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FLUORINATED β -SULTONES AS PRECURSORS TO FLUORINATED
SULFONIC ACIDS, AND NEW FLUOROSULFONYL CONTAINING
MONOMERS/POLYMERS

by

JAVID MOHTASHAM

A dissertation submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY
in
ENVIRONMENTAL SCIENCES AND RESOURCES/CHEMISTRY

Portland State University
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TO THE OFFICE OF GRADUATE STUDIES:

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dissertation of Javid Mohtasham presented February 10, 1989.

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TO MY MOTHER,
FRESHTEH MOJAB,
WHO IS NO MORE.

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AN ABSTRACT OF THE DISSERTATION OF JAVID MOHTASHAM FOR THE
DOCTOR OF PHILOSOPHY in Environmental Sciences and
Resources/Chemistry presented February 10, 1989.

Title: Fluorinated β -sultones as Precursors to Fluorinated
Sulfonic Acids, and New Fluorosulfonyl Containing
Monomers/Polymers.

APPROVED BY MEMBERS OF THE DISSERTATION COMMITTEE:

Gary L. Gard, Chairman

Dennis W. Barnum

Morris B. Silverman

Marvin H. Beeson

John Dash

Stanley S. Hillman

Sulfur trioxide (SO_3) adds to fluoroolefins of the form $\text{RCF}=\text{CF}_2$, (where $\text{R} = \text{F}, \text{SF}_5, \text{CF}_3, \text{CF}_3\text{OCF}_2, \text{CF}_2=\text{CF}(\text{CF}_2)_2, \text{CF}_3(\text{CF}_2)_3\text{O}, \text{CF}_3\text{O}(\text{CF}_2)_2\text{OCF}_2$, or $\text{CH}_2\text{ClCHClCH}_2$), yielding the fluorinated β -sultones, $\overline{\text{RCFCF}_2\text{OSO}_2}$. In the case of $\text{CF}_3(\text{CF}_2)_3\text{OCF}=\text{CF}_2$, a reverse addition occurs, giving the sultone, $\text{CF}_3(\text{CF}_2)_3\text{CF}_2\overline{\text{OCFCF}_2\text{SO}_2\text{O}}$. The fluoro β -sultones are capable of undergoing different reactions, such as rearrangement, hydrolysis, esterification, and polymerization. These reactions, will result in the formation of compounds containing the fluorosulfonyl grouping (SO_2F); it is this group that yields the corresponding sulfonic acid upon base/acid treatment.

The addition of sodium bisulfite to $\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_3(\text{CF}_2)_4\text{CF}=\text{CF}_2$ in the presence of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was also studied to produce the corresponding sulfonic acid hydrates of the general formula, $\text{R}_f\text{CFHCF}_2\text{SO}_3\text{H} \cdot n\text{H}_2\text{O}$. These acids were prepared, and thus, tested as possible fuel cell electrolytes.

Infrared, ^1H and ^{19}F nuclear magnetic resonance and mass spectra, as well as elemental analyses, will be presented in order to support the proposed structures for the resulted compounds.

CHAPTER I

FUEL CELLS

Fuel cells are devices that convert chemical energy directly into electricity without an intermediate combustion cycle. Their function is the reverse of electrolysis: they convert the chemical potential of fuel and oxidant into electrical energy (1, 2).

A fuel cell is simply a battery that has a continuous supply of reactants; it does not have any moving parts in it. The fuels and oxidants are fed into a cell and pass through porous electrodes made of platinum bonded to Teflon. The platinum serves both as electrode and catalyst for the reaction, while the Teflon is an inert support material. These electrodes are separated by a solid or liquid electrolyte which serves as an ionic conductor for specific ions (H^+). In a typical acid electrolyte fuel cell, hydrogen is fed into one compartment where it contacts the anode forming hydrogen ions and electrons. The resulting protons pass through the electrolyte while the electrons travel an external circuit to produce usable electric power. Electrons and protons combine with oxygen at the cathode and produce water; Figure 1.

Anodic Reaction

Cathodic Reaction

Figure 1. A typical acid fuel cell.

Due to the formation of water as the sole product in the acid fuel cell, it is necessary for the cell to operate at high enough temperatures to remove the water as steam to prevent dilution of the electrolyte. The operation of fuel cells at high temperatures improves their reaction kinetics, but at the same time causes electrolyte evaporation and material failure. The evaporation and material failure can be solved by using a higher boiling electrolyte, such as phosphoric acid, which operates at about 200°C, or fluorinated sulfonic acid with operation temperature around 120-150°C (3, 4).

In comparison with phosphoric acid, trifluoromethanesulfonic acid (TFMSA) shows promising results as an electrolyte for fuel cells. TFMSA is one of the strongest

protic acids known; it is capable of protonating sulfuric acid, and is much stronger than phosphoric acid. Also, TFMSA has better oxygen solubility than phosphoric acid because it can be used in a dilute form while it maintains high ionic conductivity. This high conductivity of TFMSA has made it possible for fuel cells to operate at lower temperatures (around 60°C) where TFMSA is stable (5, 6, 7).

The results obtained with TFMSA have created interest in this class of compounds as potential electrolytes. Currently, a number of laboratories are studying new or known fluorinated sulfonic acids as potential fuel cell electrolytes. In this study, new or known fluorinated β -sultones have been prepared, characterized, and used as precursors to fluorinated sulfonic acids and to monomeric/polymeric esters containing the fluorosulfonyl group (SO_2F). These esters can be converted to their corresponding ether derivatives by reaction with SF_4/HF , which in turn can be used to prepare new ether containing sulfonic acids (8). Results obtained from Dr. Ross' studies show that ethers containing sulfonic acids are good candidates as potential fuel cell electrolytes due to the presence of ether oxygen in their structures (9).

CHAPTER II

FLUORINATED β -SULTONES

Sultones are the cyclic esters derived from hydroxyalkane sulfonic acids; they may also be regarded as sulfur analogous of lactones from hydroxycarboxylic acids. As in the case of lactones, there are α -, β -, γ -, and δ -sultones along with a large number of cyclic sulfonates. Among the unsubstituted compounds, the γ -, and δ -sultones are the most stable ones, and contain five- and six-membered rings, respectively. Generally, the unsubstituted β -sultones easily decompose and have not yet been isolated, while fluorinated β -sultones are relatively stable (10,11).

Sulfur trioxide reacts with fluoroolefins to give stable β -sultones. But with some fluoroolefins such as tetrafluoroethylene, the final products are a β -sultone, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$, a β -disultone, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2\text{OSO}_2}$, and even an eight-membered ring hetrocycle, $\overline{(\text{CF}_2)_2\text{OSO}_2(\text{CF}_2)_2\text{OSO}_2}$ (12).

HISTORY OF THE β -SULTONES

The first β -sultone, 1,8-naphthosultone, was prepared and analyzed in 1887 by Schultz, who credited Menching for its discovery. Later on, this compound was studied by Eidmann in 1888, who confirmed the structure and coined the

term "sultone" (10):

One of the first fluorinated β -sultones prepared was 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone, $\text{CF}_3\text{C}(\text{CF}_3)\text{OSO}_2\text{H}$. This β -sultone, which can also be named as 3-trifluoromethyl-3,4,4-trifluoro-1,2-oxathietane-2,2-dioxide, was made by Jiang in 1957 as a result of direct reaction of sulfur trioxide on hexafluoropropene (13).

MECHANISM OF THE FORMATION OF THE FLUORINATED β -SULTONES

There are three different proposed mechanisms for the reaction of sulfur trioxide with fluoroolefins:

Electrophilic Mechanism

The reaction of sulfur trioxide and fluoroolefins is proposed as an electrophilic reaction, due to the typical electrophilic characteristic of sulfur trioxide which easily adds to amines, ethers, alcohols, alkyl halides, hydrogen halides, water, and finally fluoroolefins (14).

Sulfur trioxide reacts with fluoroolefins through an unshared electron pair of hetero atom and the π -component of the multiple bond. The resulting intermediate π -complex isomerizes into a dipole structure, where the sulfur atom is bounded covalently to the carbon atom having enhanced electron density. Finally, through cyclization of the

dipole structure, the fluorinated β -sultones are formed (14, 15):

Figure 2. Electrophilic mechanism.

Nucleophilic Mechanism

In this proposed scheme, the oxygen of sulfur trioxide attacks the carbon of the CF_2 group and forms an intermediate which has a positive charge on the sulfur and a negative charge on the carbon of the CF group. In the final step, the carbon of the CF group and the sulfur undergo ring closure forming the sultone ring (16):

Figure 3. Nucleophilic mechanism.

Concerted Mechanism

This scheme is the final possible mechanism for the formation of the mono β -sultones in which the sulfur and the oxygen of sulfur trioxide attack the carbon of the CF and CF_2 groups simultaneously, and form a β -sultone (17):

Figure 4. Concerted mechanism.

PROPERTIES AND REACTIONS OF FLUORINATED β -SULTONES

Generally, fluorinated β -sultones are colorless liquids which usually fume in air. They dissolve in saturated hydrocarbons, in their fluoro- and chloro-derivatives, and in polyhalogenoolefins. Fluoro sultones react with water and most inorganic or organic compounds in order to produce different derivatives of sulfonic acids or sulfuric acids (11). For example, it is reported that the hydrolysis of the fluoro β -sultones, such as $\overline{\text{XCFCF}_2\text{OSO}_2}$ (where X = F, and CF_3), in basic and acidic media yields the following derivatives (11):

Reactions with Metal Fluorides

The fluorinated β -sultones undergo isomerization to α -fluorosulfonyl polyfluoro carbonyl fluorides upon heating with nucleophilic reagents such as triethylamine, ammonia, dioxane, and alkali metal fluorides. In some cases, brief exposure to moist air produces some isomerization. The

Figure 5. Formation of an acyl fluoride.

$$\overbrace{\text{R}_f\text{CFCF}_2\text{OSO}_2} + \text{ROH} + \text{MF} \longrightarrow \text{R}_f\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OR} + \text{MHF}_2 \quad \text{II-6}$$

Reaction of the fluorinated β -sultones with nucleophilic compounds containing mobile hydrogen atoms, such as found in alcohols, proceeds in two steps. In the first step, the fluorinated β -sultones undergo isomerization in the presence of alkali metal fluorides to the α -fluorosulfonyl polyfluoro acyl fluoride. Finally, the resulting polyfluoro acyl fluorides react with alcohols, forming the corresponding ester along with MHF_2 (19,20,21,22):

Figure 6. Formation of esters containing the sulfonyl fluoride groupings.

Reaction with Water

In the presence of water, fluorinated β -sultones (with three or more carbon atoms) yield unstable α -fluorosulfonyl polyfluoro carboxylic acids which readily undergo decarboxylation. The two carbon acids, fluorosulfonylfluoroacetic acid and fluorosulfonyldifluoroacetic, give carbon dioxide only on heating; higher homologs decarboxylate at room temperature to give hydryl α -monosubstituted polyfluoroalkanesulfonyl fluorides (11,23,24,25,26):

Figure 7. Formation of polyfluorosulfonyl fluorides.

Reaction with Strong Base/Acid

Treatment of the fluorinated β -sultones (with three carbons or more) with base, either $\text{Ca}(\text{OH})_2$ or NaOH , produced the corresponding calcium or sodium sulfonate salts. The resulting sodium or calcium salts, with 100% H_2SO_4 or concentrated $\text{HCl}_{(\text{aq})}$ produce the desired fluorinated sulfonic acids ($\text{R}_f\text{SO}_3\text{H}$, where R_f is any fluorocarbon moiety). The same results are obtained, if the isomeric fluorosulfonyl fluorides are used in place of the fluorinated β -sultones (16,24):

Figure 8. Formation of fluorosulfonic acids.

LITERATURE REVIEW

A survey of the literature shows that the fluorinated β -sultones are useful precursors to perfluoro and polyfluoro derivatives of sulfuric and sulfonic acids; some of these derivatives have had wide chemical applications such as additives to fuel cell electrolytes, surfactants, or in the systems requiring thermally and hydrolytically stable strong acids (11,21). Due to the importance of β -sultones, this section is divided into three parts: in the first part, the preparation of fluorinated β -sultones will be described and in the last two parts explain the reactions of the β -sultones along with their spectral data are explained.

Preparation of Fluorinated β -Sultones

Synthesis of the fluorinated β -sultones depends on the conditions (i.e., temperature, time, and solvent) under which monomer SO_3 reacts with fluoroolefins. Because of

this, all fluorinated sultones are reported with their methods of preparation, and presented in the order which have been published in the literature. At the end, all of these β -sultones are summarized in Table I, according to the number of carbon atoms in their structures.

2-Hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone. $\text{CF}_3\overline{\text{CFCF}_2}\text{OSO}_2$ was made in the form of a mixture as a result of spontaneous reaction of SO_3 and $\text{CF}_3\text{CF}=\text{CF}_2$ (13). Later on, the above β -sultone was obtained by heating a mixture of sulfur trioxide and hexafluoropropene at 100°C for 15 hours (18,27), or 60°C in a Carius tube or autoclave (14); b.p. 46.5°C , with an 85 or 92% yield.

2-Hydroxy-1-chloro-1,2,2-trifluoroethanesulfonic acid sultone and 2-hydroxy-2-chloro-1,1,2-trifluoroethanesulfonic acid sultone. The $\overline{\text{CF}_2\text{CFClo}}\text{SO}_2$ (I) and $\text{Cl}\overline{\text{CFCF}_2}\text{OSO}_2$ (II) mixture was obtained through reaction of sulfur trioxide with chlorotrifluoroethylene between -28°C to -21°C . The reaction mixture was then refluxed for 3 hours under a dry ice condenser. Finally after 8 days the product was distilled to give 68% of (I) and 32% of (II); b.p. $76.0-76.5^\circ\text{C}$ (13). In 1960, there were two reports on preparation of these sultones. The first preparation method consists of heating a mixture of chlorotrifluoro-ethylene and sulfur trioxide (stabilized with dimethylsulfate) in an autoclave at temperatures up to 70°C . The yield for the

production of the sultone was 95% (14). The second method was as follows: freshly distilled sulfur trioxide was added dropwise to the chlorotrifluoro-ethylene in the parr apparatus. The product mixtures of (I) and (II) were collected in -78°C bath with a 85% yield; b.p. $76-78^{\circ}\text{C}$ (18). Later, sulfur trioxide was added to liquid trifluorochloroethylene over a period of one hour with stirring in a dry ice slush bath. The resultant homogeneous solution was at 10°C and was kept at this temperature for 2 hours. The resulting β -sultone was fractionated at atmospheric pressure with 55.8% yield; b.p. $73-77^{\circ}\text{C}$ (28).

4,5-Dichloroperfluoropentane-1,2-sultone. $\text{CF}_2\text{ClCFCl}-\overline{\text{CF}_2\text{CFCF}_2}\text{OSO}_2$ was prepared by the slow addition of sulfur trioxide to 4,5-dichloroperfluoropentene between $45-48^{\circ}\text{C}$ over a period of 20 hours. The resulting sultone was obtained with 72.3% yield; b.p. $79.8-80^{\circ}\text{C}/63.7\text{ mm}$ (13). Later, this sultone was obtained through distillation of 4,5-dichloro-perfluoropentene-1 and SO_3 into a dry flask. The mixture was then refluxed for 20 hours; while the temperature rose from 40 to 54°C . Excess SO_3 was distilled out. The β -sultone was formed in 92% yield; b.p. $55^{\circ}\text{C}/25\text{ mm}$ (29).

4,6,7-Trichloroperfluoroheptane-1,2-sultone. $\text{CF}_2\text{Cl}-(\text{CF}_2\text{CFCl})_2\overline{\text{CFCF}_2}\text{OSO}_2$ was obtained through the addition of sulfur trioxide to 4, 6, 7-trichloroperfluoroheptene at 50°C for 48 hours. The resulting β -sultone ring, $\text{CF}_2\text{Cl}-$

$(\text{CFClCF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$, was produced in 77.5% yield; b.p. 69-72.5°C/0.22 mm (13,28).

4,6,8,9-Tetrachloroperfluorononane-1,2-sultone. $\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_3\overline{\text{CFCF}_2\text{OSO}_2}$ was made by the addition of sulfur trioxide to 4,6,8,9-tetrachloroperfluorononene between 40-45°C for 90 hours. The β -sultone was obtained in 16.6% yield; b.p. 81-82°C/0.08 mm (13,28).

4,6,8,10,11-Pentachloroperfluorohendecane-1,2-sultone. $\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_4\overline{\text{CFCF}_2\text{OSO}_2}$ was produced through the addition of sulfur trioxide to 4,6,8,10,11-pentachloroperfluorohendecane at 45°C for 27 hours. The β -sultone was formed with 14.2% yield; b.p. 115-116°C/0.4 mm (13,28).

4,4-Dichloroperfluorobutane-1,2-sultone. 4,4-Dichloroperfluorobutene-1 was reacted with sulfur trioxide at room temperature for 3 days. The resulting β -sultone, $\text{CFCl}_2\text{CF}_2\overline{\text{CFCF}_2\text{OSO}_2}$, was obtained in 42.5% yield; b.p. 136.7°C (13,28).

2,3-Dichloroperfluorobutane-2-3-sultone. A mixture of sym. dichloroperfluorobutene and sulfur trioxide was kept between 40-45°C for 13 days. The final β -sultone, $\text{CF}_3\text{CCl}(\text{O})\text{CCl}(\text{SO}_2)\text{CF}_3$, was obtained in 59.8% yield; b.p. 132-133.8°C (28).

2-Hydroxytetrafluoroethanesulfonic acid β -sultone. Originally, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ was prepared by the reaction of freshly distilled sulfur trioxide, which was stabilized with dimethyl sulfate, and tetrafluoroethylene in an 100ml auto-

clave at -100°C . The reaction vessel was then warmed up to -10°C in 2 hours and later to 60°C . The resulting β -sultone was obtained in 90% yield; b.p. 33°C (14,30). Later, this β -sultone was obtained using a Parr low-pressure hydrogenation apparatus in which freshly distilled sulfur trioxide reacted with tetrafluoroethylene while the temperature was kept below 80°C . The β -sultone was produced in 93% yield; b.p. 42°C (18,27).

2-Hydroxy-1,2,2-trifluoroethanesulfonic acid β -sultone. $\overline{\text{CFHCF}_2\text{OSO}_2}$ was produced by reaction of sulfur trioxide, which was stabilized with dimethyl sulfate, and trifluoroethylene at 50°C . The resulting sultone was obtained in 94% yield; b.p. $104-105^{\circ}\text{C}$ (14,30). This sultone was also made in a similar manner as explained previously for $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ (18), but in 1985, this sultone was prepared by the reaction of monomer SO_3 and trifluoroethylene at room temperature. The resulting β -sultone was formed in 78% yield, b.p. 97°C (31).

2-Hydroxy-1,2-dichloro-1,2-difluoroethanesulfonic acid sultone. $\overline{\text{CFClCFClOSO}_2}$ was made by reacting 1,2-dichloro-1,2-difluoroethylene and freshly distilled sulfur trioxide at an ice bath temperature. The resulting sultone was produced in 80% yield; b.p. $110-113^{\circ}\text{C}$ (18).

2-Hydroxy-1,1-dichloro-2,2-difluoroethanesulfonic acid sultone. $\overline{\text{CCl}_2\text{CF}_2\text{OSO}_2}$ was prepared for the first time in 1960 through the addition of freshly sulfur trioxide to 1,1-

dichloro-2,2-difluoroethylene at -78°C . The mixture was heated overnight and produced the sultone in 56% yield; b.p. $110-112^{\circ}\text{C}$ (18).

2-Hydroxy-1-(ω -hydroperfluorohexyl)-1,2,2-trifluoroethane-sulfonic acid sultone. $\text{H}(\text{CF}_2)_6\overline{\text{CFCF}_2}\text{OSO}_2$ was made by heating a mixture of ω -hydroperfluoro-1-octene and freshly distilled sulfur trioxide in a sealed glass tube. The sultone was formed in 90% yield; b.p. $76^{\circ}\text{C}/22\text{ mm}$ (18).

2-Hydroxy-1-butyl-1,2,2-trifluoroethanesulfonic acid sultone. $\text{C}_4\text{H}_9\overline{\text{CFCF}_2}\text{OSO}_2$ was formed by addition of freshly distilled sulfur trioxide to butyltrifluoroethylene at an ice bath temperature. The mixture was warmed to room temperature and distillation of the mixture gave rise to sultone in 72% yield; b.p. $63-65^{\circ}\text{C}/20\text{ mm}$ (18).

3-Perfluoropentyl-3,4,4-trifluoro-1,2-oxathietane-2,2-dioxide. $\text{C}_5\text{F}_{11}\overline{\text{CFCF}_2}\text{OSO}_2$ was prepared by heating an excess amount of freshly distilled sulfur trioxide with perfluoro-1-heptene for 3 hours at 150°C . The resulted sultone was obtained in 58% yield; b.p. $134.5-136.5^{\circ}\text{C}$ (32).

β -Methoxy- α,β -difluoro- α -chloroethane- β -sultone. $\text{CH}_3\text{O}\overline{\text{CFCFC}_1}\text{SO}_2\text{O}$ was prepared by the addition of freshly distilled SO_3 to methyl 1,2-difluoro-2-chloro-vinyl ether at -10°C . The mixture was stirred at room temperature for 3 hours and it was then distilled to produce the β -sultone in 95% yield; b.p. $39-40^{\circ}\text{C}/3\text{ mm}$ (33).

β -Ethoxy- α,β -difluoro- α -chloroethane- β -sultone.

$\text{C}_2\text{H}_5\text{O}\overline{\text{CFCFC}}\text{ClSO}_2\text{O}$ was obtained similarly from freshly distilled SO_3 and ethyl 1,2-difluoro-2-chlorovinyl ether. This sultone was formed in 93% yield; b.p. $41-42^\circ\text{C}/3\text{ mm}$ (33).

Bis- α -trifluoromethyldifluoroethane- β -sultone.

$(\text{CF}_3)_2\overline{\text{CCF}_2}\text{OSO}_2$ was made through a mixture of octafluoroisobutylene and freshly distilled SO_3 which was heated between $170-190^\circ\text{C}$ for 12 hours. The resulting β -sultone was obtained in 19% yield; b.p. 63°C (34).

1-(Heptafluoro-3-yl)trifluoroethane- β -sultone.

$\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2}\text{OSO}_2$ was made through distillation of SO_3 into a dry flask containing 1,5-perfluorohexadiene. The mixture was then refluxed for 24 hours; temperature rose from $42-61^\circ\text{C}$. Distillation of the mixture gave the mono β -sultone, b.p. 115°C (29).

Trifluorobromo-1,2-oxathietane-2,2-dioxides and trifluoroiodo-1,2-oxathietane-2,2-dioxides. $\overline{\text{CFBrCF}_2}\text{OSO}_2$ and $\overline{\text{CFICF}_2}\text{OSO}_2$ were prepared by heating a mixture of SO_3 with trifluorobromoethene-1 and trifluoroiodo-ethene-1. Distillation of each mixture gave the desired β -sultone (35).

2-Hydropentafluoropropane-2- β -sultone. $\text{CF}_3\overline{\text{CHCF}_2}\text{OSO}_2$

was prepared by heating a mixture of 2-hydropentafluoropropylene and freshly distilled SO_3 between $90-100^\circ\text{C}$ for 2 h. The β -sultone was formed in 90% yield; b.p. 92°C (36).

Ethoxy-2-trifluoromethyl-1,1-difluoroethane-1-sulfonic acid β -sultone. $\text{C}_2\text{F}_5\text{OC}(\text{CF}_3)\text{CF}_2\text{SO}_2\text{O}$ was prepared by addition of SO_3 to ethyl pentafluoroisopropenyl ether between -10 to -5°C . The resulting β -sultone was decomposed upon heating to room temperature (37).

2-Heptafluoropropoxy-2-hydroxytrifluoroethane-1-sulfonic acid β -sultone. $\text{C}_3\text{F}_7\text{OCFCF}_2\text{SO}_2\text{O}$ was prepared through warming a mixture of SO_3 and heptafluoro-n-propyltrifluorovinyl ether in a heavy-walled glass tube. After exothermic reaction had occurred, the reaction mixture was kept overnight at 25°C . The mixture was distilled in 67% yield; b.p. $66^\circ\text{C}/180$ mm (37).

1-Fluorosulfonyl-1-H-difluoroethane- β -sultone. $\text{FSO}_2\text{CHCF}_2\text{OSO}_2$ was made through heating a mixture of freshly distilled SO_3 and 2,2-difluoroethylene sulfonyl fluoride between 150 - 160°C for 2 hours. The β -sultone was obtained in 67.5% yield; b.p. 49 - $51^\circ\text{C}/15$ mm (38).

1,4-Bis(2,2-dioxotrifluoro-1,2-oxthietane-3-yl) octafluorobutane. $[\text{CF}_2(\text{O})\text{CF}(\text{SO}_2)(\text{CF}_2)_2]_2$ was produced by heating a mixture of SO_3 and 1,7-perfluorooctadiene in a steel test tube at 120°C for 3 hours. The bis β -sultone was obtained in 91% yield; b.p. 91 - $92^\circ\text{C}/15$ mm (39).

1-(Undecafluorohexen-5-yl)trifluoroethane- β -sultone. $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{CFCF}_2\text{OSO}_2$ was obtained through heating a mixture of freshly distilled SO_3 and 1,7-perfluorooctadiene in a steel test tube for 4 hours at 110°C . The

mono β -sultone was obtained in 89% yield; b.p. 62-63°C/15 mm (39).

3-Pentafluorophenylpentafluoropropene-1,2-sultone.

$\text{C}_6\text{F}_5\text{CF}_2\overline{\text{CFCF}_2\text{OSO}_2}$ was formed by condensing a mixture of freshly distilled SO_3 and perfluoroalkylbenzene in a sealed ampul, which resulted in an exothermic reaction. The resulting β -sultone was formed in 69% yield; b.p. 75°C/6 mm (40).

2-Nonafluorobutyltrifluoroethane-2- β -sultone. $\text{C}_4\text{F}_9\overline{\text{CF}-\text{CF}_2\text{OSO}_2}$

was prepared through heating a mixture of freshly distilled SO_3 , 1-perfluorohexene and 1.5-2.0% of B_2O_3 at 100°C for 3 hours. The final β -sultone was produced in 42% yield (40). In 1986, freshly distilled SO_3 and 1-perfluorohexene were heated in a steel autoclave at 120°C for 8 hours. Distillation of the mixture resulted in a formation of β -sultone with 65.6% yield; b.p. 114°C (41).

3-Heptafluoroisopropoxypentafluoropropane-1,2-sultone.

$(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$ was made by heating a mixture of SO_3 and F-allylisopropylether in a sealed ampul at 100°C for 4 hours. The β -sultone was obtained in 90% yield; b.p. 107-109°C (42).

1-Heptafluoroisopropoxypentafluoropropane-1,2-sultone.

$(\text{CF}_3)_2\text{CFOCF}(\overline{\text{O}})\text{CF}(\text{SO}_2)\text{CF}_3$ was prepared by addition of 3-perfluoroisopropoxy-1-hexafluoropropene to freshly distilled SO_3 . The mixture produced an exothermic reaction. When the reaction was over concentrated H_2SO_4 was added to the

mixture. Distillation of the volatile products resulted in the formation of β -sultone (mixture of erythron and threo isomers) with 98% yield; b.p. 105-107°C (42).

Trifluoro-1-(pentafluoroallyl)ethane- β -sultone. This sultone, $\text{CF}_2=\text{CFCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$, was prepared in two different methods. First, through heating a mixture of SO_3 and 1,4-perfluoropentadiene in a steel tube at 100°C for 2 hours. Then the tube was cooled to -50°C and its nonvolatile residue was distilled to produce the β -sultone with 18% yield; b.p. 100-102°C. In the second method, the fluorinated diene was added to a solution of SO_3 in SO_2 at 10°C. The mixture was kept at -10°C for 1 hour and was slowly warmed up to room temperature. Later, SO_2 was removed at -78°C and the resulting residue was distilled to produce the β -sultone with 29.1% yield and fluorinated diene (43).

2-Hydroxy-1-(pentafluoro- λ^6 -sulfanyl)-1,2,1-trifluoroethane-sulfonic acid sultone. $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$ was made by addition of freshly distilled SO_3 and trifluorovinylsulfur pentafluoride into a Pyrex-glass Carius tube. The vessel was warmed up to 80°C over a period of 6 hours and it was then heated at 100°C for 36 hours. Distillation of the mixture gave β -sultone with 58% yield; b.p. 88°C (16,45).

2-Pentafluoroethyl-, 2-(2-H-tetrafluoroethyl)- and 2-(2-chloro-tetrafluoroethyl)- β -sultones. $\text{C}_2\text{F}_5\overline{\text{CFCF}_2\text{OSO}_2}$, CF_2-

$\text{HCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$ and $\text{CF}_2\text{ClCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$ were prepared through heating of equimolar mixture of the SO_3 and polyfluoroalkenes in steel autoclave at 120°C for 8 hours. The resulting mixtures were distilled to give the above β -sultones with 78.0% yield, b.p. 66°C ; 87.0%, b.p. 90°C ; and 92%, b.p. 103°C , respectively (41).

3-Heptafluoroisopropoxy-pentafluoropropane- and 1-heptafluoroisopropoxy-2-difluoromethylenefluorosulfonate-difluoroethane-1,2-sultone. $(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$ (I) and $(\text{CF}_3)_2\text{CFOCF}(\overline{\text{O}})\text{CF}(\text{SO}_2)\text{CF}_2\text{OSO}_2\text{F}$ (II) were made by mixing SO_3 and F-allylisopropylether in a Carius tube at 5°C for 8 weeks. The resulting mixture was distilled to produce β -sultone (I) in the form of mixture; b.p. $40-5^\circ\text{C}/40$ mm. A higher fraction was also obtained which represents β -sultone (II) with 36% yield; b.p. $51^\circ\text{C}/5$ mm (44).

2-Hydroxy-1-(pentafluoro- λ^6 -sulfanyl)-2,2-difluoroethanesulfonic acid sultone. $\text{SF}_5\overline{\text{CHCF}_2}\text{OSO}_2$ was produced by heating a mixture of SO_3 and 2-H-1,1-difluorovinylsulfur pentafluoride in a Pyrex-glass Carius tube at $95\pm 5^\circ\text{C}$ for 24 hours. Distillation of the mixture gave the β -sultone with 58% yield; b.p. $108-111^\circ\text{C}/600$ mm; m.p. $47-48^\circ\text{C}$ (24,45).

TABLE I
FLUORO β -SULTONES

Sultone	bp	Ref.
$\overline{\text{CF}_2\text{CF}_2}\text{OSO}_2$	42°C	(14, 18, 27, 30)
$\overline{\text{CFBrCF}_2}\text{OSO}_2$	-	(35)
$\overline{\text{CFC1CF}_2}\text{OSO}_2$	{mixture 73-77°C	(13, 14, 18, 28)
$\overline{\text{CF}_2\text{CFC1O}}\text{SO}_2$		
$\overline{\text{CFC1CFC1O}}\text{SO}_2$	110-113°C	(18)
$\overline{\text{CCl}_2\text{CF}_2}\text{OSO}_2$	110-112°C	(18)
$\overline{\text{SF}_5\text{CFCF}_2}\text{OSO}_2$	88°C	(16, 45)
$\overline{\text{SF}_5\text{CHCF}_2}\text{OSO}_2$	108-111°C/600mm; mp 47-48°C	(24, 45)
$\overline{\text{CHF}_2\text{CF}_2}\text{OSO}_2$	97°C	(14, 18, 30, 31)
$\overline{\text{FSO}_2\text{CHCF}_2}\text{OSO}_2$	49-51°C/15mm	(38)
$\overline{\text{CFICF}_2}\text{OSO}_2$	-	(35)
$\overline{\text{CF}_3\text{CFCF}_2}\text{OSO}_2$	46.5°C	(13, 14, 18, 27)
$\overline{\text{CF}_3\text{CHCF}_2}\text{OSO}_2$	92°C	(36)

TABLE I
FLUORO β -SULTONES
(continued)

Sultone	bp	Ref.
$(\text{CF}_3)_2\overline{\text{CCF}_2\text{OSO}_2}$	63°C	(34)
$\text{CH}_3\text{O}\overline{\text{CFCClFSO}_2}\text{O}$	39-40°C/3mm	(33)
$\text{C}_2\text{F}_5\overline{\text{CFCF}_2\text{OSO}_2}$	66°C	(41)
$\text{CF}_2\text{ClCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	103°C	(41)
$\text{CFCl}_2\text{CF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	129-131.5°C	(13, 28)
$\text{CF}_2\text{HCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	90°C	(41)
$\text{C}_2\text{F}_5\text{OC}(\overline{\text{CF}_3})\text{CF}_2\text{SO}_2\text{O}$	-	(37)
$\text{C}_2\text{H}_5\text{OC}\overline{\text{FCFC}}\text{ClSO}_2\text{O}$	41-42°C/3mm	(33)
$\text{CF}_3\text{CCl}(\overline{\text{O}})\text{CCl}(\text{SO}_2)\text{CF}_3$	132-133.8°C	(28)
$\text{C}_3\text{F}_7\text{OC}\overline{\text{FCF}_2}\text{SO}_2\text{O}$	66°C/180mm	(37)
$\text{CF}_2\text{ClCFClCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	55°C/25mm	(13, 29)
$(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	107-109°C	(42, 44)
$(\text{CF}_3)_2\text{CFOCF}(\overline{\text{O}})\text{CF}(\text{SO}_2)\text{CF}_2\text{OSO}_2\text{F}$	51°C/5mm	(44)

TABLE I
FLUORO β -SULTONES
(continued)

Sultone	bp	Ref.
$\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$	115°C	(29)
$(\text{CF}_3)_2\text{CFOCF}(\text{O})\overline{\text{CF}(\text{SO}_2)}\text{CF}_3$	105-107°C	(42)
$\text{C}_4\text{F}_9\overline{\text{CFCF}_2\text{OSO}_2}$	114°C	(40, 41)
$\text{C}_4\text{H}_9\overline{\text{CFCF}_2\text{OSO}_2}$	63-65°C/20mm	(18)
$\text{C}_5\text{F}_{11}\overline{\text{CFCF}_2\text{OSO}_2}$	134-136.5°C	(32)
$\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_2\overline{\text{CFCF}_2\text{OSO}_2}$	56-58°C/0.22mm	(13, 28)
$\text{H}(\text{CF}_2)_6\overline{\text{CFCF}_2\text{OSO}_2}$	76°C/22mm	(18)
$\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_3\overline{\text{CFCF}_2\text{OSO}_2}$	81-82°C/0.08mm	(13, 28)
$\text{CF}_2=\text{CF}(\text{CF}_2)_4\overline{\text{CFCF}_2\text{OSO}_2}$	62-63°C/15mm	(39)
$[\text{CF}_2(\text{O})\overline{\text{CF}(\text{SO}_2)}(\text{CF}_2)_2]_2$	91-92°C/15mm	(39)
$\text{C}_6\text{F}_5\text{CF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	75°C/6mm	(40)
$\text{CF}_2\text{Cl}(\text{CF}_2\text{CFCl})_4\overline{\text{CFCF}_2\text{OSO}_2}$	115-116°C/0.4mm	(13, 28)

Fluorinated β -Sultones Derivatives

Reactions of the fluoro β -sultones with nucleophilic reagents result in derivatives of fluorosulfonyl carboxylic acids (the acid itself forms by reaction of two carbon atoms fluoro sultones with water; while in sultones with three carbons or more, the intermediate carboxylic acids undergo decarboxylation due to their instability). These derivatives were formed to the following reactions:

1. Reaction with Et_3N or MF

Z = SF_5 , X = F (16); and SF_5 , H (24)

Z = Cl, X = Cl; F, F; F, H; and CF_3 , F (18)

Z = FSO_2 , X = H (38); and $\text{CF}_2=\text{CF}(\text{CF}_2)_4$, F (39)

M = Na, K, and Ca

2. Reaction with H_2O

Z = SF_5 , X = F (16); and SF_5 , H (24)

Z = CF_3 , X = F (18); CF_3 , H (36); $\text{CF}_2\text{ClCFC1CF}_2$ and

but in the case of sultone derived from fluorovinyl ether, the hydrolysis reaction yields an ester:

3. Reaction with ROH

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Where bis or poly alcohol were employed for reaction with fluoro β -sultones, the following esters were reported in the literature:

Z = F (18), and Z = CF₃ (19)

Z = F and CF₃ (22)

Z = CH₃, n = 0; NO₂, 0; OC(O)CF₂SO₂F, 2; and CH₂OC(O)CF₂SO₂F, 0 (20)

and in the case of the β -sultone produced from fluoro vinyl ether, two esters were reported:

4. Reaction with Alkoxide

R_f = CF₃CH₂, and (CF₃)₂CH, M = Li (20)

M = Na (18)

5. Reaction with Other Nucleophiles

Z = F, Nu = HS (27), SCN, (Et)₂N, H₂NC(O)NH, C₄H₉NH, C₆H₅NH,

C₆H₅N(CH₃), (C₆H₅)₂N, C₈H₁₇NH, $\overline{O(CH_2)_2NCH_2CH_2}$ (18)

Z = F, CF₃, Nu = C₆H₅N(CH₃) (18)

M = H, Na (where Nu = SCN)

Nu = p-CH₃OC₆H₄NH (18)

X = C(O)CF₂SO₂F

Nu = O(CH₂)₂NCH₂CH₂, (Et)₂N (18)

Nu = O(CH₂)₂NCH₂CH₂ (36)

6. Reaction with MOH

Z = F (11), CFCl₂CF₂, CF₂Cl(CFC₁CF₂)₂, CF₂Cl(CFC₁CF₂)₃,

CF₂Cl(CFC₁CF₂)₄ (28), CF₃, C₅F₁₁ (32)

M = Li, Na, K, Sr, Ba

+ NaOH $\longrightarrow$

X = F, M = Ca, Na (16)

X = H, M = Ca (24)

7. Other Reactions

Spectral Data of Fluorinated β -Sultones

Most of the fluoro β -sultones usually show similar trends in their spectral information (i.e., SO_2 asym stretch appears between $1440\text{--}1455\text{ cm}^{-1}$ in the IR, and the $\text{CF}_{2(1,2)}(\text{O})$ (of the sultone ring) chemical shift is between $80\text{--}90$ ppm with $J_{1,2}$ in the range of $100\text{--}110$ Hz in the nmr). Knowledge of these spectral characteristics is necessary in order to determine the structures of new β -sultones. Due to this fact, the reported spectral data for all known fluorinated sultones are reproduced in this section; these data consist of the IR, NMR, MS and GC, which are shown in Tables II through VI. The chemical shifts of the β -sultones are reported relative to F-11 (CFCl_3) for ^{19}F nmr and TMS ($(\text{CH}_3)_4\text{Si}$) for ^1H and ^{13}C nmr.

TABLE II

IR DATA

Sultone	Wave Numbers (cm ⁻¹)*	Ref.
$\overline{\text{CHF}}\text{CF}_2\text{OSO}_2$	SO ₂ (asym, 1455; sym, 1239) CF (1050-1129) CH (2890)	(31)
$\overline{\text{CF}_2\text{CF}_2}\text{OSO}_2$	SO ₂ (asym, 1451; sym, 1235) CF (1030-1090)	(31)
$\overline{\text{CF}_3\text{CFCF}_2}\text{OSO}_2$	SO ₂ (asym, 1455; sym, 1237) CF (1005-1340)	(31)
$\overline{\text{SF}_5\text{CFCF}_2}\text{OSO}_2$	SO ₂ (asym, 1448; sym, 1214) CF (1020-1096) SF (stretching, 854-896) (deformation, 570-610)	(16)

TABLE II
IR DATA
(continued)

Sultone	Wave Numbers (cm ⁻¹)*	Ref.
$\overline{\text{SF}_5\text{CHCF}_2\text{OSO}_2}$	SO ₂ (asym, 1419; sym, 1203) CF (1078-1106) SF (stretching, 819-878) (deformation, 575-612)	(24)
$\text{CF}_2\text{ClCFClCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	SO ₂ (asym, 1440)	(29)
$\text{C}_5\text{F}_{11}\overline{\text{CFCF}_2\text{OSO}_2}$	SO ₂ (asym, 1450)	(32)
$\text{CF}_2=\text{CFCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	SO ₂ (asym, 1450)	(43)
	CF ₂ =CF (1795)	
$(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	SO ₂ (asym, 1445)	(44)
$(\text{CF}_3)_2\text{CFOCF}(\text{O})\overline{\text{CF}(\text{SO}_2)\text{CF}_2\text{OSO}_2\text{F}}$	SO ₂ (asym, 1445)	(44)
	CF, CO, SO ₂ , (1100-1300)	
	OSO ₂ F (1490)	

* The assignment for symmetric stretching band is complicated in some cases by the appearance of strong carbon-fluorine absorption bands in the 1110-1300 cm⁻¹ region.

TABLE III
NMR DATA

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)	Ref.
$\overline{\text{CH}}_{(4)}\text{F}_{(3)}\overline{\text{CF}_2(1,2)}\text{OSO}_2$			
	CF ₂ (-83.9 d,d,d -89.4 d,d,d)	$J_{1,2} = 111.5$	$J_{2,3} = 4.9$ (31)
	CF (-170.2 d,d,d)	$J_{1,3} = 7.3$	$J_{2,4} = 1.1$
	CH (6.4 d,d,d)	$J_{1,4} = 3.4$	$J_{3,4} = 50.2$
$\overline{\text{CF}}_{(3)}\text{ClCF}_2(1,2)\text{OSO}_2$			
	CF ₂ (1, -83.9 2, -87.6)	$J_{1,2} = 96.5$	(35)
	CF (-103.0)	$J_{2,3} = -8.2$	
$\overline{(1,2)}\overline{\text{CF}_2\text{CF}}_{(3)}\overline{\text{ClOSO}_2}$			
	CF ₂ (1, -89.7 2, -74.5)	$J_{1,2} = 119.3$	(35)
	CF (-69.0)	$J_{1,3} = 13.2$	
		$J_{2,3} = -10.1$	

TABLE III
NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)	Ref.
$\overline{\text{CF}}_{(3)}\text{BrCF}_2(1,2)\text{OSO}_2$	CF ₂ (1, -80.1 2, -87.4) CF (-103.2)	J _{1,2} = 95.6 J _{1,3} = -3.0 J _{2,3} = -8.1	(35)
$\overline{\text{CF}}_{(3)}\text{ICF}_2(1,2)\text{OSO}_2$	CF ₂ (1, -74.0 2, -88.2) CF (-104.8)	J _{1,2} = 95.5 J _{1,3} = -7.3 J _{2,3} = -7.7	(35)
$\text{F}_{(5)}\text{SF}_4(4)\overline{\text{CF}}_{(3)}\overline{\text{CF}_2(1,2)\text{OSO}_2}$	SF (62.7 m), SF ₄ (57.0 m) CF ₂ (-81.2 d,p,d -83.6 m) CF (-116.9 m)	J _{1,2} = 104 J _{2,4} = 2.4(16) J _{1,3} = 2.7 J _{2,3} = 6.4 J _{1,4} = 21.8 J _{3,5} = 3.8 J _{1,5} = 2.7 J _{4,5} = 156.7 J _{2,3} = 1.1	

TABLE III
NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)	Ref.
$\text{F}_{(5)} \text{SF}_4(4) \overline{\text{CH}(3) \text{CF}_2(1,2) \text{OSO}_2}$	SF_5 (69.4 m)	$J_{1,2} = 103$	(24)
	CF_2 (-72.8 d, -79.7 d)	$J_{4,3} = 4.6$	
	CH (6.58 m)	$J_{4,5} = 130$	
$\text{FSO}_2 \overline{\text{CHCF}_2 \text{OSO}_2}$	SO_2F (68.1 m)	-	(38)
	CF_2 (-60.2 m)	-	
	CH (4.42 m)	-	
$\overline{\text{CF}_2 \text{CF}_2 \text{OSO}_2}$	CF_2 (-93.3 m, -102.6 m)	-	(31)
$\text{CF}_3(4) \overline{\text{CH}(3) \text{CF}_2(1,2) \text{OSO}_2}$	CF_3 (-64.5 m)	$J_{1,2} = 103.9$	$J_{2,3} = 4.8$ (36)
	CF_2 (-76.9 d,q)	$J_{1,3} = 4.2$	$J_{2,4} = 12.1$
	CH (5.6 t,q)	$J_{1,4} = 3.4$	$J_{3,4} = 6.7$

TABLE III
NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)	Ref.
$\overline{\text{C}_2\text{H}_5\text{OC}(\text{CF}_3)_3\text{CF}_2(1,2)\text{SO}_2\text{O}}$			
	CF_3 (-77.6 d)	$J_{1,2} = 173$	(37)
	CF_2 (1, -94.6 d; 2, -100.5 d,q)	$J_{1,3} = 15$	
$\overline{\text{CF}_3(4)\text{CF}(3)\text{CF}_2(1,2)\text{OSO}_2}$			
	CF_3 (-74.4 d,d,d)	$J_{1,2} = 107.2$	$J_{2,3} = 1.5$ (49)
	CF_2 (-82.4m, -88.6m)	$J_{1,3} = 8.4$	$J_{2,4} = 11.4$
	CF (-153.1 d,q)	$J_{1,2} = 2.4$	$J_{2,3} = 8.5$
$\overline{(\text{CF}_3)_2\text{CCF}_2\text{OSO}_2}$			
	CF_3 (-62.0)	-	(34)
	CF_2 (-76.3)	-	

TABLE III

NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)	Ref.
CF ₂ (₄)HCF ₂ (₃)CF(₂)CF ₂ (₁)OSO ₂	CF ₂ (-82.7 m, -85.6 m)	J _{1ab} = 100.1	J _{3,H} = 3.8 (41)
	CF ₂ (3, -122.2 m)	J _{1,3} = 18.3	J _{4,H} = 51.7
	CF ₂ (4, -137.9 m)	J _{1,4} = 6.5	
	CF (-151.1 m)		
	CH (6.2 t,t)		
CF ₂ (₄)ClCF ₂ (₃)CF(₂)CF ₂ (₁)OSO ₂	CF ₂ (-81.6 m, -84.4 m)	J _{1ab} = 107	(41)
	CF ₂ (4, -86.3 m)	J _{1,2} = 3.9	
	CF ₂ (3, -114.6 m)	J _{1,3} = 16.9	
	CF (-149.3 m)		

TABLE III
NMR DATA
(continued)

Sultone	Chemical shifts (ppm)	Coupling Constant(Hz)	Ref.
CF ₃ (4) CF ₂ (3) CF ₂ (2) CF ₂ (1) OSO ₂	CF ₃ (-80.7 d,d)	J _{1ab} = 109	J _{2,3} = 5.8 (41)
	CF ₂ (-82.6 m, -85.9 m)	J _{1,3} = 17.9	J _{2,4} = 11.3
	CF ₂ (3, -121.0 m)	J _{1,4} = 5.1	
	CF (-151.3 m)		
CF ₂ (5) ClCF ₄ ClCF ₂ (3) CF ₂ (2) CF ₂ (1) OSO ₂	CF ₂ (5, -64.0)	-	(29)
	CF ₂ (1, -83.0)	-	
	CF ₂ (3, -109)	-	
	CF (4, -128)	-	
	CF (2, -148)	-	

TABLE III
NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant (Hz)	Ref.
(CF ₃) ₂ (₅)CF(₄)OCF(₃)(O)CF(₂) $\overline{\text{CF}_3}$ (₁)	CF ₃ (1, -73.6 d,d)	J _{1,2} = 7.0	J _{3,4} = 21.0 (42)
	CF ₃ (5, -80.5 m)	J _{1,3} = 1.5	
	CF (3, -83.7 m)	J _{2,3} = 4.0	
	CF (4, -143.1 d,m)		
	CF (2, -149.6 d,q)		
CF ₃ (₇)CF ₂ (₆)CF ₂ (_{4,5})OCF(₃) $\overline{\text{CF}_2}$ (_{1,2})SO ₂ O	CF ₃ (-83.5 t)	J _{1,2} = 151.0	(37)
	CF ₂ (-84.1 m, -86.5 m)	J _{4,5} = 160.0	
	CF (-90.3 m)	J _{6,7} = 7.6	
	CF ₂ O (4, -99.8, 5, -101.2 m)		
	CF ₂ (6, -131.4 s)		

TABLE III

NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant (Hz)	Ref.
(CF ₃) ₂ (6) CF ₍₅₎ OCF ₂ (4) CF ₍₃₎ CF ₂ (1,2) OSO ₂	CF ₃ (-81.3 m)	J _{1,2} = 108 J _{3,4} = 8.1	(44)
	CF ₂ (4, -74.6 m)	J _{1,3} = 7.1 J _{4,5} = 22.0	
	CF ₂ (-82.4 d,d,t, -89.5 d,t)	J _{1,4} = 2.5 J _{5,6} = 2.3	
	CF (5, -145.7 t, sep)	J _{2,4} = 12.5	
	CF (3, -151.8 t,d)		
(CF ₃) ₂ (6) CF ₍₅₎ ⁰ CF ₂ (4) CF ₍₃₎ CF ₂ (1,2) OSO ₂	CF ₃ (-80.6 br.s)	J _{1,2} = 109.0 J _{2,4} = 13.2	(42)
	CF ₂ (-83.3 d,d,t, -89.0 d,t)	J _{1,3} = 6.6 J _{3,4} = 6.6	
	CF ₂ (4, -73.9 m)	J _{1,4} = 2.5 J _{4,5} = 22.6	
	CF (5, -144.4 t,m)		
	CF (3, -151.3 d,t)		

TABLE III
NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)	Ref.
(CF ₃) ₂ (7)CF ₍₆₎ O CF ₍₅₎ (O)CF ₍₄₎ (SO ₂)CF ₂ (2,3)OSO ₂ F(1)	SO ₂ F (51.2 m)	J _{4,2} = 6.7 J _{5,6} = 18.7 (44)	
	CF ₃ (-80.9 m)	J _{4,3} = 6.7 J _{6,7} = 2.5	
	CF ₂ (-77.1 AB center)	J _{4,5} = 4.2	
	CF (5, -77.6 m)		
	CF (6, -145.2 d, sep)		
CF ₃ (6)CF ₂ (5)CF ₂ (4)CF ₂ (3) $\overline{\text{CF}(2)\text{CF}_2(1)\text{OSO}_2}$	CF (4, -149.0 t,d)		
	CF ₃ (6, -81.2 t,t)	J _{1ab} = 104.9 J _{6,3} = 2.1 (41)	
	CF ₂ (-82.6 m, -85.5 m)	J _{1,3} = 16.9 J _{6,4} = 9.9	
	CF ₂ (3, -116.7 m, 4, - 126.2 m)	J _{1,4} = 6.2	
	CF ₂ (5, -120.2 m)		
	CF (2, -151.2 m)		

TABLE III

NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)Ref.
CF ₃ (7) CF ₂ (6) CF ₂ (5) CF ₂ (4) $\overbrace{\text{CF}(3) \text{CF}_2(1,2)}^{\text{OSO}_2}$	CF ₃ (7, -81.4 m)	- (40)
	CF ₂ (1, -82.4 d,m, 2, -86.4 d,m)	
	CF ₂ (4, -125.6 m)	
	CF ₂ (5, -119.7 m, 6, -116.6 m)	
	CF (-151.2 m)	
	$\overbrace{\text{CF}(3) \text{CF}_2(1,2)}^{\text{OSO}_2}$	
C ₆ F ₅ CF ₂ (5,4) $\overbrace{\text{CF}(3) \text{CF}_2(1,2)}^{\text{OSO}_2}$	CF ₂ (1, -80.8 d,m 2, -87.6 d,m)	J _{1,2} = 109 (40)
	CF ₂ (4, -94.0 m 5, -97.2 m)	J _{4,5} = 320
	CF (3, -136.6 m)	
	C ₆ F ₅ (-137.5 m, -145.4 m, -163.5 m)	

TABLE III

NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant(Hz)Ref.
(6,7) F ₂ C=CF (5) CF ₂ (4) CF (3) CF ₂ (1,2) OSO ₂	CF ₂ (-81.4 m, AB center (1,2))	(43)
	CF ₂ (6, -88.7 d,d,t, 7, -105.1 d,d,t)	
	CF ₂ (4, -114.3 m)	
	CF (3, -147.1 d,d,t)	
	CF (5, -190.6 d,d,t)	
	CF (3) CF ₂ (1,2) OSO ₂	
(6,7) F ₂ C=CF (5) (CF ₂) ₄ (4) CF (3) CF ₂ (1,2) OSO ₂	CF ₂ (-83.6 m AB center)	J _{1,2} = 108.0 (39)
	CF ₂ (6, -87.9 d,d,t 2, 105.1 d,d,t)	J _{6,7} = 58.5
	CF ₂ (4, -115.9 m -117.4 m)	
	CF ₂ (4, -119.0 m -122.6 m)	
	CF (3, -149.9 m)	
	CF (5, -189.7 m)	

TABLE III
NMR DATA
(continued)

Sultone	Chemical Shifts (ppm)	Coupling Constant (Hz) Ref.
[CF ₂ (_{1,2}) (O) CF ₂ (₃) (SO ₂) CF ₂ (₄) CF ₂ (₄)] ₂	CF ₂ (-83.2 m AB center)	J _{1,2} = 107.2 (39)
	CF ₂ (4, -115.5 m, -118, 4 m)	
	CF (-150.2 m)	

TABLE IV
¹³C NMR DATA

Sultone	Chemical Shifts (ppm)	Coupling Constant (Hz) Ref.
F ₍₆₎ SF ₄ (₅) C ₍₄₎ H ₍₃₎ C ₍₂₎ F ₂ (₁) OSO ₂	CH (4, 99.6 d, p, m)	J _{2,1} = 293 J _{4,5} = 23 (24)
	CF ₂ (2, 112 br. p)	J _{2,5} = 3.8

TABLE V

MS DATA

Sultone	Fragment Ions (m/e)	Ref.
$\text{SF}_5\overline{\text{CFCF}_2}\text{OSO}_2$	208 (M-SO ₃) ⁺ , 161 (M-SF ₅) ⁺ , 129 (CF(SO)CF ₂) ⁺ , 127 (SF ₅) ⁺ , 113 (CF(S)CF ₂) ⁺ , 97 (CFCF ₂ O) ⁺ , 81 (CFCF ₂) ⁺ , 80 (SO ₃) ⁺ , 66 (CF ₂ O) ⁺ , 64 (SO ₂) ⁺ , SF (51) ⁺ , 48 (SO) ⁺	(16)
$\text{SF}_5\overline{\text{CHCF}_2}\text{OSO}_2$	269 (M-H) ⁻ , 142 (CCF ₂ OSO ₂) ⁻ , 127 (SF ₅) ⁻ , 123 (CCFOSO ₃) ⁻ , 83 (SF ₂ CH) ⁻ , 79 (CHCF ₂ O) ⁻	(24)

TABLE VI

GC DATA

Sultone	Retention Time	Ref.
$\text{CF}_2\text{ClCFClCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$	13.8 chromosorb column at 100°C	(29)
$\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2}\text{OSO}_2$	4.43 chromosorb column at 100°C	(29)

CHAPTER III

EXPERIMENTAL METHODS

APPARATUS

Vacuum System

In order to handle gases and volatile liquids requiring the use of high vacuum, or inert atmosphere conditions, a glass vacuum line was employed. The manifold was fabricated from 20 mm O.D. Pyrex glass tubing and fitted with four Eck and Krebs 2 mm high-vacuum stopcocks; outer standard taper 10/30 ground glass joints were attached to the stopcocks. The vacuum line was evacuated through a liquid nitrogen (-196°C) cooled trap by a Welch Duo-Seal rotary pump. The pressure inside the line was monitored by a Televac Thermo-couple gauge, and maintained below 10μ . Higher pressure within the manifold, when required, could be measured by a Heise Bourdon tube gauge to ± 1 torr. All joints and stopcock in the vacuum system were lubricated with either Apiezon-M or Fluorolube GR-290 grease. Vacuum guage connections were sealed with Halocarbon wax.

Reaction Vessels

Reaction vessels used in this study can be divided into two types: one type, for low pressure systems, are 25

ml, 50 ml, 75 ml, or 100 ml Pyrex-glass reaction vessels equipped with a Kontes high vacuum Teflon valve and Teflon stirring bar, and tipped with a Pyrex 10/30 inner joint for attachment to the vacuum line. The second type, for high pressure reactions, are either 75 ml to 100 ml Hoke Monel or stainless steel vessels equipped with a Whitey stainless steel valve, and tipped with a metal 10/30 inner joint or 60-130 ml heavy wall Pyrex-glass Carius tubes equipped with a Kontes Teflon valve, and tipped with a Pyrex 10/30 inner joint. Reactions which were not compatible with either Pyrex-glass, stainless, or Monel were carried out in a 35 ml Kel-F reaction vessel fitted with a Whitney brass valve and a brass 10/30 inner joint.

Vacuum Traps

To remove volatile materials from a reaction, a Pyrex-glass trap cooled to liquid nitrogen temperature (-196°C) or dry ice and acetone slush bath (-78°C) were used. The traps were made up of two concentric Pyrex-glass tubes of 22 mm and 10 mm I.D. The outer tube was connected to a Kontes high vacuum Teflon valve by a piece of 10 mm I.D. Pyrex-glass tubing. The inner tube was connected to another Kontes high vacuum Teflon valve. Both valves were fitted with 10/30 inner joints for attachment to the vacuum line.

Dry Box

All air sensitive compounds were handled under an

atmosphere of nitrogen gas in a Kewaunee Scientific Equipment dry box. Nitrogen gas was passed into the box through a CaSO_4 tube. The atmosphere inside the box was dried with phosphorous pentaoxide (P_4O_{10}).

Glove Bag

A plastic glove bag made of polyethylene provided a quick alternative to the dry box. The bag was always flushed with nitrogen and regularly maintained under an atmosphere of nitrogen whenever it was in use.

PHYSICAL METHODS

Infrared Spectra

The infrared spectra were recorded over the range of $4000\text{--}400\text{ cm}^{-1}$ on a FT-IR, Nicolet 20DX spectrophotometer equipped with Disk module, Data processor unit and a 7470A Hewlett-Packard plotter. Samples were run in three different forms: solid samples were run neat between KBr or KRS-5 windows. KRS-5 windows were used in case the KBr windows were not inert toward compounds. The non-volatile liquid samples were handled exactly as solid samples. Finally the gaseous samples were run in a glass gas cell fitted with glass 10/30 inner joint for attachment to the vacuum line. The cell windows were KBr or KRS-5 and the path length of the cell was 8.25 cm.

Nuclear Magnetic Resonance

The nuclear magnetic resonance spectra were recorded with a Varian Model EM-390 spectrometer operating at 90 MHz for proton and 84.67 MHz for fluorine resonance. Chemical shifts are reported relative to external TMS ($\text{Si}(\text{CH}_3)_4$) for proton, F-11 (CFCl_3), and TFA ($\text{CF}_3\text{C}(\text{O})\text{OH}$) for fluorine spectra where downfield resonance are reported as positive values.

Mass Spectra

Mass spectra were measured on a VG 7070 HS mass spectrometer operated at 70 ev. Perfluorokerosene was used as an internal standard sample.

Distillation

Products were purified by distilling in a "Bantam Ware" Kontes Pyrex-glass distillation apparatus with 14-20 or 19-22 ground joints, either at reduced or atmospheric pressure. For compounds with high boiling points, vacuum distillations were used in which the unit was connected to the vacuum line through a trap cooled to -196°C . The distillations, which were done under atmospheric pressure, had the same set up with the exception that the unit was connected to the atmosphere via a trap cooled to -78°C .

Sublimation

Purification of some solids were done by sublimation using a conventional Pyrex-glass sublimation unit. The cold

finger was cooled by flowing water, and vacuum was achieved by attachment of the sublimation unit to the vacuum line through a trap cooled to the liquid nitrogen (-196°C).

Melting Point

Melting points/decomposition of solid phase compounds were determined using sealed capillary tubes in a Mel-Temp apparatus.

Elemental Analysis

Elemental analysis of new compounds was carried out by Beller Microanalytisches Laboratorium, Göttingen, West Germany. Air sensitive samples were sealed under vacuum in Pyrex-glass tubes.

REAGENTS

Allyl Bromide

$\text{CH}_2=\text{CHCH}_2\text{Br}$ was purchased from MCB and was used without further purification.

Allyl Alcohol

$\text{CH}_2=\text{CHCH}_2\text{OH}$ was purchased from Mallinckrodt and was used without further purification.

Benzoyl Peroxide

$(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$ was purchased from Aldrich and was used without further purification.

F-2-Butoxyethylene

$C_4F_9OCF=CF_2$ was received from Dr. Fred E. Behr, 3M and was used without further purification.

1,2-Dibromoethane

$BrCH_2CH_2Br$ was purchased from MCB and was used without further purification.

2-[3,2-Dichloropropyl]trifluoroethylene

$CH_2ClCHClCH_2CF=CF_2$ was received from Dr. Donald J. Burton, University of Iowa and was used without further purification.

Diethyl Ether

$(C_2H_5)_2O$ was purchased from Mallinkrodt and was used without further purification.

Diiodomethane

CH_2I_2 was purchased from Eastman Kodak and was treated with Hg prior to use.

Ethyl Bromoacetate

$BrCH_2COOC_2H_5$ was purchased from MCB and was used without further purification.

Freon-11 (F-11)

$CFCl_3$ was purchased from Du Pont and was stored over type 5A molecular sieve prior to use.

Hexafluoroisopropoyl Alcohol

$(\text{CF}_3)_2\text{CHOH}$ was purchased from Eastman Kodak and was used without further purification.

1,5-[2,2,3,3,4,4-Hexafluoro]pentadiol

$\text{HOCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH}$ was obtained as a gift from 3M and was sublimed prior to use.

Hexafluoropropylene

$\text{CF}_3\text{CF}=\text{CF}_2$ was purchased from PCR and was used without further purification.

F-3-Methoxypropene

$\text{CF}_3\text{OCF}_2\text{CF}=\text{CF}_2$ was received from Dr. James L. Adcock, University of Tennessee and was used without further purification.

F-3-[2-Methoxyethoxy]propene

$\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}=\text{CF}_2$ was received from Dr. James L. Adcock, University of Tennessee and was used without further purification.

Mercury

Hg (analytical reagent grade) was purchased from American Scientific & Chemicals and was used without further purification.

Molecular Sieves

Type 5A molecular sieves (8 mesh beads) were purchased

from EM Science, and were dried under the vacuum line prior to use.

Pentafluorophenol

$\text{C}_6\text{F}_5\text{OH}$ was purchased from PCR and was distilled prior to use.

1,5-Perfluorohexadiene

$\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}=\text{CF}_2$ was received from Dr. Donald J. Burton, University of Iowa and was used without further purification.

1-Perfluoroheptene

$\text{CF}_3(\text{CF}_2)_5\text{CF}=\text{CF}_2$ was purchased from PCR and was used without further purification.

Silver Oxide

Ag_2O was purchased from Mallinckrodt and was used without further purification.

Sodium Bisulfite

NaHSO_3 was purchased from Aldrich and was used without further purification.

Sodium Borate, 10-Hydrate

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ purchased from Baker and was used without further purification.

Sodium Fluoride

NaF was purchased from Baker and was dried prior to use.

Sodium Hydroxide (pellets)

NaOH was purchased from Baker and was used without further purification.

Sulfur Trioxide

SO₃ was purchased from Baker or Aldrich and was distilled prior to use.

Tetrafluoroethylene

Inhibited CF₂=CF₂ was purchased from PCR and was used without further purification.

Tetramethylsilane (TMS)

Si(CH₃)₄ was purchased from Baker and was used without further purification.

Trifluoroacetic Acid (TFA)

CF₃C(O)OH was purchased from Baker and was used without further purification.

Trifluoroethanol

CF₃CH₂OH was purchased from PCR and was used without further purification.

Trifluorovinylsulfur Pentafluoride

$\text{SF}_5\text{CF}=\text{CF}_2$ was prepared according to the literature method (51).

Water

Oxygen free H_2O was obtained from the tap water, and was boiled for approximately one hour to remove air.

CHAPTER IV

THE SYNTHESIS OF NEW MONO/BIS FLUORINATED SULTONES AND THEIR DERIVATIVES

Fluorinated β -sultones are formed on addition of sulfur trioxide to fluorinated olefins. The study of the reactions of fluorinated olefins with sulfur trioxide shows that terminal fluoroolefins normally undergo cycloaddition to form β -sultones (12,18,44). Fluorinated β -sultones undergo a number of interesting reactions that produce molecular systems containing the fluorosulfonyl group (16,18,29,39,43). The incorporation of the fluorosulfonyl group leads to compounds useful as ion-exchange resins, comonomers with tetrafluoroethylene, surface active agents and strong sulfonic acids (16,29,52). Recent studies (39,43) show that the reaction of sulfur trioxide with fluorinated polyene is a good pathway for preparation of new fluorinated monomers and polymers containing the fluorosulfonyl group (SO_2F); thus the reaction of perfluoro 1,5-hexadiene, $[\text{CF}_2=\text{CFCF}_2]_2$, with sulfur trioxide was studied in order to obtain mono and bis β -sultones. The product of the reaction is dependent on the ratio between reactants; when a 1:1 molar ratio composition of fluorinated diene and SO_3 is heated, a mixture containing mono and bis sultones is formed. If the molar ratio of fluorinated diene to SO_3 is

increased to 1.26:1, mono β -sultone is formed, and at a 1:3.00 (or more) ratio, bis β -sultone is obtained:

I and II are thermally stable and colorless liquids; they undergo rearrangement in the presence of MX (where M = Na or K, and X = F) to give the corresponding isomeric fluoro-sulfonyl acyl fluorides:

In the presence of water and heat, I undergoes rearrangement, and a concerted hydrolysis/decarboxylation reaction:

The $\text{FSO}_2\text{CFH(CF}_2)_2\text{CFHSO}_2\text{F}$ product is a stable crystalline solid which melts at 43-44°C.

Allyl alcohol, with sodium fluoride, reacts with the bis/mono fluorosultones I and II according to the following equations:

VI

VII

The new esters, VI and VII, are thermally stable, clear and colorless liquids. In the presence of ultraviolet irradiation they undergo polymerization:

VIII

IX

When washed with CCl_3F , the polydiester in eq. IV-8 gave an off-white solid polymer, which decomposed at 265°C . The polyester in eq. IV-9 is a viscous liquid.

The reaction of the perfluoro 1,5-hexadiene and sulfur trioxide was carried out in a modified 130 ml Pyrex-glass Carius tube under autogeneous pressure at $115 \pm 5^\circ\text{C}$ for 10-14 hours. The conversion of the mono/bis β -sultones to the fluorosulfonyl acyl fluorides and allyl esters was done in a 25 or 50 ml Pyrex-glass round bottom flask under reflux at 80 - 150°C for 48 hours. The hydrolysis reaction of bis β -sultone, I, was performed in a 40 ml Kel-F vessel due to the formation of HF which etches glassware, at 0 - 40°C for 12 h.

The irradiation of the mono/bis fluorosulfonyl allyl esters was carried out in a 80 ml quartz reaction vessel with ultra-violet light in the presence of CFCl_3 for 7-23 hours. The purification of the mono/bis β -sultones, fluorosulfonyl acyl fluorides, and fluorosulfonyl allyl esters was done by fractional distillation at reduced pressure. The elemental analyses confirmed the molecular formulas for all new mono/bis β -sultones, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$ and $[\text{CF}_2(\overline{\text{O}})\overline{\text{CF}}(\text{SO}_2)\text{CF}_2]_2$, and their derivatives.

EXPERIMENTAL

Synthesis of $[\text{CF}_2(\overline{\text{O}})\overline{\text{CF}}(\text{SO}_2)\text{CF}_2]_2$

To 85.0 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube, equipped with a Kontes Teflon valve, 23.8 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}=\text{CF}_2$ was added. The mixture was heated at $115\pm 5^\circ\text{C}$ for 14 h. Distillation of the mixture gave 21.7 mmol of a clear liquid, $[\text{CF}_2(\overline{\text{O}})\overline{\text{CF}}(\text{SO}_2)\text{CF}_2]_2$, in 91.4% yield, b.p. $69\pm 1^\circ\text{C}/15\text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 1441(vs), 1427(sh), 1342(m), 1314(ms), 1272(ms), 1216(s), 1180(sh), 1124(ms), 1096(ms), 1061(ms), 984(m), 955(sh), 920(m), 892(m), 857(vw), 815(sh), 787(ms), 773(sh), 738(ms), 695(w), 653(ms), 639(m), 611(m), 604(sh), 583(w), 569(w), 541(sh), 520(m), 498(vw), 484(m), 456(w), 442(w), 407(m).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_2 (1.0, 1.0), CF_2 (2.0), and CF (1.0).

The positive ion (CI)⁺ mass spectrum (m/e species):
 423, MH⁺; 404, (MH-F)⁺; 403, M-F⁺; 342, (M-SO₃)⁺; 339, (M-SO₂F)⁺; 323, (M-SO₃F)⁺; 259, C₆F₉O⁺; 255, (M-C₂F₅O₃)⁺; 247, (M-SO₃F₅)⁺; 243, C₆F₉⁺; 231, C₆F₅SO₂⁺; 211, (M-CF₂CFCF₂SO₃)⁺; 209, C₅F₇O⁺; 193, C₅F₇⁺; 181, C₄F₇⁺; 171, C₅F₅O⁺; 169, C₄F₃SO₂⁺; 162, C₄F₆⁺; 159, C₄F₅O⁺; 143, C₄F₅⁺; 140, C₄F₄O⁺; 109, C₃F₃O⁺; 97, C₂F₃O⁺; 95, CFSO₂⁺; 93, C₃F₃⁺; 81, C₂F₃⁺; 79, CFSO⁺; 74, C₃F₂⁺; 67, SOF⁺; 66, CF₂O⁺; 64, SO₂⁺; 63, CSF⁺; 62, C₂F₂⁺.

Synthesis of [FC(O)CF(SO₂F)CF₂]₂

To a 50 ml Pyrex-glass round bottom flask, equipped with a Teflon coated stirring bar, were added 73.8 mmol of dry NaF, and 30.8 mmol of [CF₂(O)CF(SO₂)CF]₂. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C. The reaction mixture was heated to 80-100°C (48 h). Distillation of the mixture gave 1.90 mmol of a colorless liquid, [FC(O)CF(SO₂F)CF₂]₂, in 62% yield; b.p. 61±1°C/13 mm.

The infrared spectrum had the following bands (cm⁻¹): 1877(s), 1863(ms), 1455(vs), 1237(vw), 1230(vs), 1209(s), 1159(s), 1138(s), 1082(m), 1040(w), 991(m), 963(m), 934(vw), 913(vw), 829(s), 773(vw), 752(vw), 716(m), 653(m), 611(m), 590(m), 576(m), 562(sh), 541(ms), 464(m), 456(m).

The ¹⁹F nmr spectrum gave the following relative peak areas: SO₂F (1.0), C(O)F (1.0), CF (1.0), and CF₂ (1.8).

The positive ion (CI)⁺ mass spectrum (m/e, species):

404, (MH-F)⁺; 403, (M-F)⁺; 339, (M-SO₂F)⁺; 323, (M-SO₃F)⁺; 255, (M-C₂F₅O₃)⁺; 247, (M-SO₃F₅)⁺; 211, (M-SO₃C₃F₅)⁺; 191, (C₄F₅SO)⁺; 171, (C₅F₅O)⁺; 169, C₄F₃SO₂⁺; 162, C₄F₆⁺; 159, C₄F₅O⁺; 143, C₄F₅⁺; 140, C₄F₄O⁺; 131, C₃F₅⁺; 128, C₃F₄O⁺; 119, C₃FSO₂⁺; 112, C₃F₄⁺; 109, C₃F₃O⁺; 100, C₂F₄⁺; 97, C₂F₃O⁺; 93, C₃F₃⁺; 90, C₃F₂O⁺; 87, C₃FS⁺; 83, SO₂F⁺; 82, CFSF⁺; 81, C₂F₃⁺; 79, CFSO⁺; 75, C₂FS⁺; 74, C₃F₂⁺; 67, SOF⁺; 64, SO₂⁺; 63, CFS⁺; 59, C₂FO⁺; 51, SF⁺.

Synthesis of [FSO₂CFHCF₂]₂

To a 40 ml Kel-F vessel, equipped with a Teflon stirring bar, was added 17.1 mmol of [CF₂($\overline{\text{O}}$)CF(SO₂)CF₂]₂. The reaction vessel was cooled to 0°C and 341.1 mmol of distilled H₂O was added dropwise over a period of 3 h. The mixture was heated at 40°C (12 h). The solid was recovered via filtration and sublimed in vacuo at 55°C. The white solid [FSO₂CFHCF₂]₂, 12.09 mmol, was formed in 71% yield; m.p. 43-44°C.

The infrared spectrum had the following bands (cm⁻¹): 2973(m), 1468(sh), 1441(s), 1420(sh), 1328(m), 1307(m), 1293(m), 1265(w), 1251(sh), 1237(sh), 1209(ms), 1181(vw), 1152(m), 1131(m), 1033(vw), 1019(vw), 991(m), 871(m), 850(sh), 836(m), 829(sh), 808(m), 801(sh), 773(m), 759(m), 752(m), 702(m), 625(vw), 597(m), 569(sh), 555(ms), 548(ms), 527(m), 498(vw), 477(ms), 470(m), 449(sh), 435(w), 428(sh), 407(m).

The ^{19}F nmr spectrum gave the following peak areas:
 SO_2F (1.0), CF (1.2), and CF_2 (2.1).

The positive ion $(\text{CI})^+$ mass spectrum (m/e, species):
 331, MH^+ ; 311, $(\text{M}-\text{F})^+$; 291, $(\text{M}-\text{HF}_2)^+$; 249, $(\text{MH}_2-\text{SO}_2\text{F})^+$; 248,
 $(\text{MH}-\text{SO}_2\text{F})^+$; 247*, $(\text{M}-\text{SO}_2\text{F})^+$; 227, $(\text{M}-\text{HSO}_2\text{F}_2)^+$; 195,
 $\text{CF}_2\text{CF}_2\text{CFSO}_2^+$; 165, $\text{FSO}_2\text{CFHCF}_2^+$; 163, $\text{CF}_2\text{CF}_2\text{CFS}^+$; 162,
 $\text{CF}(\text{CF}_2)_2\text{CF}^+$; 161, $\text{FSOCFHCF}_2\text{C}^+$; 151, $\text{FSO}_2\text{CFHC}_3^+$; 143,
 $\text{CCF}_2\text{CF}_2\text{CF}^+$; 141, $\text{CF}_2\text{CFCSo}^+$; 131, $\text{CFCF}_2\text{CF}_2^+$; 115, FSO_2CFH^+ ;
 114, FSO_2CF^+ ; 113, $\text{CF}_2\text{CF}_2\text{CH}^+$; 111, SOCHCF_2^+ ; 101, CFHCCCHS^+ ;
 95, FSO_2C^+ ; 93, CF_2CFC^+ ; 91, SOCCF^+ ; 79, CFSO^+ ; 75, CFCS^+ ;
 69, CFHC_3H^+ ; 67, SOF^+ ; 64, SO_2^+ or SCFH^+ ; 63, SCF^+ or
 CFHCF^+ ; 57, C_2SH^+ ; 51, SF^+ ; 50, CF_2^+ ; 48, SO^+ .

Synthesis of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$

To a 12.5 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube with a Kontes Teflon valve, 15.7 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}=\text{CF}_2$ was added. The mixture was heated for 10 h at $115\pm 5^\circ\text{C}$. Distillation of the mixture gave 7.34 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$ in 47% yield; b.p. $79\pm 1^\circ\text{C}/226$ mm.

The infrared spectrum had the following bands (cm^{-1}):
 1785(s), 1441(vs), 1370(s), 1335(sh), 1321(s), 1279(s),
 1272(sh), 1216(vs), 1195(sh), 1110(s), 1089(s), 1075(sh),
 998(m), 977(m), 970(sh), 913(m), 864(m), 850(sh), 815(m),
 787(s), 766(s), 745(vw), 709(vw), 695(vw), 674(sh), 660(s),
 646(sh), 604(w), 590(w), 569(vw), 540(m), 519(m), 484(w),
 428(w), 407(m).

The ^{19}F nmr spectrum gave the following relative peak areas: CF (1.0), CF (1.0), CF_2_{ab} (1.0, 1.0), CF_2 (4.1), and CF_2_{ab} (1.0, 1.0).

The positive ion (CI) $^+$ mass spectrum (m/e, species): 342, M^+ ; 323, $(\text{M}-\text{F})^+$; 243, $(\text{M}-\text{SO}_3\text{F})^+$; 231, $(\text{C}_5\text{F}_9)^+$; 212, C_5F_8^+ ; 193, $(\text{M}-\text{CF}_3\text{SO}_3)^+$; 181, C_4F_7^+ ; 155, C_5F_5^+ ; 143, C_4F_5^+ ; 131, C_3F_5^+ ; 124, C_4F_4^+ ; 112, C_3F_4^+ ; 109, $\text{C}_3\text{F}_3\text{O}^+$; 100, C_2F_4^+ ; 95, SO_2CF^+ ; 93, C_3F_3^+ ; 81, C_2F_3^+ ; 79, CFSO^+ ; 74, C_3F_2^+ ; 64, SO_2 ; 62, C_2F_2^+ ; 48, SO^+ ; 47, CFO^+ ; 44, CS^+ .

Synthesis of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

To a 50 ml Pyrex-glass round bottom flask, equipped with a Teflon coated stirring bar, were added 1.19 mmol of dry NaF, and 4.50 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C . The mixture was heated for 48 h at $147\pm 3^\circ\text{C}$. Distillation of the mixture gave 2.92 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$, in 65% yield; b.p. $84-5^\circ\text{C}/244$ mm.

The infrared spectrum had the following bands (cm^{-1}): 1884(s), 1870(sh), 1785(vs), 1462(vs), 1377(s), 1321(vs), 1272(m), 1244(sh), 1223(vs), 1195(s), 1181(s), 1166(sh), 1138(s), 1082(s), 1005(m), 984(m), 955(ms), 857(m), 829(ms), 794(ms), 766(ms), 745(vw), 723(m), 695(m), 660(m), 646(sh), 639(sh), 625(sh), 611(m), 590(sh), 583(m), 576(sh), 555(ms), 505(w), 497(m), 463(m), 435(m).

The ^{19}F nmr spectrum gave the following relative peak

areas: SO_2F (1.0), COF (1.0), CF (1.1), CF (1.3), CF_2ab (1.0, 1.1), and CF_2 (4.2).

The positive ion $(\text{CI})^+$ mass spectrum (m/e , species): P 343, MH^+ ; 342, M^+ ; 324, $(\text{MH}-\text{F})^+$; 323, $(\text{M}-\text{F})^+$; 276, $(\text{MH}-\text{SOF})^+$; 259, $(\text{M}-\text{SO}_2\text{F})^+$; 243, $(\text{M}-\text{SO}_3\text{F})^+$; 237, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CSC}^+$; 231, $\text{CF}_2=\text{CFCF}_2\text{CC}(\text{SO}_2)\text{C}^+$; 213, $(\text{MH}-\text{SO}_2\text{F}, \text{COF})^+$; 212, $(\text{M}-\text{SO}_2\text{F}, \text{COF})^+$; 209, $\text{CFCF}_2\text{CF}_2\text{CFCOF}^+$; 193, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{C}^+$; 181, $\text{CF}_2=\text{CF}(\text{CF}_2)_2^+$; 171, $\text{CFCF}_2\text{CF}_2\text{CCO}^+$; 163, $\text{CF}_2\text{CF}_2\text{CFS}^+$; 162, $\text{CFCF}_2\text{CF}_2\text{CF}^+$; 143, $\text{CF}_2=\text{CFCF}_2\text{C}^+$; 131, $\text{CF}_2=\text{CFCF}_2^+$; 109, CF_2CFCO^+ ; 100, CF_2CF_2^+ ; 93, $\text{CF}_2=\text{CFC}^+$; 83, SO_2F^+ ; 81, CF_2CF^+ ; 79, CFSO^+ ; 67, SOF^+ ; 64, SO_2^+ .

Synthesis of $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$

To a 25 ml Pyrex-glass round bottom flask, equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 3.57 mmol of dried NaF, 5.31 mmol of $[\text{CF}_2(\overline{\text{O}})\text{CF}(\text{SO}_2)-\text{CF}_2]_2$, and 10.34 mmol of $\text{CH}_2=\text{CHCH}_2\text{OH}$. The mixture was stirred for 3 h at room temperature. Distillation of the volatile material gave 2.61 mmol of $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})-\text{CF}_2]_2$ in 49% yield; b.p. $111\pm 2^\circ\text{C}/36$ mm.

The infrared spectrum had the following bands (cm^{-1}): 3093(vw), 3037(vw), 2995(vw), 2966(w), 2889(vw), 1792(s), 1771(s), 1652(w), 1455(vs), 1384(sh), 1363(m), 1307(ms), 1272(s), 1258(ms), 1223(s), 1188(ms), 1152(ms), 1117(sh), 1082(m), 1019(m), 984(m), 970(vw), 941(m), 899(w), 829(m), 801(sh), 787(m), 759(vw), 752(m), 688(sh), 667(m), 646(sh), 604(m), 576(vw), 548(m), 505(sh), 484(m), 456(m).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.1), CF (1.0), and CF_2 (1.7). The ^1H nmr spectrum gave the following peak areas: CH_2 (1.8) and C_2H_3 (2.9).

The positive ion $(\text{CI})^+$ mass spectrum (m/e , species): 499, MH^+ ; 457, $(\text{M}-\text{C}_3\text{H}_5)^+$; 312, $\text{FSO}_2\text{CF}(\text{CF}_2)_2\text{CFSOF}^+$; 311, $\text{C}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{COOC}_3\text{H}_5^+$; 293, $\text{FSO}_2\text{CF}(\text{CF}_2)_2\text{CFSO}^+$; 291, $\text{CCFCF}_2\text{CF}(\text{SO}_2\text{F})\text{COOC}_3\text{H}_4^+$; 261, $\text{CCF}_2\text{CF}(\text{SO}_2\text{F})\text{COOC}_3\text{H}_5^+$; 235, $\text{CF}_2\text{CF}(\text{SO}_2\text{F})\text{COOC}_2\text{H}_3^+$; 227, $\text{CFCF}(\text{SO}_2\text{F})\text{COOC}_3\text{H}_2^+$; 209, $\text{CCF}(\text{SO}_2\text{F})\text{COOC}_3\text{H}_3^+$; 197, $\text{FSO}_2\text{CFCOOC}_3\text{H}_3^+$; 195, $\text{FSO}_2\text{CFCOOC}_3\text{H}^+$; 171, $\text{CF}(\text{CF}_2)_2\text{CCO}^+$; 169, $\text{CFCF}_2\text{CCSO}_2^+$; 163, $\text{CF}_2\text{CF}_2\text{CFS}^+$; 145, $\text{CF}_2\text{CFSO}_2^+$; 140, $\text{CF}_2\text{CF}_2\text{CCO}^+$; 131, $\text{CF}_2\text{CF}_2\text{CF}^+$; 121, SCFCOOCH_2^+ ; 115, $\text{CFCOOC}_3\text{H}_4^+$; 112, $\text{CFCOOC}_3\text{H}^+$; 101, $\text{CFCOOC}_2\text{H}_2^+$; 100, CF_2CF_2^+ ; 95, FSO_2C^+ ; 87, CFCOOC^+ ; 85, SCCOCH^+ ; 83, SO_2F^+ ; 81, CCOOCHC^+ ; 79, FSOC^+ ; 71, CFCOO^+ ; 69, CCOOCH^+ ; 67, SOF^+ ; 64, SO_2^+ ; 63, SFC^+ .

Synthesis of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

To a 50 ml Pyrex-glass round bottom flask, equipped with a Teflon coated stirring bar, were added 3.1 mmol of dry NaF , 5.34 mmol of $\text{CH}_2=\text{CHCH}_2\text{OH}$, and 5.53 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CFCF}_2\text{OSO}_2$. The mixture was heated for 20 h at $55\pm 5^\circ\text{C}$. Distillation of the mixture gave 3.76 mmol of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$, in 68% yield; b.p. $84\pm 2^\circ\text{C}/12\text{mm}$.

The infrared spectrum had the following bands (cm^{-1}): 3100(w), 3037(vw), 2995(vw), 2966(w), 2896(vw), 1785(vs),

1652(m), 1455(vs), 1420(sh), 1363(s), 1321(s), 1286(s), 1251(s), 1216(s), 1173(s), 1089(s), 1019(m), 991(m), 970(ms), 941(ms), 892(m), 857(m), 829(ms), 794(ms), 780(ms), 766(ms), 738(sh), 698(w), 681(m), 653(m), 618(ms), 590(ms), 569(ms), 498(m), 484(m), 456(m), 434(m).

The ^{19}F nmr spectrum gave the following relative peak areas: SO_2F (1.0), CF (1.0), CF (1.1), $\text{CF}_{2\text{ab}}$ (1.0,1.1) and CF_2 (3.8). The ^1H nmr spectrum gave the following relative peak areas: CH_2 (2.0) and C_2H_3 (3.0).

The positive ion $(\text{CI})^+$ mass spectrum (m/e, species): 381, MH^+ ; 380, M^+ ; 379, $(\text{M}-\text{H})^+$; 297, $(\text{M}-\text{SO}_2\text{F})^+$; 296, $(\text{M}-\text{H}, \text{SO}_2\text{F})^+$; 277, $(\text{M}-\text{HF}, \text{SO}_2\text{F})^+$; 268, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CFCOOC}^+$; 249, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CCOOC}^+$; 240, $\text{CF}_2=\text{CFCF}_2\text{CFCCOC}_3\text{H}_2^+$; 231, $\text{CF}(\text{CF}_2)_2-\text{CFCOOCHC}^+$; 221, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CCO}^+$; 213, $\text{CF}(\text{CF}_2)_2\text{CCOOC}_2\text{H}_2^+$; 212, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}^+$; 209, $\text{CCF}(\text{SO}_2\text{F})\text{COOC}_3\text{H}_3^+$; 201, $\text{CF}(\text{CF}_2)_2-\text{CCOOCH}_2^+$; 194, $\text{FSO}_2\text{CFCOOC}^+$; 193, $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{C}^+$; 181, $\text{CF}_2=\text{CF}(\text{CF}_2)_2^+$; 171, $\text{CF}(\text{CF}_2)_2\text{CCO}^+$; 165, $\text{CF}_2\text{C}(\text{S})\text{COOC}_2\text{H}_3^+$; 163, $\text{CF}_2\text{CF}_2\text{CFS}^+$; 159, $\text{CF}_2\text{CF}_2\text{CFCO}^+$; 151, $\text{CCCCFCOOCH}_2\text{CHCH}^+$; 145, $\text{CF}_2\text{CFSO}_2^+$; 143, $\text{CF}(\text{CF}_2)_2\text{C}^+$; 132, $\text{SCFCOOC}_2\text{H}^+$; 131, $\text{CF}_2\text{CF}_2\text{CF}^+$; 127, $\text{CCFCOOC}_3\text{H}_4^+$; 124, $\text{CF}_2\text{CF}_2\text{CC}^+$; 121, SCFCOOCH_2^+ ; 115, $\text{CFCOOC}_3\text{H}_4^+$; 114, CFSO_2F^+ ; 113, $\text{CFCOOCH}_2\text{CC}^+$; 109, CF_2CFCO^+ ; 101, $\text{CFCOOC}_2\text{H}_2^+$; 100, CF_2CF_2^+ ; 95, FSO_2C^+ ; 94, CF_2COO^+ ; 93, CF_2CFC^+ ; 91, SCFCO^+ ; 87, CFCOOC^+ ; 83, SO_2F^+ ; 81, CCOOC_2H^+ ; 79, FSOC^+ ; 75, CFCOO^+ ; 69, CCOOCH^+ ; 67, SOF^+ ; 64, SO_2^+ ; 63, SCF^+ ; 62, CFCF^+ .

Synthesis of $[(-\text{CH}_2-\overset{1}{\text{CH}}-)_n\text{CH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.610 g (1.22 mmol) of $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$ in 1.52 g (11.1 mmol) of CFCl_3 was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 7 h. The solution was transferred from the reaction vessel, and CFCl_3 removed under vacuum to give 0.588 g (1.18 mmol) of an off-white solid, $[(-\text{CH}_2-\overset{1}{\text{CH}}-)_n\text{CH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$; the polydiester was formed in 96% yield. A sample washed with CCl_3F decomposed at 265°C .

The infrared spectrum had the following bands (cm^{-1}): 3100(vw), 2973(w), 1799(s), 1764(ms), 1448(vs), 1391(vw), 1363(w), 1307(sh), 1279(m), 1258(m), 1230(s), 1195(m), 1159(ms), 1082(w), 1047(sh), 1019(w), 991(w), 970(vw), 934(w), 899(sh), 885(vw), 829(m), 801(sh), 787(m), 766(vw), 752(w), 667(w), 604(sh), 548(sh), 513(vs).

Synthesis of $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{1}{\text{CH}}-\text{CH}_2-]_n$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.52 g (1.38 mmol) of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ in 1.77 g (12.9 mmol) of CFCl_3 was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 23 h. The liquid was drained from the reaction vessel and CFCl_3 was removed under vacuum to give 0.480 g (1.26 mmol) of the light brown viscous liquid, $[\text{CF}_2 = \text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{1}{\text{CH}}-\text{CH}_2]_n$,

which was formed in 92% yield.

The infrared spectrum had the following bands (cm^{-1}): 3100(vw), 2973(w), 2875(vw), 1785(s), 1455(s), 1420(sh), 1370(s), 1321(s), 1286(s), 1251(s), 1223(s), 1173(s), 1089(s), 1012(m), 970(ms), 934(sh), 892(m), 864(m), 829(ms), 794(ms), 766(sh), 738(sh), 709(w), 681(w), 646(w), 618(ms), 597(ms), 569(ms), 505(w), 491(m), 463(w), 435(w), 407(w).

The ^{19}F nmr spectrum gave the following relative peak areas: SO_2F (1.0), CF (0.9), CF (1.2), CF_2_{ab} (1.0,1.0), and CF_2 (4.6).

ELEMENTAL ANALYSIS

The elemental analysis of mono/bis β -sultones and their derivatives are tabulated in Table VII. There is good agreement between the calculated and experimental values.

TABLE VII
ELEMENTAL ANALYSIS OF MONO/BIS β -SULTONES
AND THEIR DERIVATIVES

Compound	Calc.		Found
<hr/>			
I. $[\text{CF}_2(\overline{\text{O}}\text{CF}(\text{SO}_2)\text{CF}_2)]_2$	C	17.06	17.18
	F	45.00	44.17
	S	15.17	15.01
II. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$	C	21.06	21.15
	F	55.50	55.00
	S	9.37	8.69
III. $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	C	17.06	17.42
	F	45.00	44.20
	S	15.17	16.09
IV. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$	C	21.06	21.52
	F	55.50	55.20
	S	9.37	9.74

TABLE VII
ELEMENTAL ANALYSIS OF MONO/BIS β -SULTONES
AND THEIR DERIVATIVES
(continued)

Compound	Calc.	Found
V. $[\text{FSO}_2\text{CFHCF}_2]_2$		
	C 14.55	14.57
	H 0.61	0.62
	F 46.10	46.40
	S 19.40	19.62
VI. $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$		
	C 28.92	28.65
	H 2.02	2.01
	F 30.50	30.00
	S 12.87	12.70
VII. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$		
	C 28.43	28.44
	H 1.33	1.44
	F 45.00	45.50
	S 8.43	8.21

TABLE VII
 ELEMENTAL ANALYSIS OF MONO/BIS β -SULTONES
 AND THEIR DERIVATIVES
 (continued)

Compound	Calc.	Found
VIII. $[(-\text{CH}_2-\overset{ }{\text{CH}}-)_n\text{CH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$		
	C 28.92	28.62
	H 2.02	2.01
	F 30.50	30.70
	S 12.87	12.83
IX. $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{ }{\text{CH}}-\text{CH}_2-]_n$		
	C 28.43	28.51
	H 1.55	1.36
	F 45.00	44.40
	S 8.43	8.25

INFRARED SPECTRA

The infrared spectral data for mono/bis β -sultones and their derivatives are presented in the experimental section, and the spectra are also shown in the appendix.

The infrared spectra for compounds I through V contain the asymmetric and symmetric SO_2 stretching vibrations at $1462\text{--}1441\text{ cm}^{-1}$ and $1223\text{--}1209\text{ cm}^{-1}$, respectively; these values are in agreement with other fluorosultones and comparable derivatives (16,24). In compounds III and IV, the carbonyl stretching frequency is found in the $1863\text{--}1884\text{ cm}^{-1}$ region, respectively; for compound IV the olefinic stretching mode is located at 1785 cm^{-1} . The S-F stretching vibration of the fluorosulfonyl group in compounds III-V is found near the 800 cm^{-1} region.

In the new allyl esters, the group frequencies and assignments are: carbonyl stretching vibration ($1977\text{--}1764\text{ cm}^{-1}$); olefinic stretching frequencies ($\text{H}_2\text{C}=\text{CH}$, 1652 cm^{-1} and $\text{F}_2\text{C}=\text{CF}-$, 1785 cm^{-1}); sulfur-fluorine stretching (near 800 cm^{-1}); SO_2 asymmetric and symmetric vibrational frequencies ($1455\text{--}1448\text{ cm}^{-1}$ and $1223\text{--}1216\text{ cm}^{-1}$); and C-H vibrational bands ($2875\text{--}3100\text{ cm}^{-1}$). It is to be noted that for polymeric systems the olefinic stretching vibration at 1652 cm^{-1} is absent.

In all cases these assignments are in excellent agreement with literature values (19,20,22).

NMR SPECTRA

The nmr chemical shifts and coupling constants for the mono/bis β -sultones and all of their derivatives are shown in Tables VIII through XI and the spectra are reproduced in the appendix.

The ^{19}F nmr spectra for all compounds were self consistent with respect to the expected chemical shifts. The ^{19}F nmr chemical shift values are summarized in Table 8. The nonequivalent CF_2 fluorines in the mono/bis β -sultones rings are found in the -84.0 to -87.7 ppm range; for other fluorinated sultones, $[\text{CF}_2(\text{O})\text{CF}(\text{SO}_2)\text{CF}_2\text{CF}_2]_2$, $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{CF}(\text{CF}_2)\text{OSO}_2$, $\text{CF}_2\text{ClCFClCF}_2\text{CF}(\text{CF}_2)\text{OSO}_2$, and $\text{SF}_5\text{CF}(\text{CF}_2)\text{OSO}_2$, the CF_2 resonance bands are located in -72.8 to -88.5 ppm range (16,29,39). The resonance for the CF group in the four membered ring is located at -153.4 and -152.9 ppm for compounds I and II, respectively; in other sultones systems such as $\text{CF}_2\text{ClCFClCF}_2\text{CF}(\text{CF}_2)\text{OSO}_2$ and the bis β -sultone of perfluoro-1,7-octadiene, the CF fluorine resonance is located at -148 and -150.1 ppm, respectively (29,39). The ^{19}F nmr spectra for the CF_2 group in all compounds consisted in general of a complex multiplet with a band center in the range -113.2 to -126.3 ppm. The ^{19}F nmr values for the following functional groupings or arrangements, $-\text{C}(\text{O})\text{F}$, $-\text{SO}_2\text{F}$, $-\text{CFH}$, $-\text{CF}(\text{SO}_2\text{F})$, and $\text{CF}_2=\text{CF}$, in compounds II to IX are all in excellent agreement with literature values (16,29,39).

The ^1H nmr data (chemical shifts and coupling constants) for the new esters are reported in Table X through XI. The chemical shifts and coupling constants for the $-\text{CH}_2\text{CH}=\text{CH}_2$ moiety are in agreement with values reported for allyl alcohol and $\text{R}_f\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ derivatives (19,22,53). The proton nmr spectrum for the polymeric ester IX showed, in general, broad peaks similar to that reported for other polymeric esters (22). The nmr spectrum of the polyester VIII formed from the bis β -sultone was not obtained because of its insolubility in a number of solvents.

MASS SPECTRA

The major mass spectral peaks for these compounds are listed in the experimental section. A molecular ion was observed for compound II and the MH^+ peak found for compounds I, IV, V, VI and VIII. Additional M-X peaks, such as a M-F^+ , $\text{M-SO}_2\text{F}^+$, $\text{M-SO}_3\text{F}^+$, M-SO_3^+ , were also found. The remainder of the fragmentation patterns are consistent with the structures assigned to these compounds.

TABLE VIII

FLUORINE NMR CHEMICAL SHIFTS^{1,2,3,4}

	FSO ₂	C(O)F	F ₁	CF ₂ ^a F ₂
I. $\overline{[\text{CF}_2(\text{O})\text{CF}(\text{SO}_2)\text{CF}_2]_2}$	-	-	-84.0(d,t)	-86.7(d,m)
II. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$	-	-	-84.5(d,t)	-87.7(d,d,t)
III. $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	55.8(m)	1.8(d,m)	-	-
IV. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$	54.7(m)	31.3(m)	-	-
V. $[\text{FSO}_2\text{CFHCF}_2]_2$	56.0(m)	-	-	-
VI. $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	53.2(m)	-	-	-
VII. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$	52.3(m)	-	-	-
IX. $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-]_n$	52.1(br,s)	-	-	-

1. Fluorine chemical shifts in ppm from external F-11.

2. d = doublet, t = triplet, m = multiplet, br = broadened.

3. a = $\overline{\text{CF}_2\text{O}}$

TABLE VIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3,4}
(continued)

	CF ₂ ^b		CF ₂ ^c	
	F ₁	F ₂		
I. $\overline{[\text{CF}_2(\text{O})\text{CF}(\text{SO}_2)\text{CF}_2]_2}$	-	-	-116.3 (d,m)	
II. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CFCF}_2\text{OSO}_2}$	-89.3 (d,d,t)	-106.5 (d,d,t,t)	-119.9 (d,d,m) -118 (m)	
III. $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	-	-	-113.6 (d,m)	
IV. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$	-89.3 (d,d,t)	-106.2 (d,d,m)	-119.7 (m) -117.8 (m)	
V. $[\text{FSO}_2\text{CFHCF}_2]_2$	-	-	-	
VI. $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	-	-	-113.2 (m)	
VII. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$	-89.3 (d,d,t)	-106.2 (d,d,m)	-118.8 (m) -118.0 (m)	
IX. $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{ }{\text{CH}}-\text{CH}_2-]_n$	-87.8 (m)	-105.8 (br,d)	-118.2 (m)	

1. Fluorine chemical shifts in ppm from external F-11.
2. d = doublet, t = triplet, m = multiplet, br = broadened.
3. b = $\overline{\text{CF}_2}=\text{CF}$, c = $\text{CF}\overline{\text{CF}_2}\text{CF}_2\text{F}$.

TABLE VIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3,4}
(continued)

	CF ^d	CF ^e	CF ₂ ^f
I. $[\text{CF}_2(\text{O})\overline{\text{CF}(\text{SO}_2)\text{CF}_2}]_2$	-153.4 (m)	-	-
II. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\overline{\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2)\text{CF}_2}$	-152.9 (m)	-192.8 (d,d,m)	-
III. $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	-160.3 (d,m)	-	-
IV. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$	-119.7 (m)	-192.8 (d,d,m)	-
V. $[\text{FSO}_2\text{CFHCF}_2]_2$	-	-	-119.0 (d,m)
VI. $[\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$	-159.3 (d,m)	-	-126.3 (d,m)
VII. $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$	-160.3 (m)	-192.2 (d,d,m)	-
IX. $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\text{CH}-\text{CH}_2-]_n$	-160.3 (m)	-192.8 (m)	-

1. Fluorine chemical shifts in ppm from external F-11.
2. d = doublet, t = triplet, q = quartet, m = multiplet.
3. d = $\overline{\text{CF}(\text{SO}_2)}$, e = $\text{CF}_2=\overline{\text{CF}}$, f = $\overline{\text{CF}_2\text{CFH}}$.
4. The $\overline{\text{CFH}}\text{SO}_2\text{F}$ resonance is located at -190.1 (m) ppm for compound V.

TABLE IX
FLUORINE NMR COUPLING CONSTANTS

	Coupling Constants (Hz)
I. $[(1,2)F_2C(O)CF(SO_2)CF_2]_2$	$J_{1,2} = 110.8$
II. $(4,5)F_2=CF_{(3)}(CF_2)_2CF_{(1,2)}CF_2OSO_2$	$J_{1,2} = 110.1$ $J_{4,5} = 50.5$ $J_{3,4} = 40.9$ $J_{3,5} = 118.5$
IV. $(2,3)F_2C=CF_{(1)}(CF_2)_2CF(SO_2F)C(O)F$	$J_{1,2} = 41.5$ $J_{1,3} = 122.8$ $J_{2,3} = 50.8$
V. $[(3)FSO_2CF_{(2)}H_{(1)}CF_2]_2$	$J_{1,2} = 44.1$ $J_{1,3} = 42.6$ $J_{2,3} = 11.3$
VII. $(2,3)CF_2=CF_{(1)}(CF_2)_2CF(SO_2F)C(O)OCH_2CH=CH_2$	$J_{1,2} = 40.9$ $J_{1,3} = 119.9$ $J_{2,3} = 55.0$

TABLE X

PROTON NMR CHEMICAL SHIFTS^{1,2,3,4,5}

	H _a	H _b	H _c	CH ₂ d
VI. $[(a,b)H_2C=CH(c)CH_2(d)OC(O)CF(SO_2F)CF_2]_2$	5.68 (d,d,t)	5.75 (d,d,t)	6.27 (d,d,t)	5.23 (d,d,d)
VII. $CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2(d)CH(c)=CH_2(a,b)$	5.57 (d,d,t)	5.66 (d,d,t)	6.17 (d,d,t)	5.10 (d,d,d)

1. Proton chemical shifts in ppm downfield from external TMS.
2. d = doublet, t = triplet
3. In compounds VI and VII, H_b and H_c are trans to each other.
4. For $CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2(-CH-CH_2-)_n$, the spectrum contained a broad peak at 4.53 ppm and a series of peaks between 1 and 3.5 ppm.
5. For $[FSO_2CFHCF_2]_2$, the CH chemical shift is 7.1 ppm.

TABLE XI
PROTON NMR COUPLING CONSTANTS^{1,2}

	Coupling Constants (Hz)	
<hr/>		
VI. $[(a,b)H_2C=CH_{(c)}CH_2_{(d)}OC(O)CF(SO_2F)CF_2]_2$		
	$J_{a,b} = 1.0$	$J_{c,d} = 6.0$
	$J_{a,c} = 10.8$	
	$J_{b,c} = 16.5$	
VII. $CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2_{(d)}CH_{(c)}=CH_2_{(a,b)}$		
	$J_{a,b} = 0.9$	$J_{b,c} = 17.2$
	$J_{a,c} = 10.5$	$J_{b,d} = 0.8$
	$J_{a,d} = 0.8$	$J_{c,d} = 6.1$

1. The coupling constants for $CF_2=CF(CF_2)_2CF(SO_2F)C(O)OCH_2CH=CH_2$ were obtained with a General Electric QE-300 NMR Spectrometer. Thanks are expressed to Dr. David H. Peyton for obtaining the 1H nmr spectrum of this compound.
2. $J_{b,c}$ is trans coupling.

CHAPTER V

SULFUR TRIOXIDATION OF ACYCLIC FLUORO-ALLYL ETHERS

Fluorinated ethers have a variety of uses including lubricants, fire extinguishers, solvents and blood substitutes. Those containing sulfonyl fluoride groupings lead to compounds useful as ion-exchange resins, comonomers with tetrafluoro-ethylene, surface active agents, and strong sulfonic acids (22,24,54). The fluorinated ethers containing sulfonyl fluoride groupings are also a good source for fluorinated ethers, because upon heating, they decompose to give fluorinated ether and SO₂ (55):

F-allyl ethers represent a class of compounds capable of producing unsymmetrical allylic cation intermediates in reactions with sulfur trioxide (44). In the case of both ethers, CF₃OC₂F₄OCF₂CF=CF₂ and CF₃OCF₂CF=CF₂, which were used in this study, the predominant reaction with monomeric sulfur trioxide was sulfonation at the terminal positions, along with the disappearance of double bonds giving the following β-sultones:

II

The above reactions were carried out in a modified Carius tube under autogeneous pressure at temperatures greater than 100°C.

The products in reactions V-2 and V-3 result from the stereospecific addition of SO_3 without isomer formation. By comparison, with F-vinyl ethers ($\text{R}_f\text{OCF}=\text{CF}_2$), the cycloaddition reaction with sulfur trioxide occurs in a reverse order (37); i.e., the oxygen and SO_2 of sulfur trioxide bonds with the olefinic carbon of the CF and the terminal CF_2 groups, respectively; incorporation of the unpaired electron from the ether oxygen into the electron cloud of the π -olefinic system creates a conjugated system such that the olefinic CF_2 carbon carries a partial negative charge and bonds with the sulfur portion of SO_3 .

The β -sultones, I and II, are thermally stable, colorless liquids. Treatment of these β -sultones with metal halides, MX, (where M = Na or K, and X = F, Br) produced the corresponding isomeric fluorosulfonyl acylfluorides:

In the presence of water, I and II undergo rearrangement, and a concerted hydrolysis/decarboxylation

reaction:

V

VI

The products, V and VI, are also stable colorless liquids.

Allyl alcohol in the presence of dried sodium fluoride reacts with the β -sultones I and II to produce new fluorosulfonyl allyl esters according to the following equations:

VII

VIII

The new allyl esters, VII and VIII, are thermally stable and colorless liquids; in the presence of ultraviolet irradiation, the new fluorosulfonyl allyl esters undergo polymerization:

IX

X

The fluorosulfonyl polyesters, IX and X, are brownish viscous liquids.

The syntheses of the two β -sultones, I and II, were carried out by heating in a 130 ml Pyrex-glass Carius tube at 105-120°C for 2-6 days, while the rearrangement reactions of these β -sultones were carried out in a 50 ml Pyrex-glass round bottom flask at 95-100°C for 1-2 days, and at room temperature for 8 more days in case of the $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$ rearrangement. The hydrolysis process of the β -sultones was done in a Kel-F vessel due to the formation of HF, which etches the glassware. The esterification reactions of β -sultones were also carried out in 50 ml Pyrex-glass round bottomed flasks at room temperature for 1-7 days; an extra 6 days of heating at 61-65°C for $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$ esterification was needed. In order to polymerize the allylic esters, they were placed in a 80 ml quartz vessel and irradiated with ultraviolet light in the presence of CFCl_3 for 21.5 hours. The purification of the β -sultones and their derivatives was done either through fractional distillation at reduced or atmospheric pressure, or direct transfer from the reaction vessel. The results of the elemental analyses confirmed the molecular formulas of all new β -sultones and their derivatives, except for $[\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{|}{\text{CH}}-\text{CH}_2-]_n$, which was not sent for elemental analysis due to its decomposition prior to the analysis.

EXPERIMENTAL

Synthesis of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_3\overline{\text{CFCF}_2}\text{OSO}_2$

To 21.3 mmol of SO_3 in a 130 ml Pyrex-glass Carius tube equipped with a Kontes Teflon valve, 17.5 mmol of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}=\text{CF}_2$ was added. The mixture was heated at $115\pm 5^\circ\text{C}$ for 48 h. Distillation of the mixture gave 13.4 mmol of a clear liquid, $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$ in 76.6% yield, b.p. $88^\circ\text{C}/336$ mm.

The infrared spectrum had the following bands (cm^{-1}): 1508(w), 1497(m), 1473(w), 1449(s), 1429(w), 1403(w), 1337(ms), 1293(s), 1225(vs), 1149(s), 1131(s), 1107(s), 1090(s), 1061(sh), 1024(sh), 1000(ms), 921(ms), 901(ms), 846(m), 831(m), 814(w), 785(ms), 763(ms), 744(ms), 684(ms), 671(sh), 660(ms), 623(sh), 579(w), 566(sh), 557(sh), 531(ms), 503(m), 476(m), 428(sh), 409(w).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_3 (3.5), CF_2 (2.5), CF_2CF_2 (2.0,2.0), CF_2ab (1.0,1.0), and CF (1.0).

The positive ion (CI) $^+$ mass spectrum (m/e, species): 413, MH^+ ; 393, $(\text{M}-\text{F})^+$; 332, $(\text{M}-\text{SO}_3)^+$; 328, $(\text{MH}-\text{CF}_3\text{O})^+$; 327, $(\text{M}-\text{CF}_3\text{O})^+$; 313, $(\text{M}-\text{SO}_3\text{F})^+$; 213, $\text{CF}_3\text{OC}_2\text{F}_4\text{OC}^+$; 185, $\text{CF}_3\text{OCF}_2\text{CF}_2^+$; 169, $\text{CF}_2\text{OCFC}(\text{SO})\text{C}^+$; 163, $\text{CF}_3\text{OCFCFO}^+$; 150, $\text{CF}_2\text{OCC}(\text{SO})\text{C}^+$; 147, $\text{CF}_3\text{OCF}_2\text{C}^+$; 135, $\text{CF}_3\text{OCF}_2^+$; 133, $\text{CF}_2\text{CFOCCC}^+$; 132, $\text{OCF}_2\text{CF}_2\text{O}^+$; 131, $\text{CF}_2\text{CFCF}_2^+$; 129, $\text{CF}(\text{SO})\text{CF}_2^+$; 128, CF_3OCFC^+ ; 119, $\text{OCFC}(\text{SO})\text{C}^+$; 109, CF_3OCC^+ ; 100, CF_2CF_2^+ ;

97, CF_3OC^+ ; 95, CFSO_2^+ ; 81, CF_2CF^+ ; 79, CFSO^+ ; 75, OCFCO^+ ; 69, CF_3^+ ; 64, SO_2^+ .

Synthesis of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

To a 50 ml Pyrex-glass round bottom flask, equipped with a Teflon coated stirring bar, were added 3.10 mmol of dry NaF, and 4.85 mmol of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C . The reaction mixture was heated to $100\pm 5^\circ\text{C}$ for 48 h. Distillation of the mixture gave 2.74 mmol of a colorless liquid, $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$, in 56.5% yield; b.p. $82\pm 1^\circ\text{C}/343\text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 1881(s), 1871(s), 1844(m), 1469(s), 1402(m), 1290(s), 1236(vs), 1195(sh), 1152(vs), 1118(vs), 1094(s), 996(ms), 976(ms), 901(s), 824(s), 807(s), 763(ms), 746(sh), 709(ms), 682(ms), 672(m), 621(sh), 597(s), 560(sh), 526(w), 486(m), 459(m), 418(vw).

The ^{19}F nmr spectrum gave the following relative peak areas: SO_2F (1.0), $\text{C}(\text{O})\text{F}$ (1.0), CF_3 (3.5), CF_2 (2.1), CF_2CF_2 (2.2, 2.1), and CF (1.0).

The positive ion (CI) $^+$ mass spectrum (m/e, species): 393, $(\text{M}-\text{F})^+$; 330, $(\text{MH}-\text{SO}_2\text{F})^+$; 327, $(\text{M}-\text{CF}_3\text{O})^+$; 313, $(\text{M}-\text{SO}_3\text{F})^+$; 213, $\text{CF}_3\text{OC}_2\text{F}_4\text{OC}^+$; 211, $\text{OCF}_2\text{CF}(\text{SOF})\text{COF}^+$; 185, $\text{CF}_3\text{OCF}_2\text{CF}_2^+$; 169, $\text{CF}_2\text{OCFC}(\text{SO})\text{C}^+$; 163, $\text{CF}_3\text{OCFCFO}^+$; 150, $\text{CF}_2\text{OCC}(\text{SO})\text{C}^+$; 147, $\text{CF}_3\text{OCF}_2\text{C}^+$; 145, $\text{CF}(\text{SO}_2\text{F})\text{CF}^+$; 135,

$\text{CF}_3\text{OCF}_2^+$; 133, $\text{CF}_2\text{CFOCCC}^+$; 132, $\text{OC}_2\text{F}_4\text{O}^+$; 129, CF_2CFSO^+ ; 128, CF_3OCFC^+ ; 119, $\text{CC}(\text{SO}_2\text{F})\text{C}^+$; 109, CF_3OCC^+ ; 100, CF_2CF_2^+ ; 97, CF_3OC^+ ; 95, CSO_2F^+ ; 83, SO_2F^+ ; 81, CF_2CF^+ ; 79, CFSO^+ ; 78, CFCOF^+ ; 69, CF_3^+ ; 67, SOF^+ ; 64, SO_2^+ ; 56, CCS^+ .

Synthesis of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFHSO}_2\text{F}$

To a 40 ml Kel-F vessel, equipped with a Teflon stirring bar, was added 6.36 mmol of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\overline{\text{CFCF}_2\text{O}}\text{SO}_2$. The reaction vessel was cooled to 0°C and 10 ml of distilled H_2O was added dropwise over a period of 45 min. The mixture was allowed to stand at room temperature for 3 h after which the lower layer was separated, and dried over MgSO_4 . Distillation gave 1.45 mmol of colorless liquid, $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFHSO}_2\text{F}$, in 22.8% yield; b.p. $86^\circ\text{C}/336\text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 2988(vw), 1455(s), 1406(m), 1356(ms), 1289(s), 1253(s), 1231(s), 1197(s), 1147(vs), 1123(sh), 1092(ms), 934(sh), 916(m), 907(m), 894(m), 882(m), 866(w), 824(ms), 810(sh), 788(m), 753(m), 734(w), 721(sh), 683(w), 671(m), 647(sh), 599(ms), 561(sh), 527(vw), 497(vw), 477(vw), 458(vw).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), CF_3 (3.1), CF_2 (2.0), CF_2CF_2 (2.1, 2.0), and CH (1.1).

The positive ion $(\text{CI})^+$ mass spectrum (m/e, species): 349, $(\text{M}-\text{OH})^+$; 347, $(\text{M}-\text{F})^+$; 281, $(\text{M}-\text{CF}_3\text{O})^+$; 195, $\text{CF}_2\text{OCF}_2-\text{CFSO}^+$; 185, $\text{CF}_3\text{OCF}_2\text{CF}_2^+$; 165, $\text{CF}_2\text{CFHSO}_2\text{F}^+$; 164, $\text{CF}_2\text{CFSO}_2\text{F}^+$; 163, OCFCOCCSO_2^+ ; 147, CFCOCCSO_2^+ ; 145, $\text{OCCOCC}(\text{SO}_2)\text{H}^+$; 143,

CFOCCOCCS⁺; 135, CFOCCSO₂⁺; 119, CFOCCSO⁺; 117, COCC(SO₂)H⁺; 101, COCC(SO)H⁺; 100, CF₂CF₂; 97, OCF₂CF⁺; 95, CFSO₂⁺; 87, CFOCCO⁺; 83, SO₂F⁺; 82, CF₂CFH⁺; 81, CF₂CF⁺; 79, CFSO⁺; 75, CFCS⁺; 69, CF₃⁺; 67, SOF⁺; 64, SO₂⁺; 59, CFCO⁺.

Synthesis of CF₃OCF₂ $\overline{\text{CFCF}_2}$ OSO₂

To a 24.4 mmol of SO₃ in a 130 ml Pyrex-glass Carius tube with a Kontes Teflon valve, 22.2 mmol of CF₃OCF₂CF=CF₂ was added. The mixture was heated for 6 days at 110±5°C. Distillation of the mixture gave 14.8 mmol of CF₃OCF₂ $\overline{\text{CFCF}_2}$ OSO₂ in 66.5% yield; b.p. 69-72°C/atm.

The infrared spectrum had the following bands (cm⁻¹): 1485(w), 1470(m), 1446(s), 1428(m), 1344(s), 1317(s), 1275(sh), 1249(vs), 1210(sh), 1180(s), 1138(s), 1096(s), 1021(ms), 1007(ms), 971(sh), 932(m), 920(m), 908(sh), 890(w), 863(m), 848(w), 824(ms), 785(s), 690(w), 675(m), 657(s), 621(vw), 603(vw), 582(w), 546(m), 523(ms), 505(ms), 469(sh), 448(m), 418(vw).

The ¹⁹F nmr spectrum gave the following relative peak areas: CF₃ (3.0), CF₂ (1.9), CF₂_{ab} (1.0,1.0), and CF (0.9).

The positive ion (CI)⁺ mass spectrum (m/e, species): 297, MH⁺; 277, (MH-HF)⁺; 216, (M-SO₃)⁺; 211, (M-CF₃O)⁺; 197, (M-SO₃F)⁺; 189, OCCFCF₂OSO₂⁺; 179, CF₃OCF₂CS⁺; 151, OCFCCOSO₂⁺; 150, CF₂OCC(SO)C⁺; 147, CF₃OCF₂C⁺; 145, CF(SO₂)CF₂⁺; 135, CF₃OCF₂⁺; 132, OCCCO₂SO₂⁺; 131, CF₂CFCF₂⁺; 129, CF(SO)CF₂⁺; 128, CF₃OCFC⁺; 125, OCCFCF₂O⁺; 119, OCFC(SO)C⁺; 109, CF₃OCC⁺; 100, OCC(SO)C⁺; 97, CF₃OC⁺; 95,

CFSO_2^+ ; 81, CF_2CF^+ ; 80, SO_3^+ ; 79, CFSO^+ ; 69, CF_3^+ ; 64, SO_2^+ .

Synthesis of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

To a 50 ml Pyrex-glass round bottom flask equipped with a Teflon coated stirring bar, were added 4.76 mmol of dry NaF, and 7.67 mmol of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$. The reaction vessel was connected to a reflux condenser which was attached to a trap cooled to -78°C . The mixture was heated for 24 h at 100°C and room temperature for 8 days. Trap-to-trap distillation of the reaction mixture gave 3.38 mmol of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$ in 44.1% yield at liquid nitrogen temperature (-196°C).

The infrared spectrum had the following bands (cm^{-1}): 1883(s), 1867(sh), 1845(sh), 1489(sh), 1467(s), 1445(s), 1432(sh), 1345(sh), 1317(s), 1242(vs), 1176(sh), 1145(vs), 1129(vs), 1095(s), 1004(ms), 973(m), 932(w), 920(w), 888(w), 860(m), 826(ms), 801(ms), 782(ms), 716(m), 676(m), 657(ms), 619(ms), 585(ms), 544(vw), 523(w), 504(vw), 481(w), 457(w), 422(vw), 410(vw).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (0.9), $\text{C}(\text{O})\text{F}$ (0.9), CF_3 (3.0), CF_2 (1.5), and CF (1.0).

The positive ion $(\text{CI})^+$ mass spectrum (m/e, species): 297, MH^+ ; 278, $(\text{MH}-\text{F})^+$; 277, $(\text{M}-\text{F})^+$; 231, $(\text{MH}-\text{COF}, \text{F})^+$; 211, $(\text{M}-\text{CF}_3\text{O})^+$; 197, $(\text{M}-\text{SO}_2\text{F}, \text{O})^+$; 189, $\text{OCF}_2\text{CF}(\text{SO}_2)\text{CO}^+$; 151, $\text{OCFC}(\text{SO}_2)\text{CO}^+$; 150, $\text{CF}_2\text{OCC}(\text{SO})\text{C}^+$; 147, $\text{CF}_3\text{OCF}_2\text{C}^+$; 145,

CF(SO₂)-CF₂⁺; 135, CF₃OCF₂⁺; 129, CF(SF)COF⁺; 128, CF₃OCFC⁺; 119, CFC(SO₂)C⁺; 109, CF₃OCC⁺; 107, CFC(SO₂)⁺; 100, CC(SO₂)C⁺; 97, CF₃OC; 95, CSO₂F⁺; 85, CF₃O⁺; 83, SO₂F⁺; 81, CF₂CF⁺; 79, CFSO⁺; 69, CF₃⁺; 67, SOF⁺; 64, SO₂⁺.

Synthesis of CF₃OCF₂CFHSO₂F

To a 40 ml Kel-F vessel equipped with a Teflon stirring bar was added 12.8 mmol of CF₃OCF₂ $\overline{\text{CFCF}_2\text{OSO}_2}$. The reaction vessel was cooled to 0°C and 10 ml of distilled H₂O was added dropwise over a period of 45 minutes. The mixture was distilled and the resulted product was dried over MgSO₄. Distillation gave 5.12 mmol of CF₃OCF₂CFHSO₂F, in 39.9% yield; b.p. 72°C/atm.

The infrared spectrum had the following bands (cm⁻¹): 2992(m), 1483(ms), 1450(vs), 1360(s), 1310(s), 1255(vs), 1231(vs), 1199(sh), 1150(vs), 1131(vs), 1085(sh), 1002(m), 963(w), 942(m), 934(m), 919(ms), 885(m), 857(ms), 829(s), 795(s), 782(sh), 752(ms), 705(sh), 681(m), 666(vw), 632(m), 617(ms), 581(s), 530(w), 493(m), 489(sh), 470(m), 440(m).

The ¹⁹F nmr spectrum gave the following relative peak areas: FSO₂ (1.0), CF₃ (2.8), CF₂ (2.0), and CF (1.0).

The positive ion (CI)⁺ mass spectrum (m/e, species): 251, MH⁺; 233, (M-OH)⁺; 232, (MH-F)⁺; 231, (M-F)⁺; 165, CF₂CFHSO₂F⁺; 164, CF₂CFSO₂F⁺; 145, CF₂CFSO₂⁺; 135, CFOCCSO₂⁺; 129, CF₃OCFH⁺; 128, CF₃OCFC⁺; 113, CF₂CFS⁺; 101, COCC(SO)H⁺; 100, COCCSO⁺; 97, OCF₂CF⁺; 83, SO₂F⁺; 82, CF₂CFH⁺; 81, CF₂CF⁺; 79, CFSO₂⁺; 69, CF₃⁺; 67, SOF⁺; 64,

SO_2^+ ; 59, OCFC^+ .

Synthesis of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

To a 25 ml Pyrex-glass round bottom flask, equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 6.90 mmol of dried NaF, 3.76 mmol of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ and 3.79 mmol of $\text{CH}_2=\text{CHCH}_2\text{OH}$. The mixture was stirred for 24 h at room temperature. Distillation of the volatile material gave 2.37 mmol of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ in 62.9% yield; b.p. 96-99°C/50 mm.

The infrared spectrum had the following bands (cm^{-1}): 3100(vw), 3030(vw), 2995(vw), 2966(w), 1792(s), 1771(s), 1652(w), 1458(vs), 1398(w), 1363(w), 1281(s), 1251(sh), 1230(vs), 1205(sh), 1159(vs), 1124(vs), 1096(ms), 1026(m), 991(m), 970(w), 941(m), 899(ms), 822(ms), 787(ms), 752(ms), 688(m), 674(m), 625(sh), 604(ms), 562(w), 527(vw), 491(w), 470(w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.1), CF_3 (3.3), CF_2 (1.9), CF_2CF_2 (2.0,2.0), and CF (1.0). The relative band areas for ^1H nmr spectrum were: C_2H_3 (3.2) and CH_2 (2.0).

The positive ion (CI) $^+$ mass spectrum (m/e, species): 451, MH^+ ; 450, M^+ ; 368, $(\text{MH}-\text{SO}_2\text{F})^+$; 367, $(\text{M}-\text{SO}_2\text{F})^+$; 366, $(\text{M}-\text{H},\text{SO}_2\text{F})^+$; 347, $(\text{MH}-\text{F},\text{COOC}_3\text{H}_5)^+$; 338, $(\text{M}-\text{SO}_2\text{F},\text{C}_2\text{H}_5)^+$; 305, $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CCOCH}_2^+$; 207, $\text{CCF}_2\text{OCF}_2\text{CFSO}^+$; 195, $\text{CF}_2\text{OCF}_2\text{CFSO}^+$; 185, $\text{CF}_3\text{OCF}_2\text{CF}_2^+$; 164, $\text{CF}_2\text{CFSO}_2\text{F}^+$; 163, $\text{CF}_3\text{OCFCFO}^+$; 145,

$\text{CF}_2\text{CFSO}_2^+$; 143, $\text{OCCFCOOC}_3\text{H}_4^+$; 142, $\text{OCCFCOOC}_3\text{H}_3^+$; 137, $\text{COC}_2\text{COOC}_3\text{H}_5^+$; 136, $\text{COC}_2\text{COOC}_3\text{H}_4^+$; 135, CFOCCSO_2^+ ; 128, $\text{SCFCOC}_3\text{H}^+$; 123, $\text{OC}_2\text{COOC}_3\text{H}_3^+$; 121, $\text{OC}_2\text{COOC}_3\text{H}^+$; 119, CFOCCSO^+ ; 117, $\text{SO}_2\text{CCOCH}^+$; 109, $\text{CCCOOC}_3\text{H}_5^+$; 106, $\text{CCCOOC}_3\text{H}_2^+$; 103, $\text{CFCOOC}_2\text{H}_4^+$; 101, $\text{CFCOOC}_2\text{H}_2^+$; 100, CF_2CF_2^+ ; 99, $\text{CFCOC}_3\text{H}_4^+$; 97, OCF_2CF^+ ; 95, CFSO_2^+ ; 89, CFCOOCH_2^+ ; 85, $\text{COOC}_3\text{H}_5^+$; 83, SO_2F^+ ; 82, $\text{COOC}_3\text{H}_2^+$; 81, COOC_3H^+ ; 80, COOC_3^+ ; 79, CFSO^+ ; 71, $\text{COOC}_2\text{H}_3^+$; 69, CF_3^+ ; 67, SOF^+ ; 64, SO_2^+ ; 63, SCF^+ .

Synthesis of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

To a 50 ml Pyrex-glass round bottom flask, equipped with a Teflon coated stirring bar, were added 4.52 mmol of dry NaF, 4.83 mmol of $\text{CH}_2=\text{CHCH}_2\text{OH}$, and 6.71 mmol of $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$. The mixture was stirred for 7 days at room temperature and was heated for 6 days at $63\pm 2^\circ\text{C}$. Distillation of the mixture gave 4.62 mmol of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CH}=\text{CH}_2$ in 68.9% yield; b.p. $65\pm 1^\circ\text{C}/22\text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 3100(vw), 3037(vw), 3002(vw), 2966(vw), 1785(s), 1778(s), 1652(w), 1455(s), 1363(m), 1321(s), 1293(sh), 1286(s), 1237(vs), 1159(s), 1124(vs), 1023(m), 990(m), 973(m), 940(ms), 896(m), 862(w), 830(m), 818(ms), 794(ms), 780(sh), 744(vw), 707(w), 680(w), 658(sh), 622(ms), 590(s), 530(vw), 513(vw), 488(w), 461(w), 440(vw), 420(vw), 410(vw).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (0.9), CF_3 (3.1), CF_2 (1.9), and CF (1.0).

The relative band areas for ^1H nmr spectrum were: C_2H_3 (3.2) and CH_2 (2.0).

The positive ion $(\text{CI})^+$ mass spectrum (m/e , species): 335, MH^+ ; 334, M^+ ; 251, $(\text{M}-\text{SO}_2\text{F})^+$; 250, $(\text{MH}-\text{CF}_3\text{O})^+$; 231, $(\text{MH}-\text{CF}_3\text{O}, \text{F})^+$; 222, $\text{CF}_2\text{CF}(\text{SO}_2\text{F})\text{COOCH}_2^+$; 203, $\text{CF}_2\text{CF}(\text{SO}_2)\text{COOCH}_2^+$; 194, $\text{CF}_2\text{C}(\text{SO}_2)\text{COOCC}^+$; 189, $\text{CF}_2\text{CF}(\text{SO}_2)\text{COO}^+$; 175, $\text{CFC}(\text{SO}_2)\text{COOCC}^+$; 165, $\text{CFC}(\text{SO}_2)\text{COOCH}_2^+$; 164, $\text{CF}_2\text{CFSO}_2\text{F}^+$; 157, $\text{CF}_2\text{CF}(\text{SO}_2)\text{C}^+$; 145, $\text{CF}_2\text{CFSO}_2^+$; 135, $\text{COC}_2\text{COOC}_3\text{H}_3^+$; 128, $\text{SCFCOC}_3\text{H}^+$; 121, $\text{OC}_2\text{COOC}_3\text{H}^+$; 119, CFOCCSO^+ ; 117, $\text{SO}_2\text{CCOCH}^+$; 109, $\text{CCCOOC}_3\text{H}_5^+$; 106, $\text{CCCOOC}_3\text{H}_2^+$; 101, $\text{CFCOOC}_2\text{H}_2^+$; 100, $\text{CFCOC}_3\text{H}_5^+$; 99, $\text{CFCOC}_3\text{H}_4^+$; 97, OCF_2CF^+ ; 91, CCFSO^+ ; 87, CFCOOC^+ ; 85, CF_3O^+ ; 83, SO_2F^+ ; 82, $\text{COOC}_3\text{H}_2^+$; 81, COOC_3H^+ ; 79, CFSO^+ ; 73, $\text{COOC}_2\text{H}_5^+$; 71, $\text{COOC}_2\text{H}_3^+$; 70, $\text{COOC}_2\text{H}_2^+$; 69, CF_3^+ ; 68, COOC_2^+ ; 67, SOF^+ ; 64, SO_2^+ ; 59, CFCO^+ ; 57, OC_3H_5^+ ; 55, COC_2H_3^+ ; 54, COC_2H_2^+ .

Synthesis of $[\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{1}{\text{CH}}-\text{CH}_2-\text{I}]_n$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.345 g (0.766 mmol) of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ in 1.08 g (7.85 mmol) of CFCl_3 was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 21.5 hours. The solution was transferred from the reaction vessel and the CFCl_3 was removed under vacuum to give 0.272 g (0.604 mmol) of the light brown viscous liquid $[\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{1}{\text{CH}}-\text{CH}_2-\text{I}]_n$ which was formed in 78.8% yield.

The infrared spectrum had the following bands (cm^{-1}): 2968(vw), 2878(vw), 1791(ms), 1456(ms), 1419(vw), 1399(w), 1291(vs), 1236(vs), 1236(vs), 1196(vs), 1148(vs), 1125(vs), 1028(m), 902(ms), 822(m), 747(w), 681(w), 670(w), 647(vw), 619(sh), 599(m), 562(sh), 527(vw), 490(vw), 459(vw), 439(vw).

Synthesis of $[\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{|}{\text{CH}}-\text{CH}_2-]_n$

To a 80 ml quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 0.348 g (1.04 mmol) of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ in 1.36 g (9.89 mmol) of CFCl_3 was irradiated with ultraviolet light from a 100 watt Hanovia lamp for 21.5 hours. The liquid was drained from the reaction vessel and CFCl_3 was removed under vacuum to give 0.302 g (0.903 mmol) of the light brown viscous liquid $[\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{|}{\text{CH}}-\text{CH}_2-]_n$ which was formed in 86.6% yield.

The infrared spectrum had the following bands (cm^{-1}): 2968(w), 2878(vw), 1791(s), 1454(s), 1417(vw), 1316(s), 1291(s), 1243(vs), 1228(vs), 1165(s), 1130(vs), 1023(m), 976(m), 891(m), 762(m), 818(ms), 796(ms), 736(vw), 702(vw), 683(w), 658(sh), 620(m), 588(ms), 532(w), 510(vw), 488(w), 459(w), 422(vw).

ELEMENTAL ANALYSIS

The data for the elemental analysis of the resulted β -sultones and their derivatives are shown below (Table XII). There is good agreement between the experimental and calculated values.

TABLE XII

ELEMENTAL ANALYSIS OF β -SULTONES AND THEIR DERIVATIVES

Compound		Calc.	Found
I. $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$			
	C	17.49	17.47
	F	55.30	54.80
	S	7.78	7.62
II. $\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2}\text{OSO}_2$			
	C	16.22	16.33
	F	51.30	50.80
	S	10.81	10.74
III. $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$			
	C	17.49	17.51
	F	55.30	55.60
	S	7.78	7.66

TABLE XII
ELEMENTAL ANALYSIS OF β -SULTONES AND THEIR DERIVATIVES
(continued)

Compound		Calc.	Found
IV. $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$			
	C	16.22	16.26
	F	51.30	51.40
	S	10.81	10.95
V. $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFHSO}_2\text{F}$			
	C	16.40	16.52
	H	0.28	0.27
	F	57.10	57.40
	S	8.76	8.81
VI. $\text{CF}_3\text{OCF}_2\text{CFHSO}_2\text{F}$			
	C	14.41	14.64
	H	0.40	0.43
	F	53.20	53.50
	S	12.82	12.79
VII. $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$			
	C	24.01	24.00
	H	1.12	1.04
	F	46.40	46.80
	S	7.12	7.28

TABLE XII
ELEMENTAL ANALYSIS OF β -SULTONES AND THEIR DERIVATIVES
(continued)

Compound		Calc.	Found
VIII. $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$			
	C	25.16	25.34
	H	1.51	1.54
	F	39.80	39.60
	S	9.59	9.43
IX. $[\text{CF}_3\text{OCF}_2\text{F}_4\text{OCF}_2(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{ }{\text{CH}}-\text{CH}_2-]_n$			
	C	24.01	-
	H	1.12	-
	F	46.40	-
	S	7.12	-
X. $[\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{ }{\text{CH}}-\text{CH}_2-]_n$			
	C	25.16	25.28
	H	1.51	1.55
	F	39.80	39.71
	S	9.59	9.23

INFRARED SPECTRA

The infrared spectral data for all new fluorinated β -sultones, fluorosulfonyl acylfluorides, fluorosulfonyl fluorides, fluoroallylic esters, and fluorosulfonyl polymers are compiled in the experimental section, and the spectra are reproduced in the appendix.

The infrared spectra of the new compounds have several common features. The compounds I through VI contain the asymmetric and symmetric SO_2 stretching vibrations at 1469-1449 and 1242-1220 cm^{-1} , respectively; these values are in good agreement with the other fluorinated β -sultones and their derivatives (16,24). The carbonyl stretching frequency for compounds III and IV is found in the 1883-1867 cm^{-1} region. The S-F stretching vibration of the fluorosulfonyl group in compounds III-VI is found near the 800 cm^{-1} region. The carbon-hydrogen vibrational bands are located in the 2992-2988 cm^{-1} region.

For the new monomeric and polymeric esters, VII-X, the frequencies and assignments are as follows: carbonyl stretching vibrations are found in 1792-1771 cm^{-1} region; the olefinic stretching frequencies for compounds VII and VIII are located at 1652 cm^{-1} . It is to be noted that for polymeric systems (compounds IX and X) the olefinic stretching vibration at 1652 cm^{-1} is absent. The sulfur-fluorine stretching of the fluorosulfonyl group in monomeric and polymeric systems is located near 800 cm^{-1} . The SO_2

asymmetric and symmetric vibrational frequencies for the compounds are found in the region 1458-1454 and 1237-1228 cm^{-1} region, respectively. The C-H vibrational bands for compounds VII-X are found in the region of 3100-2966 cm^{-1} .

In all cases these assignments are in excellent agreement with literature values (19,20,21).

NMR SPECTRA

The nmr chemical shifts and coupling constants for all of the new fluoroether derivatives are shown in Tables VIII through XVI and the spectra are reproduced in the appendix.

The ^{19}F nmr chemical shift values are summarized in Table XIII. The nonequivalent CF_2 fluorines in the sultones, I and II, are found in the -85.3 to -91.7 ppm range; for sultones such as $(\text{CF}_3)_2\text{CFOCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$, the CF_2 resonance bands are located at -82.4 and -89.5 ppm (42), while for other similar sultones, $\text{CF}_3\text{CF}_2\text{CF}_2\overline{\text{OCFCF}_2\text{SO}_2\text{O}}$ and $\text{C}_2\text{H}_5\text{OC}(\overline{\text{CF}_3\text{CF}_2\text{SO}_2\text{O}})$, the CF_2 resonance bands are located in the -84.1 to -100.5 ppm range (37). Generally, the range for nonequivalent CF_2 fluorines of fluorinated sultones is reported in the range -72.8 to -88.5 ppm (16,18,24,29,39). The CF resonance in the sultone ring is located at -154.7 and -135.9 ppm for compounds I and II, respectively; in other sultone systems such as $(\text{CF}_3)_2\text{CFOCF}(\text{O})\text{CF}(\text{SO}_2)\text{CF}_2\text{OSO}_2\text{F}$, the CF fluorine resonance is located at -151.8 and -149.0 ppm, respectively (44). The ^{19}F nmr resonance for the CF_3

group in all compounds consisted in general of a triplet in the range of -54.8 to -57.8 ppm. The ^{19}F nmr values for the following functional groupings or arrangements, $-\text{C}(\text{O})\text{F}$, $-\text{SO}_2\text{F}$, $-\text{CF}_2$, $-\text{OCF}_2\text{CFO}$, $-\text{CF}(\text{SO}_2\text{F})$ and $-\text{CFH}$, in compounds I to X are all in excellent agreement with literature values (16,18,24,29,39).

The ^1H nmr data (chemical shifts and coupling constants) for the new compounds are reported in Tables XV and XVI. The chemical shifts and coupling constants for the $-\text{CH}_2\text{CH}=\text{CH}_2$ moiety are in agreement with values reported for allyl alcohol and $\text{R}_f\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ derivatives (19,22,53). The proton nmr spectra for the polymeric esters IX and X showed, in general, broad peaks similar to that reported for other polymeric esters (22).

MASS SPECTRA

The major mass spectral peaks for these compounds are listed in the experimental section. The molecular ions were observed for compounds VII and VIII and the MH^+ peak found for compounds, I, II, IV, VI, VII and VIII. Additional M-X^+ or MH-X^+ peaks, such as a MH-F^+ , M-F^+ , M-OH^+ , $\text{M-SO}_2\text{F}^+$, $\text{M-CH}_3\text{O}^+$, were also found.

TABLE XIII

FLUORINE NMR CHEMICAL SHIFTS^{1,2,3,4}

	FSO ₂	C(O)F	CF ₃
I. CF ₃ OCF ₂ CF ₂ OCF ₂ $\overbrace{\text{CFCF}_2\text{OSO}_2}^{\text{ }}$	-	-	-58.4 (t)
II. CF ₃ OCF ₂ $\overbrace{\text{CFCF}_2\text{OSO}_2}^{\text{ }}$	-	-	-57.3 (t)
III. CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)F	52.8 (d, t, d)	31.6 (d, d, t)	-57.5 (t)
IV. CF ₃ OCF ₂ CF(SO ₂ F)C(O)F	55.6 (d, t, d)	34.6 (d, d, t)	-55.6 (t)
V. CF ₃ OCF ₂ CF ₂ OCF ₂ CFHSO ₂ F	53.9 (m)	-	-55.5 (t)
VI. CF ₃ OCF ₂ CFHSO ₂ F	51.5 (m)	-	-57.4 (t)
VII. CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	50.2 (d, t)	-	-57.8 (t)
VIII. CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	52.6 (d, t)	-	-54.8 (t)
IX. [CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ - $\overset{ }{\text{CH}}$ -CH ₂] _n	50.5 (br, m)	-	-57.3 (br, m)
X. [CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ - $\overset{ }{\text{CH}}$ -CH ₂] _n	49.8 (br, m)	-	-57.2 (br, m)

1. Fluorine chemical shifts in ppm from external CFCI₃.
2. d = doublet, t = triplet, m = multiplet, br = broadened.

TABLE XIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3,4}
(continued)

	CF ₂ ^a	F ₁	CF ₂ ^b	F ₂
I. CF ₃ OCF ₂ CF ₂ OCF ₂ $\overline{\text{CFCF}_2\text{OSO}_2}$	-79.5(m)	-85.3(d,d,t)	-91.7(d,t)	
II. CF ₃ OCF ₂ $\overline{\text{CFCF}_2\text{OSO}_2}$	-80.7(m)	-85.4(d,d,t)	-90.6(d,t)	
III. CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)F	-76.9(m)	-	-	
IV. CF ₃ OCF ₂ CF(SO ₂ F)C(O)F	-77.5(m)	-	-	
V. CF ₃ OCF ₂ CF ₂ OCF ₂ CFHSO ₂ F	-76.9(m)	-	-	
VI. CF ₃ OCF ₂ CFHSO ₂ F	-82.5(m)	-	-	
VII. CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	-77.6(m)	-	-	
VIII. CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	-77.8(m)	-	-	
IX. [CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ $\overset{ }{\text{CH}}\text{-CH}_2\text{-}]_n$	-76.9(br,m)	-	-	
X. [CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ $\overset{ }{\text{CH}}\text{-CH}_2\text{-}]_n$	-79.6(br,m)	-	-	

1. Fluorine chemical shifts in ppm from external CFCl₃.
2. d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened.
3. a = OCF_2CF , b = CFCF_2O

TABLE XIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3,4}
(continued)

	CF ₂ ^c	CF ₂ ^d	CF ^e
I. CF ₃ OCF ₂ CF ₂ OCF ₂ $\overline{\text{CFCF}_2\text{OSO}_2}$	-90.0 (m)	-93.2 (q)	-154.7 (d, t)
II. CF ₃ OCF ₂ $\overline{\text{CFCF}_2\text{OSO}_2}$	-	-	-153.9 (d, t)
III. CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)F	-90.3 (m)	-92.4 (q)	-161.0 (d, t, d)
IV. CF ₃ OCF ₂ CF(SO ₂ F)C(O)F	-	-	-160.1 (d, t, d)
V. CF ₃ OCF ₂ CF ₂ OCF ₂ CFHSO ₂ F	-89.0 (m)	-91.0 (q)	-
VI. CF ₃ OCF ₂ CFHSO ₂ F	-	-	-
VII. CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	-90.7 (m)	-92.7 (q)	-161.7 (d, t)
VIII. CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	-	-	-159.8 (d, t)
IX. [CF ₃ OCF ₂ CF ₂ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ - $\overset{ }{\text{CH}}$ -CH ₂ -] _n	-90.5 (br, m)	-92.6 (br, m)	-161.1 (br, m)
X. [CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ - $\overset{ }{\text{CH}}$ -CH ₂ -] _n	-	-	-161.4 (br, m)

1. Fluorine chemical shifts in ppm from external CFCl₃.

2. d = doublet, t = triplet, q = quartet, m = multiplet, br = broadened.

3. c = CF₃OCF₂CF₂, d = CF₃OCF₂CF₂, e = CF(SO₂).

4. The CFHSO₂F resonance is located at -190.2 (d, t, d), and 192.5 (d, t, d) ppm for compounds V and VI.

TABLE XIV
FLUORINE NMR COUPLING CONSTANTS

	Coupling Constants (Hz)
I. $\text{CF}_3(7) \text{OCF}_2(6) \text{CF}_2(5) \text{OCF}_2(4) \overbrace{\text{CF}(3) \text{CF}_2(1,2)}^{\text{OSO}_2}$	$J_{1,2} = 112.9$ $J_{2,4} = 12.7$ $J_{1,3} = 6.3$ $J_{3,4} = 7.7$ $J_{1,4} = 2.4$ $J_{6,7} = 9.4$
II. $\text{CF}_3(5) \text{OCF}_2(4) \overbrace{\text{CF}(3) \text{CF}_2(1,2)}^{\text{OSO}_2}$	$J_{1,2} = 112.9$ $J_{2,4} = 14.1$ $J_{1,3} = 6.6$ $J_{3,4} = 6.8$ $J_{1,4} = 2.8$ $J_{4,5} = 9.2$
III. $\text{CF}_3(7) \text{OCF}_2(6) \text{CF}_2(5) \text{OCF}_2(4) \text{CF}(3) (\text{SO}_2\text{F})_2 \text{C(O)F}(1)$	$J_{1,2} = 16.7$ $J_{2,4} = 6.5$ $J_{1,3} = 23.8$ $J_{3,4} = 8.2$ $J_{1,4} = 7.6$ $J_{6,7} = 9.9$ $J_{2,3} = 3.8$

TABLE XIV
FLUORINE NMR COUPLING CONSTANTS
(continued)

	Coupling Constants (Hz)
IV. CF_3 (5) OCF_2 (4) CF (3) (SO_2F) (2) $\text{C}(\text{O})\text{F}$ (1)	$J_{1,2} = 16.1$ $J_{2,3} = 4.0$ $J_{1,3} = 24.0$ $J_{3,4} = 8.0$ $J_{1,4} = 7.3$ $J_{4,5} = 9.4$
V. CF_3 (7) OCF_2 (6) CF_2 (5) OCF (4) CF (3) H (2) SO_2F (1)	$J_{1,2} = 2.0$ $J_{2,4} = 5.8$ $J_{1,3} = 6.6$ $J_{3,4} = 11.7$ $J_{2,3} = 44.6$ $J_{6,7} = 9.17$
VI. CF_3 (5) OCF_2 (4) CF (3) H (2) SO_2F (1)	$J_{1,2} = 2.1$ $J_{4,2} = 5.8$ $J_{1,3} = 5.9$ $J_{4,5} = 9.3$ $J_{3,2} = 45.2$

TABLE XIV
FLUORINE NMR COUPLING CONSTANTS
(continued)

	Coupling Constants (Hz)
VII. CF_3 OCF_2 CF_2 OCF_2 CF $\text{(SO}_2\text{F)}$ $\text{C(O)OCH}_2\text{CH=CH}_2$	
	$J_{1,2} = 4.2$ $J_{5,6} = 9.4$
	$J_{1,3} = 9.9$
	$J_{2,3} = 8.2$
VIII. CF_3 OCF_2 CF $\text{(SO}_2\text{F)}$ $\text{C(O)OCH}_2\text{CH=CH}_2$	
	$J_{1,2} = 4.0$ $J_{3,4} = 8.9$
	$J_{1,3} = 9.7$
	$J_{2,3} = 8.2$

TABLE XV

PROTON NMR CHEMICAL SHIFTS^{1,2,3,4,5,6,7}

	H _a	H _b	H _c	CH _{2d}
VII. CF ₃ OCF ₂ F ₄ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ (d) CH _(c) =CH ₂ (a,b)	5.56 (d,d,t)	5.65 (d,d,t)	6.04 (d,d,t)	5.10 (d,d,d)
VIII. CF ₃ OCF ₂ CF(SO ₂ F)C(O)OCH ₂ (d) CH _(c) =CH ₂ (a,b)	5.54 (d,d)	5.61 (d,d)	6.10 (d,t)	5.06 (d)

1. Proton chemical shifts in ppm downfield from external TMS.
2. d = doublet, t = triplet
3. In compounds VII and VIII, H_b and H_c are trans to each other.
4. For CF₃OCF₂CF₂OCF₂CF(SO₂F)C(O)OCH₂(-CH-CH₂-)_n, the spectrum contained a broad peak at 4.57 ppm and a series of peaks between 0.7 and 3.0 ppm.
5. For CF₃OCF₂CF(SO₂F)C(O)OCH₂(-CH-CH₂-)_n, the spectrum contained a broad peak at 4.55 ppm and a series of peaks between 0.7 and 3.5 ppm.
6. For CF₃OCF₂CF₂OCF₂CFHSO₂F, the CH chemical shift is 5.9 ppm.
7. For CF₃OCF₂CFHSO₂F, the CH chemical shift is 5.9 ppm.

TABLE XVI

PROTON NMR COUPLING CONSTANTS^{1,2}

	Coupling Constants (Hz)
VII. $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{(d)}\text{CH}^{\text{(c)}}=\text{CH}_2\text{(a,b)}$	$J_{a,b} = 1.3$ $J_{b,c} = 17.1$ $J_{a,c} = 10.4$ $J_{b,d} = 1.2$ $J_{a,d} = 1.2$ $J_{c',d} = 6.1$
VIII. $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{(d)}\text{CH}^{\text{(c)}}=\text{CH}_2\text{(a,b)}$	$J_{a,c} = 10.6$ $J_{b,c} = 17.7$ $J_{c,d} = 6.0$

1. The coupling constants for $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ were obtained with a General Electric QE-300 NMR Spectrometer. Thanks are expressed to Dr. David H. Peyton for obtaining the ^1H nmr spectrum of this compound.
2. $J_{b,c}$ is trans coupling.

CHAPTER VI

SYNTHESIS OF FLUOROSULFONYL ESTERS

In order to obtain precursors to new fluorinated sulfonic acids for use as fuel cell electrolytes, two fluorinated β -sultones, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ and $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$, were used to prepare a variety of new mono- and di-fluorosulfonyl esters. To meet this objective, two different routes were employed: the first method involved direct reaction of fluorinated β -sultones with fluorinated and non-fluorinated alcohols in the presence of dried NaF; the second method involved using $\text{AgOC(O)CF}_2\text{SO}_2\text{F}$, and will be discussed later.

Generally, treatment of the fluorinated β -sultones with different nucleophiles such as amines, mercaptans, alcohols, hydrogen sulfide and carboxylic acids, gives rise to the corresponding derivatives of fluorosulfonylfluoroacetic acid. In this process, the fluoro sultone isomerizes to a linear α -fluorosulfonyl polyfluoroacyl fluoride which finally acylates the nucleophile to give different derivatives of fluorosulfonylfluoroacetic acid, $\text{R}_f\text{CF}(\text{SO}_2\text{F})\text{C(O)Nu}$ (11,18,32,56).

where Nu = NH_2- , $\text{RS}-$, $\text{RO}-$, $\text{HS}-$, and RC(O)O ; R_f = could be

any fluorinated radicals.

In the case where the nucleophile is an alcohol, the final product will be a fluorosulfonyl ester. As mentioned in Chapter II, in the ester formation, the dried NaF serves not only as a catalyst for the rearrangement of the β -sultone to the acid fluoride form but reacts with the HF by product (19,20,21,22):

The resulting acid fluoride reacts with alcohols, in the presence of dried NaF, forming the corresponding ester and NaHF_2 :

where R = any radicals.

The reactions of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ and $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$ with polyfluoro/perfluoro alcohols and hydrocarbon alcohols provided a convenient route to the following fluorosulfonyl esters:

where $\text{R}_f = \text{CF}_3\text{CH}_2$, and $(\text{CF}_3)_2\text{CH}$

With a fluorinated bis-alcohol and $\text{SF}_5\overline{\text{CFCF}_2}\text{OSO}_2$ the following diester was produced:

The syntheses of the above fluorosulfonyl esters were carried out in a 100 to 125 ml Pyrex-glass reaction vessel at 40-70°C for 5-24 days. The purification of these esters was done through fractional distillation, which was performed either at reduced pressure or atmospheric pressure. The elemental analyses confirmed the molecular formulas for all new fluorosulfonyl esters produced from $\overline{\text{CF}_2\text{CF}_2}\text{OSO}_2$ and $\text{SF}_5\overline{\text{CFCF}_2}\text{OSO}_2$, except for the diester, $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$, in which analyses were off by a small factor (see p. 123) due to the presence of trace amount of fluoride ion (NaF and HF).

It is known that the silver salt of fluorocarboxylic acids can be used to prepare fluorinated esters through its reactions with alkyl iodides (57). Therefore, a method was developed for the preparation of fluorosulfonyl esters via the silver salt route in which the new $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ salt was treated with a series of alkyl halides. Thus, the silver salt of difluoro(fluorosulfonyl)acetic acid was prepared from $\overline{\text{CF}_2\text{CF}_2}\text{OSO}_2$ according to the following route:

The resulting silver difluorosulfonyl acetate is a white solid and sensitive to light. It is soluble in water at room temperature.

The silver salt can be used to prepare fluorosulfonyl esters via its reactions with different alkyl bromides or iodides:

where R = $\text{BrCH}_2\text{CH}_2-$, $\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{CH}_2-$, $\text{CH}_2=\text{CHCH}_2-$

While it was not possible to replace both bromines in $\text{BrCH}_2\text{CH}_2\text{Br}$, replacement of both iodines in CH_2I_2 was observed:

Generally, these esters were synthesized in a 90 to 150 ml Pyrex-glass reaction vessel; the silver salt was added to the reaction vessel under an atmosphere of nitrogen. The iodo- and bromo- alkyl derivatives were added either through vacuum transfer or directly added in a dry box while the reaction vessel was kept at -196°C . The reaction vessels were protected from light and allowed to warm slowly to room temperature over a period of 24 h. The purification of the resulting fluorosulfonyl esters was done either by trap-to-trap distillation, direct transfer from the reaction vessel, or fractional distillation. The elemental analyses confirmed the molecular formulas for all

new esters obtained from this route, except for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$, which gave C, 29.97; H, 4.52; F, 8.90; S, 8.10 (theor. C, 27.28; H, 2.67; F, 21.57; S, 12.4). These results are attributed to the decomposition of the ester over a period of time.

The new sulfonyl fluoride esters, either from the β -sultone method or the silver salt route, are clear and colorless liquids.

EXPERIMENTAL

Synthesis of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$

Into a 130 mL Pyrex-glass Carius tube equipped with a Kontes Teflon valve was added 224 mmol of trimer SO_3 . The Carius tube was heated for 2 h at $125 \pm 5^\circ\text{C}$ in order to monomerize the trimer SO_3 . The monomer SO_3 was then exposed to one atmospheric pressure of gaseous $\text{CF}_2=\text{CF}_2$ at room temperature with agitation for 2 h. Distillation of the mixture gave 178 mmol of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ in 82.4% yield; b.p. 42.5°C .

Synthesis of $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$

Into the same Carius tube previously described were added 77.0 mmol of trimer SO_3 and 89.7 mmol of $\text{SF}_5\text{CF}=\text{CF}_2$. The mixture was heated for 72 h at $110 \pm 5^\circ\text{C}$. Distillation gave 47.5 mmol of $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$ in 61.7% yield; b.p. 88.0°C .

Synthesis of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$

$\text{CF}_2\text{CF}_2\text{OSO}_2$ with H_2O . Into a 40 mL Kel-F vessel equipped with a Teflon stirring bar was added 55.5 mmol of $\text{CF}_2\text{CF}_2\text{OSO}_2$. The reaction vessel was cooled to 0°C and 66.7 mmol of distilled H_2O was added dropwise over a period of 1.5 h. The mixture was magnetically stirred at room temperature overnight. Distillation gave 40.5 mmol of $\text{FSO}_2\text{CF}_2\text{COOH}$ in 73.0% yield; b.p. $91\pm 1^\circ\text{C}/51\text{ mm}$.

$\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OH}$ with Ag_2O . To a 200 mL Pyrex-glass three neck reaction vessel equipped with a reflux condenser and containing a Teflon stirring bar, were added 19.5 mmol of Ag_2O and 25 mL diethyl ether. The 200 mL reaction vessel was covered with aluminum foil and 37.8 mmol of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OH}$ was added slowly with stirring over a period of 0.75 h; stirring was continued for an additional 15 h at room temperature. The mixture was then filtered and pumped on through a trap cooled to -196°C . The salt, $\text{FSO}_2\text{CF}_2\text{CO}_2\text{Ag}$ (15.4 mmol), was dried by pumping under vacuum line for 6 days. The yield was 82%, mp $159\pm 1^\circ\text{C}$ with dec.

The infrared spectrum had the following bands (cm^{-1}): 1708(s), 1687(s, with sh. 1652), 1427(s), 1384(m), 1230(m), 1180(ms, sh. at 1138), 998(m, sh. at 955), 899(w), 843(m), 808(m, sh. at 787, 752), 738(wm), 716(wm), 649(m), 604(m), 562(w), 541(w), 484(wm), 456(wm).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.2) and CF_2 (2.0).

Synthesis of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OC}_6\text{F}_5$

Into a 100 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 35.71 mmol of dried NaF, 14.20 mmol of $\text{C}_6\text{F}_5\text{OH}$, and 10.86 mmol of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$. The mixture was stirred magnetically for 6 h at 55-70°C. Distillation of the volatile material gave 5.10 mmol of $\text{C}_6\text{F}_5\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$ in 47% yield; b.p. 102.5±0.5°C/40 mm.

The infrared spectrum had the following bands (cm^{-1}): 1820(ms), 1650(w), 1522(vs), 1457(s), 1290(m), 1234(ms), 1210(m), 1150(m), 1123(ms), 1011(ms), 1000(ms), 976(m, sh. at 953), 861(w), 812(m,br), 728(vw), 709(vw), 659(w), 621(m), 591(w), 557(wm), 487(w), 466(w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), CF_2 (1.9), ortho (2.0), meta (2.0), and para (1.0).

Synthesis of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$

Into a 100 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 116.7 mmol of dried NaF, 13.9 mmol of $\text{CF}_3\text{CH}_2\text{OH}$, and 13.5 mmol of $\overline{\text{SF}_5\text{CFCF}_2\text{OSO}_2}$. The mixture was stirred for 5 days at 40-50°C. Distillation of the mixture gave 10.35 mmol of the ester, $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$, in 76.45% yield; b.p. 88°C/101 mm.

The infrared spectrum had the following bands (cm^{-1}): 3051(vw), 2995(vw), 1806(s), 1455(s), 1413(m), 1321(s),

1293(s), 1259(s), 1230(s), 1195(vs), 1166(vs), 1054(m), 1026(w), 991(m), 977(m), 955(m), 927(s), 913(vs), 892(vs), 871(vs), 850(s), 808(ms), 787(s), 681(m), 667(m), 653(m), 646(m), 639(m), 611(ms), 597(s), 576(s), 534(w), 520(vw), 491(wm), 477(w), 438(wm).

The ^{19}F nmr spectrum gave the following relative peak areas: SF (0.9), SF_4 (4.0), SO_2F (1.1), CF (1.0), and CF_3 (3.0).

The positive ion (CI^+) mass spectrum (m/e, species): 369, $\text{M}+\text{H}^+$; 349, $\text{M}-\text{F}^+$; 127, SF_5^+ or FSCSO_2^+ or $\text{OCH}_2\text{CF}_3^+$; 89, SF_3^+ ; 83, SO_2F^+ or CF_3CH_2^+ ; 69, CF_3^+ ; 67, SOF^+ ; 64, SO_2^+ ; 63, CFS^+ .

Synthesis of $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$

Into a 100 mL Pyrex-glass reaction vessel containing a Teflon-coated stirring bar, were added 115.2 mmol of dried NaF , 9.25 mmol of $\text{HOCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH}$, and 23.8 mmol of $\text{SF}_5\text{CFCF}_2\text{OSO}_2$. The mixture was stirred for 4 days at 40-50°C and 5 days at 60-70°C. Distillation of the mixture gave 7.29 mmol of $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$ in 78.9% yield; b.p. 152°C/15 mm.

The infrared spectrum had the following bands (cm^{-1}): 3044(w), 2988(w), 1806(vs), 1785(vs), 1462(vs), 1406(m), 1286(vs), 1272(vs), 1237(vs), 1216(vs), 1202(s), 1181(s), 1159(s), 1124(s), 1103(m), 1082(w), 1054(m), 1019(w), 977(ms), 963(ms), 934(vs), 899(vs), 878(vs), 865(vs), 850(vs), 815(vs), 801(vs), 779(vs), 766(s), 738(w), 731(w),

716(w), 709(vw), 695(m), 681(m), 674(m), 667(m), 646(w), 618(s), 597(s), 582(s), 569(s), 550(w), 541(m), 527(w), 513(vw), 491(m), 470(w), 456(w), 435(w), 414(w).

The ^{19}F nmr spectrum have the following relative peak areas: SF (0.9), SF_4 (4.0), SO_2F (1.0), CF (1.0), and CF_2 (2.1 for CF_2 external and 1.0 for CF_2 internal).

The positive ion (CI^+) mass spectrum (m/e, species): 621, M-SF_5^+ ; 269, $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}^+$; 143, $\text{C}_3\text{C}(\text{O})\text{OCFS}^+$; 175, $\text{CH}(\text{CF}_2)_3\text{C}^+$; 127, SF_5^+ ; 113, SF_2CFC^+ ; 95, CSO_2F^+ ; 89, SF_3^+ ; 83, SO_2F^+ ; 69, $\text{C}(\text{O})\text{OCHC}^+$; 67, SOF^+ ; 65, C_4HO^+ ; 64, SO_2^+ ; 51, SF^+ ; 48, SO^+ ; 41, COCH^+ .

Synthesis of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$

Into a 100 mL Pyrex-glass reaction vessel containing a Teflon-coated stirring bar and 102.1 mmol of dry NaF were added 138.2 mmol $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$ and 140.5 mmol $(\text{CF}_3)_2\text{CHOH}$. The mixture was heated for 24 days at 40–50°C. Distillation of the mixture gave 107.6 mmol of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$ in 77.5% yield; b.p. 124±2C/455 mm.

The infrared spectrum had the following bands (cm^{-1}): 2988(w), 1813(s), 1469(s), 1462(s), 1384(s), 1363(ms), 1300(s), 1258(vs), 1237(vs), 1209(vs), 1166(s), 1117(vs), 1082(m), 1061(wm), 998(w), 997(mw), 948(m), 906–892(vs, b), 857(s), 822(m), 787(s), 730(m), 688(s), 660(w), 625(mw), 583(s), 576(s), 548(w), 527(w), 512(w), 491(w), 470(w), 428(w).

The ^{19}F nmr spectrum gave the following relative peak

areas: SF (1.0), SF₄ (3.6), FSO₂ (1.0), and CF₃ (6.0).

The positive ion (CI⁺) mass spectrum (mass, species): 290, SF₂CCOCC₂⁺; 225, SF₅CF(SOF)⁺; 195, FSO₂CFC(O)OCHC₂⁺; 151, CH(CF₃)₂⁺ or SF₅C₂⁺; 131, C₂O₂CHC₂F₄⁺; 89, SF₃⁺; 79, CFSO⁺; 78, OC₂F₂⁺; 70, SF₂⁺; 69, CF₃⁺; 67, SOF⁺; 64, SO₂⁺; 51, SF⁺; 50, CF₂⁺; 48, SO⁺.

Synthesis of SF₅CF(SO₂F)C(O)OCH₂CH=CH₂

Into a 125 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 114.8 mmol of anhydrous sodium fluoride, 22.6 mmol allyl alcohol, and 21.4 mmol of SF₅ $\overline{\text{CFCF}_2\text{OSO}_2}$. This mixture was magnetically stirred for 5 days at room temperature and 9 days at 40-50°C. Distillation of the volatile material gave 15.0 mmol of SF₅CF(SO₂F)C(O)OCH₂CH=CH₂ in 70% yield; b.p. 103±1C/74 mm.

The infrared spectrum had the following bands (cm⁻¹): 3100(vw), 2995(w), 2966(w), 1792(s), 1652(w), 1455(s), 1348(w), 1279(s), 1258(m), 1230(s), 1166(s), 1082(w), 1019(w), 991(w), 934(m), 885(vs), 850(s), 808(m), 780(m), 674(m), 668(w), 618(m), 597(s), 576(s), 491(m), 456(w), 421(w).

The ¹⁹F nmr spectrum gave the following relative peak areas: SF (1.4), SF₄ (4.0), SO₂F (1.0), and CF (1.0). The relative band areas in ¹H nmr spectrum were: C₂H₃ (3.1), and CH₂ (2.0).

The positive ion (CI⁺) mass spectrum (m/e, species):

326, M^+ ; 243, $M-SO_2F^+$; 199, $M-SF_5^+$; 186, SF_5CFCO^+ ; 143, $FSCO_2C_4^+$; 127, SF_5^+ ; 116, $M-SF_5SO_2F^+$; 108, SF_4^+ ; 101, SF_3C^+ ; 91, $SCFCO^+$; 89, SF_3^+ ; 85, $CO_2C_3H_5^+$; 83, $CO_2C_3H_3^+$, SO_2F^+ ; 71, $CFCOC^+$; 70, SF_2^+ ; 69, $C_3H_5CO^+$; 67, SOF^+ , $C_4H_3O^+$; 65, C_4HO^+ ; 64, C_4O , SO_2^+ ; 63, FSC^+ ; 59, $CFCO^+$; 57, $C_3H_5O^+$; 56, $C_3H_4O^+$; 55, $C_3H_3O^+$; 51, SF^+ ; 48, SO^+ ; 44, CS^+ , CO_2^+ ; 42, $C_2H_2O^+$; 41, $C_3H_5^+$.

Synthesis of $FSO_2CF_2C(O)OCH_2CH_2Br$

Into a 100 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve, were added 21.73 mmol of $FSO_2CF_2C(O)OAg$ and 10.0 mmol $BrCH_2CH_2Br$. The mixture was protected from light and warmed slowly to room temperature in 24 h. Trap-to-trap distillation of the mixture gave 3.51 mmol of the ester $FSO_2CF_2C(O)OCH_2CH_2Br$ at $-196^\circ C$ trap in 35% yield.

The infrared spectrum had the following bands (cm^{-1}): 2959(vw), 2917(w), 2854(w), 1792(s), 1448(s), 1384(w), 1314(s), 1279(m), 1237(s), 1188(s), 1152(s), 1068(w), 1012(m), 976(w), 948(vw), 927(vw), 843(m), 808(s,b), 723(vw), 646(ms), 611(m), 590(ms), 484(w), 456(w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0) and CF_2 (2.0). The relative band areas for 1H nmr the spectrum were: CH_2 (1.0) and CH_2 (1.0).

The positive ion (CI^+) mass spectrum (m/e, species): 267, $M-FH^+$; 205, $M-Br^+$; 153, $CO_2C_2H_4Br^+$ or $FSCF_2C_3O^+$; 151, $CO_2C_2H_4Br^+$ or $CO_2C_2H_2Br^+$; 149, $CO_2C_2H_2Br^+$ or $CO_2C_2Br^+$; 141,

$\text{FSCF}_2\text{C}_2\text{O}^+$; 135, $\text{SCF}_2\text{C}_3\text{HO}^+$ or $\text{C}_3\text{H}_4\text{OBr}^+$ or $\text{C}_3\text{H}_2\text{OBr}^+$; 133, $\text{FSO}_2\text{CF}_2^+$ or C_3OBr^+ or $\text{C}_3\text{H}_2\text{Br}^+$; 123, $\text{OC}_2\text{H}_2\text{Br}^+$ or $\text{OC}_2\text{H}_4\text{Br}^+$; 122, $\text{OC}_2\text{H}_3\text{Br}^+$ or OC_2HBr^+ ; 121, OC_2Br^+ ; 119, OC_2Br^+ or $\text{SC}_4\text{FH}_4\text{O}^+$; 113, FSCF_2C^+ ; 110, $\text{SC}_2\text{F}_2\text{O}^+$; 109, $\text{C}_2\text{H}_4\text{Br}^+$; 108, $\text{C}_2\text{H}_3\text{Br}^+$ or $\text{CF}_2\text{C}_2\text{O}_2\text{H}_2^+$; 107, $\text{C}_2\text{H}_4\text{Br}^+$ or $\text{C}_2\text{H}_2\text{Br}^+$ or FSO_2C_2^+ or $\text{CF}_2\text{CO}_2\text{CH}^+$; 106, $\text{C}_2\text{H}_3\text{Br}^+$ or C_2HBr^+ or $\text{CF}_2\text{C}_2\text{O}_2^+$; 103, SC_3FO^+ or C_2Br^+ ; 101, FSCF_2^+ ; 99, $\text{SC}_2\text{OC}_2\text{H}_4^+$.

Synthesis of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$

Into a 100 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 12.4 mmol of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ and 12.6 mmol $\text{BrCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$. The volatile material was removed at -78°C . The remaining liquid, 10.9 mmol of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$, was collected at -196°C in 88% yield.

The infrared spectrum had the following bands (cm^{-1}): 2988(wm), 1792(s), 1757(s), 1448(s), 1434(m), 1398(wm), 1384(m), 1363(mw), 1314(m), 1279(m), 1223(s, sh at 1237), 1202(s), 1152(s), 1096(w), 1068(wm), 1047(m), 1026(m), 970(w), 864(w), 829(m), 808-794(ms, b), 723(w), 646(m), 604(wm), 569(wm).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), and CF_2 (2.0). The relative band areas for ^1H nmr spectrum were: CH_2 (2.0), CH_2 (2.0), and CH_3 (3.0).

The positive ion (CI^+) mass spectrum (m/e, species): 265, MH^+ ; 239, M-FH_7^+ ; 237, $\text{MH}_2\text{-C}_2\text{H}_5^+$; 220, $\text{FSO}_2\text{C}_6\text{O}_4\text{H}^+$;

219, $\text{M-OC}_2\text{H}_5^+$; 191, $\text{FSO}_2\text{CF}_2\text{CO}_2\text{CH}_2^+$; 155, $\text{FSCF}_2\text{C}_3\text{H}_2\text{O}^+$; 153, $\text{FSCF}_2\text{C}_3\text{O}^+$; 108, $\text{CF}_2\text{C}_2\text{H}_2\text{O}_2^+$; 97, C_4SHO^+ ; 87, $\text{C}_4\text{H}_7\text{O}^+$; 80, C_4O^+ ; 78, $\text{C}_2\text{F}_2\text{O}^+$; 67, $\text{C}_4\text{H}_3\text{O}^+$ or FSO^+ ; 65, C_4OH^+ ; 59, C_2FO^+ ; 57, $\text{C}_2\text{O}_2\text{H}^+$.

Synthesis of $[\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{O}]_2\text{CH}_2$

To the same reaction vessel previously described, 19.51 mmol $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ and 9.70 mmol CH_2I_2 were added. The mixture was magnetically stirred for 7 days at room temperature. Distillation of the volatiles gave 6.20 mmol of $(\text{FSO}_2\text{CF}_2\text{CO}_2)_2\text{CH}_2$ in 64% yield; b.p. $63^\circ\text{C}/100\ \mu$.

The infrared spectrum had the following bands (cm^{-1}): 3079(vw), 3009(vw), 1813(s), 1455(vs), 1321(m), 1286(m), 1237(s), 1209(ms), 1166(s), 1117(s), 1054(m), 1033(m), 998(ms), 963(m), 822(ms), 808(ms), 723(w), 653(m), 604(m with sh at 562), 513(vw), 491(w), 423(w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), and CF_2 (2.0).

The positive ion (CI^+) mass spectrum (m/e, species): 369, MH^+ ; 193, $(\text{MH}_2-\text{OCOCF}_2\text{SO}_2\text{F})^+$; 192, $(\text{MH}-\text{OCOCF}_2\text{SO}_2\text{F})^+$; 191, $(\text{M}-\text{FSO}_2\text{CF}_2\text{COO})^+$; 177, $\text{FSO}_2\text{CF}_2\text{COO}^+$; 161, $\text{FSO}_2\text{CF}_2\text{CO}^+$; 133, $\text{COOCH}_2\text{COOCF}^+$; 132, $\text{CFCOCH}_2\text{OCCF}^+$; 127, CFCOOCOC^+ ; 111, CFCOCOC^+ ; 109, CCOOCHOC^+ ; 107, $\text{CF}_2\text{COOCH}^+$; 105, SCFCOCH_2^+ ; 103, CFCOOCO^+ ; 101, $\text{CFCOCH}_2\text{OC}^+$; 100, CFCOCHOC^+ ; 99, CFCOCOC^+ ; 98, FSOCF^+ ; 97, CCOOCHOC^+ ; 96, CCOOCOC^+ ; 95, FSO_2C^+ ; 94, CF_2COO^+ ; 91, SCFCO^+ ; 87, CFCOOC^+ ; 85, SCCOCH^+ ; 83, SO_2F^+ ; 81, CCOCHOC^+ ; 80, CCOCOC^+ ; 79, FSOC^+ ; 78,

CF_2CO^+ ; 75, CFCOO^+ ; 71, CFCOC^+ ; 70, CCOOCH_2^+ ; 69, CCOOCH^+ ; 68, CCOOC^+ ; 67, SOF^+ ; 64, SO_2^+ , 100; 63, SFC^+ ; 62, CF_2C^+ .

Synthesis of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

The above compound was synthesized via two different methods, first was through usage of $\text{CF}_2\text{CF}_2\text{OSO}_2$ and $\text{CH}_2=\text{CHCH}_2\text{OH}$ and the second method was via reaction of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ and $\text{BrCH}_2\text{CH}=\text{CH}_2$.

1. Into a 100 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 122.5 mmol of anhydrous sodium fluoride, 22.3 mmol of allyl alcohol, and 22.4 mmol of $\text{CF}_2\text{CF}_2\text{OSO}_2$. This mixture was magnetically stirred for 6 days at room temperature and then heated at 40-50°C for 18 d. Distillation of the volatile material gave 15.4 mmol of $\text{FSO}_2\text{CF}_2\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$ in 69% yield; b.p. 141-142°C.

The infrared spectrum had the following bands (cm^{-1}): 3100(w), 3037(w), 2995(w), 1785(vs), 1652(w), 1448(s), 1370(m), 1314(s with sh. at 1293), 1237(s), 1195(s), 1152(s), 1082(w), 1041(wm), 1019(m), 991(m), 977(w), 941(m), 899(wm), 829(s), 801(s), 723(w), 680(w), 656(w), 646(m), 597(wm), 569(m), 526(w), 484(w), 456(w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), and CF_2 (2.0). The relative band areas for ^1H nmr spectrum were: C_2H_3 (3.1), and CH_2 (2.0).

The positive ion (CI^+) mass spectrum (m/e, species): 218, M^+ ; 135, $\text{M-SO}_2\text{F}^+$; 134, $\text{M-SO}_2\text{FH}^+$; 133, $\text{M-SO}_2\text{FH}_2^+$, M-

$\text{CO}_2\text{C}_3\text{H}_5^+$; 106, $\text{CF}_2\text{COC}_2\text{H}_4^+$; 85, $\text{CO}_2\text{C}_3\text{H}_5^+$; 84, $\text{CO}_2\text{C}_3\text{H}_4^+$; 83, $\text{CO}_2\text{C}_3\text{H}_3^+$, SO_2F^+ ; 79, SOFC^+ ; 78, CF_2CO^+ ; 69, $\text{C}_4\text{H}_5\text{O}^+$; 67, $\text{C}_4\text{H}_3\text{O}$, SOF^+ ; 64, SO_2^+ ; 57, OC_3H_5^+ ; 56, $\text{C}_3\text{H}_5\text{O}^+$; 55, $\text{C}_3\text{H}_3\text{O}^+$; 51, SF^+ ; 48, SO^+ ; 44, CS^+ , CO_2^+ ; 43, $\text{C}_2\text{H}_3\text{O}^+$; 42, OCH_2C^+ ; 41, C_3H_5^+ .

2. To the reaction vessel previously described were added 16.72 mmol $\text{BrCH}_2\text{CH}=\text{CH}_2$ and 16.49 mmol $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$. Distillation of the product gave 11.2 mmol of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ in 67% yield; b.p. 141-142°C. The infrared, ^{19}F nmr and ^1H nmr chemical shift spectral data agreed with that previously reported in the first method for this ester.

ELEMENTAL ANALYSIS

The elemental analyses of fluorinated esters containing the sulfonyl fluoride grouping and prepared by the β -sultone or the silver salt methods are tabulated below (Table XVII). The agreement between the calculated and experimental values was excellent except for two esters, $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$ and $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$.

TABLE XVII
ELEMENTAL ANALYSIS OF FLUORINATED ESTERS

Compound	Calc.		Found
I. $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$			
	C	8.43	8.74
	F	20.00	20.50
	S	11.25	11.35
	Ag	37.86	37.51
II. $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OC}_6\text{F}_5$			
	C	27.92	27.86
	F	44.20	44.90
	S	9.32	9.37
III. $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$			
	C	13.04	13.09
	H	0.54	0.55
	F	51.60	52.30
	S	17.39	17.14
IV. $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$			
	C	14.44	14.67
	H	0.54	0.46
	F	50.70	50.60
	S	17.14	15.90

TABLE XVII
ELEMENTAL ANALYSIS OF FLUORINATED ESTERS
(continued)

Compound		Calc.	Found
V. $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$			
	C	13.70	13.90
	H	0.23	0.34
	F	56.60	57.20
	S	17.42	17.14
VI. $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$			
	C	18.41	18.56
	H	1.54	1.41
	F	40.77	41.10
	S	19.66	19.48
VII. $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{Br}$			
	C	16.86	16.68
	H	1.41	1.60
	F	20.00	20.30
	S	11.25	11.20
	Br	28.03	28.02
VIII. $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$			
	C	27.28	29.97
	H	2.67	4.52
	F	21.57	8.90
	S	12.14	8.10

TABLE XVII
ELEMENTAL ANALYSIS OF FLUORINATED ESTERS
(continued)

Compound	Calc.		Found
<hr/>			
IX. $[\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{O}]_2\text{CH}_2$			
	C	16.31	16.42
	H	0.55	0.54
	F	31.00	30.80
	S	17.41	17.26
X. $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$			
	C	27.53	27.58
	H	2.31	2.36
	F	26.10	26.50
	S	14.69	14.52

INFRARED SPECTRA

The infrared spectral data for all fluorinated esters containing the sulfonyl fluoride group are shown in the experimental section, and the spectra are also shown in the appendix. These sulfonyl fluoride esters have several features in common: the stretching frequency for the carbonyl group adjacent to CF_2 is found in the 1785-1834 cm^{-1} region; for the carbonyl group next to the CH_2 group the corresponding frequency is located at 1757 cm^{-1} . These values are in good agreement with other fluorinated esters (19,22,57,58,59). In the silver salt, $\text{FSO}_2\text{CF}_2\text{C(O)OAg}$, the carbonyl frequency is found at 1708 cm^{-1} ; while in CF_3COOAg , this stretching frequency is located at 1720 cm^{-1} (60).

In all sulfonyl fluoride esters, as well as the silver salt, the asymmetric and symmetric SO_2 stretching frequencies are assigned to the 1427-1469 cm^{-1} region and 1209-1259 cm^{-1} region, respectively. The above assignment for the SO_2 group agrees closely with that found for other fluorosulfonyl derivatives (19,20,22). The intense S-F absorption band is located, as expected, near the 800 cm^{-1} region (19,20,22). For compounds containing a C-F group and a CF_3 group, the C-F stretching vibration is usually located in the 1000-1200 cm^{-1} region while marked absorption in the range 1230-1390 cm^{-1} can be correlated with the CF_3 group (61). For the SF_5 containing esters, the absorption band,

in the 815-913 cm^{-1} region, assigned to the S-F stretching vibrations. The S-F deformation modes are found near 600 cm^{-1} . These assignments are in good agreement with the reported values in the literature (62).

The infrared spectra of the hydrogen containing esters have C-H absorption bands in the 2960-3100 cm^{-1} region. The C=C stretching frequency is located near the 1650 cm^{-1} region.

NMR SPECTRA

The nmr chemical shifts and coupling constants for all of the fluorosulfonyl esters are presented in Tables XVIII through XXI and the spectra are reproduced in the appendix. In some cases, the coupling constants were not calculated due to the complexity of the splitting patterns (second-order effects). Fluorine chemical shifts and proton chemical shifts are reported in ppm from CFCl_3 and downfield from TMS, respectively.

The ^{19}F nmr spectra of all reported esters exhibit several common features. The chemical shifts for the FSO_2 -group range from 38.0 to 49.6 ppm. The SF_5 -group appears as an AB_4 pattern in all SF_5 -containing esters, with the axial-SF appearing as a nine-line pattern and the equatorial $-\text{SF}_4-$ as a complex doublet. Line 6 was used as the band center for the axial $-\text{SF}$, while the midpoint of the doublet for the $-\text{SF}_4-$ position was used as its band center. The chemical

shifts of the AB₄ pattern of these esters range from 61.5-64.3 (A) and 56.3-57.2 (B) ppm. The chemical shifts for the SF₅ group in all esters fall within the expected range (51,63). The CF₃ group is found in the range of -75.2 to -76.2 ppm in SF₅-containing esters. The chemical shifts of the CF₂ group of the fluorosulfonyl esters that resulted from the $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ sultone are located between -100.9 to -109.0 ppm and in the case of [SF₅CF(SO₂F)CH₂CF₂]₂CF₂ the CF₂ falls in the range of -121.3 to -127.0 ppm. In all esters, the CF group chemical shift range is -119 to -123.5 ppm. The resulted chemical shifts for CF₃, CF₂ and CF groups are consistent with those reported in the literature (18,29,39,64). The resonance signals for the C₆F₅ group (ortho, para, and meta) of FSO₂CF₂COOC₆F₅ are found at -155.7, -159.2, and -166.7 ppm, and are in good agreement with other perfluorophenyl systems (65,66).

The ¹H nmr spectra for all esters were self consistent with respect to the expected chemical shifts for CH and CH₂ groups. In monosubstituted esters that were prepared from FSO₂CF₂COOAg, the proton nmr spectra gave splitting patterns similar to the starting alkyl bromide; for the diester prepared from CH₂I₂, a peak at 6.53 ppm was found (CH₂). The spectrum of FSO₂CF₂C(O)OCH₂CH₂Br contained peaks at 3.98 ppm (CH₂Br) and 5.13 ppm (OCH₂). The chemical shifts for the -CHCH₂=CH₂ moiety are in agreement with values reported for allyl alcohol esters (17,20). For the SF₅

containing mono- and diesters that were prepared from $(\text{CF}_3)_2\text{CHOH}$, $\text{CF}_3\text{CH}_2\text{OH}$, and $(\text{HOCH}_2\text{CF}_2)_2\text{CF}_2$ resonance peaks at 6.25, 4.97, and 5.22 ppm were found, respectively.

The fluorine-fluorine and fluorine-proton coupling constants in the new sulfonyl fluoride esters are self consistent. In the esters that were prepared from $\text{SF}_5\text{CFCF}_2\text{OSO}_2$, the coupling constants for the $\text{SF}_{(\text{ax})}$ to $\text{SF}_{4(\text{eq})}$ fluorines are in the range of 136-141 Hz; by comparison, the ester $\text{SF}_5\text{CF}(\text{CF}_3)\text{COOCH}_3$ has a $J_{1,2}=144$ Hz (51). The sulfonyl fluoride grouping (SO_2F) vicinal to the $\text{SF}_{4(\text{ax})}$ have values ranging from $J_{2,4}=9.2$ to 11.6 Hz. In these esters the $J_{1,3}$ and $J_{2,3}$ values are the same, ≈ 3.0 Hz. The coupling $J_{5,6}$ in SF_5 containing esters III-V vary considerably, 7.4, 5.6 and 12.0 Hz, respectively. These values reflect the differences in structure with different group attachments to the SF_5CF moiety.

Esters derived from $\text{CF}_2\text{CF}_2\text{OSO}_2$ show similar trends in their coupling constants based on their structural differences as a result of different group attachments. The coupling constants for the sulfonyl fluoride group (see Table XX) range from 5.3-5.5 Hz for compounds VII to X. $J_{1,2}$, the couplings in compounds I and II are found to be 3.5 and 6.3, respectively and are due to the attachments of the more negative C_6F_5 and more positive Ag to the $\text{FSO}_2\text{CF}_2\text{COO}$ moiety. The J values for the C_6F_5 group ($J_{\text{o-p}}$, $J_{\text{m-o}}$, and $J_{\text{m-p}}$) are found to be 24.6, 12.7 and 12.9 Hz. The

coupling constants for the CH_2 groups and CH_2 to CH_3 in compounds VII and VIII are found to be 6.0 and 7.2 Hz, respectively. The proton couplings of the allyl group in the fluorosulfonyl esters VI and X are shown in Table XXI. The resulted couplings are in good agreement with literature (25,26).

MASS SPECTRA

The mass spectra of all fluorosulfonyl esters are reported in the experimental section. There are similar fragments in the fluorosulfonyl esters derived from $\text{SF}_5\text{CFCF}_2\text{OSO}_2$ and $\text{CF}_2\text{CF}_2\text{OSO}_2$ sultones. These similarities are more apparent in the lower molecular weight fragments. The molecular ions (M^+) are observed for compounds VI and X, while for compounds VIII and IX and VII the MH^+ fragments are found. Fragments at m/e values of 127 (SF_5)⁺, 89 (SF_3)⁺, 70 (SF_2)⁺, and 51 (SF)⁺ provide strong evidence for the presence of the SF_5 -group in esters derived from $\text{SF}_5\text{CFCF}_2\text{OSO}_2$. The remainder of the fragments are consistent with the structures assigned to these esters.

TABLE XVIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2}

	SF _{ax}	SF _{4eq}	SO ₂ F	CF ₃	CF ₂
I. FSO ₂ CF ₂ C(O)OAg	-	-	30.8 (t)	-	-100.9(d)
II. FSO ₂ CF ₂ C(O)OC ₆ F ₅	-	-	40.5(t)	-	-106.2(d)
III. SF ₅ CF(SO ₂ F)C(O)OCH ₂ CF ₃	62.3(9-line)	56.5(d)	48.9(p)	-76.2(t)	-
IV. [SF ₅ CF(SO ₂ F)C(O)OCH ₂ CF ₂] ₂ CF	62.9(9-line)	56.7(d)	49.1(br.p)	-	-121.3(br.t)
V. SF ₅ CF(SO ₂ F)C(O)OCH(CF ₃) ₂	61.5(9-line)	57.2(d)	49.6(p)	-75.2(d)	-
VI. SF ₅ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	64.3(9-line)	56.3(d)	48.6(p)	-	-
VII. FSO ₂ CF ₂ C(O)OCH ₂ CH ₂ Br	-	-	38.3(y)	-	-109.0(d)
VIII. FSO ₂ CF ₂ C(O)OCH ₂ C(O)OC ₂ H ₅	-	-	40.4(t)	-	-105.5(d)
IX. [FSO ₂ CF ₂ C(O)O] ₂ CH ₂	-	-	39.2(t)	-	-105.6(d)
X. FSO ₂ CF ₂ C(O)OCH ₂ CH=CH ₂	-	-	39.9(t)	-	-104.9(d)

1. Fluorine chemical shifts in ppm from external F-11.
2. s = singlet, d = doublet, t = triplet, p = pentet, br = broadened.

TABLE XVIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2}
(continued)

	CF	ortho	C ₆ F ₅ para	meta
I. FSO ₂ CF ₂ C(O)OAg	-	-	-	-
II. FSO ₂ CF ₂ C(O)OC ₆ F ₅	-	-155.7(d)	-159.2(t)	-166.7(t)
III. SF ₅ CF(SO ₂ F)C(O)OCH ₂ CF ₃	-123.5(d,p)	-	-	-
IV. [SF ₅ CF(SO ₂ F)C(O)OCH ₂ CF ₂] ₂ CF	-123.4	-	-	-
V. SF ₅ CF(SO ₂ F)C(O)OCH(CF ₃) ₂	-119.0(d,p)	-	-	-
VI. SF ₅ CF(SO ₂ F)C(O)OCH ₂ =CH ₂	-121.9(s)	-	-	-
VII. FSO ₂ CF ₂ C(O)OCH ₂ CH ₂ Br	-	-	-	-
VIII. FSO ₂ CF ₂ C(O)OCH ₂ C(O)OC ₂ H ₅	-	-	-	-
IX. [FSO ₂ CF ₂ C(O)O] ₂ CH ₂	-	-	-	-
X. FSO ₂ CF ₂ C(O)OCH ₂ CH=CH ₂	-	-	-	-

1. Fluorine chemical shifts in ppm from external F-11.

2. s = singlet, d = doublet, t = triplet, p = pentet, br = broadened.

TABLE XIX
PROTON NMR CHEMICAL SHIFTS^{1,2,3}

	CH	CH ₂	CH ₃	H _a	H _b	H _c	CH ₂ d
I. FSO ₂ CF ₂ C(O)OAg	-	-	-	-	-	-	-
II. FSO ₂ CF ₂ C(O)OC ₆ F ₅	-	-	-	-	-	-	-
III. SF ₅ CF(SO ₂ F)C(O)OCH ₂ CF ₃	-	4.97 (q)	-	-	-	-	-
IV. [SF ₅ CF(SO ₂ F)C(O)OCH ₂ CF ₂] ₂ CF ₂	-	5.22 (t)	-	-	-	-	-
V. SF ₅ CF(SO ₂ F)C(O)OCH(CF ₃) ₂	-	-	-	-	-	-	-
VI. SF ₅ CF(SO ₂ F)C(O)OCH ₂ CH=CH ₂	-	-	-	5.58 (d,d)	5.82 (d,d)	6.12 (d,t)	5.07 (d)
VII. FSO ₂ CF ₂ C(O)OCH ₂ CH ₂ Br	5.13 (t),	3.98 (t)	-	-	-	-	-
VIII. FSO ₂ CF ₂ C(O)OCH ₂ C(O)OCH ₂ CH ₃	5.12 (s),	4.40 (q)	1.40 (t)	-	-	-	-
IX. [FSO ₂ CF ₂ C(O)O] ₂ CH ₂	-	6.53 (s)	-	-	-	-	-
X. FSO ₂ CF ₂ C(O)OCH ₂ CH=CH ₂	-	-	-	5.43 (d,d)	5.72 (d,d)	6.02 (d,t)	4.95 (d)

1. Proton chemical shifts in ppm downfield from external TMS.

2. s = singlet, d = doublet, t = triplet, q = quartet.

3. R_f-CH₂ CH₂ = CH^H (c) (a) (b)', where H_b and H_c are trans.

TABLE XX

PROTON AND FLUORINE NMR COUPLING CONSTANTS

		Coupling Constants (Hz)	
I.	$F_{(1)}SO_2CF_2_{(2)}C(O)OAg$	$J_{1,2} = 3.5$	
II.	$F_{(1)}SO_2CF_2_{(2)}C(O)OC_6F_5_{(o,m,p)}$	$J_{1,2} = 6.3$	$J_{m,o} = 12.7$
		$J_{o,p} = 24.6$	$J_{m,p} = 12.9$
III.	$F_{(1)}SF_4_{(2)}CF_{(3)}(SO_2F)_{(4)}C(O)OCH_2_{(5)}CF_3_{(6)}$	$J_{1,2} = 141$	$J_{2,4} = 9.2$
		$J_{1,3} = 3.0$	$J_{5,6} = 7.4$
		$J_{2,3} = 3.0$	
IV.	$[F_{(1)}SF_4_{(2)}CF_{(3)}(SO_2F)_{(4)}C(O)OCH_{(5)}CF_2_{(6)}]_2CF_2_{(7)}$	$J_{1,2} = 136$	$J_{2,4} = 9.2$
		$J_{1,3} = 3.0$	$J_{5,6} = 12.0$
		$J_{2,3} = 3.0$	
V.	$F_{(1)}SF_4_{(2)}CF_{(3)}(SO_2F)_{(4)}C(O)OCH_{(5)}(CF_3)_2_{(6)}$	$J_{1,2} = 136$	$J_{2,4} = 10.1$
		$J_{1,3} = 3.0$	$J_{5,6} = 5.6$
		$J_{2,3} = 3.0$	
VI.	$F_{(1)}SF_4_{(2)}CF_{(3)}(SO_2F)_{(4)}C(O)OCH_2CH=CH_2$	$J_{1,2} = 141$	$J_{2,3} = 3.1$
		$J_{1,3} = 3.1$	$J_{2,4} = 11.6$
VII.	$F_{(1)}SO_2CF_2_{(2)}C(O)OCH_2_{(3)}CH_2_{(4)}Br$	$J_{1,2} = 5.5$	$J_{3,4} = 6.0$

TABLE XX
PROTON AND FLUORINE NMR COUPLING CONSTANTS
(continued)

	Coupling Constants (Hz)
VIII. $F_{(1)}SO_2CF_2_{(2)}C(O)OCH_2C(O)OCH_2_{(3)}CH_3_{(4)}$	$J_{1,2} = 5.4 \quad J_{3,4} = 7.2$
IX. $[F_{(1)}SO_2CF_2_{(2)}C(O)O]_2CH_2$	$J_{1,2} = 5.5$
X. $F_{(1)}SO_2CF_2_{(2)}C(O)OCH_2CH=CH_2$	$J_{1,2} = 5.3$

TABLE XXI
PROTON NMR COUPLING CONSTANTS OF FLUORO-ALLYLIC ESTERS^{1,2}

	Coupling Constants (Hz)
VI. $SF_5CF(SO_2F)C(O)OCH_2_{(d)}CH_{(c)}=CH_2_{(a,b)}$	$J_{a,b} = 1.8 \quad J_{c,d} = 5.7$ $J_{a,c} = 9.9$ $J_{b,c} = 17.1$
X. $FSO_2CF_2C(O)OCH_2_{(d)}CH_{(c)}=CH_2_{(a,b)}$	$J_{a,b} = 1.2 \quad J_{b,c} = 17.2$ $J_{a,d} = 1.2 \quad J_{b,d} = 1.2$ $J_{a,c} = 10.4 \quad J_{c,d} = 6.0$

1. The coupling constants for $FSO_2CF_2C(O)OCH_2CH=CH_2$ were obtained with a General Electric QE-300 NMR spectrometer. Thanks are expressed to Dr. David H. Peyton for obtaining the 1H nmr spectrum of the compound.
2. $J_{b,c}$ is trans coupling.

CHAPTER VII

SYNTHESIS OF FLUORINATED SULFONIC ACIDS

The objective of this research was the synthesis of fluorinated sulfonic acids ($R_f\text{SO}_3\text{H}$, where R_f is any fluorocarbon moieties) that would serve as potential fuel cell electrolytes. Currently, phosphoric acid (H_3PO_4) is in use as an electrolyte in fuel cells. For a sulfonic acid to be an effective fuel cell electrolyte, it should be thermally stable, have a low vapor pressure, be inert toward oxygen and hydrogen as well as metallic systems, be able to conduct ions and dissolve oxygen, and finally, not wet or coat the electrodes (17). As mentioned previously in Chapter I, trifluoromethane sulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$, TFMSA) shows promising results as an electrolyte for a fuel cell electrolyte due to its superiority to H_3PO_4 from the standpoint of electrode kinetics. But there are some undesirable characteristics in TFMSA which include volatility and wetting of the Teflon based electrodes (54). This result led to this research for a better fuel cell electrolyte.

The literature discusses a limited number of methods for preparation of fluorosulfonic acids. In one method, bis(trifluoro-methyl)disulfide is used to prepare TFMSA via

three different routes, as shown below (67,68):

or

The electrochemical fluorination of methane sulfonyl fluoride or chloride ($\text{CH}_3\text{SO}_2\text{X}$, where $\text{X} = \text{F}$ or Cl) is another source for the preparation of TFMSA or other fluorinated alkyl sulfonic acids:

The above method gives high yields of TFMSA and represents a general method for preparation of perfluoroalkane sulfonic acids (6).

Partially fluorinated aromatic sulfonic acids can be made through electrophilic substitution (70).

Sulfonation of perfluorinated aromatic systems such as pentafluorobenzene take place under rather mild conditions (71):

A good method, the metal bisulfite route, involves the addition reaction between a fluoroolefin and aqueous NaHSO_3 or Na_2SO_3 (buffered to pH 5-7 with $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in the presence of benzoyl peroxide; the product is a sodium salt. Reaction and distillation from the sodium salt with 100% H_2SO_4 will result in the formation of a fluorosulfonic acid (72):

The low molecular weight partially fluorinated alkane-sulfonic acids containing α -methylene groups can be prepared from the *p*-toluenesulfonates of the corresponding alcohols via a reaction with benzyl mercaptan, followed by an oxidative chlorination of the resulting sulfides, with subsequent hydrolysis of the sulfonyl chloride (54):

The reaction of partially fluorinated alkyl halides with sodium sulfites is another method for preparation of

fluorosulfonic acids. It is reported that this method produces fluorosulfonic acids in very low yield, and the resulted sulfonate salts are also difficult to characterize and purify (54):

Another method used to prepare sulfonic acids is the sultone method in which fluorinated olefins react with monomeric sulfur trioxide to form a β -sultone. The β -sultone reacts with water to form sulfonyl fluoride (R_fSO_2F) from which the sulfonic acid can be produced in two different pathways: first, treatment of the sulfonyl fluoride (R_fSO_2F) with an aqueous suspension of $Ba(OH)_2$ to give the barium sulfonate salt; further reaction of the barium salt with 100% H_2SO_4 will yield sulfonic acid. The second pathway involves reaction of the sulfonyl fluoride (R_fSO_2F) with anhydrous pyridine which results in the formation of a fluoro-sulfonene ($R_fCF=SO_2NC_5H_5$). The fluorosulfonene is then hydrolyzed with aqueous $Ba(OH)_2$ and finally treated with 100% H_2SO_4 to give sulfonic acid (73,74,75).

In order to prepare a number of fluorosulfonic acids with different structural parameters, the metal bisulfite and β -sultone methods were used in this study.

In the metal bisulfite route, $\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{C}_5\text{F}_{11}\text{CF}=\text{CF}_2$ were utilized as starting fluoro-olefins:

The resulting sodium salt from the reaction VII-26 was extracted twice with hot ethanol prior to its treatment with 100% H_2SO_4 . The sodium salt resulting from the $\text{C}_5\text{F}_{11}\text{CF}=\text{CF}_2$ fluoro-olefin could not be extracted due to its insolubility in hot ethanol. However, the subsequent treatment of sodium salts with 100% H_2SO_4 resulted in the production of the desired fluorosulfonic acids:

The syntheses of the sodium salts were carried out in a 75 ml stainless steel autoclave, with agitation; at $115 \pm 5^\circ\text{C}$ for 10-18 h; acidification of salts with 100% H_2SO_4 and subsequent distillation yielded the desired acids. In the literature (72), it is reported that liquid $\text{C}_5\text{F}_{11}\text{CFHCF}_2$

SO₃H boils at 119-120°C/3 mm; while it was found in our laboratory that the acid is a solid and is in the hydrated form with 0.5 mole of H₂O; b.p. 125-130°C/5 μ and m.p. 58±3°C.

In the sultone method, CF₃ $\overline{\text{CFCF}_2\text{OSO}_2}$ was used as a starting material:

subsequent treatment with H₂O, NaOH, and 100% H₂SO₄ gave the corresponding acid:

The resulted sodium salt was extracted twice with hot ethanol before its treatment with 100% H₂SO₄.

In the literature (73), it is reported that the acid is in the hydrated form, CH₃CFHSO₃H•2H₂O, with a b.p. 115°C/2 mm, but we found the acid to have only 0.5 mole of H₂O, CF₃CFHSO₃H•0.5H₂O, and boiled at 119±1°C/20 mm. The results of the elemental analysis showed that all three acids are in the hydrated forms:

EXPERIMENTAL

Synthesis $\text{CF}_3\text{CFHSO}_3\text{H}$

$\text{CF}_3\text{CF}=\text{CF}_2$ with SO_3 . Into a 130 ml Pyrex-glass Carius tube equipped with a Kontes Teflon valve, were added 407 mmol of SO_3 and 430 mmol $\text{CF}_3\text{CF}=\text{CF}_2$. The mixture was heated for 48 h at $105\pm 5^\circ\text{C}$. Distillation gave 327 mmol of a clear liquid, $\text{CF}_3\text{CFCF}_2\text{OSO}_2$, in 80% yield; b.p. $46.5^\circ\text{C}/\text{atm}$.

$\text{CF}_3\text{CFCF}_2\text{OSO}_2$ with H_2O . Into a 40 ml Kel-F vessel equipped with a Teflon stirring bar was added 50 g ice; 265 mmol of $\text{CF}_3\text{CFCF}_2\text{OSO}_2$ was then slowly added with stirring over a period of 0.5 h while the temperature of the mixture was kept below 5°C . The mixture was stirred at room temperature for 25 min, after which the lower layer was separated and dried over MgSO_4 . Distillation gave 174 mmol of $\text{CF}_3\text{CFHSO}_2\text{F}$ in 65.6% yield; b.p. $61\text{--}66^\circ\text{C}/\text{atm}$.

$\text{CF}_3\text{CFHSO}_2\text{F}$ with NaOH . Into a 50 ml Pyrex-glass round-bottom flask, equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 25 ml (1389 mmol) of distilled H_2O and 101.8 mmol of NaOH pellets. To this solution, cooled to 0°C , 48.8 mmol of $\text{CF}_3\text{CFHSO}_2\text{F}$ was slowly added (1 h). The mixture was refluxed with stirring for 24 h at room temperature. The solvent was then removed, the residue was extracted twice with hot ethanol, and the extracts were dried under vacuum. The resulted white solid, $\text{CF}_3\text{CFHSO}_3\text{Na}$, was formed in 74.1% yield; the compound was stable to 300°C .

The infrared spectrum had the following bands (cm^{-1}): 3670(m), 3452(m), 3374(w), 2966(w), 1628(m), 1358(ms), 1299(s), 1275(vs), 1262(sh), 1231(vs), 1192(s), 1167(sh), 1151(s), 1138(s), 1097(s), 1060(s), 1047(s), 889(ms), 811(w), 708(ms), 640(s), 589(m), 542(m), 529(m), 516(m), 506(m), 480(m), 469(sh), 438(m), 405(m).

$\text{CF}_3\text{CFHSO}_3\text{Na}$ with 100% H_2SO_4 . Into a 100 ml Pyrex-glass round-bottom flask equipped with a Teflon stirring bar were added 34.8 mmol of $\text{CF}_3\text{CFHSO}_3\text{Na}$ and 61.2 mmol of 100% H_2SO_4 . The mixture was slowly distilled under reduced pressure, giving 24.6 mmol $\text{CF}_3\text{CFHSO}_3\text{H}\cdot 0.5\text{H}_2\text{O}$ in 70.6% yield; b.p. $119\pm 1^\circ\text{C}/20\text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 2973(br. s), 2411(w), 2179(w), 1652(br. m), 1391(s), 1349(s), 1272(vs), 1230(vs), 1202(vs), 1158(vs), 1112(sh), 1053(s), 954(br. s), 881(ms), 808(w), 789(w), 703(s), 637(sh), 604(s), 577(m), 524(w), 505(ms), 485(w), 445(w), 439(w).

The positive ion (CI^+) mass spectrum (m/e, species): 163, M-F^+ ; 124, $\text{C}_2\text{FHSO}_3^+$; 101, CF_3CFH^+ ; 82, CF_2CFH^+ ; 81, C_2F_3^+ , SO_3H^+ ; 80, SO_3^+ ; 69, CF^+ ; 65, SO_2H^+ ; 64, CFHS^+ , SO_2^+ ; 63, $\text{C}_2\text{F}_2\text{H}^+$, CFS^+ ; 62, C_2F_2^+ ; 52, CF_2^+ ; 49, SOH^+ ; 48, SO^+ ; 44, SC^+ .

Synthesis of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}$

$\text{CF}_3\text{CF}=\text{CF}_2$ with NaHSO_3 . Into a 75 ml stainless steel autoclave were added 113 mmol of $\text{CF}_3\text{CF}=\text{CF}_2$, 100 mmol NaHSO_3 ,

12.5 mmol of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 2.12 mmol of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$, and 29 ml of distilled H_2O . The contents of the autoclave were heated with agitation for 10 h at $115 \pm 5^\circ\text{C}$. The solvent was removed and the residue was extracted twice with hot ethanol; the extracts were dried under vacuum. The resulted white solid, $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$, was formed in 59.4% yield; the compound was stable to 150°C .

The infrared spectrum had the following bands (cm^{-1}): 3670(m), 3466(ms), 3191(br. ms), 1654(m), 1636(m), 1377(m), 1355(w), 1293(sh), 1273(s), 1242(vs), 1201(s), 1180(s), 1094(s), 1043(sh), 1002(m), 941(vw), 913(vw), 885(vw), 850(ms), 827(ms), 780(w), 752(w), 709(w), 660(sh), 654(m), 644(m), 620(w), 597(w), 589(w), 556(m), 535(w), 527(m), 498(w), 488(w), 469(w), 459(m), 450(sh), 441(sh), 430(m).

$\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$ with 100% H_2SO_4 . Into a 100 ml Pyrex-glass round-bottom flask equipped with a Teflon stirring bar were added 64.8 mmol of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$ and 170 mmol of 100% H_2SO_4 . The mixture was slowly distilled under reduced pressure, giving 30.3 mmol of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H} \cdot 1.5\text{H}_2\text{O}$ in 46.8% yield; b.p. $110\text{--}111^\circ\text{C}/20\text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 2985(br. s), 2213(br. ms), 1714(br. s), 1384(s), 1351(ms), 1343(vs), 1261(vs), 1181(s), 1085(s), 1053(sh), 1029(sh), 992(s), 885(w), 851(ms), 883(ms), 744(vw), 727(w), 718(w), 699(vw), 646(vs), 620(ms), 562(s), 542(sh), 533(sh), 525(m), 494(vw), 475(m), 438(vw), 418(vw), 403(m).

The positive ion (CI^+) mass spectrum (m/e , species):
 151, $\text{CF}_3\text{CFHCF}_2^+$; 150, $\text{CF}_3\text{CFCF}_2^+$; 131, C_3F_5^+ , $\text{CF}_2\text{SO}_3\text{H}^+$; 113, $\text{C}_3\text{F}_4\text{H}^+$; 101, CF_3CFH^+ ; 100 CF_3CF^+ ; 82, CF_2CFH^+ ; 81, SO_3H^+ ; 69, CF_3^+ ; 65, SO_2H^+ ; 64, SO_2^+ ; 63, $\text{C}_2\text{F}_2\text{H}^+$, CFS^+ ; 62, C_2F_2 ; 50, CF_2^+ ; 49, SOH^+ ; 48, SO^+ ; 44, SC^+ .

Synthesis of $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{H}$

$\text{C}_5\text{F}_{11}\text{CF}=\text{CF}_2$ with NaHSO_3 . Into a 75 ml stainless steel autoclave were added 47.1 mmol of $\text{C}_5\text{F}_{11}\text{CF}=\text{CF}_2$, 47.1 mmol of NaHSO_3 , 5.87 mmol of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 2.12 mmol of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$, and 10 ml of distilled H_2O . The contents of the autoclave were heated with agitation for 18 h at $115 \pm 5^\circ\text{C}$. The solvent was then removed, the residue was extracted with the mixture of hot ethanol and water (75:25), and the extracts were dried under vacuum. The resulted white solid, $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{Na}$, was formed in 81.3% yield; the compound was stable to 300°C .

The infrared spectrum had the following bands (cm^{-1}):
 3677(m), 3487(m), 3395(vw), 3206(vw), 1650(vw), 1628(m), 1490(br.s), 1362(vw), 1349(w), 1299(s), 1276(s), 1239(vs), 1206(vs), 1176(sh), 1146(s), 1132(s), 1113(s), 1099(s), 1055(ms), 1011(w), 992(ms), 950(m), 873(w), 860(m), 834(m), 818(m), 771(w), 750(m), 734(ms), 713(vw), 692(m), 678(vw), 653(ms), 641(vw), 630(m), 611(m), 597(ms), 567(m), 527(ms), 509(w), 490(vw), 439(vw), 430(w), 411(vw), 404(w).

$\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{Na}$ with 100% H_2SO_4 . Into a 100 ml Pyrex-glass round-bottom flask equipped with a Teflon

stirring bar were added 28.7 mmol of $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{Na}$ and 66.5 mmol of 100% H_2SO_4 . The mixture was slowly distilled under reduced pressure, giving 17.7 mmol of $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{H}\cdot 0.5\text{H}_2\text{O}$ in 66.5% yield; b.p. $125-130^\circ\text{C}/5\text{ }\mu$; m.p. $58\pm 3^\circ\text{C}$.

The infrared spectrum had the following bands (cm^{-1}): 3677(ms), 3481(ms), 3234(vw), 2995(vw), 1632(vw), 1363(vw), 1344(w), 1300(s), 1270(s), 1236(vs), 1204(vs), 1173(sh), 1148(s), 1136(vs), 1099(m), 1053(ms), 1007(w), 994(m), 891(w), 859(w), 836(m), 820(w), 796(vw), 771(m), 750(w), 734(m), 712(w), 688(m), 678(vw), 654(m), 504(vw), 490(vw), 451(vw).

The positive ion (CI^+) mass spectrum (m/e, species): 726, $(2\text{M}-2\text{CF}_3)^+$; 613, $(2\text{M H}_2\text{O}-\text{C}_5\text{F}_{11})^+$; 595, $(2\text{M}-\text{C}_5\text{F}_{11})^+$; 563, $(2\text{M}-\text{C}_5\text{F}_{11}\text{CFH})^+$; 449, $(\text{M H}_2\text{O}-\text{H})^+$; 413, $(\text{M}-\text{F})^+$; 349, $\text{C}_5\text{F}_{11}\text{SO}_3^+$; 344, $(2\text{M H}_2\text{O}-2\text{C}_5\text{F}_4)^+$; 332, $(\text{M}-\text{FSO}_3\text{H})^+$; 331, $(\text{M}-\text{HFSO}_3\text{H})^+$; 326, $(2\text{M}-2\text{C}_5\text{F}_{11})^+$; 279, $(2\text{M H}_2\text{O}-2\text{C}_5\text{F}_{11}\text{CFH})^+$; 269, $\text{C}_5\text{F}_{11}^+$; 262, $(2\text{M}-2\text{C}_5\text{F}_{11}\text{CFH})^+$; 251, $\text{C}_4\text{F}_9\text{CFH}^+$; 237, $\text{CF}_2\text{CFCF}_2\text{SO}_2^+$; 236, $\text{CF}_2\text{CFHCF}_2\text{SO}_2^+$; 219, C_4F_9^+ ; 213, $(\text{M}-\text{C}_4\text{F}_9)^+$; 201, $\text{C}_3\text{F}_7\text{CFH}$; 184, $\text{C}_2\text{F}_5\text{SO}_2\text{H}^+$; 169, C_3F_7^+ ; 151, $\text{C}_2\text{F}_5\text{CFH}^+$; 130, CF_2SO_3^+ ; 119, C_2F_5^+ .

ELEMENTAL ANALYSIS

The results of the elemental analyses for the fluorosulfonic acids prepared via the metal bisulfite or β -sultone routes are shown below (Table XXII). The analyses showed all fluorosulfonic acids were in hydrated forms; they contained 0.5 to 1.5 moles of water in their structures. Based on the degree of hydration the agreement between calculated and found values was good.

TABLE XXII
ELEMENTAL ANALYSIS OF FLUOROSULFONIC ACID HYDRATES

Compound		Calcd.	Found
II. $\text{CF}_3\text{CFHSO}_3\text{H}\cdot 0.5\text{H}_2\text{O}$			
	C	12.56	12.69
	H	1.57	1.30
	F	39.79	38.90
	S	16.75	16.56
IV. $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}\cdot 1.5\text{H}_2\text{O}$			
	C	13.9	14.44
	H	1.93	2.17
	F	38.68	42.10
	S	12.56	10.17

TABLE XXII
ELEMENTAL ANALYSIS OF FLUOROSULFONIC ACID HYDRATES
(continued)

Compound		Calcd.	Found
VI. $C_5F_{11}CFHCF_2SO_3H \cdot 0.5H_2O$			
	C	19.04	18.67
	H	0.68	0.73
	F	60.32	57.20
	S	7.26	6.94

INFRARED SPECTRA

The infrared spectral data for all fluorosulfonic acids and their salts are presented in the experimental section, and the spectra are also shown in the appendix. The most prominent feature of these spectra are the SO_3 symmetric and asymmetric stretching modes in the region from 1054 to 1100 cm^{-1} and 1170 to 1296 cm^{-1} , respectively. These assignments are in agreement with the reported values for SO_3 symmetric and asymmetric in the literature (16,24,76). The CF stretching modes for all three fluorosulfonic acids and their salts are in the range of 984-1100 cm^{-1} and 1202-1381 cm^{-1} . The reported values for the CF vibration is 1000-1100 cm^{-1} (61) while marked absorption in the range of 1200-1360 cm^{-1} are correlated with the CF_2 and CF_3 groups (61). The CH stretching frequencies appeared between

2988 and 2991 cm^{-1} . The OH stretching and bending modes for sulfonic acids are around 3400 cm^{-1} and 1620-1726 cm^{-1} , respectively. All of these assignments are in good agreement with reported values in the literature (16,24,77).

NMR SPECTRA

The nmr chemical shifts and coupling constants for the three fluorosulfonic acids and their salts are shown in Tables XXIII through XXV and the spectra are reproduced in the appendix. In the case of $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{Na}$ and $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{H}$, the coupling constants were not calculated due to the complexity of the splitting patterns. Fluorine and proton chemical shifts are reported in ppm from CFCl_3 and downfield from TMS, respectively.

The ^{19}F nmr resonance for the CF_3 group in the sodium salts is found in the range of -71.9 to -82.7 ppm, while for the corresponding acids the fluorine chemical shifts of this group range from -70.3 to -82.9 ppm. In the other fluorosulfonic acid, $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{H}$, the CF_3 resonance band is located at -82.3 ppm, (21,78). The nonequivalent CF_2 fluorines, which are adjacent to $-\text{SO}_3\text{Na}$ and $-\text{SO}_3\text{H}$ in compounds III to VI, are found in the range of -112.8 to -121.0 ppm; for compounds V and VI, the range is -135.3 to -173.6 ppm. The resulted chemical shifts for the nonequivalent CF_2 are in good agreement with values reported in the literature (4). The CF_2 groups in $\text{CF}_3(\text{CF}_2)_4\text{CFHCF}_2\text{SO}_3\text{Na}$

and $\text{CF}_3(\text{CF}_2)_4\text{CFHCF}_2\text{SO}_3\text{H}$ appeared as complex patterns and their chemical shifts range from -112.3 to -128.2 ppm. The CF fluorine resonance is located in the range of -192.4 to -210.5 ppm for all compounds except $\text{CF}_3(\text{CF}_2)_4\text{CFHCF}_2\text{SO}_3\text{Na}$, which is not observed. Generally, fluorine chemical shifts reported for these compounds show consistency with those found in similar compounds (4,14,22,76).

The fluorine-fluorine or fluorine-proton coupling constants are not found for compounds V and VI due to the complexity of their splitting patterns; while the other four salts and acids coupling constants were found.

The ^1H nmr data for all acids/salts were self consistent with respect to the expected chemical shifts for CH and SO_3H groups.

TABLE XXIII

FLUORINE NMR CHEMICAL SHIFTS^{1,2,3}

	CF ₃	F ₁	CF ₂ ^a	F ₂
I. CF ₃ CFHSO ₃ Na	-72.4 (d,d)	-	-	-
II. CF ₃ CFHSO ₃ H•0.5H ₂ O	-70.3 (d,d)	-	-	-
III. CF ₃ CFHCF ₂ SO ₃ Na	-71.9 (d,d,d,d)	-112.8 (d,d,d,q)	-121.0 (d,d,q,d)	
IV. CF ₃ CFHCF ₂ SO ₃ H•1.5H ₂ O	-75.2 (d,d,d,d)	-113.2 (d,d,d,q)	-118.5 (d,d,q,d)	
V. CF ₃ (CF ₂) ₄ CFHCF ₂ SO ₃ Na	-82.7 (m)	-165.0 (m)	-173.6 (m)	
VI. CF ₂ (CF ₂) ₄ CFHCF ₂ SO ₃ H•0.5H ₂ O	-82.9 (m)	-153.3 (m)	-161.7 (m)	

1. Fluorine chemical shifts in ppm and F-11.
2. s = singlet, d = doublet, q = quartet, m = multiplet, br = broadened.
3. a = CFHCF₂.

TABLE XXIII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3}
(continued)

	F ₁	CF ₂ ^b	F ₂	CF
I. CF ₃ CFHSO ₃ Na	-		-	-192.4 (d,q)
II. CF ₃ CFHSO ₃ H•0.5H ₂ O	-		-	-196.5 (d,q)
III. CF ₃ CFHCF ₂ SO ₃ Na	-		-	-208.5 (d,d,q,d)
IV. CF ₃ CFHCF ₂ SO ₃ H•1.5H ₂ O	-		-	-210.5 (d,d,q,d)
V. CF ₃ (CF ₂) ₄ CFHCF ₂ SO ₃ Na	-112.3	to	-128.2 (m)	-
VI. CF ₂ (CF ₂) ₄ CFHCF ₂ SO ₃ H•0.5H ₂ O	-122.5	to	-128.4 (m)	-209.4 (m)

1. Fluorine chemical shifts in ppm from F-11.
2. s = singlet, d = doublet, q = quartet, m = multiplet, br = broadened.
3. b = CF₃(CF₂)₄.

TABLE XXIV
PROTON NMR CHEMICAL SHIFTS^{1,2}

	CH	SO ₃ H	H ₂ O
I. CF ₃ CFHSO ₃ Na	6.16 (d,q)	-	-
II. CF ₃ CFHSO ₃ H•0.5H ₂ O	5.73 (d,q)	11.94 (br,s)	-
III. CF ₃ CFHCF ₂ SO ₃ Na	6.20 (d,d,q,d)	-	-
IV. CF ₃ CFHCF ₂ SO ₃ H•1.5H ₂ O	5.6 (d,d,q,d)	10.65 (s)	8.9 (s)
V. CF ₃ (CF ₂) ₄ CFHCF ₂ SO ₃ Na	6.05 (m)	-	-
VI. CF ₂ (CF ₂) ₄ CFHCF ₂ SO ₃ H•0.5H ₂ O	5.73 (m)	11.5 (br,s)	-

1. Proton chemical shifts in ppm downfield from TMS.
2. s = singlet, d = doublet, q = quartet, m = multiplet, br = broadened.

TABLE XXV
FLUORINE AND PROTON NMR COUPLING CONSTANTS

	Coupling Constants (Hz) *	
I. $\text{CF}_3^{(1)} \text{CF}^{(2)} \text{H}^{(3)} \text{SO}_3\text{Na}$	$J_{1,2} = 11.7$	
	$J_{1,3} = 6.1$	
	$J_{2,3} = 44.1$	
II. $\text{CF}_3^{(1)} \text{CF}^{(2)} \text{H}^{(3)} \text{SO}_3\text{H} \cdot 0.5\text{H}_2\text{O}$	$J_{1,2} = 11.2$	
	$J_{1,3} = 5.6$	
	$J_{2,3} = 44.0$	
III. $\text{CF}_3^{(1)} \text{CF}^{(2)} \text{H}^{(3)} \text{CF}^{(4)} \text{F}^{(5)} \text{SO}_3\text{Na}$	$J_{1,2} = 6.0$	$J_{2,4} = 17.5$
	$J_{1,3} = 11.3$	$J_{2,5} = 3.4$
	$J_{1,4} = 8.9$	$J_{2,4} = 13.5$
	$J_{1,5} = 11.7$	$J_{3,5} = 10.6$
	$J_{2,3} = 42.3$	$J_{4,5} = 266$
IV. $\text{CF}_3^{(1)} \text{CF}^{(2)} \text{H}^{(3)} \text{CF}^{(4)} \text{F}^{(5)} \text{SO}_3\text{H} \cdot 1.5\text{H}_2\text{O}$	$J_{1,2} = 6.0$	$J_{2,4} = 17.5$
	$J_{1,3} = 10.8$	$J_{2,5} = 3.5$
	$J_{1,4} = 8.6$	$J_{3,4} = 12.8$
	$J_{1,5} = 12.8$	$J_{3,5} = 10.7$
	$J_{2,3} = 42.6$	$J_{4,5} = 262$

* The proton and fluorine nmr spectra of all acids/salts, along with the interpretation of the data, were done by Dr. Roger M. Sheets and Mr. Robert J. Willenbring. Thanks are expressed to them.

MASS SPECTRA

The mass spectra of all fluorosulfonic acids are reported in the experimental section. There are similar fragments in all fluorosulfonic acids, and these similarities are more apparent in the lower molecular weight fragments. The molecular ions (M^+) are not observed for any of the three acids. The highest fragment observed for $CF_3(CF_2)_4CFHCF_2SO_3H$ is found at m/e values of 726 ($2M - 2CF_3$) $^+$; while in the case of CF_3CFHSO_3H and $CF_3CFHCF_2SO_3H$, the highest fragments are observed at 163 ($M - F$) $^+$ and 151 ($M - SO_3H$) $^+$, respectively. The remainder of fragments are consistent with the structures assigned to these fluorosulfonic acids.

CHAPTER VIII

NOVEL β -SULTONES

The reaction of sulfur trioxide with $\text{CH}_2\text{ClCHClCH}_2\text{-CF=CF}_2$ and $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\text{OCF=CF}_2$ was studied. The result of this study was the production of the two new compounds, $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}_2}\text{OSO}_2$ and $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\overline{\text{OCFCF}_2}\text{SO}_2\text{O}$, which represent an important class of fluorinated β -sultones because of the location of different atoms in their structures. In the case of $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}_2}\text{OSO}_2$, due to the presence of Cl, F, and H, its reaction with different nucleophiles will lead to several different products containing sulfonyl fluoride (SO_2F). However, if there is functionalization of the Cl atoms, additional compounds can be formed. With $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\overline{\text{OCFCF}_2}\text{SO}_2\text{O}$, because of the closeness of the oxygen atom to the olefinic carbon of the CF group, the sultone ring is formed in the reverse manner (see p. 81). Thus, this sultone enables the study of the effect of the oxygen bonding to the carbon of the CF group from both a synthetic and spectral points of view.

The preliminary studies done in our laboratory were:

II

III

The β -sultones, I and III, are thermally stable and colorless liquids; I undergoes rearrangement in the presence of MX (where M = Na or K, and X = F) to give the corresponding isomeric fluorosulfonyl acylfluoride (II).

The syntheses of the two β -sultones, I and III, were carried out in a 130 mL Pyrex-glass Carius tube at 0°C and 105±5°C for 7 days, respectively. The rearrangement reaction of the β -sultone I was carried out in a 50 mL Pyrex-glass round bottom flask at 40-50°C for 7 days. The purification of the two β -sultones and one rearranged product was done by fractional distillation at reduced pressure. The result of the elemental analyses confirmed the molecular formulas of all new β -sultones and rearranged product.

EXPERIMENTAL

Synthesis of $\text{CH}_2\text{ClCHClCH}_2\text{CF}(\text{CF}_2\text{OSO}_2)$

To 26.2 mmol of $\text{CH}_2\text{ClCHClCH}_2\text{CF}=\text{CF}_2$ at 0°C in a 130 mL Pyrex-glass Carius tube equipped with a Kontes Teflon valve, 30.0 mmol of monomer SO_3 was added. The mixture was kept at room temperature for 2-3 h. Distillation of the mixture

gave 11.6 mmol of clear liquid, $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}_2\text{OSO}_2}$, in 44.3% yield, b.p. 72-73°C/4 μ .

The infrared spectrum had the following bands (cm^{-1}): 3044(vw), 2973(w), 1482(m), 1447(sh), 1413(vs), 1375(w), 1337(m), 1314(m), 1292(m), 1268(m), 1243(sh), 1203(vs), 1122(ms), 1059(s), 1017(sh), 1003(w), 968(w), 943(w), 914(vw), 869(vw), 782(s), 753(m), 730(w), 719(w), 699(vw), 679(m), 656(s), 638(ms), 607(sh), 580(ms), 531(ms), 520(ms), 504(sh), 484(vw), 450(vw), 424(vw), 412(w), 406(sh).

The ^{19}F nmr spectrum gave the following relative peak areas: $\text{CF}_{2\text{ab}}$ (1.0,1.0), and CF (1.0). The relative band areas for ^1H nmr were: CH_2 (2.1), CH_2Cl (2.2), and CHCl (1.0).

The positive ion mass spectrum (m/e) species: 237, $(\text{M}-\text{CHl})^+$; 223, $(\text{M}-\text{HCl}, \text{CH}_2)^+$; 193, $(\text{M}-\text{SO}_3)^+$; 189, $(\text{M}-\text{HCl}, \text{CCl})^+$ or $(\text{M}-\text{SO}_3, 4\text{H})^+$; 161, $(\text{M}-\text{C}_3\text{H}_5\text{Cl}_2)^+$; 153, $\text{CF}_2\text{CFCCCCl}^+$; 143, $\text{CF}_2\text{CFCH}_2\text{CCl}^+$; 142, $\text{CF}_2\text{CSO}_3^+$; 127, $(\text{M}-\text{SO}_3, \text{CFCl})^+$; 125, $(\text{M}-\text{SO}_3, \text{CH}_2\text{FCl})^+$; 117, $\text{CF}_2\text{CFCCC}^+$; 111, $\text{CH}_2\text{C}_2\text{H}_2\text{Cl}_2^+$; 109, $\text{CH}_2\text{C}_2\text{Cl}_2^+$; 108, $\text{CHC}_2\text{Cl}_2^+$ or $\text{CF}_2\text{CFC}_2\text{H}_3^+$; 107, CC_2Cl_2^+ ; 98, $\text{C}_2\text{H}_3\text{Cl}_2^+$; 97, $\text{C}_2\text{H}_2\text{Cl}_2^+$; 96, C_2HCl_2^+ ; 95, C_2Cl_2^+ or CFSO_2^+ ; 93, CF_2CFC^+ ; 81, CF_2CF^+ ; 80, SO_3^+ ; 77, $\text{CH}_2\text{C}_2\text{H}_3\text{Cl}^+$; 75, $\text{CH}_2\text{C}_2\text{HCl}^+$; 72, CCCCl^+ ; 64, SO_2^+ .

Synthesis of $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}}$

To a 25 mL Pyrex-glass round bottom flask, equipped with a Teflon-coated stirring bar, were added 10.2 mmol of dry NaF, and 9.89 mmol of $\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}_2\text{OSO}_2}$. The

reaction vessel was heated to 40-50°C for 7 days. Distillation of the mixture gave 5.60 mmol of a clear liquid, $\text{CH}_2\text{ClCHClCH}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$, in 56.6% yield, b.p. $55 \pm 1^\circ\text{C}/4 \mu$.

The infrared spectrum had the following bands (cm^{-1}): 2992(w), 2964(w), 1871(vs), 1885(sh), 1482(m), 1443(vs), 1391(m), 1332(ms), 1302(ms), 1276(ms), 1224(vs), 1201(sh), 1172(s), 1123(sh), 1080(ms), 1054(ms), 1028(sh), 1015(ms), 966(w), 946(w), 917(w), 868(m), 851(sh), 805(s), 770(sh), 747(ms), 724(m), 691(m), 658(w), 639(w), 609(s), 580(s), 537(m), 521(w), 495(w), 485(w), 459(m), 426(vw), 410(w).

The ^{19}F nmr spectrum gave the following relative peak areas: FSO_2 (1.0), and COF (1.0). The relative band areas for ^1H nmr spectrum were: CH_2 (2.0), CH_2Cl (2.0), and CHCl (1.0).

Synthesis of $\text{C}_4\text{F}_9\text{OCFCF}_2\text{SO}_2\text{O}$

To 40 mmol of SO_3 in a 130 mL Pyrex-glass Carius tube, equipped with a Kontes Teflon valve, 19.9 mmol of $\text{C}_4\text{F}_9\text{OCF}=\text{CF}_2$ was added. The mixture was heated at $105 \pm 5^\circ\text{C}$ for 7 days. Distillation of the mixture gave 8.84 mmol of a clear liquid, $\text{C}_4\text{F}_9\text{OCFCF}_2\text{SO}_2\text{O}$, in 44.4% yield, b.p. $85-90^\circ\text{C}/197 \text{ mm}$.

The infrared spectrum had the following bands (cm^{-1}): 1473(m), 1449(vs), 1346(ms), 1307(vs), 1260(vs), 1221(s), 1199(sh), 1152(s), 1144(sh), 1125(sh), 1112(w), 1088(vw), 1059(ms), 1027(s), 997(w), 995(m), 936(w), 924(vw), 896(ms), 821(m), 779(m), 742(s), 717(vw), 701(vw), 666(w), 634(w),

604(sh), 594(w), 573(vw), 538(vw), 534(w), 484(m), 459(w), 443(w), 437(w), 418(w), 406(w).

The ^{19}F nmr spectrum gave the following relative peak areas: CF_3 (3.0), $\text{CF}_{2\text{ab}}$ (1.0,1.0), CF_2 (1.8), $(\text{CF}_2)_2$ (4.5), and CF (1.0).

The positive ion $(\text{CI})^+$ mass spectrum (m/e species): 397, MH^+ ; 316, $(\text{M}-\text{SO}_3)^+$; 263, $(\text{M}-\text{CF}_2\text{SO}_2\text{F})^+$; 225, $\text{C}_4\text{F}_7\text{OC}(\text{O})^+$; 219, C_4F_9^+ ; 197, $\text{C}_3\text{F}_7\text{CO}^+$; 181, $\text{C}_3\text{F}_7\text{C}^+$; 177, $\text{OCF}(\text{O})\text{CF}_2\text{SO}_2^+$; 170, $\text{CF}_2\text{OC}(\text{O})\text{CSO}_2^+$; 169, C_3F_7^+ ; 161, $\text{CF}(\text{O})\text{CF}_2\text{SO}_2^+$; 155, $\text{C}_4\text{OCCFSO}^+$; 151, $\text{COCF}(\text{O})\text{CSO}_2^+$; 150 C_3F_6^+ ; 131, C_3F_5^+ ; 119, C_2F_5^+ ; 113, CFCF_2S^+ or $\text{OCF}(\text{O})\text{CF}_2^+$; 100, C_2F_4^+ ; 99, $\text{C}_2\text{OCF}(\text{O})\text{C}^+$; 98, CF_2SO^+ ; 97, OCFCF_2^+ ; 95, CFSO_2^+ ; 93, CF_3CC^+ ; 87, $\text{CFOC}(\text{O})\text{C}^+$; 83, CFCCCO^+ ; 81, CF_2CF^+ ; 78, CF_2CO^+ ; 75, $\text{OCF}(\text{O})\text{C}^+$; 71, CFOCC^+ ; 69, CF_3^+ ; 64, SO_2^+ ; 63, CFS^+ ; 59, OCFC^+ .

ELEMENTAL ANALYSIS

The elemental analysis of the two β -sultones and the fluorosulfonyl acylfluoride are shown in Table XXVI. There is good agreement between the calculated and experimental values.

TABLE XXVI
ELEMENTAL ANALYSIS OF β -SULTONES AND FLUOROSULFONYL
ACYLFLUORIDE

Compound	Calc.		Found
<hr/>			
I. $\text{CH}_2\text{ClCHClCH}_2\overbrace{\text{CFCF}_2\text{OSO}_2}$			
	C	21.98	22.07
	Cl	26.01	25.90
	H	1.83	1.81
	F	20.88	20.50
	S	11.72	11.46
II. $\text{CH}_2\text{ClCHClCH}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$			
	C	21.98	22.28
	Cl	26.01	26.37
	H	1.83	1.74
	F	20.88	20.90
	S	11.72	11.42
III. $\text{C}_4\text{F}_9\text{O}\overbrace{\text{CFCF}_2\text{SO}_2}\text{O}$			
	C	18.18	17.82
	F	57.58	57.10
	S	8.08	8.27

INFRARED SPECTRA

The infrared spectra data for the newly fluorinated β -sultones and the fluorosulfonyl acylfluoride are shown in the experimental section, and the spectra are reproduced in the Appendix.

The group frequencies and assignments in the infrared spectra of compounds I through III are: carbonyl stretching vibration (1871 cm^{-1}), SO_2 asymmetric and symmetric vibrational frequencies ($1449\text{--}1413\text{ cm}^{-1}$ and $1224\text{--}1203\text{ cm}^{-1}$); carbon-fluorine absorption bands ($1330\text{--}1100\text{ cm}^{-1}$); C-H vibrational bands ($3044\text{--}2964\text{ cm}^{-1}$), and the intense S-F absorption band (near 800 cm^{-1}).

In all cases these assignments are in excellent agreement with literature values (16,24,25,26).

NMR SPECTRA

The nmr chemical shifts and coupling constants for the two new fluoro β -sultones and one fluorosulfonyl acylfluoride are shown in Tables XXVII through XXIX and the spectra are reproduced in the Appendix.

The ^{19}F nmr chemical shift values are summarized in Table XXVII. The nonequivalent CF_2 fluorines in the sultone rings, I and III, are found in the -82.3 to -87.0 ppm range; for other similar fluorinated sultones, $\text{C}_3\text{F}_7\text{OCFCF}_2\text{SO}_2\text{O}$ and $\text{CF}_2\text{ClCFClCF}_2\text{CF}_2\text{OSO}_2$, the CF_2 resonance bands are located in the 83.0 to 86.5 ppm range (37,29). The resonance for

the CF group in the four membered ring is located at -143.0 and -91.8 ppm for sultones I and III, respectively. The difference between these two CF chemical shifts arise from the fact that the sultone ring in compound III is reversed, -CF₂SO₂, not -CF₂O (see p. 81). The ¹⁹F nmr values for the following functional groupings CF₃(CF₂)₂, CF₃(CF₂)₂, and CF₃(CF₂)₂CF₂O in compound III are in excellent agreement with literature values, except for the splitting pattern of the CF₃(CF₂)₂ group. For example, for a similar sultone, CF₃CF₂CF₂OCFCF₂SO₂O, CF₃CF₂ is reported as a singlet (37). While in our laboratory, it was found that in CF₃(CF₂)₂-CF₂OCFCF₂SO₂O sultone, the CF₃(CF₂)₂ is a multiplet.

The ¹H nmr data for the new sultone (I) and its rearranged product (II) are reported in Table XXVIX. The chemical shifts for CH₂ClCHClCH₂- moiety are self-consistent with respect to the expected chemical shifts.

MASS SPECTRA

The major mass spectral peaks for these compounds are listed in the experimental section. The MH⁺ peak was found for compound III. Additional (M-X)⁺ or (MH-X)⁺ peaks, such as MH-SO₃⁺, M-SO₃⁺, M-C₃H₅Cl₂⁺, and M-C₄F₉⁺ were also found.

TABLE XVII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3}

	FSO ₂	C(O)F	CF ₃	F ₁	CF ₂ ^a	F ₂
I. CH ₂ ClCHClCH ₂ <u>CF</u> CF ₂ OSO ₂	-	-	-	-82.3(d,d)	-86.8(d,d)	
II. CH ₂ ClCHClCH ₂ CF(SO ₂ F)C(O)F	43.9(d,d)	32.1(d,d,m)	-	-	-	
III. CF ₃ (CF ₂) ₂ CF ₂ OC <u>FCF</u> CF ₂ SO ₂ O	-	-	-84.5(t)	-84.2(d,m)	-87.0(d,m)	

TABLE XXVII
FLUORINE NMR CHEMICAL SHIFTS^{1,2,3}
(continued)

	CF ₂ ^b	CF ₂ ^c	CF
I. CH ₂ ClCHClCH ₂ <u>CF</u> CF ₂ OSO ₂	-	-	-143.0(d,m)
II. CH ₂ ClCHClCH ₂ CF(SO ₂ F)C(O)F	-	-	-160.6(m)
III. CF ₃ (CF ₂) ₂ CF ₂ OC <u>FCF</u> CF ₂ SO ₂ O	105.0(m)	129.5(m)	- 91.8(m)

1. Fluorine chemical shifts in ppm from external CFC1₃.

2. d = doublet, t = triplet, m = multiplet

3. a = CFCF₂, b = CF₂O, c = CF₃(CF₂)₂.

TABLE XXVIII
FLUORINE NMR COUPLING CONSTANTS

	Coupling Constants (Hz)
I. $\text{CH}_2\text{ClCHClCH}_2\text{CF}_{(3)}\text{CF}_{2(1,2)}\text{OSO}_2$	$J_{1,2} = 107.2$ $J_{1,3} = 7.1$ $J_{2,3} = 3.5$
II. $\text{CH}_2\text{ClCHClCH}_2\text{CF}_{(3)}(\text{SO}_2\text{F})_{(2)}\text{C}(\text{O})\text{F}_{(1)}$	$J_{1,2} = 6.1$ $J_{2,3} = 2.3$
III. $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\text{OCFCF}_{2(1,2)}\text{SO}_2\text{O}$	$J_{1,2} = 153.3$

TABLE XXIX
PROTON NMR CHEMICAL SHIFTS^{1,2}

	CHCl	CH ₂ Cl	CH ₂
I. $\text{CH}_2\text{ClCHClCH}_2\text{CFCF}_2\text{OSO}_2$	4.8 (m)	4.2 (m)	3.6 (m)
II. $\text{CH}_2\text{ClCHClCH}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$	4.6 (m)	4.03 (m)	3.4 (m)

1. Proton chemical shifts in ppm downfield from external TMS.

2. m = multiplet.

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APPENDIX

INFRARED AND NMR SPECTRA

IR Spectrum of $[\text{CF}_2(\text{O})\text{CF}(\text{SO}_2)\text{CF}_2]_2$

IR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CFCF}_2\text{OSO}_2$

IR Spectrum of $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$

IR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

IR Spectrum of $[\text{FSO}_2\text{CFHCF}_2]_2$

IR Spectrum of $[\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{OCF}(\text{SO}_2\text{F})\text{CF}_2]_2$

IR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

IR Spectrum of $[(-\text{CH}_2-\overset{|}{\text{CH}}-)_{\text{n}}\text{CH}_2\text{C}(\text{O})\text{OCF}(\text{SO}_2\text{F})\text{CF}_2]_2$

IR Spectrum of $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\text{CH}-\text{CH}_2-]_n$

IR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFCF}_2\text{OSO}_2$

IR Spectrum of $\text{CF}_3\text{OCF}_2\text{CFCF}_2\text{OSO}_2$

IR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

IR Spectrum of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

IR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFHSO}_2\text{F}$

IR spectrum of $\text{CF}_3\text{OCF}_2\text{CFHSO}_2\text{F}$

IR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

IR Spectrum of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

IR Spectrum of $[\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{-CH-CH}_2\text{-}]_n$

IR Spectrum of $[\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{-CH-CH}_2\text{-}]_n$

IR Spectrum of $\text{FSO}_2\text{CF}_2\text{C(O)OAg}$

IR Spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OC}_6\text{F}_5$

IR Spectrum of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$

IR Spectrum of $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$

IR Spectrum of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$

IR spectrum of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

IR Spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{Br}$

IR Spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$

IR Spectrum of $[\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2]_2\text{CH}_2$

IR Spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

IR Spectrum of $\text{CF}_3\text{CFHSO}_3\text{Na}$

IR Spectrum of $\text{CF}_3\text{CFHSO}_3\text{H} \cdot 0.5\text{H}_2\text{O}$

IR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$

IR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H} \cdot 1.5\text{H}_2\text{O}$

IR Spectrum of $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{Na}$

IR Spectrum of $\text{C}_5\text{F}_{11}\text{CFHCF}_2\text{SO}_3\text{H} \cdot 0.5\text{H}_2\text{O}$

IR Spectrum of $\text{CH}_2\text{ClCHClCH}_2\text{CFCF}_2\text{OSO}_2$

IR Spectrum of $\text{CH}_2\text{ClCHClCH}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

IR Spectrum of $\text{CF}_3(\text{CF}_2)_2\text{CF}_2\text{OCFCF}_2\text{SO}_2\text{O}$

^{19}F NMR Spectrum of $[\text{CF}_2(\text{O})\overline{\text{CF}}(\text{SO}_2)\text{CF}_2]_2$

^{19}F NMR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}_2\text{OSO}_2$

^{19}F NMR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CFCF}_2\text{OSO}_2$

^{19}F NMR Spectrum of $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$

^{19}F NMR Spectrum of $[\text{FC}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_2]_2$

^{19}F NMR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C(O)F}$

^{19}F NMR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

^1H NMR Spectrum of $[\text{FSO}_2\text{CFHCF}_2]_2$

^{19}F NMR spectrum of $[\text{FSO}_2\text{CFHCF}_2]_2$

¹⁹F NMR spectrum of [CH₂=CHCH₂C(O)OCF(SO₂F)CF₂]₂

^{19}F NMR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

^{19}F NMR Spectrum of $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

^1H NMR Spectrum of $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-]_n$

^{19}F NMR Spectrum of $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{|}{\text{CH}}-\text{CH}_2-]_n$

$=\text{CF}$

^{19}F NMR Spectrum of $[\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\text{CH}-\text{CH}_2-]_n$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}_2\text{OSO}_2$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}_2\text{CF}_2\text{OSO}_2$

^{19}F NMR Spectrum of $\text{CF}_3\text{OCF}_2\text{CFCF}_2\text{OSO}_2$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

^{19}F NMR Spectrum of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

^{19}F NMR Spectrum of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$

^1H NMR spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFHSO}_2\text{F}$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFH}\text{SO}_2\text{F}$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CFHSO}_2\text{F}$

^1H NMR Spectrum of $\text{CF}_3\text{OCF}_2\text{CFHSO}_2\text{F}$

^{19}F NMR Spectrum of $\text{CF}_3\text{OCF}_2\text{CFH}\text{SO}_2\text{F}$

^1H NMR Spectrum of $\text{R}_f\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

^{19}F NMR Spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

^{19}F NMR spectrum of $\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

^{19}F NMR Spectrum of $\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$

C_3H_5

1H NMR Spectrum of $[CF_3OC_2F_4OCF_2CF(SO_2F)C(O)OCH_2-\overset{|}{CH}-CH_2-]_n$

^{19}F NMR Spectrum of $[\text{CF}_3\text{OC}_2\text{F}_4\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-]_n$

^1H NMR spectrum of $[\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\overset{|}{\text{CH}}-\text{CH}_2-]_n$

^{19}F NMR Spectrum of $[\text{CF}_3\text{OCF}_2\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2-\text{CH}-\text{CH}_2-]_n$

^{19}F NMR Spectrum of $FSO_2CF_2C(O)OC_6F_5$

^{19}F NMR Spectrum of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OR}$

^1H and ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$

^1H NMR spectrum of $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$

^{19}F NMR spectrum of $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$

^1H and ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$

^1H NMR Spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{Br}$

CH_3

^1H NMR Spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$

^1H NMR Spectrum of $[\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{O}]_2\text{CH}_2$

CH

^1H NMR Spectrum of $\text{CF}_3\text{CFH}\text{SO}_3\text{Na}$

^1H NMR Spectrum of $\text{CF}_3\text{CFHSO}_3\text{H}\cdot 0.5\text{H}_2\text{O}$

^{19}F NMR Spectrum of $\text{CF}_3\text{CFH}\text{SO}_3\text{H}\cdot 0.5\text{H}_2\text{O}$

CH

^1H NMR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$

CF_2 ^{19}F NMR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$

CF

^{19}F NMR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{Na}$

^1H NMR spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}\cdot 1.5\text{H}_2\text{O}$

^{19}F NMR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}\cdot 1.5\text{H}_2\text{O}$

^{19}F NMR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}\cdot 1.5\text{H}_2\text{O}$

^{19}F NMR Spectrum of $\text{CF}_3\text{CFHCF}_2\text{SO}_3\text{H}\cdot 1.5\text{H}_2\text{O}$

^1H NMR Spectrum of $\text{R}_f\text{CH}_2\text{CHClCH}_2\text{CH}_2\text{Cl}$

^{19}F NMR Spectrum of $\text{CH}_2\text{ClCHClCH}_2\text{CF}_2\text{OSO}_2$

CF

^{19}F NMR Spectrum of $\text{CH}_2\text{ClCHClCH}_2\text{CFCF}_2\text{OSO}_2$

^{19}F NMR Spectrum of $\text{CH}_2\text{ClCHClCH}_2\text{CF}(\text{SO}_2\text{F})\text{C(O)F}$