoride $CF_3CF_2CF_2OC(CF_3)FSO_2F$.

Anal. Calcd for $C_5F_{11}SO_3$: C, 16.3; F, 61.7; S, 8.7. Found: C, 16.4; F, 61.5; S, 8.5.

The infrared spectrum shows a strong band at 6.78 μ. The nmr spectrum for

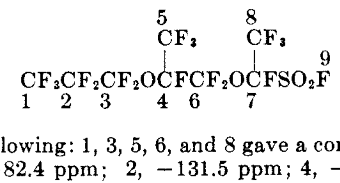


$$\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}O\underset{\underset{5}{CF_3}}{\overset{4}{C}}F\overset{6}{SO_2F}$$

showed 1, 3, 5 as a complex multiplet centered at −82.6 ppm; 2, −131.6 ppm; 4, −128.3 ppm; and 6, +43.6 ppm.

The calcium salt of the free acid was prepared by hydrolysis of the acid fluoride with a slurry of the stoichiometric amount of CaO in water, filtration from CaF_2, and evaporation to dryness. The nmr spectrum of the calcium salt showed the following: 1, −82.5 ppm, J_{13} = 8 cps; 2, −130.4 ppm, J_{24} = 4 cps; 3, −81.6 ppm, J_{34} = 21 cps; 4, −132.5 ppm, J_{35} = 2 cps; 5, −79.9 ppm, J_{45} = 7 cps.

Reaction of Perfluoro(3,6-dioxa-5-methyl-1-nonene) with Sulfuryl Fluoride.—The above compound (78 g, 0.17 mole) 5 g of CsF, and 50 ml of diglyme were treated with 17.7 g (0.17 mole) of SO_2F_2 in a Fischer–Porter aerosol pressure bottle at 60°. The reaction was worked up as in the previous experiment and 39.5 g (46%) of the sulfonyl fluoride (III) was obtained distilling at 80–81° (100 mm). The analysis is given in Table I. The infrared spectrum showed a band of 6.79 μ. The nmr spectrum for

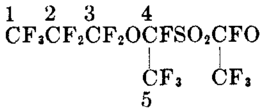


$$\underset{1}{CF_3}\underset{2}{CF_2}\underset{3}{CF_2}O\underset{4}{C}\overset{\overset{5}{CF_3}}{F}\underset{6}{CF_2}O\underset{7}{C}\overset{\overset{8}{CF_3}}{F}\overset{9}{SO_2F}$$

showed the following: 1, 3, 5, 6, and 8 gave a complex multiplet centered at −82.4 ppm; 2, −131.5 ppm; 4, −146.0 ppm; 7, −128.2 ppm, and 9, +43.6 ppm. The mass spectrum is given in Figure 2.

Compounds XI, XII, and XIII were prepared in perfectly analogous fashion and gave similar infrared spectra and nmr chemical shifts. The yields, boiling points, and analyses are given in Table I.

Preparation of Perfluoro[bis(2-oxa-1-methylpentyl) Sulfone].—Perfluoro(propyl vinyl ether) (133 g, 0.5 mole) and 26 g of sulfuryl fluoride were reacted at 80° in a Hastelloy C bomb in the presence of 10 ml of diglyme and 5 g of anhydrous CsF. The reaction appeared to be complete in 1 hr and the bomb was cooled, vented, and discharged. The nonvolatile reaction product was washed with ice water and dried over anhydrous $MgSO_4$. Upon distillation, 38 g (23%) of sulfone IV, bp 84° (100 mm), was obtained. The infrared spectrum showed a strong band at 7.05 μ. The nmr spectrum for

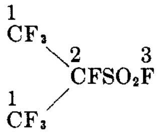


$$\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}\overset{4}{O}\underset{\underset{5}{CF_3}}{CF}SO_2\underset{CF_3}{CF}OCF_2CF_2CF_3$$

IV

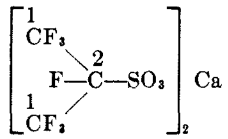
was as follows: 1, −81.6 ppm; 2, −130.9 ppm; 3, −79.9 ppm; 4, −124.0 ppm; 5, −77.0 ppm. The mass spectrum was consistent with the proposed structure.

Attempted Preparation of Bis(perfluoroisopropyl) Sulfones. A. With CsF in Diglyme.—Into a clean dry Hastelloy C lined bomb were loaded 40 g of CsF and 150 ml of diglyme. The bomb was sealed, flushed with dry nitrogen, evacuated, and cooled in a Dry Ice–acetone mixture and loaded with 51 g of SO_2F_2 and 150 g of hexafluoropropene (HFP). The bomb was placed in the shaker and heated to 100°. After 8 hr the bomb was cooled and vented. The lower layer of reaction mixture was separated and distilled to give 31 g of perfluoro-2-propanesulfonyl fluoride, bp 38–39.5°. The major products were linear dimers and trimers. The sulfonyl fluoride showed a strong infrared band at 6.77 μ. The nmr spectrum for



was as follows: 1, −74.4 ppm, multiplet; 2, −170.0 ppm, multiplet; 3, +46.1 ppm, multiplet; J_{12} = 7.5 cps; J_{13} = 10 cps; J_{23} = 4 cps. The mass spectrum was consistent with the proposed structure.

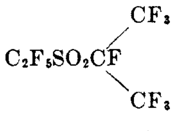
The calcium salt of heptafluoro-2-propanesulfonic acid



gave an nmr spectrum as follows: 1, −73.2 ppm, doublet; 2, −171.8 ppm, heptaplet; J_{12} = 7 cps.

B. With Tetraethylammonium Bromide in 3-Chloro-1,1,2,2-tetrafluoropropane.—When the attempted preparation of the sulfone was carried out using 10 g of $(C_2H_5)_4NBr$ (Eastman, recrystallized) in 150 ml of $HCF_2CF_2CH_2Cl$, a temperature of 120° appeared to be necessary. Distillation now gave 86.5 g of perfluoro-2-propanesulfonyl fluoride and 34.5 g of a mixture of the sulfonyl fluoride with the solvent. The higher boiling components consisted of solvent and linear HFP dimer and trimer.

Attempted Preparation of Perfluoroethylisopropyl Sulfone.—All attempts to prepare



from TFE, SO_2F_2, and HFP in stepwise fashion in either direction gave mixtures of perfluorodiethyl sulfone and fluoroolefins. When HFP was added first, heptafluoro-2-propanesulfonyl fluoride was an additional product.

Registry No.—Sulfuryl fluoride, 2699-79-8; I, 14930-22-4; II, 14856-91-8; $C_2F_5SO_2(CF_2)_6SO_2C_2F_5$, 14856-92-9; $C_8H_5F_5O_2S$, 14856-93-0; IV, 15079-63-7; IX, 14856-94-1; Ca salt of the free acid of IX, 14856-95-2; X, 14856-96-3; XI, 14856-97-4; XII, 14856-98-5; XIII, 14856-99-6; Ca salt of heptafluoro-2-propanesulfonic acid, 14857-00-2; $(CF_2ClCF_2)SO_2$, 14857-01-3.

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