used for the different α-disulfones were as follows: p-CH_3O, 284 mμ; p-CH_3, 257 mμ; p-Br, 266 mμ; p-Cl, 259 mμ. At selected time intervals thereafter, additional aliquots were removed and their absorbance was measured in the same way.

Products of the Decomposition of 5a in Diglyme.—p-Tolyl α-disulfone (1.25 g, 0.004 mol) and 1 l. of freshly distilled diglyme were placed in a 2-l., three-necked flask fitted with a gas-inlet tube and a condenser. The top of the condenser was connected with a length of tubing to a trap that contained a solution of 2.5 g of $BaCl_2 \cdot 2H_2O$ and 10 ml of 30% hydrogen peroxide in 90 ml of water. A vigorous stream of nitrogen was passed through the solution and the rest of the system for 10 min at room temperature before the flask was warmed and gently swirled to dissolve the α-disulfone. Once the α-disulfone had dissolved, a sheet of aluminum foil was wrapped around the flask, the nitrogen stream was reduced to a gentle flow, and the solution was heated to reflux. After 20 hr at reflux, the solution was allowed to cool and trap was disconnected from the condenser. The amount of sulfur dioxide which had been liberated in the decomposition was determined from the amount of barium sulfate formed in the trap.

The solvent was removed from the final solution under reduced pressure and the residue was dissolved in chloroform. The chloroform solution was washed with several portions of water. The water washings were combined and one half was titrated with 0.10 N sodium hydroxide. The other half was treated with S-benzylisothiouronium chloride, using the procedure described by Donleavy[19] and S-benzylisothiouronium p-toluenesulfonate, mp 179–180° (lit.[19] mp 178°), was isolated in a yield equivalent to 94% of the amount expected from the titration results, assuming that all the acid being titrated was p-toluenesulfonic acid.

The chloroform solution was then evaporated and the residue was chromatographed on alumina in the usual way. Elution with hexane and 80:20 hexane–benzene gave fractions which were a mixture of p-tolyl disulfide and p-tolyl sulfide. A pure sample of each was isolated by repeated fractional crystallizations from ethanol of those fractions richest in each component. To determine quantitatively the relative amounts of sulfide and disulfide present, the combined fractions from a run were dissolved in alcohol, excess sodium borohydride was added, and the mixture was stirred for 10 hr at room temperature. Then dilute hydrochloric acid was added to decompose the excess borohydride, and an equal volume of a 50:50 pyridine–water solution was added. The resulting solution was then titrated with standard iodine. Control runs with known mixtures of p-tolyl sulfide and disulfide showed that this method was quantitative for determining the amount of disulfide. The remainder of the material in the combined fractions was assumed to be p-tolyl sulfide.

A large amount of a dark oil was eluted with benzene. Its infrared spectrum in chloroform showed two strong bands at 7.35 and 8.50 μ, indicating the presence of a sulfonyl group. The presence of a wide band of medium intnsity centered at 3.4 μ suggests that the oil possesses aliphatic protons and therefore contains one or more solvent-derived fragments.

Products of the Decomposition of 5a in Bromobenzene.—The same procedure as was used with diglyme was employed to investigate the products of the decomposition of **5a** in bromobenzene. The decomposition was carried out at the reflux temperature (156°) in bromobenzene.

Besides the mixture of p-tolyl sulfide and disulfide, the chromatography on alumina gave a sizable fraction which was eluted with benzene. Recrystallization of this material from 95% ethanol gave pure phenyl p-tolyl sulfone, mp 126–127°, identical in all respects with a known sample of this compound prepared by the method of Buehler and Masters.[4]

Products of the Decomposition of 5a in Diphenylmethane.—The decomposition was carried out at 156° in the same general manner as the decompositions in diglyme or bromobenzene except that no estimate was made of whether any sulfur dioxide was evolved in the decomposition.

After removal of the solvent and extraction of the residue with water, the water washings were titrated with standard base, but, inadvertently, the experiment with S-benzylisothiouronium chloride to determine what fraction of the total acidity was due to sulfonic acid was not carried out, so that we do not know what fraction is due to sulfonic acid and what fraction to sulfinic acid.

Chromatography of the residue on alumina gave a large amount of *sym*-tetraphenylethane, eluted with 80:20 hexane–benzene, mp 210–212°, identical in all respects with a known sample[20] of this compound.

Registry No.—**5a**, 10409-07-1; **5** (Ar = p-BrC_6H_4), 14039-87-3; **5** (Ar = p-ClC_6H_4), 22040-25-1; **5** (Ar = p-$CH_3OC_6H_4$), 13603-79-7.

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Fluorinated Dialkyl Mono- and Polysulfates.
I. Preparation and Some Reactions[1]

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Bis(1H,1H,2H,2H-perfluoroalkyl) and bis(1H,1H,2H,2H-perfluoroisopropoxyalkyl) polysulfates are prepared by the reaction of sulfur trioxide with the corresponding 1-iodo-1H,1H,2H,2H-perfluoro- and 1-iodo-1H,1H,2H,-2H-perfluoroisopropoxyalkanes. Fluorinated dialkyl polysulfates, $R_FCH_2CH_2O(SO_2O)_zCH_2CH_2R_F$, where $z > 3$, have not been isolated owing to the instability of the longer sulfate chain length. The di- and trisulfates (where $z > 1$) are readily decomposed to the lower sulfates and sulfur trioxide when heated for extended periods above 80°. Reaction of the polysulfates with mineral or organic acids gave the corresponding alcohols or alkyl esters, respectively, whereas the monosulfates were unreactive under similar conditions.

The chemistry of fluorosulfur compounds has received an extensive amount of study during the last few years; yet fluorinated dialkyl sulfates are virtually unknown. Apparently, only a few such compounds have been reported: bis(difluorodiethyl) sulfate,[2] bis(trifluoromethyl) mono- and pyrosulfate,[3] bis(hexafluoroisopropyl) pyrosulfate,[4] bis(1H,1H,ωH-perfluoroalkyl) sulfates,[5] and bis(1H,1H,2H,2H-perfluoroalkyl) sulfates.[6]

Related compounds such as fluorocarbon cyclic sulfonate–sulfate anhydrides as well as β-sulfones and novel fluorocarbon halosulfates have also been discussed by recent workers.[7,8]

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TABLE I

REACTIONS OF POLYFLUOROALKYL IODIDES WITH SULFUR TRIOXIDE

Fluoroalkyl iodides $X(CF_2)_m(CH_2)_nI$			Products $X(CF_2)_m(CH_2)_nO(SO_2O)_z(CH_2)_n(CF_2)_mX$						
X	*m*	*n*	X	*m*	*n*	*z*	%	Compd	Bp (mm) or mp, °C
F	3	1	F	3	1	3	25	I	<25
F	3	2	F	3	2	3	75	II	116 (2)
F	7	2	F	7	2	2	76	III	94–96
F	7	2	F	7	2	3	>95	IV	102–104
i-C_3F_7O	2	2	*i*-C_3F_7O	2	2	3	>95	V	2–4
i-C_3F_7O	4	2	*i*-C_3F_7O	4	2	2	>95	VI	30–31
i-C_3F_7O	6	2	*i*-C_3F_7O	6	2	2	74	VII	57–58
i-C_3F_7O	6	2	*i*-C_3F_7O	6	2	3	80	VIII	64–66

TABLE II

PERFLUOROALKYL MONOSULFATES PREPARED BY DECOMPOSITION OF THE CORRESPONDING POLYSULFATES

Polyfluoroalkyl polysulfate $X(CF_2)_m(CH_2)_nO(SO_2O)_z(CH_2)_n(CF_2)_mX$				Polyfluoroalkyl monosulfate $X(CF_2)_m(CH_2)_nOSO_2O(CH_2)_n(CF_2)_mX$					
X	*m*	*n*	*z*	X	*m*	*n*	%	Compd	Bp (mm) or mp, °C
F	3	1	3	F	3	1	50	IX	120–125 (6)
F	3	2	3	F	3	2	62	X	103–105 (2)
F	7	2	2	F	7	2	91	XI	88–90
i-C_3F_7O	2	2	2	*i*-C_3F_7O	2	2	100	XII	98–100 (1)
i-C_3F_7O	4	2	2	*i*-C_3F_7O	4	2	86	XIII	140–142 (1)
i-C_3F_7O	6	2	2	*i*-C_3F_7O	6	2	100	XIV	35–36

The present paper describes the synthesis and some reactions of fluorinated dialkyl mono- and polysulfates.

Discussion

We have found that the sulfation of polyfluoroalkyl iodides with sulfur trioxide provides a convenient route to a family of fluorinated dialkyl polysulfates, as shown in eq 1. The reactions were generally carried

$$2R_F(CH_2)_nI + (z + 1)SO_3 \longrightarrow R_F(CH_2)_nO(SO_2O)_z(CH_2)_nR_F + SO_2 + I_2 \quad (1)$$

$$R_F = \text{fluoroalkyl}$$
$$n = 1, 2$$
$$z = 2, 3$$

out at temperatures in the range of 25–70° at atmospheric pressure. The di- and trisulfates, *i.e.*, where $z = 2$ and 3, were formed in 75–100% yields. Sulfur dioxide and elemental iodine were the inorganic products formed in the reaction. When a molar excess of sulfur trioxide is used (eq 1), the iodine is recovered in the form of a liquid sulfur trioxide–iodine complex. The conversion of the polyfluoroalkyl iodides into the corresponding polysulfates depends on the ratio of sulfur trioxide to the fluoroalkyl iodide, with best conversions being obtained at a 1.5:1 or greater ratio of sulfur trioxide to fluoroalkyl iodide. If less than enough sulfur trioxide is used, a lower conversion of the iodide into the polysulfate is obtained rather than a conversion of the iodide into the monosulfate (eq 1, where $z = 1$) as might be expected from the stoichiometry of the reaction.

At this time, of the polysulfates prepared, only the di- and trisulfate species have been clearly identified. Higher species of the polysulfates, $R_F(CH_2)_nO(SO_2O)_z(CH_2)_nR_F$, where $z > 3$, have not been isolated. The physical properties of the polysulfates and the results of each experiment are presented in Table I.

It seems reasonable to suppose that higher concentrations of sulfur trioxide and moderate pressure could result in the formation of z values >3, probably 4 or higher. However, one of the difficulties in the isolation of the individual polysulfates is that they cannot be purified by fractional distillation or crystallization. They are thermally unstable and tend to dissociate to the lower dialkyl sulfates and sulfur trioxide. This dissociation, in fact, provided a ready and convenient means for obtaining the monosulfates in high yields, and temperatures above 80° were used to induce a rapid dissociation. The monosulfates, unlike the polysulfates or their hydrocarbon analogs,[9,10] are thermally stable, and no decomposition to the dialkyl ethers was observed. The physical properties of the monosulfates and the results of the decomposition experiments are presented in Table II.

Effect of Increasing Methylene Units between the Polyfluoroalkyl Group and Iodide Atom.—There have been many reports on the influence exerted on organic reactions by fluorine in the molecule. This is ascribed to the electron-withdrawing effect caused by the electronegativity of the fluoroalkyl groups. In our studies, evidence for the inductive effect exerted by the perfluoroalkyl groups was demonstrated when perfluoroalkyl iodides, R_FI, with the fluoroalkyl group adjacent to the iodine atom failed to give any fluorinated dialkyl polysulfates when treated with sulfur trioxide[11] but gave instead the corresponding perfluoroacyl fluorides and perfluoropyrosulfuryl fluorides. The influence of the perfluoroalkyl groups was reduced considerably when insulating methylene units were present between the fluoroalkyl group and the iodine atom. This was supported by the increased rate of reaction as well as a sharp increase in percentage conversion of iodides to polysulfates when the iodides were treated with sulfur trioxide as one proceeded from R_FCH_2I to $R_FCH_2CH_2I$.

Thus, the reaction of perfluoropropyl or perfluoroheptyl iodide with sulfur trioxide proceeded only at

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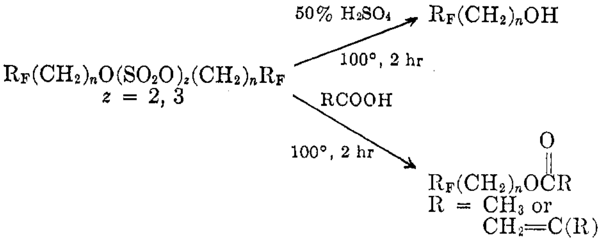
temperatures >*ca.* 100° and at autogenous pressures of about 140 psig over a period of 24 hr to give the corresponding perfluoroacyl fluorides and perfluoropyrosulfuryl fluorides in 49 and 18% conversions, respectively. In contrast, 1-iodo-1H,1H-perfluorobutane reacted comparatively faster at the reflux temperature of sulfur trioxide (46°) to give the corresponding dialkyl trisulfate as the only organic product in a 25% conversion. 1-Iodo-1H,1H,2H,2H-perfluoropentane reacted so exothermically at 25° that ice–water cooling was necessary to moderate the reaction and contain the mixture in the reaction flask. A 75% conversion into the trisulfate was obtained under these conditions.

Equilibrium between the Monosulfate and Sulfur Trioxide.—Several early papers have been published on methoxyl-terminated polysulfates, $CH_3O(SO_2O)_zCH_3$,[9] polysulfuryl fluorides, $F(SO_2O)_zSOF$,[12,13] and polysulfonic acids, $CH_3(SO_2O)_zH$,[14] in which an equilibrium could be achieved with respect to an exchange of parts between the molecules. On the assumption that similar equilibrium mixtures could also be produced from solutions of fluorinated monosulfates and free sulfur trioxide (eq 2), the two compounds were combined in a Fischer–Porter aerosol compatibility tube in a mole ratio of 1:4.3. After the tube was sealed, heated to 100° for 18 hr, and cooled, an examination of the liquid mixture showed that about 50% of the monosulfate was converted into the disulfate. The results are interpreted to show that at high concentrations of sulfur trioxide, it is probable that the polysulfate compounds, free sulfur trioxide, and the monosulfates are in equilibrium and that the equilibrium is directed toward the monosulfates.

$$R_F(CH_2)_nOSO_2O(CH_2)_nR_F + zSO_3 \rightleftharpoons R_F(CH_2)_nO(SO_2O)_{z+1}(CH_2)_nR_F \quad (2)$$

Reactions of the Dialkyl Sulfates.—A study of the reactions of the fluorinated mono- and polysulfates under hydrolytic and esterifying conditions showed an unexpected difference in reactivity. Nonfluorinated dialkyl mono- and polysulfates show equal reactivity under similar conditions and have been extensively employed as alkylating agents both in industry and in the laboratory.[10,15] The ease with which such reactions occur is usually governed by the nucleophilicity of the reactants and the considerable degree of cleavage shown by the carbon–oxygen bond of the monosulfates and the sulfur–oxygen bond of the polysulfates.

It was expected that the fluorinated dialkyl mono- and polysulfates would behave similarly. However, the monosulfates showed remarkable hydrolytic stability, and attempts to prepare fluoro alcohols and fluoro esters by reaction with concentrated sulfuric acid or organic acids, respectively, at 100° for extended periods of time were unsuccessful. The polysulfates, on the other hand, hydrolyzed readily to the fluoro alcohols in the presence of 35–50% sulfuric acid to give a 75% yield of the alcohol. Similarly, treatment of the polysulfates with either excess acetic or acrylic acid gave the corresponding fluoro esters in about the same yields (eq 3). It would seem then that fluorinated dialkyl polysulfates of this type have potential as fluoroalkylating agents and the facile cleavage of the sulfur–oxygen bond can give products not obtainable from the corresponding monosulfates.



$$R_F(CH_2)_nO(SO_2O)_z(CH_2)_nR_F \;(z = 2, 3)\; \xrightarrow[100°,\ 2\ hr]{50\%\ H_2SO_4} R_F(CH_2)_nOH; \quad \xrightarrow[100°,\ 2\ hr]{RCOOH} R_F(CH_2)_nOC(=O)R,\ R = CH_3 \text{ or } CH_2{=}C(R) \quad (3)$$

Additional work is expected to show the versatility of these fluorinated mono- and polysulfates. We have started studies on their reactions with other nucleophilic reagents and this work will be reported at a later date.

Experimental Section[16]

Bis(1H,1H-heptafluorobutyl) Trisulfate (I).—1-Iodo-1H,1H-heptafluorobutane (102 g, 0.33 mol) was treated with stabilized liquid sulfur trioxide (106 g, 1.32 mol).[17] Although there was a slight exotherm, ice–water cooling was not necessary. The sulfur dioxide evolved was condensed in a Dry Ice–acetone-cooled trap. The mixture was maintained at reflux (47°) for 24 hr, cooled, and poured into a separatory funnel where the upper organic phase was separated from the dark, lower inorganic phase. Unreacted and by-product materials, *e.g.*, sulfur trioxide, iodine, etc., were removed by heating the crude product to 80° for 5 hr under a vacuum of 2 mm. A dark brown liquid, the trisulfate, was obtained in 25% yield.

Anal. Calcd for $C_8H_4F_{14}O_{10}S_3$: C, 15.44; H, 0.63; F, 42.74; S, 15.46. Found: C, 15.45; H, 0.72; F, 42.51; S, 15.84.

Fractionation of the trisulfate gave 19 g (0.041 mol) of bis(1H,1H-heptafluorobutyl) sulfate (IX), bp 120–125° (6 mm).

Anal. Calcd for $C_8H_4F_{14}O_4S$: C, 20.61; H, 0.87; F, 57.57; S, 6.93. Found: C, 20.79; H, 0.95; F, 58.02; S, 7.14.

Bis(1H,1H,2H,2H-heptafluoropentyl) Trisulfate (II).—Sulfur trioxide (40 g, 0.50 mol) was added dropwise to 1-iodo-1H,1H,-2H,2H-heptafluoropentane (43 g, 0.13 mol) over a 30-min period; the temperature was maintained at 25–30° with ice–water cooling. The sulfur dioxide evolved was condensed in a Dry Ice–acetone-cooled trap. The mixture was stirred for an additional 2 hr at 70° and poured into a separatory funnel, where the upper organic phase was separated from the dark, lower inorganic phase. Unreacted and by-product materials were removed by heating the crude product to 80° for 2 hr under a vacuum of 2 mm. A tan liquid, the trisulfate, was obtained in 75% yield.

Anal. Calcd for $C_{10}H_8F_{14}O_{10}S_3$: C, 18.46; H, 1.23; F, 40.92; S, 14.77. Found: C, 19.01; H, 1.14; F, 41.16; S, 14.54.

Fractionation of the trisulfate gave bis(1H,1H,2H,2H-heptafluoropentyl) sulfate (X, 30 g, 0.06 mol), bp 103–105° (2 mm), and bis(1H,1H,2H,2H-heptafluoropentyl) pyrosulfate (13 g, 0.023 mol) as a high boiler.

Anal. Calcd for $C_{10}H_8F_{14}O_4S$: C, 24.50; H, 1.63; F, 54.05; S, 6.53. Found: C, 24.32; H, 1.46; F. 53.42; S, 6.71.

Anal. Calcd for $C_{10}H_8F_{14}O_7S_2$: C, 21.05; H, 1.40; F, 46.67; S, 11.23. Found: C, 22.31; H, 1.62; F, 46.46; S, 10.54.

Bis(1H,1H,2H,2H-pentadecafluorononyl) Pyrosulfate (III).—1-Iodo-1H,1H,2H,2H-pentadecafluorononane (40 g, 0.076 mol) treated with sulfur trioxide (21 g, 0.27 mol) as previously described gave a tan residue. The tan residue was recrystallized from carbon tetrachloride to give the pyrosulfate (28 g, 0.029 mol, 76% yield), mp 94–96°.

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(16) Boiling points and melting points are uncorrected; melting points were taken on a Fisher-Johns hot-stage melting point apparatus. The elemental analyses were performed by the Galbraith Analytical Laboratories, Knoxville, Tenn.

(17) Sulfan R (Baker and Adamson reagent grade sulfur trioxide containing 0.25% stabilizing additive), Specialty Chemicals Division, Allied Chemical Corp.

Anal. Calcd for $C_{18}H_8F_{30}O_7S_2$: C, 22.23; H, 0.82; F, 58.76; S, 6.60. Found: C, 21.62; H, 0.72; F, 59.30; S, 6.65.

Bis(1H,1H,2H,2H-pentadecafluorononyl) Trisulfate (IV).—1-Iodo-1H,1H,2H,2H-pentadecafluorononane (50 g, 0.095 mol) treated with sulfur trioxide (48 g, 0.60 mol) as previously described gave the trisulfate, a tan solid, mp 102–104°, in a quantitative yield.

Anal. Calcd for $C_{18}H_8F_{30}O_{10}S_3$: C, 20.57; H, 0.76; F, 54.28; S, 9.16. Found: C, 21.22; H, 0.81; F, 55.42; S, 9.14.

Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Trisulfate (V).—1-Iodo-1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutane[18] (68 g, 0.15 mol) treated with sulfur trioxide (70 g, 0.75 mol) as previously described gave the trisulfate, a liquid, in a quantitative yield.

Anal. Calcd for $C_{14}H_8F_{22}O_{12}S_3$: C, 19.04; H, 0.91; F, 47.40; S, 10.81. Found: C, 19.10; H, 0.97; F, 47.74; S, 10.62.

Fractionation of the trisulfate gave bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) sulfate (50 g, 0.069 mol), bp 98–100° (1 mm).

Anal. Calcd for $C_{14}H_8F_{22}O_6S$: C, 23.27; H, 1.11; F, 57.89; S, 4.43. Found: C, 23.62; H, 1.29; F, 57.24; S, 4.27.

Bis(1H,1H,2H,2H-octafluoro-6-heptafluoroisopropoxyhexyl) Pyrosulfate (VI).—1-Iodo-1H,1H,2H,2H-octafluoro-6-heptafluoroisopropoxyhexane (61 g, 0.11 mol) treated with sulfur trioxide (35 g, 0.44 mol) as previously described gave the pyrosulfate, mp 30°, in a quantitative yield.

Anal. Calcd for $C_{18}H_8F_{30}O_9S_2$: C, 21.54; H, 0.81; F, 56.96; S, 6.39. Found: C, 21.70; H, 0.75; F, 56.21; S, 6.75.

Bis(1H,1H,2H,2H-dodecafluoro-8-hetafluoroisopropoxyoctyl) Pyrosulfate (VII).—1-Iodo-1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctane (56 g, 0.087 mol) treated with sulfur trioxide (33 g, 0.41 mol) gave the pyrosulfate, mp 57–58°, in 74% yield.

Anal. Calcd for $C_{22}H_8F_{38}O_9S_2$: C, 21.93; H, 0.67; F, 60.00; S, 5.32. Found: C, 22.23; H, 0.85; F, 59.46; S, 6.00.

Bis(1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctyl) Trisulfate (VIII).—1-Iodo-1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctane (60 g, 0.094 mol) treated with sulfur trioxide (40 g, 0.41 mol) gave the trisulfate, mp 64–66°, in 80% yield.

Anal. Calcd for $C_{22}H_8F_{38}O_{12}S_3$: C, 20.60; H, 0.62; F, 56.29; S, 7.50. Found: C, 21.22; H, 0.71; F, 57.16; S, 7.25.

Bis(1H,1H,2H,2H-pentadecafluorononyl) Sulfate (XI).—Fractionation of bis(1H,1H,2H,2H-pentadecafluorononyl) pyrosulfate (56 g, 0.058 mol) gave the monosulfate (47 g, 0.053 mol), mp 88–90°.

Anal. Calcd for $C_{18}H_8F_{30}O_4S$: C, 24.27; H, 0.90; F, 64.04; S, 3.60. Found: C, 24.72; H, 1.02; F, 64.35; S, 3.82.

Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Sulfate (XII).—Fractionation of bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) pyrosulfate (250 g, 0.284 mol) gave the monosulfate (228 g, 0.28 mol), bp 98–100° (1 mm), and sulfur trioxide (18 g, 0.225 mol).

Anal. Calcd for $C_{14}H_8F_{22}O_6S$: C, 23.27; H, 1.11; F, 57.89; S. 4.43. Found: C, 23.75; H, 1.09; F, 57.54; S, 4.62.

Bis(1H,1H,2H,2H-octafluoro-6-heptafluoroisopropoxyhexyl) Sulfate (XIII).—Fractionation of bis(1H,1H,2H,2H-octafluoro-6-heptafluoroisopropoxyhexyl) pyrosulfate (291 g, 0.288 mol) gave the monosulfate (230 g, 0.284 mol), bp 140–142° (1 mm), and sulfur trioxide (19 g, 0.24 mol).

Anal. Calcd for $C_{18}H_8F_{30}O_6S$: C, 23.42; H, 0.87; F, 61.82; S, 3.47. Found: C, 23.03; H, 0.98; F, 61.14; S, 3.75.

Bis(1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctyl) Sulfate (XIV).—Fractionation of bis(1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctyl) pyrosulfate (400 g, 0.30 mol) gave the monosulfate (336 g, 0.30 mol), mp 35–36°, and sulfur trioxide (24 g, 0.30 mol).

Anal. Calcd for $C_{22}H_8F_{38}O_6S$: 23.53; H, 0.72; F, 64.35; S, 2.85. Found: C, 23.12; H, 0.82; F, 64.72; S, 2.24.

Reaction of Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Sulfate with Sulfur Trioxide.—Into a 100-ml Fischer–Porter aerosol compatibility tube equipped with a pressure gauge was placed bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) sulfate (26.5 g, 0.037 mol) and sulfur trioxide (13 g, 0.16 mol). This mixture was heated to 100° for 18 hr. Fractionation of the liquid product gave a fore-cut (9.5 g, 0.12 mol) of unreacted sulfur trioxide, a main fraction (13 g, 0.018 mol) of starting sulfate, bp 98–100° (1 mm), and bis-(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) pyrosulfate (12 g, 0.016 mol), bp 110–117° (1 mm).

Anal. Calcd for $C_{14}H_8F_{22}O_9S_2$: C, 20.95; H, 0.99; F, 52.12; S, 7.91. Found: C, 19.85; H, 1.50; F, 51.72; S, 7.43.

Reaction of Perfluoropropyl Iodide with Sulfur Trioxide.—A Fischer–Porter reaction vessel was charged with perfluoropropyl iodide (30 g, 0.10 mol) and sulfur trioxide (16 g, 0.20 mol). The reaction vessel was flushed with nitrogen and sealed. The reaction mixture was heated to 100° with stirring, the pressure rising to 140 psig within 1 hr and gradually to 165 psig. After 23 hr, the mixture was cooled to −78° and the vessel was vented to the atmosphere. The light upper organic layer (27 g) was separated from the lower inorganic layer and distilled to give perfluoropropionyl fluoride (7 g, 0.042 mol), bp −27°, recovered perfluoropropyl iodide (6 g, 0.02 mol), bp 39.5°, and material boiling above 88° (12 g). The infrared spectrum of this last fraction showed a strong absorption in the form of a doublet at 6.65–6.72 μ, indicating the formation of perfluoropyrosulfuryl fluoride.

The reaction of perfluoropropyl iodide with sulfur trioxide at reflux (39°) for 12 hr gave only unreacted perfluoropropyl iodide after work-up and distillation.

Reaction of Bis(1H,1H,2H,2H-pentadecafluorononyl) Pyrosulfate with Methacrylic Acid.—Bis(1H,1H,2H,2H-pentadecafluorononyl) pyrosulfate (30 g, 0.031 mol) was allowed to react with methacrylic acid (12 g, 0.14 mol) at a temperature of 100–105° for 8 hr. Work-up and distillation of the product gave 18 g (0.037 mol) of 1H,1H,2H,2H-pentadecafluorononyl methacrylate, bp 68–72° (1 mm), and 9 g (0.009 mol) of starting pyrosulfate.

Anal. Calcd for $C_{13}H_9F_{15}O_2$: C, 32.38; H, 1.87; F, 59.10. Found: C, 32.50; H, 1.75; F, 58.72.

Reaction of Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Pyrosulfate with Acrylic Acid.—Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) pyrosulfate (32 g, 0.038 mol) was allowed to react with acrylic acid (10 g, 0.14 mol) at a temperature of 110° for 20 hr. The mixture was washed with water, dried, and distilled. 1H,1H,2H,2H-Tetrafluoro-4-heptafluoroisopropoxybutyl acrylate (20 g, 0.052 mol) was recovered, bp 50–54° (4 mm).

Anal. Calcd for $C_{10}H_7F_{11}O_3$: C, 31.25; H, 1.82; F, 54.43. Found: C, 31.61; H, 1.92; F, 54.89.

Reaction of Bis(1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctyl) Pyrosulfate with Acrylic Acid.—Bis(1H,1H,2H,2H-dodecafluoro-8-heptafluorooctyl) pyrosulfate (46 g, 0.038 mol) was allowed to react with acrylic acid (15 g, 0.20 mol) at a temperature of 100–110° for a period of 15 hr. The organic product was extracted with ether, dried, and distilled to give 1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctyl acrylate (19 g, 0.032 mol), bp 82–83° (2 mm), and starting pyrosulfate (21 g, 0.017 mol).

Anal. Calcd for $C_{14}H_7F_{19}O_3$: C, 28.77; H, 1.20; F, 61.81. Found: C, 28.52; H, 1.05; F, 61.34.

Reaction of Bis(1H,1H,2H,2H-pentadecafluorononyl) Pyrosulfate with Sulfuric Acid.—Bis(1H,1H,2H,2H-pentadecafluorononyl) pyrosulfate (28 g, 0.029 mol) was allowed to react with 25% H_2SO_4 (200 ml) at 100° for 2 hr. The organic product was dried and distilled to give 1H,1H,2H,2H-pentadecafluorononanol (16 g, 0.04 mol), bp 82–84° (10 mm).

Anal. Calcd for $C_9H_5F_{15}O$: C, 26.09; H, 1.21; F, 68.83. Found: C, 26.54; H, 1.18; F, 69.12.

Reaction of Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Pyrosulfate with Sulfuric Acid.—Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) pyrosulfate (35 g, 0.043 mol) was allowed to react with 35% H_2SO_4 (100 ml) at 105° for 1 hr. The organic phase was extracted with ether, dried, and distilled to give 1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutanol (19 g, 0.060 mol), bp 84° (59 mm).

Anal. Calcd for $C_7H_5F_{11}O_2$: C, 25.45; H, 1.55; F, 63.33. Found: C, 24.92; H, 1.55; F, 62.68.

Reaction of Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Sulfate with Acrylic Acid.—Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) sulfate (42 g, 0.058 mol)

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[18] F. W. Evans, M. H. Litt, A. M. Weidler-Kubanek, and F. P. Avonda, *J. Org. Chem.*, **33**, 1839 (1968).

Table III

Major Infrared Absorption Bands[a]

—Wavenumbers, cm^{-1}— Mono-sulfate XII	Tri-sulfate V	Remarks
1465 w		CH deformation
1400 m	1430 m	Asymmetrical O=S=O stretch
1300 s	1300 s	
1240 s	1240 s	CF stretch
1180 s	1175 s	
1130 s	1140 s	Symmetrical O=S=O stretch and CF stretch
1060 m	1050 m	
980 s	980 m	Characteristic of $(CF_3)_2CFOC$
900 m	900 m	
875 m	875 m	
850 m	840 m	
800 m	790 m	Symmetrical OSO stretch
775 m	765 m	
720 m	715 m	

[a] Perkin-Elmer Model 525 grating infrared spectrophotometer; determined from a film. Intensities are indicated as follows: s, strong; m, medium; w, weak.

Table IV

Proton Nmr Data[a]

Compd	Compd no.	Chemical shift, ppm	Assignment
$[(CF_3)_2CFOCF_2CF_2CH_2CH_2O]_2SO_2$	XII	4.55 (triplet)	α
β α		2.58 (triplet of triplets)	β
		J_{HH} = 6.5 cps	
		J_{HF} = 17.0 cps	
$[(CF_3)_2CFOCF_2CF_2CH_2CH_2]_2O(SO_3)_3$	V	4.37 (triplet)	α Disulfate[b]
β α		4.14 (triplet)	α Trisulfate
		2.18 (triplet of triplets)	β Disulfate[b]
		2.12 (triplet of triplets)	β Trisulfate
		J_{HH} = 6.6 cps	
		J_{HF} = 17.1 cps	

[a] Data were obtained on a Varian Model A-60 operating at 60.0 Mcps using TMS as an internal zero reference, deuterated chloroform solution. [b] Small amounts of disulfate present in the sample.

was heated with acrylic acid (11 g, 0.15 mol) at a temperature of 105° for a period of 18 hr. The lower phase (44 g) was washed with water, dried, and distilled. 1H,1H,2H,2H-Tetrafluoro-4-heptafluoroisopropoxybutyl acrylate (4 g, 0.01 mol, 1% conversion), bp 50–54° (4 mm), and unreacted starting sulfate (31 g, 0.043 mol) were obtained.

Reaction of Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) Sulfate with Sulfuric Acid.—Bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) sulfate (19 g, 0.026 mol) was allowed to react with 50% H_2SO_4 (55 ml) at a temperature of 105° for 3 hr. The organic product was extracted with ether, dried, and distilled to give only the unreacted starting sulfate.

Infrared and Nmr Spectra.—The infrared spectra of the monosulfate, $[(CF_3)_2CFOCF_2CF_2CH_2CH_2O]_2SO_2$, and the trisulfate, $[(CF_3)_2CFOCF_2CF_2CH_2CH_2]_2O(SO_3)_3$, are given in Table III. Proton nuclear magnetic resonance data for the compounds are given in Table IV.

Registry No.—I, 22040-33-1; II, 22040-34-2; III, 22040-35-3; IV, 22040-36-4; V, 22040-37-5; VI, 22040-38-6; VII, 22103-93-1; VIII, 22040-39-7; IX, 22103-94-2; X, 22040-40-0; XI, 22040-41-1; XII, 22040-42-2; XIII, 22040-43-3; XIV, 22103-95-3; bis(1H,1H,2H,2H-heptafluoropentyl) pyrosulfate, 22040-44-4; bis(1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl) pyrosulfate, 22040-45-5; perfluoropropionyl fluoride, 422-61-7; 1H,1H,2H,2H-pentadecafluorononyl methacrylate, 1815-18-5; 1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutyl acrylate, 22040-48-8; 1H,1H,2H,2H-dodecafluoro-8-heptafluoroisopropoxyoctyl acrylate, 22040-49-9; 1H,1H,2H,2H-pentadecanonanol, 755-02-2; 1H,1H,2H,2H-tetrafluoro-4-heptafluoroisopropoxybutanol, 22040-51-3.

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