The Chemistry of Sulfonyl Fluorides: SF$_5$ and/or SO$_2$F Containing Compounds as Precursors to Sulfonic Acids

Robin Joyce Terjeson

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THE CHEMISTRY OF SULFONYL FLUORIDES:
SF₅ AND/OR SO₂F CONTAINING COMPOUNDS
AS PRECURSORS TO SULFONIC ACIDS

by

ROBIN JOYCE TERJESON

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

DOCTOR OF PHILOSOPHY
in
ENVIRONMENTAL SCIENCE AND RESOURCES:
CHEMISTRY

Portland State University
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TO THE OFFICE OF GRADUATE STUDIES:

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Title: The Chemistry of Sulfonyl Fluorides: SF₅ and/or SO₂F Containing Compounds as Precursors to Sulfonic Acids

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Sulfonyl fluoride systems and their derivatives, RSO₂F, where R represents hydrocarbon/fluorocarbon moieties continue to be of considerable interest. The incorporation of the sulfonyl fluoride group (SO₂F) into molecular systems can lead to compounds that are useful as ion-exchange resins, surface active agents, fuel cell electrolytes, and strong sulfonic acids/salts.

Interest in preparing SF₅ containing sulfonyl fluorides led to the synthesis of the β-sultone, SF₅CHCF₂OSO₂, and its rearranged product. Hydrolysis of the sultone gave SF₅CH₂SO₂F which led to the sulfonic acid and salt, SF₅CH₂SO₃H•H₂O and (SF₅CH₂SO₃)₂Ca. Esters of the sultone were prepared by reaction of the sultone with fluorinated alcohols in the presence of NaF to give SF₅CH(SO₂F)C(O)OR where R = CH₂CF₃ and CH(CF₃)₂.

Polymeric SF₅/SO₂F containing esters were prepared by reaction of allyl esters, RCX(SO₂F)C(O)OCH₂CH=CH₂, in ultraviolet light where R = CF₃ or SF₅ and X = H or F.

Fluorinated silver carboxylate salts have been useful in preparing fluoroesters from alkyl iodides. Therefore, a new silver salt, FSO₂CF₂C(O)OAg was prepared and characterized; its reaction with (CH₃)₃SiI, HOCH₂CH₂I and alkyl bromides and iodides are reported.

In addition, new SF₅ containing fluoropolymers were synthesized via reaction of fluorinated olefins with SF₅Br. Reactions of SF₅ containing olefins with CF₃OC1, ClF and Cl₂
provide reagents that may be of potential use as precursors to sulfonyl fluoride containing systems.

All new compounds were characterized by their respective infrared, nmr and mass spectra.
ACKNOWLEDGEMENTS

The author extends appreciation to Dr. Gary Gard for his helpfulness, guidance and patience; to Dr. Gary Knerr (University of Idaho) for the mass spectra, Roger Kohnert (Oregon State University) for $^{13}\text{C}$ nmr and $^{19}\text{F}$ nmr spectra, Dr. Horace White for helpful discussions about nmr and the Gas Research Institute for funding. A special thank-you goes to my family and my colleagues at Clark College for their support and encouragement.
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Fuel cell power plants which cogenerate electricity and heat on site are entering extensive field testing. The electrochemical process that generates the power occurs in the individually stacked cells and provides direct current voltage. Each cell consists of an anode, a cathode, an electrolytic solution, and fuel cavities. The hydrogen rich fuel is passed over the catalytic anode releasing electrons and H\(^+\) ions. The H\(^+\) ions are carried via the electrolyte to the cathode where they react with oxygen from air and the electrons from the anode that have passed through an external circuit. The reaction of the H\(^+\) ion and oxygen produces heat and liquid water. The electrons passing through the external circuit provide the direct current power which is converted to alternating current power.\(^1\)

\[
H_2 \rightarrow 2H^+ + 2e^- \\
2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O
\]

Figure 1. A typical fuel cell.
ELECTROLYTES

Significant research in providing stable materials for anodes, cathodes, and electrolytes of fuel cells is continuing. Of particular interest in our laboratories are fluorocarbon sulfonyl halide \((RSO_2X)\) systems which can be converted to sulfonic acid electrolytes \((R=SF_5CH_2, SF_5CHF, CH_3, CF_3CF_2, \text{etc.}, \ X=\text{F, Cl})\). Currently, phosphoric acid is the electrolyte of choice in fuel cells, but it has limited oxygen solubility. Fluorine-containing sulfonic acids possess properties which are desirable for fuel cell electrolytes. It is expected that these acids alone or in combination with phosphoric acid, will result in enhanced performance of the fuel cell.

Electrolytes for fuel cells need to be thermally stable, non-reactive with hydrogen and oxygen as well as metallic systems, able to conduct ions, and to dissolve oxygen for increased reaction efficiency. "Wetting" or coating of electrodes is an additional concern in finding an appropriate electrolyte, as is high volatility or loss of the electrolyte in the system. The thermodynamics and kinetics of the fuel cell are such that the efficiency increases at higher temperatures.
SULFONIC ACIDS AND SULFONYL FLUORIDES

Interesting properties associated with fluorine containing sulfonic acids include:

1. Acid strength for acids that depend on the amount and position of fluorine in the fluorocarbon "tail". (CF$_3$SO$_3$H is a stronger acid than CH$_3$SO$_3$H)
2. Increased oxygen solubility.
3. Good ionic conductivity.
4. High boiling points (low vapor pressure).
5. Non-toxic and non-corrosive compounds.
6. Excellent electrochemical and thermal stability.
7. Relatively low concentrations of acid optimize efficiency thereby lowering costs.
8. Variable surfactant activity depending on the chain length and heteroatoms (i.e. oxygen, nitrogen or phosphorous in the carbon chain).

Trifluoromethanesulfonic acid, prepared from CF$_3$SO$_2$X, X=Cl,F, is comparable to phosphoric acid as an electrolyte for fuel cells. Preliminary testing of SF$_5$CHFSO$_3$H prepared in our laboratory also showed potential as an electrolyte.

Preparation of sulfonyl fluorides and their conversion to sulfonic acids have been reported previously. Important factors influencing the properties of fluorine-containing sulfonic acids include substituent and terminal group effects, chain length, and heteroatom effects. For
example: different end groups, such as the SF₅ grouping, may stabilize the sulfonic acid systems. Preparation of compounds containing oxygen as ethers, and variation in the number of carbons are other ways of changing the properties of sulfonic acids. The relationship between the number of fluorine atoms versus the number of hydrogen atoms in the chain influences the acidity. Longer carbon chains and more fluorination increases oxygen solubility and acidity of sulfonic acids, and stabilizes the systems as well.

Polymeric sulfonic acids have been successfully used as solid electrolytes on some space flights. Sulfonyl fluoride systems may also lead to compounds that are of interest as ion-exchange resins and surface-active agents. See Table V.

Compounds containing sulfonyl fluoride (SO₂F) group(s) can easily be converted to sulfonic acids via formation of the sodium or calcium salt and treatment with sulfuric or hydrochloric acid. For this reason we are interested in investigating methods of preparing compounds containing the sulfonyl fluoride grouping as well as ways of incorporating heteroatoms into their structures. Chapter II reviews methods of producing sulfonyl fluoride systems.
SULFONYLFLUORIDE/SULFONIC ACID PRECURSORS

In order to prepare new sulfonyl fluoride systems, a number of new olefins and/or halogen containing compounds are needed as starting materials. Reactions of hypochlorite compounds with fluoro-olefins as well as reactions of SF$_5$Br with these olefins give rise to new olefinic systems. The SF$_5$ group potentially may bring about significant changes in the chemical, physical and biological properties of the sulfonyl fluoride molecules as it does in other systems. These properties are manifested by applications such as solvents for polymers, perfluorinated blood substitutes, surface-active agents, fumigants, and as thermally and chemically stable systems. Fluoroalkyl ethers are useful as monomers for polymerization as well as for their own physical properties.

Polymeric SF$_5$-containing compounds were noted during preparation of some adducts/olefins. It is possible that these SF$_5$-containing polymers have potential use as non-reactive Teflon-like waxes and greases. Gaskets made of polytetrafluoroethylene or other heat resistant, corrosion resistant fluoropolymers form reliable seals in phosphoric acid fuel cells.
Fluorinated sulfonyl fluoride (SO$_2$F) compounds may be prepared by a variety of methods and have widespread use as mentioned in Chapter I. In our laboratory, sulfonyl fluoride systems are made as precursors to sulfonic acids for potential evaluation as fuel cell electrolytes. The properties of fluorinated esters and ethers containing the SO$_2$F moiety are a part of our ongoing studies. Short chain sulfonic acids are of interest due to the fact that long chain fluorinated compounds wet Teflon (serves as mounting material for fuel cell electrodes) more readily. The need for low volatility and high stability toward oxidation in these acids leads to our interest in attaching the SF$_5$ grouping to a fluorocarbon group. Investigating the properties of fluorinated esters and ethers containing the SO$_2$F moiety are of interest for the same reason.

Fluorinated polymeric solids and viscous oils with the SO$_2$F group also incur growing interest as potential ion exchange resins, as precursors to polymeric sulfonic acids similar to Nafion$^\text{TM}$, and as copolymers. (See Table V) In this chapter we will review a variety of methods used for preparing SO$_2$F containing compounds and polymers.
METHODS OF PREPARATION

Electrochemical Fluorination

One method of preparing fluorinated sulfonyl fluoride compounds is by electrochemical fluorination of hydrocarbons containing the sulfonyl fluoride/chloride moiety; however, the percent yield decreases as the number of carbons in the system increase:\textsuperscript{4,11,12}

\[
\text{HF} \text{CH}_3\text{SO}_2\text{Cl/CH}_3\text{SO}_2\text{F} \xrightarrow{\text{HF}} \text{CF}_3\text{SO}_2\text{F} \quad (1)
\]

87%\textbar{}96% yield

This method is sometimes used to increase the amount of fluorine in the hydrocarbon chain.

Reactions of ClSO$_2$F/SO$_2$F$_2$ with Olefins

Addition of ClSO$_2$F or SO$_2$F$_2$ to olefins has been used to prepare some SO$_2$F containing compounds in reactions such as:\textsuperscript{13}

\[
\text{rad. init.} \quad \text{ClSO}_2\text{F} + n\text{RCH=CH}_2 \xrightarrow{\text{rad. init.}} \text{Cl(CHRCH}_2)_n\text{SO}_2\text{F} \quad (2)
\]

Temple, in 1968, reported a series of interesting reactions that lead to sulfonyl fluorides and sulfones:\textsuperscript{5}

\[
\text{C}_6\text{H}_5\text{F} + n\text{CF}_2=\text{CF}_2 + \text{SO}_2\text{F}_2 \xrightarrow{\text{C}_6\text{H}_5\text{F}} \text{CF}_3\text{CF}_2\text{SO}_2\text{CF}_2\text{CF}_3 \quad (3)
\]

\[
\text{CF}_2=\text{CF}_2 + \text{RSO}_2\text{F} \xrightarrow{\text{diglyme}} \text{RSO}_2\text{CF}_2\text{CF}_3 \quad (4)
\]

(R = benzene sulfonyl fluoride and perfluorohexane disulfonyl fluoride)

\[
\text{CF}_3\text{CF}=\text{CF}_2(\text{HFP}) + \text{SO}_2\text{F}_2 \xrightarrow{(\text{C}_2\text{H}_5)_4\text{N}^+\text{F}^-} \text{FC(CF}_3)_2\text{SO}_2\text{F} + \text{HFP} \quad (5)
\]

HCF$_2$CF$_2$CH$_2$Cl dimer/trimer
Sultones and Derivatives

Fluorinated β-sultones have proven to be the most effective precursors to formation of sulfonyl fluoride containing systems.

Reactions of sulfur trioxide (SO₃) with hydrocarbon olefins proceed readily and are so exothermic that any sultone produced is difficult to isolate. When electronegative groups are attached to the olefin, the reaction is more moderate; with fluoroolefins, β-sultones are produced:

\[
\text{XFC---cYZ} \quad \text{where X may be F, H, CF₃, Cl or other}
\]

\[
\text{O₂S---O} \quad \text{fluorinated substituents and Y and Z are F or H.}^{6,14,15}
\]

Trifluoroethylene, for example, undergoes the following reaction to form 2-hydroxy-1,2,2-trifluoroethanesulfonic acid β-sultone and the 1,3,2,4-dioxadithiane-2,2,4,4-tetraoxide:\(^6\)

\[
2\text{CHF}=\text{CF}_2 + 3\text{SO}_3 \rightarrow \text{CHFCF}_2 + \text{CHF}---\text{CF}_2
\]

\[
\text{O₂S---O} \quad \text{O₂S---O} \quad \text{O---SO₂}
\]

With tetrafluoroethylene in addition to the β-sultone \(\text{CF}_2\text{CF}_2\text{OSO}_2\), the cyclic sulfite, \(\text{OCF}_2---\text{CF}_2\text{O}\) is also found
when Sulfan is used instead of freshly distilled monomeric sulfur trioxide.

Most fluorinated \( \beta \)-sultones undergo hydrolysis via the following reaction to give a sulfonyl fluoride compound:

\[
\text{CFXCF}_2\text{OSO}_2 + \text{H}_2\text{O} \rightarrow \text{HCFXSO}_2\text{F} - \text{CO}_2, -\text{HF}
\]  

(8)

Rearrangement of the sultone in the presence of a Lewis base produces the bifunctional carbonyl fluoride and sulfonyl fluoride:

\[
\text{CFXCF}_2\text{OSO}_2 \rightarrow \text{CFX(SO}_2\text{F})\text{C(O)F}
\]  

(9)

With tetrafluoroethylene \( \beta \)-sultone, the carboxylic acid, \( \text{FSO}_2\text{CF}_2\text{C(O)OH} \), difluoro(sulfonylfluoride)acetic acid, is formed in the hydrolysis reaction. Proposed mechanisms for these reactions are given in Chapter IV. Some products/derivatives of the hydrolysis and rearrangement reactions of selected fluorinated \( \beta \)-sultones are given in Table I. A review by Knunyants and Sokolskii done in 1972 gives a variety of reactions possible with fluorinated \( \beta \)-sultones, many of which produce fluorinated sulfonyl fluorides. The reactions of the interesting disultone gives fluorosulfate/sulfonyl fluoride products:

\[
\text{CHF—CF}_2 \xrightarrow{\text{KF}} \text{CF}_2=\text{CFOSO}_2\text{O}_2\text{SO}_2\text{F}
\]  

(10)

\[
\text{O}_2\text{S} \xrightarrow{\Delta} \text{FC(O)CF}_2\text{SO}_2\text{O}_2\text{SO}_2\text{F}
\]  

(11)

Of particular interest are the sultones prepared from \( \text{CF}_3\text{CH}=\text{CF}_2 \) and \( \text{SF}_5\text{CF}=\text{CF}_2 \) as well as their derivatives.
In addition to the expected hydrolysis and rearrangement products, the sulfonic acid, SF₅CHFSO₃H, prepared from the sultone, SF₅CFCF₂O₅S (2-hydroxy-1-(pentafluoro-α₆-sulfanyl)-1,2,2-trifluoroethanesulfonic acid sultone), is currently under evaluation as a potential fuel cell electrolyte. The products of the reaction of CF₃CHCF₂OSO₂ with alcohols give esters which have been shown to have a labile proton as observed via nmr by stabilization with base (eqn. 14):

\[
\text{CF}_3\text{CHCF}_2\text{OSO}_2 + \text{ROH} \rightarrow \text{CF}_3\text{CH(SO}_2\text{F)}\text{C(O)OR} + \text{HF} \quad (12)
\]
\[
\text{CF}_3\text{CH(SO}_2\text{F)}\text{C(O)OR} + 7\text{OH}^- \rightarrow \text{-OOCCH}_2\text{SO}_2\text{O}^- + 4\text{F}^- + 2\text{H}_2\text{O} \quad (13)
\]
\[
- + \text{HCO}_3^- + \text{ROH}
\]
\[
\text{CF}_3\text{CHCF}_2\text{OSO}_2 + \text{OH}^-/\text{R}_3\text{N} \rightarrow \text{CF}_3\text{C(SO}_2\text{F)}\text{C(O)OR} + \text{HOH}/\text{R}_3\text{NH}^+ \quad (14)
\]

R = CH₃, C₂H₅

In a number of cases it is possible to replace the proton in the esters CF₃CH(SO₂F)CO(O)R to form the derivatives CF₃CBr(SO₂F)COOR and CF₃CCl(SO₂F)COOR; and in one reaction, CF₃CCl₂SO₂F (also obtained by chlorination of CF₃CH₂SO₂F in a proposed two step process). Other studies by the same group show the CH acidity of α-hydro containing sulfonyl fluorides to fall in the following order: CF₃CHFSO₂F < CF₃CH₂SO₂F < CF₃CHClSO₂F = CF₃CH(SO₂F)C(O)OR. Based upon proton nmr data, the CH acidity of some SF₅-containing sulfonyl fluoride systems occurs in the following order: SF₅CH₂SO₂F < SF₅CHFSO₂F = SF₅CH(SO₂F)C(O)OR (Table VIII).
Esters/Ethers Prepared via Reaction of Sultones with Alcohols

An early study found that 2-hydroxy-tetrafluoroethane-β-sultone, \( \text{CF}_2\text{CF}_2\text{SO}_2 \) (I), or its acid, \( \text{FSO}_2\text{CF}_2\text{C(O)OH} \) (II), when reacted with alcohols under mild conditions (0 to 10°C) produced the corresponding esters, \( \text{FSO}_2\text{CF}_2\text{C(O)OR} \) (\( R = \text{C}_3\text{H}_7, \text{C}_8\text{H}_{17}, \text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{CHCH}_2, \) and \( \text{H(CF}_2\text{)}_4\text{CH}_2 \) and the diester \( (\text{CH}_2\text{OC(O)CF}_2\text{SO}_2\text{F})_2 \).\(^6\) Similar reactions produce \( \text{FSO}_2\text{CF}_2\text{C(O)OCH}_3, \text{FSO}_2\text{CF}_2\text{C(O)OC}_2\text{H}_5, \) and \( \text{FSO}_2\text{CF}_2\text{C(O)OCH(CH}_3\text{)}_2.\(^{15}\) Reaction of 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone, \( \text{CF}_3\text{CF}_2\text{SO}_2 \), with the alcohols \( \text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{CHCH}_2\text{OH}, \text{CH}_3\text{OH}, \) and \( \text{(CH}_3\text{)}_2\text{CHOH} \) also gave esters.\(^6,^{16}\) In more recent studies, the β-sultones, \( \text{CF}_2\text{CF}_2\text{SO}_2 \) and \( \text{CF}_3\text{CF}_2\text{SO}_2 \), when reacted with fluorinated and nonfluorinated alcohols produce the sulfonyl fluoride (SO₂F) containing esters; with appropriate alkane diols, triols, or tetraols the corresponding di, tri, and tetra-esters are formed.\(^{20,21}\) (See Table II)

Direct reaction of a number of the SO₂F containing esters with SF₄ acting as a fluorinating agent and a large excess of anhydrous HF has been shown to produce the corresponding ether derivatives.\(^{22}\)

\[
R_f\text{OC(O)CF}_2\text{SO}_2\text{F} + \text{SF}_4/\text{HF} \rightarrow R_f\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \tag{15}
\]

\( R_f = \text{CF}_3\text{CH}_2, \text{CF}_3\text{CF}_2\text{CH}_2, \text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2, \text{CH}_3\text{CH}_2, \text{C(CF}_3\text{)}_2\text{H}, \text{CF}_3\text{CH(CF}_3\text{), CH}_3\text{C(CF}_2\text{)}_2, \text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2, \) and \( \text{C(CH}_2\text{O)}_4 \)
TABLE I
PRODUCTS/DERIVATIVES OF SULTONE REARRANGEMENT
AND HYDROLYSIS REACTIONS

<table>
<thead>
<tr>
<th>Sultone</th>
<th>Product</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₂CF₂OSO₂ (I)</td>
<td>FSO₂CF₂C(O)OH (II)</td>
<td>6, 15, 16</td>
</tr>
<tr>
<td></td>
<td>FSO₂CF₂C(O)F</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>FSO₂CF₂C(O)Cl (from II)</td>
<td>16</td>
</tr>
<tr>
<td>CHFCF₂OSO₂ (III)</td>
<td>FSO₂CHFC(O)F</td>
<td>6</td>
</tr>
<tr>
<td>CF₃CFCF₂OSO₂ (IV)</td>
<td>CF₃CF(SO₂F)C(O)F</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>CF₃CHFSO₂F</td>
<td>6</td>
</tr>
<tr>
<td>CF₂CFC₁OSO₂ (V)</td>
<td>ClSO₂CF₂C(O)F</td>
<td>6</td>
</tr>
<tr>
<td>CF₃CFC₂OSO₂ (VI)</td>
<td>FSO₂CF₂C(O)F</td>
<td>6</td>
</tr>
</tbody>
</table>

Formation of Multiple Bond/SO₂F Systems from Sultones

Sulfonyl fluoride systems containing carbon-carbon double bonds are of particular interest because they can act as precursors to polymeric and copolymeric sulfonic acids. Fluorinated compounds containing multiple SO₂F groups are also under study as precursors to polysulfonic acids.

Beckerbauer produced a series of sulfonyl fluoride containing fluoroolefins of the form CF₂=CF(CFR)ₙCFHSO₂F (n= 1 to 5 and R = F or a perfluoroalkyl group with 1 to 5 carbons) by reacting diolefins with SO₃ in a 1:1 ratio and subsequent hydrolysis. He also patented a preferred reaction where one double bond is protected by chlorination then, after hydrolysis, the chlorines are removed by
TABLE II

ESTERS PREPARED FROM SULTONES AND ALCOHOLS

<table>
<thead>
<tr>
<th>Esters of CF₂CF₂OSO₂²⁰</th>
<th>Esters of CF₂CF₂OSO₂²¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃CH₂OC(O)CF₂SO₂F</td>
<td>CF₃CH₂OC(O)CF₂SO₂F</td>
</tr>
<tr>
<td>CF₃CF₂CH₂OC(O)CF₂SO₂F</td>
<td>(CF₃)₃COC(O)CF₂SO₂F</td>
</tr>
<tr>
<td>CF₃CF₂CF₂CH₂OC(O)CF₂SO₂F</td>
<td>CF₆SO₅C(O)CF₂SO₂F</td>
</tr>
<tr>
<td>(CF₃)₂C(CH₃)OC(O)CF₂SO₂F</td>
<td>CF₆SO₅C(O)CF₂SO₂F</td>
</tr>
<tr>
<td>CF₃CH(CH₃)OC(O)CF₂SO₂F</td>
<td>Esters of CF₃CFCEF₂OSO₂²¹</td>
</tr>
<tr>
<td>(CF₃)₂CHOC(O)CF₂SO₂F</td>
<td>[FSO₂CF(CF₃)C(O)OCH₂]₂</td>
</tr>
<tr>
<td>C₇F₁₅CH₂OC(O)CF₂SO₂F</td>
<td>(CF₃)₂CHOC(O)CF(CF₃)SO₂F</td>
</tr>
<tr>
<td>CH₂(CF₂)₃CH₂OC(O)CF₂SO₂F</td>
<td>CF₆SO₅C(O)CF(CF₃)SO₂F</td>
</tr>
<tr>
<td>CH₃C(CH₂OC(O)CF₂SO₂F)₃</td>
<td>CF₃CH₂OC(O)CF(CF₃)SO₂F</td>
</tr>
<tr>
<td>[FSO₂CF₂(O)OC(OH)₂]₂</td>
<td></td>
</tr>
<tr>
<td>C(CH₂OC(O)CF₂SO₂F)₄</td>
<td></td>
</tr>
</tbody>
</table>

reaction with zinc in dioxane to regenerate the olefin functionality.²³

CF₂=CFCF₂CF=CF₂ + Cl₂ → CF₂ClCFClCF₂CF=CF₂ = CF₂ (16)

CF₂ClCFClCF₂CF=CF₂ + SO₃ → CF₂ClCFClCF₂CF-CF₂ = CF₂

H₂O

CF₂ClCFClCF₂CF-CF₂ → CF₂ClCFClCF₂CFH

O₂S—O

-HF, -CO₂

SO₂F

Zn/dioxane

CF₂ClCFClCF₂CFHSO₂F → CF₂=CFCF₂CFHSO₂F (19)
Similar to Beckerbauer's work, Russian groups have reacted another series of perfluoro diolefins (1,3-pentadiene, 1,5-hexadiene, and 1,7-octadiene) with SO₃ to give both the mono-β-sultone with olefin functionality and bis-β-sultones which produce products containing two SO₂F groupings. The monosultone is predominately produced when the ratio of olefin to SO₃ is 1.25 to 1 and the bis-sultone when the ratio is 1 to 3. Rearrangement and hydrolysis of these sultones give a variety of SO₂F containing compounds similar to those listed here for the mono and bis-β-sultone prepared from 1,7-octadiene.²⁴,²⁵

\[
\begin{align*}
& \text{CF}_2=\text{CF} (\text{CF}_2)_4 \text{CFCF}_2 \text{OSO}_2 \\
& \text{CF}_2=\text{CF} (\text{CF}_2)_4 \text{CF(SO}_2\text{F}) \text{COF} \\
& \text{CF}_2=\text{CF} (\text{CF}_2)_4 \text{CFHSO}_2\text{F} \\
& \text{Perfluoroethenesulfonyl fluoride, CF}_2=\text{CFSO}_2\text{F, is prepared by heating CF}_3 \text{CHFSO}_2\text{F to 500°C via a radical reaction:}^{16}
\end{align*}
\]

\[
\begin{align*}
& \text{CF}_3 \text{CHFSO}_2\text{F} \xrightarrow{\sim 500°C} \text{CF}_3 \text{CFSO}_2\text{F} \xrightarrow{-\text{HF}} \text{CF}_2=\text{CFSO}_2\text{F}
\end{align*}
\]

A number of nucleophilic addition products to this olefin have been reported.¹⁶

Pentafluoro-1-propene-1-sulfonyl fluoride, \(\text{CF}_3\text{CF} = \text{C(SO}_2\text{F})\text{F}\), 2,2-difluoroethenesulfonyl fluoride, \(\text{FSO}_2\text{CH} = \text{CF}_2\), and pentafluoropropene-2-sulfonyl fluoride, \(\text{CF}_2 = \text{C(SO}_2\text{F})\text{CF}_3\), have also been prepared by Russian workers.
A variety of reactions of these olefins with both nucleophilic and electrophilic reagents have been studied, most of which involve addition/dehydrohalogenation reactions. Examples of these reactions are (See Table III for additional compounds):26

\[
\text{RCF}_2\text{CHFSO}_2\text{F} \rightarrow \text{RCF}==\text{CFSO}_2\text{F} \quad (R=\text{CF}_2\text{H}, \text{CF}_2\text{Cl}, \text{C}_3\text{F}_7) \quad (21)
\]

\[
\text{RCF}==\text{CFSO}_2\text{F} + \text{CH}_3\text{OH} \rightarrow \text{RCF}==\text{CFSO}_2\text{F} + \text{RCF}==\text{CFSO}_2\text{F} \quad (22)
\]

erythro threeo

Reaction of \(\text{FSO}_2\text{CH}==\text{CF}_2\), prepared from a 10% aqueous solution of triethylamine and \(\text{CF}_3\text{CH}_2\text{SO}_2\text{F}\),27 with \(\text{SO}_3\) and subsequent rearrangement gives an acyl fluoride with two \(\text{SO}_2\text{F}\) groups; ketenes were also produced.31

\[
\text{FSO}_2\text{CH}==\text{CF}_2 + \text{SO}_3 \rightarrow \text{FSO}_2\text{CHCF}_2\text{OSO}_2 \quad (67.5\%) \quad (23)
\]

\[
\text{FSO}_2\text{CHCF}_2\text{OSO}_2 \rightarrow (\text{FSO}_2)_2\text{CHCOF} \rightarrow (\text{FSO}_2)_2\text{C}==\text{C}=\text{O} \quad (91\%) \quad (24)
\]

\[
\text{FSO}_2\text{C(CF}_3\text{)}==\text{C}=\text{O} + \text{SO}_3 \rightarrow (\text{FSO}_2)_2\text{C}==\text{CF}_2 \quad (60.7\%) \quad (25)
\]

\[
(\text{FSO}_2)_2\text{C}==\text{CF}_2 + \text{FSO}_3\text{Cl} \rightarrow (\text{FSO}_2)_2\text{CClCF}_2\text{OSO}_2\text{F} \quad (68.5\%) \quad (26)
\]

\[
(\text{FSO}_2)_2\text{CHCOF}/(\text{FSO}_2)_2\text{C}==\text{C}=\text{O}/(\text{FSO}_2)_2\text{C}==\text{CF}_2 + \text{MeOH} \rightarrow \text{FSO}_2\text{CH}_2\text{C(O)OMe} \quad (47-85\%) \quad (27)
\]

Synthesis of the ketene containing \(\text{SO}_2\text{F}\) compound, \(\text{FSO}_2\text{C(CF}_3\text{)}==\text{C}=\text{O}\), was first reported by Krespan via the following reaction:32
A more general method for producing fluorine containing ketenes consists of formation of an ester from the sultone and subsequent reaction with phosphoric anhydride:

\[
\begin{align*}
\text{FSO}_2\text{C}(\text{CF}_3)=\text{C}=\text{O} + [\text{HOR} + \text{P}_4\text{O}_{10}] &\rightarrow \text{FSO}_2\text{C}(\text{CF}_3)=\text{C}=\text{O} \\
\end{align*}
\]

Another route involves treating the rearranged product with the boron trifluoride-triethylamine complex:

\[
\begin{align*}
\text{FSO}_2\text{CH(CF}_3\text{)C(O)F} + [\text{BF}_3\cdot\text{NEt}_3] &\rightarrow \text{FSO}_2\text{C}(\text{CF}_3)=\text{C}=\text{O} \\
-\text{[BF}_4^-\cdot\text{HNEt}_3^+] &\rightarrow \text{FSO}_2\text{C}(\text{CF}_3)=\text{C}=\text{O} \\
\end{align*}
\]
### TABLE III

**LISTING OF DERIVATIVES OF SULFONYL FLUORIDES CONTAINING A DOUBLE BOND**

**Derivatives of** $\text{CF}_3\text{C} = \text{C}_\text{SO}_2\text{F}$; reference 26

<table>
<thead>
<tr>
<th>Derivatives</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CF}_3\text{C}(\text{O})\text{CHFSO}_2\text{F}$</td>
<td>![Structure 1]</td>
</tr>
<tr>
<td>$\text{CF}_3\text{CFClCHFSO}_2\text{F}$</td>
<td>![Structure 2]</td>
</tr>
<tr>
<td>$\text{FSO}_2\text{CFHCF(OCH}_3\text{)}\text{CF}_3$</td>
<td>![Structure 3]</td>
</tr>
<tr>
<td>$\text{CF}_3\text{C(NEt}_3\text{)}=\text{CF(SO}_2\text{F)}$</td>
<td>![Structure 4]</td>
</tr>
</tbody>
</table>

**Derivatives of** $\text{CF}_2=\text{C(CE)}\text{SO}_2\text{F}$; reference 28

<table>
<thead>
<tr>
<th>Derivatives</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ROCF}_2\text{CH(CE)}\text{SO}_2\text{F}$ (R=CH$_3$, C$_2$H$_5$, CH(CE)$_2$, CH(CE)$_2$4H, CH$_2$CF$_2$NO$_2$, CH$_3$CH$_2$CF$_2$NO$_2$)</td>
<td>![Structure 5]</td>
</tr>
<tr>
<td>$\text{C}_4\text{H}_9\text{SCF}_2\text{CH(CE)}\text{SO}_2\text{F}$</td>
<td>![Structure 6]</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_2\text{NC(CE)}=\text{C(CE)}\text{SO}_2\text{F}$ (isomers)</td>
<td>![Structure 7]</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OCF}_2\text{C(CE)}\text{SO}_2\text{F(OCH}_3\text{)}=\text{C(CE)}\text{SO}_2\text{F}$</td>
<td>![Structure 8]</td>
</tr>
<tr>
<td>$\text{XCF}_2\text{CH(CE)}\text{SO}_2\text{F}$ (X=Cl, Br)</td>
<td>![Structure 9]</td>
</tr>
<tr>
<td>$\text{4-CH}_3\text{OC}_6\text{H}_4\text{CF}=\text{C(CE)}\text{SO}_2\text{F}$ (isomers)</td>
<td>![Structure 10]</td>
</tr>
<tr>
<td>$\text{FSO}_2\text{OCF}_2\text{C(SO}_2\text{F)}=\text{CF}_2$</td>
<td>![Structure 11]</td>
</tr>
</tbody>
</table>
TABLE III

LISTING OF DERIVATIVES OF SULFONYL FLUORIDES
CONTAINING A DOUBLE BOND
(continued)

<table>
<thead>
<tr>
<th>Derivatives of FSO₂CH=CF₂; reference 29</th>
<th>Others; reference 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSO₂CH₂CF₂OR (R=CH₃, C₂H₅)</td>
<td>RC(NEt₂)=C(SO₂F)F (R=CF₂H, C₃F₇)</td>
</tr>
<tr>
<td>FSO₂CH₂CF₂SC₃H₇</td>
<td>RCF=CFSO₂F (R=HCF₂, CF₂Cl)</td>
</tr>
<tr>
<td>FSO₂CH=CFNR₂ (R=CH₃, C₂H₅)</td>
<td>RCFClCHFOSO₂F (R=CF₂Cl, CF₂H, C₃F₇)</td>
</tr>
<tr>
<td>FSO₂CHClCF₂Cl</td>
<td>HCF₂CF(X)CF(X)SO₂F (isomers, X=Cl, Br)</td>
</tr>
<tr>
<td>FSO₂CCl₂CF₂Cl</td>
<td></td>
</tr>
</tbody>
</table>

Others:
RC(NEt₂)=C(SO₂F)F (R=CF₂H, C₃F₇)
RCF=CFSO₂F (R=HCF₂, CF₂Cl)
RCFClCHFOSO₂F (R=CF₂Cl, CF₂H, C₃F₇)
HCF₂CF(X)CF(X)SO₂F (isomers, X=Cl, Br)
Preparation of Iodine Containing Sulfonyl Fluoride Systems and Derivatives Prepared From CF$_2$CF$_2$OSO$_2$

The Chinese group at the Shanghai Institute has synthesized sulfonyl fluoride containing ether systems from the β-sultone, CF$_2$CF$_2$OSO$_2$, by reaction with ICl and C$_2$F$_4$ in the presence of fluoride ion:

$$\text{CF}_2\text{CF}_2\text{OSO}_2 + \text{IX} + \text{nCF}_2=\text{CF}_2 \xrightarrow{\text{KF}} \text{I(CF}_2)^n\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \text{ (31) diglyme}$$

A number of olefins have also been prepared via IF elimination from the above compounds utilizing Grignard reagent. Compounds like those produced in (31), react with CH$_2$=CH$_2$ and may undergo dehydroiodination to give CH$_2$=CH(CF$_2$)$_n$O-CF$_2$CF$_2$SO$_2$F. In this study a variety of products containing chlorine and the SO$_2$F grouping are reported as well as the corresponding olefins. In some cases, the coupling products were formed from the iodine compounds. Table IV lists products from a number of references; silyl and amine derivatives are included as well.

Formation of the sulfonyl chlorides along with sulfinate salts has been accomplished via the reaction of sodium dithionite with fluorooxodide compounds.

$$\text{Na}_2\text{S}_2\text{O}_4 \xrightarrow{\text{IRf'I}} \text{NaO}_2\text{SRf'SO}_2\text{Na} \text{ (33)}$$
Sulfonyl Fluoride Containing Fluoropolymers

Preparation of fluoropolymers containing the SO₂F group often involves formation of the mono-sultone from a diolefin and subsequent polymerization or copolymerization; or the formation of the iodine containing ethers as discussed in the previous section. These ethers may be part of a long chain fluorocarbon or can be dehydrohalogenated to form olefins which can then be polymerized or copolymerized.

Several perfluorosulfonyl fluorides were irradiated with UV light as shown in the following reactions. The primary products are indicated.⁴¹

\[
\text{F(O)C(CF₃)F} \xrightarrow{\text{UV}} \text{CF₃CFOCF₂CF₂SO₂F} \quad \text{(erythroc, threo)}
\]

\[
\text{nCF₂=CFOCF₂CF(CF₃)OCF₂CF₂SO₂F} \xrightarrow{\text{a)UV}} \xrightarrow{\text{b)H₂O, NaHCO₃}} \text{-(CF₂CF)n-₁CF₂C(O)ONa}
\]

\[
\text{Cl₂} \xrightarrow{\text{b)KOH}} \text{ClO₂SR' SO₂Cl} \quad \text{(34)}
\]

\[
\text{R' = CF₂CF₂OCF₂CF₂, (CF₂)₆, (CF₂)₈, (CF₂)₁}
\]
Fluoropolymers containing SO₂F are important as precursors to ion-exchange membranes, moldable, conductive materials, fuel cell electrolytes, and may themselves serve as solvents for co-polymers and membrane repair. They also may serve as precursors to Nafion™ like sulfonic acid systems. Table V lists representative examples and in some cases their potential use.
<table>
<thead>
<tr>
<th>Reference 37</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃(CF₂)₅OCF₂CF₂SO₃K</td>
<td>Cl₃CF₂(CF₂)₅OCF₂CF₂SO₃K</td>
</tr>
<tr>
<td>(CF₂CF₂OCF₂CF₂SO₃K)₂</td>
<td>Cl₂CF₂CF₂OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>BrCF₂CF₂OCF₂CF₂SO₂F</td>
<td>Cl₂CF₂CF₂OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>BrCFC₁CF₂OCF₂CF₂SO₂F</td>
<td>IClCFC₁CF₂OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>CF₃CFC₁CF₂OCF₂CF₂SO₂F</td>
<td>CF₃CFBrOCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>ClCH₂CF₂OCF₂CF₂SO₂F</td>
<td>BrCH₂CF₂OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>Cl₂CFCFC₁OCF₂CF₂SO₂F</td>
<td>Cl₂(CF₂CF₂)₃OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>Cl(CF₂CF₂)₃OCF₂CF₂SO₂F</td>
<td>Cl(CF₂CF₂)₄OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>(FSO₂CF₂CF₂OCF₂CF₂₂)₂</td>
<td>[FSO₂CF₂CF₂OCF₂CF₂₂]²</td>
</tr>
<tr>
<td>[FSO₂CF₂CF₂OCF₂CF₂]₂</td>
<td>[FSO₂CF₂CF₂OCF₂CF₂]²</td>
</tr>
<tr>
<td>CH₃OCF₂CF₂SO₂F</td>
<td>CH₂═CHCH₂OCF₂CF₂SO₂F</td>
</tr>
<tr>
<td>CH₃OCF₂OCF₂CF₂SO₂F</td>
<td>ICF₂OCF₂CF₂SO₂F</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Reference 38</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I(CF₂)₂O(CF₂)₂SO₃H</td>
<td>Cl₂ FCCF₂O(CF₂)₂SO₃H</td>
</tr>
<tr>
<td>Cl(CF₂)₂O(CF₂)₂SO₃H</td>
<td>H(CF₂)₂O(CF₂)₂SO₃H</td>
</tr>
<tr>
<td>[I(CF₂)₂O(CF₂)₂SO₂]₂O</td>
<td>[Cl(CF₂)₂O(CF₂)₂SO₂]₂O</td>
</tr>
<tr>
<td>[Cl₂ FCCF₂O(CF₂)₂SO₂]₂O</td>
<td>[H(CF₂)₂O(CF₂)₂SO₂]₂O</td>
</tr>
<tr>
<td>I(CF₂)₂O(CF₂)₂SO₃CH₃</td>
<td>I(CF₂)₂O(CF₂)₂SO₃CH(CH₃)₂</td>
</tr>
<tr>
<td>I(CF₂)₂O(CF₂)₂SO₃CH₂CH₂Cl</td>
<td>I(CF₂)₂O(CF₂)₂SO₃CH₂CF₃</td>
</tr>
<tr>
<td>I(CF₂)₂O(CF₂)₂SO₃CH₂(CF₂)₄H</td>
<td>I(CF₂)₂O(CF₂)₂SO₃C₆F₅</td>
</tr>
<tr>
<td>I(CF₂)₂O(CF₂)₂SO₃C₆H₃(NO₂)₂</td>
<td>FO₂S(CF₂)₂OCF₂CF₀</td>
</tr>
<tr>
<td>TABLE IV</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>DERIVATIVES OF ( \text{CF}_2\text{CF}_2\text{SO}_2 )</td>
<td></td>
</tr>
<tr>
<td>(continued)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{FO}_2\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{H} )</td>
<td>( \text{HO}_3\text{S(CF}_2)\text{2OOCF}_2\text{CO}_2\text{H} )</td>
</tr>
<tr>
<td>( [\text{FO}_2\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{O}]_2 )</td>
<td>( \text{HO}_3\text{SCF}_2\text{CO}_2\text{H} )</td>
</tr>
<tr>
<td>( \text{FO}_2\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{CH}_3 )</td>
<td>( \text{FO}_2\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{CH}_2(\text{CF}_2)\text{H} )</td>
</tr>
<tr>
<td>( \text{H(CF}_2)\text{2CH}_2\text{O}_3\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{CH}_3 )</td>
<td>( \text{C}_6\text{H}_5\text{O}_3\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{CH}_3 )</td>
</tr>
<tr>
<td>( \text{H(CF}_2)\text{2CH}_2\text{O}_3\text{C(CF}_2)\text{2} )</td>
<td>( \text{C}_6\text{H}_5\text{O}_3\text{S(CF}_2)\text{2OCF}_2\text{CO}_2\text{C}_6\text{H}_5 )</td>
</tr>
<tr>
<td>( \text{H(CF}_2)\text{2CH}_2\text{O}_2\text{C-CF}_2 )</td>
<td>( \text{FO}_2\text{S(CF}_2)\text{2O(CF}_2)\text{2OCH}_3 )</td>
</tr>
<tr>
<td>( \text{FO}_2\text{S(CF}_2)\text{2O(CF}_2)\text{2OCH}_2\text{CH}=\text{CH}_2 )</td>
<td>( \text{CCl}_2=\text{CFO(CF}_2)\text{2SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{COCF}_2\text{O(CF}_2)\text{2SO}_2\text{F} )</td>
<td>( \text{p=CH}_3\text{C}_6\text{H}_4\text{COCF}_2\text{O(CF}_2)\text{2SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{p=CH}_3\text{O}_3\text{C}_6\text{H}_4\text{COCF}_2\text{O(CF}_2)\text{2SO}_2\text{F} )</td>
<td>( \text{FO}_2\text{S(CF}_2)\text{2OCF}_2\text{CCl}_0 )</td>
</tr>
</tbody>
</table>

Reference 34

<table>
<thead>
<tr>
<th>Reference 34</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ICF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{I(CF}_2\text{CF}_2)\text{3OCF}_2\text{CF}_2\text{SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{I(CF}_2\text{CF}_2)\text{5OCF}_2\text{CF}_2\text{SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{3OCF}_2\text{CF}_2\text{SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{7OCF}_2\text{CF}_2\text{SO}_2\text{F} )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{3OCF}_2\text{CF}_2\text{SO}_3\text{K} )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{7OCF}_2\text{CF}_2\text{SO}_3\text{K} )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{3O(CF}_2)\text{2SO}_2\text{N(C}_3\text{H}_7)\text{C}_2\text{H}_5\text{OH} )</td>
</tr>
<tr>
<td>( \text{CF}_2\text{CF}_2\text{O(CF}_2)\text{SO}_2\text{N(C}_3\text{H}_7)(\text{C}_2\text{H}_4)\text{OH} )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{3O(CF}_2)\text{2SO}_2\text{N(C}_3\text{H}_7)(\text{CH}_2)\text{4H} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reference 34</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CF}_3\text{(CF}_2)\text{3O(CF}_2)\text{2SO}_2\text{N(CH}_2)_3\text{N(C}_2\text{H}_5)_2 )</td>
</tr>
<tr>
<td>Chemical Structure</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>CF$_3$(CF$_2$)$_2$ O(CF$_2$)$_2$SO$_2$(CH$_2$)$_3$N(C$_2$H$_5$)$_2$</td>
</tr>
<tr>
<td>CF$_3$(CF$_2$)$_2$O(CF$_2$)$_2$SO$_2$NH(CH$_2$)$_3$N(C$_2$H$_5$)$_2$</td>
</tr>
<tr>
<td>CF$_3$(CF$_2$)$_7$O(CF$_2$)$_2$SO$_2$NH(CH$_2$)$_3$N(C$_2$H$_5$)$_2$</td>
</tr>
<tr>
<td>CF$_3$(CF$_2$)$_7$O(CF$_2$)$_2$SO$_2$NH(CH$_2$)$_3$N(C$_2$H$_5$)$_2$ + (CH$_3$SO$_4^-$)</td>
</tr>
<tr>
<td>CH$_3$</td>
</tr>
</tbody>
</table>

Reference 39

CF$_2$(CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$F ($n = 1, 3, 5, 7$)

CF$_3$(CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$NHCH$_2$CH=CH$_2$ ($n = 1, 3, 5, 7$)

CF$_3$(CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$NH(CH$_2$)$_3$SiCl$_3$ ($n = 1, 3, 5, 7$)

CF$_3$(CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$N(CH$_3$)CH$_2$CH=CH$_2$ ($n = 1, 3, 5, 7$)

CF$_3$(CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$N(CH$_3$)(CH$_2$)$_3$SiCl$_3$ ($n = 1, 3, 5, 7$)

CF$_3$(CF$_2$)$_n$OCF$_2$CF$_2$SO$_2$N(CH$_3$)(CH$_2$)$_3$Si(OCH$_3$)$_3$

Reference 40

I(CF$_2$)$_2$nO(CF$_2$)$_2$SO$_2$F ($n = 1, 2, 3$)

I(CH$_2$)$_2$O(CF$_2$)$_2$nO(CF$_2$)$_2$SO$_2$F ($n = 1, 2, 3$)

CH$_2$=CH(CF$_2$)$_2$nO(CF$_2$)$_2$SO$_2$F ($n = 1, 2, 3$)

CH$_3$SiCl$_2$(CH$_2$)$_2$O(CF$_2$)$_2$nO(CF$_2$)$_2$SO$_2$F ($n = 1, 2, 3$)

CH$_3$Si(OCH$_3$)$_2$(CH$_2$)$_2$O(CF$_2$)$_2$nO(CF$_2$)$_2$SO$_2$F ($n = 1, 2, 3$)

CH$_3$ - [OSi]$_m$ (X=SO$_2$F, SO$_3$H, SO$_3$M; M=Na, K; n=1,2,3)
<table>
<thead>
<tr>
<th>Compound/preparation/use</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂F₄ + CF=CFOCF₂CF(CF₃)OCF₂CF₂SO₂F and similar</td>
<td>42</td>
</tr>
<tr>
<td>membranes including amine derivatives are used to form chlor-alkali cells.</td>
<td></td>
</tr>
<tr>
<td>CF₂=CFOCF₂CF(CF₃)OCF₂CF₂SO₂F is copolymerized with tetrafluoroethylene and trifluoroethylene and hydrolyzed to give ion exchange materials.</td>
<td>43</td>
</tr>
<tr>
<td>CF₂=CFCF₃ + SO₃ (with BF₃ or B₂O₃)</td>
<td>44</td>
</tr>
<tr>
<td>CF₂-CFCF₂OSO₂F which rearranges to give [ \text{FCOF(SO}_2\text{F)}\text{CF}_2\text{OSO}_2\text{F} ]; CF₂=CFCF₂OSO₂F is copolymerized with CH₂=CF₂, CH₂=CHF and CF₂=CF₂. The polymers are useful in the preparation of ion exchangers and catalysts.</td>
<td></td>
</tr>
<tr>
<td>ClCF₂ClFOCF₂CF(CF₃)OCF₂CF₂SO₂F, FSO₂CF₂CF₂OCF(CF₃)CF₂OCF(CF₃)SO₂F and similar compounds are used as solvents for copolymers and membrane repair.</td>
<td>45</td>
</tr>
<tr>
<td>CF₂=CFCF₂OSO₂F + FS0₂CF₂COF (KF, diglyme, 25-28°C) [ \rightarrow \text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F} ]; this compound and similar ones are copolymerized</td>
<td>46</td>
</tr>
</tbody>
</table>
TABLE V

FLUOROPOLYMERS CONTAINING SO₂F
(continued)

with CF₂=CF₂ and other vinyl compounds and
hydrolyzed to give moldable, conductive systems.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>47</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₂XCFXO[CF₂CF(CF₃)O]ₙ(CF₂)ₘY where X = halogen; n = 0,1; m = 1,2,3; Y = CO₂Me, SO₂F; form</td>
<td></td>
</tr>
<tr>
<td>compounds used in casting reverse osmosis membranes.</td>
<td></td>
</tr>
<tr>
<td>(Nafion™ eq. wt. ~1200)SO₃H + HF + SF₄ ——&gt;</td>
<td>48</td>
</tr>
<tr>
<td>(Nafion™ eq. wt. ~1200)SO₂F</td>
<td></td>
</tr>
</tbody>
</table>

Compounds like FSO₂CF₂OC(CF₃)FOCF=CF₂ are used as intermediates for polymerization (CsF is a catalyst).
Sulfonyl fluorides react with nucleophiles such as in base hydrolysis to give products of the form R-SO₂-Nu. Mechanistic alternatives for the reaction include Sₙ2 or elimination/addition as are shown in this example:

\[
\begin{align*}
\text{Sn}_2 & \quad \text{F}_3\text{CCHFSO}_2\text{F} \quad +\text{Nu} \quad \rightarrow \quad \text{E/A} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad } \end{align*}
\]

Isolation of the unstable sulfene (or sulfonene, C=SO₂), has been accomplished in the above reaction where the nucleophile was pyridine. Knunyants proposes in eq.38 that the sulfene intermediate, CF₃CF=SO₂, is more likely than the process of the Sn₂ mechanism due to the stability of the SO₂F grouping. Sn₂ substitution occurs when no α-hydrogen exists and those reactions are much slower; CF₃CFClSO₂F undergoes alkaline hydrolysis with a rate constant of 3.3 L x mol⁻¹ x sec⁻¹ whereas CF₃CFHSO₂F has a rate constant of 923 L x mol⁻¹ x sec⁻¹. Other rate constants are shown in Table VI.17

The sulfene intermediate is also proposed in the formation of the carbene (CF₃CF⁺):50
The scheme was confirmed by the decomposition of 3-oxoperfluorobutane-2-sulfonyl fluoride, CF₃C(O)CF(SO₂F)CF₃, by potassium fluoride in pyridine solution when the tri-fluoromethylfluorosulfene was detected in the form of the pyridine adduct; in air the complex is converted to CF₃CFHSO₂OH•Py.50 In the Wedekind-Staudinger reaction, the compound C₃F₇C(O)CHFSO₂F reacts to form the sulfene, C₃F₇-C(O)CF=SO₂, and carbene, C₃F₇C(O)CF:, and give isomers of the episulfone 4,7-dioxoperfluoro-5-decene episulfone, C₃F₇C(O)CF-CFC(O)C₃F₇.57

The Chinese group at the Shanghai Institute of Organic Chemistry studied the reactions of difluoromethanesulfonyl fluoride, HCF₂SO₂F, and found that usually nucleophilic attack occurred at the sulfur atom of the SO₂F group. However, with reagents of stronger basicity, RO⁻ (R=H, C₂H₅, HCF₂CF₂CH₂, C₆H₅, etc.), the attack may occur either at the
sulfur site to give the sulfonate derivatives; or the RO− may abstract the α-hydrogen then eliminate SO2 and F− producing compounds of the form ROCF2H. In the latter scheme the carbene, :CF2, acts as an intermediate. The formation of sulfonates does not involve a sulfene intermediate.52

\[
RO^- + HCF2SO2F \rightarrow \text{ROCF2H} \quad (42)
\]

\[
\begin{align*}
\text{RO}^- & \quad \rightarrow \quad \text{HCF2SO3R} \quad \rightarrow \quad \text{R2O} + 2\text{HCF2SO2}^- \\
\text{RO}^- + \text{HCF2SO2F} \rightarrow & \quad \text{[–CF2SO2F]} \quad \rightarrow \quad \text{:CF2} \\
& \quad \rightarrow \quad \text{[–CF2SO2F]} \quad \rightarrow \quad \text{:CF2} \\
\text{F}^- & \quad \rightarrow \quad \text{CF3}^- \quad \rightarrow \quad \text{HCF3} + \text{RO}^- \\
\text{ROH} & \quad \rightarrow \quad \text{ROCF2H} \quad (43)
\end{align*}
\]

R = Et, Ph, HCF2CF2CH2

Reaction with the α-hydro-containing fluorinated sulfonyl fluoride, (CF3)2CHSO2F, and tertiary amines gives the carbanion complex, [(CF3)2CSO2F]−·[HNR3]+ as determined by 1H and 19F nmr. The proton-fluorine coupling is not observed even with only 2 mole percent of base present.53,54 Comparisons of the CH acidity in the above sulfonyl fluoride, (CF3)2CHSO2F, with nitriles and other esters were also studied.53
TABLE VI
RATE CONSTANTS OF ALKALINE HYDROLYSIS $K_c$ OF SULFONYL FLUORIDES IN THE PRESENCE OF POTASSIUM CHLORIDE AT 25°C AND pH 10.0.

<table>
<thead>
<tr>
<th>R-SO$_2$F</th>
<th>$K_c$ (1 x mol$^{-1}$ x s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$CFCl</td>
<td>3.3</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>8.2</td>
</tr>
<tr>
<td>CH$_2$=CH</td>
<td>18.3</td>
</tr>
<tr>
<td>H$_3$C</td>
<td>46.1</td>
</tr>
<tr>
<td>C$_6$H$_5$-CH$_2$</td>
<td>912</td>
</tr>
<tr>
<td>F$_3$C-CHF</td>
<td>923</td>
</tr>
</tbody>
</table>


The following series of reactions is an example of those that proceed via the carbanion intermediate.$^{53}$

\[(\text{CF}_3)_2\text{CHSO}_2\text{F} + \text{BF}_3\cdot\text{NC}_5\text{H}_5 \rightarrow \text{CF}_2\text{C}=(\text{CF}_3)\text{SO}_2\text{F} + \left[\text{BF}_4^-\cdot\text{HNC}_5\text{H}_5^+\right] \tag{44}\]

\[\text{CF}_2\text{C}=(\text{CF}_3)\text{SO}_2\text{F} + \text{CsF} \leftrightarrow [(\text{CF}_3)_2\text{CSO}_2\text{F}]^-\cdot\text{Cs}^+ \tag{45}\]

\[([(\text{CF}_3)_2\text{CSO}_2\text{F}]^-\cdot\text{Cs}^+ + \text{Br}_2 \rightarrow (\text{CF}_3)_2\text{CBrSO}_2\text{F} + \text{CsBr} \tag{46}\]

\[([(\text{CF}_3)_2\text{CSO}_2\text{F}]^-\cdot\text{Cs}^+ + \text{SO}_2\text{Cl}_2 \rightarrow (\text{CF}_3)_2\text{CClSO}_2\text{F} + \text{SO}_2 + \text{CsCl} \tag{47}\]

\[([(\text{CF}_3)_2\text{CSO}_2\text{F}]^-\cdot\text{Cs}^+ + \text{CF}_3\text{C(O)ONO} \rightarrow (\text{CF}_3)_2\text{C(NO)SO}_2\text{F} + \text{CF}_3\text{C(O)OCs} \tag{48}\]
Many of the sulfonyl fluoride containing olefins reported in Table III result from the stabilized carbanion intermediate:55

\[
\text{[RCF}_2\text{CFSO}_2\text{F}^- \rightarrow R\text{-C} = \text{C-SO}_2\text{F} \quad (50)
\]

\[
\text{F} \\
\text{[RCF}_2\text{CFSO}_2\text{F}^- \rightarrow R\text{-C} = \text{C-SO}_2\text{F} \\
\text{-F}^- \\
\text{F}
\]

\[
R = \text{CF}_3, \text{CF}_2\text{Cl}, \text{C}_3\text{F}_7
\]

NEW COMPOUNDS PREPARED AND REPORTED IN THIS DISSERTATION

Chapter IV Sulfonyl Fluoride Systems

Included in Chapter IV are the preparation and reactions of the β-sultone SF5\text{CHCF}_2\text{OSO}_2, and ester formation; preparation of SO2F containing polymer esters; and the preparation of FSO2CF2C(O)OAg and its ester derivatives. Compounds prepared and characterized are listed in Table VII.

Chapter V Related Reactions

Preparation of fluoroethers by reacting olefins, especially SF5-containing systems with trifluoromethyl hypochlorite (CF3OCl)/ClF/Cl2 are reported. In some cases, new fluorooolefins are produced. New polymers containing the SF5 group were prepared again utilizing fluorooolefins and reacting them with SF5Br. Pertinent references for these
TABLE VII
NEW COMPOUNDS REPORTED

Chapter IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₅CHCF₂OSO₂</td>
<td>[CF₃CF(SO₂F)C(O)OCH₂CHCH₂⁻]ₙ</td>
</tr>
<tr>
<td>SF₅CH(SO₂F)C(O)F</td>
<td>[SF₅CF(SO₂F)C(O)OCH₂CHCH₂⁻]ₙ</td>
</tr>
<tr>
<td>SF₅CH₂SO₂F</td>
<td>[SF₅CH(SO₂F)C(O)OCH₂CHCH₂⁻]ₙ</td>
</tr>
<tr>
<td>SF₅CH₂SO₃Na/Ca</td>
<td>FSO₂CF₂C(O) OAg</td>
</tr>
<tr>
<td>SF₅CH₂SO₃H.H₂O</td>
<td>FSO₂CF₂C(O) OCH₃</td>
</tr>
<tr>
<td>SF₅CH(SO₂F)C(O)OCH₂CF₃</td>
<td>FSO₂CF₂C(O)OCH₂CH₂CH₃</td>
</tr>
<tr>
<td>SF₅CH(SO₂F)C(O)OCH(CF₃)₂</td>
<td>FSO₂CF₂C(O)OSi(CH₃)₃</td>
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<tr>
<td>[FSO₂CF₂C(O)OCH₂]₂</td>
<td>SF₅CH=CF₂•2SO₃</td>
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</table>

Chapter V

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₅CHClCH₂OCF₃</td>
<td>SF₅(CH₂CHF)₁₀Br</td>
</tr>
<tr>
<td>SF₅CFClCF₂OCF₃</td>
<td>SF₅(CH₂CF₂)₈Br</td>
</tr>
<tr>
<td>SF₅CHClCF₃</td>
<td>SF₅(CF₂CF₂)₁₆Br₀.₃</td>
</tr>
<tr>
<td>(SF₅CCl₂CH₂)₂</td>
<td>SF₅CF₂CF₂Br (adduct)</td>
</tr>
<tr>
<td>SF₅CHClCF₂Cl</td>
<td></td>
</tr>
<tr>
<td>SF₅CCl=CH₂</td>
<td></td>
</tr>
</tbody>
</table>

related reactions are included. New compounds are listed in Table VII.
CHAPTER III

EXPERIMENTAL METHODS

VACUUM SYSTEM

The all glass vacuum system used in this work consisted of a manifold connected to a Welch Duo-Seal rotary pump. The manifold consisted of 8 mm and 22 mm I.D. Pyrex glass tubing which was connected to the pump by a concentric liquid nitrogen cooled trap. The manifold was connected to a two leg mercury manometer and also had four taps for attaching vessels. The taps were Eck and Krebs 2 mm high vacuum stopcocks to which Pyrex 10/30 outer glass joints were attached. A Televac gauge was used to monitor the system which usually attained a vacuum of $10^{-2} - 10^{-3}$ torr. All joints were lubricated with Fluorolube or Apiezon-M grease. The system is illustrated in Figure 2.

REACTION VESSELS

**Pyrex-glass Vessels**

The low temperature/low pressure reactions were run in 80 ml to 3 liter Pyrex-glass vessels. The 2 and 3 liter vessels were equipped with a cold finger at the bottom for condensing reactants and all had 2 mm high vacuum Teflon
stopcocks for an outlet. The connecting portion consisted of 10/30 inner joints for attaching to the vacuum line. Quartz vessels (80 mL) were used for reactions in UV light and were equipped in a similar manner as described for the Pyrex-glass vessels. For moderate temperature/pressure reactions, heavy wall Pyrex-glass Carius tubes equipped with high vacuum Teflon valves and 10/30 inner joints for connection to the vacuum line were utilized.

**Metal High Pressure Vessels**

Pentafluorosulfur bromide was prepared in a 75 ml monel or stainless steel vessel equipped with a Whitey stainless steel valve and tipped with a brass 10/30 inner joint. High temperature/high pressure reactions were carried out in various monel or stainless steel vessels with brass or stainless steel valves and 10/30 joints. The vessels were heated in an oven or oil bath to the desired temperature.

**PHYSICAL METHODS AND INSTRUMENTATION**

**Distillations**

Products were purified either by distillation at atmospheric pressure or under vacuum with a -78°C or -196°C trap to collect volatile products. Trap-to-trap distillation under high vacuum was used to purify some volatile products. A spinning band distillation system was also utilized in some cases.
Gas Chromatography

The purity or separation of products was checked via gas chromatography by using an Aerograph Autoprep (Model A-700) gas chromatograph. Separations were carried out with a 10' x 3/8" column containing 20% Carbowax absorbed on "Chromosorb W."

Molecular Weights

Molecular weights were determined on the vacuum line using the vapor density method. The Pyrex-glass bulb was equipped with a Teflon stopcock and had a volume of 209.6 cm³.

Infrared Spectra

Infrared spectra were obtained by using a Pyrex-glass gas cell equipped with KBr windows or as liquids or solids between KBr or KRS-5 disks on a Nicolet 20DX spectrometer.

Nuclear Magnetic Resonance

The nmr spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances or on a Bruker AM400 spectrometer operating at 400.1 MHz for proton, 376.5 MHz for fluorine and 100.6 MHz for carbon. TMS, CFCl₃ or CDCl₃ were used as external/internal standards.
**Mass Spectra**

The mass spectra were recorded with a VG 7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluorokerosene was used as an internal standard.

**Chemical Analysis**

Elemental analyses were determined by Beller Mikroanalytisches Laboratorium, Gottingen, West Germany, or by Micanal, Tucson, Arizona.

**REAGENTS**

The compounds used in this work were obtained from commercial sources: SO$_3$, BrCH$_2$CO$_2$C$_2$H$_5$, BrC$_2$H$_4$Br, BrCH$_2$CH=CH$_2$ (MCB); NaOH, Ca(OH)$_2$, KOH (Baker); (CF$_3$)$_2$CHOH (Eastman); HCl (Matheson); MgSO$_4$, Ag$_2$O, CH$_3$OH, (C$_2$H$_5$)$_2$O (Mallinckrodt); COF$_2$, ClF (Pennwalt Chemicals); Cl$_2$ (Matheson); HOCH$_2$CH$_2$I, C$_3$H$_7$I, (CH$_3$)$_3$SiI (Aldrich); CH$_3$I (Kodak); CF$_3$CH$_2$OH, CF$_2$=CF$_2$, CFH=CF$_2$, CH$_2$=CF$_2$, CHF=CH$_2$ and CH$_2$=CH$_2$ were obtained from SCM Specialty Chemicals. The above reagents were used without further purification. CF$_3$COCl, CF$_2$(SO$_2$F)COOH, SF$_5$CH(SO$_2$F)CO$_2$CH$_2$CH$_2$=CH$_2$, SF$_5$CF(SO$_2$F)CO$_2$CH$_2$CH=CH$_2$ and CF$_3$CF(SO$_2$F)CO$_2$CH$_2$CH=CH$_2$ were prepared according to literature methods$^{56,57,58}$. The olefins, SF$_5$CH=CH$_2$, SF$_5$CH=CF$_2$ and SF$_5$CF=CF$_2$, were prepared by the dehydrohalogenation of the appropriate fluoroalkyl
bromide$^{59,60,61}$. SF$_5$Br was prepared as previously reported$^{60}$ and used without further purification.

Sodium fluoride (Baker) was dried under vacuum before use. CFCl$_3$ (Dupont) was dried with silica gel prior to use. Carbon tetrachloride (Mallinckrodt Spectra grade) was dried over 4A molecular sieves.
Figure 2. Vacuum System.

A. Eck and Krebs 2 mm high vacuum stopcock
B. 10/30 g Outer Joint
C. Two-leg Mercury Manometer
D. Thermocouple Gauge
E. 18/9 Ball Joints
F. Glass Trap
CHAPTER IV

SULFONYL FLUORIDE SYSTEMS

Compounds containing the SO$_2$F grouping have created much interest in recent years as precursors to sulfonic acids and in their own right as ion exchange resins and as surface-active agents. We have prepared a number of new sulfonyle fluoride compounds via several routes described earlier. We also include the preparation of SF$_5$-containing monomeric and polymeric sulfonyle fluoride systems.

Included for comparison in the SF$_5$ sultone and derivatives discussion are esters prepared from the sultone SF$_5$CF$_2$OSO$_2$ by Javid Mohtasham. The same is true for the silver salt and ester derivatives where several additional esters were prepared by Mr. Mohtasham. The discussion section on the -SO$_2$F- containing polymer esters includes data from the monomer esters. Preparation of the polymer esters was done in conjunction with Dr. Roger Sheets.

SF$_5$ SULTONE AND DERIVATIVES

The new pentafluorothio b-sultone, 2-hydroxyl-1-(pentafluoro-\(\lambda^6\)-sulfanyl)-2,2-difluorooethanesulfonic acid sultone, SF$_5$CHCF$_2$OSO$_2$, was prepared via the reaction of
SF₅CH=CF₂ with monomeric sulfur trioxide in a Carius tube under autogeneous pressure at 100°C:

\[ \text{SF}_5\text{CH} = \text{CF}_2 + 3\text{SO}_3 \rightarrow \text{SF}_5\text{CHCF}_2\text{OSO}_2 + \text{SF}_5\text{CHCF}_2\cdot 2\text{SO}_3 \quad (1) \]

The SF₅CHCF₂OSO₂ product is a stable crystalline solid with a vapor pressure of 9 torr at 22°C; it melts at 47-48°C. Interpretation of the ¹H and ¹⁹F nmr for the interesting compound, SF₅CHCF₂•2SO₃, was not accomplished. Elemental analysis confirmed the empirical formula. Possible structures include: SF₅CH — CF₂, the rearranged product(s), or a mixture.

The SF₅ sultone undergoes rearrangement in the presence of NaX (X = I, F) giving the isomeric bifunctional fluoride, 2-(fluorosulfonyl)-2-(pentafluoro-λ⁶-sulfanyl) acetyl fluoride:

\[ \text{SF}_5\text{CHCF}_2\text{OSO}_2 \xrightarrow{\text{NaF}} \text{SF}_5\text{C(SO}_2\text{F})\text{HC(O)F} \quad (2) \]

In the presence of water, SF₅CHCF₂OSO₂ undergoes rearrangement, followed by a concerted hydrolysis decarboxylation reaction:

\[ \text{SF}_5\text{C(SO}_2\text{F})\text{HC(O)F} \rightarrow [\text{SF}_5\text{C(SO}_2\text{F})\text{HCOOH}] + \text{HF} \quad (3) \]

\[ [\text{SF}_5\text{C(SO}_2\text{F})\text{HCOOH}] \rightarrow \text{SF}_5\text{CH}_2\text{SO}_2\text{F} + \text{CO}_2 \quad (4) \]

Attempts to isolate the acid intermediate prior to decomposition failed. The final SF₅ containing product,
SF₅CH₂SO₂F, hydrylic(pentafluoro-λ⁶-sulfanyl)methanesulfonyl fluoride is a stable, colorless liquid that boils at 110-111°C. Treatment of the SF₅-sulfonyl fluoride with an aqueous sodium hydroxide solution gives, in solution, the corresponding sodium sulfonate salt which, when treated with gaseous hydrogen chloride, produces the desired SF₅ sulfinic acid:

\[
\text{SF₅CH₂SO₂F} + 2\text{NaOH(aq)} \rightarrow [\text{SF₅CH₂SO₃Na}] + \text{NaF} + \text{H₂O} \quad (5)
\]

\[
[\text{SF₅CH₂SO₃Na}] + \text{HCl(g)} \rightarrow \text{SF₅CH₂SO₃H(aq)} + \text{NaCl(s)} \quad (6)
\]

The new SF₅ containing acid, hydrylic(pentafluoro-λ⁶-sulfanyl)methanesulfonic acid monohydrate is isolated from solution and purified by sublimation; it is a white solid which melts at 97±1°C. The corresponding salt of this acid can be prepared by reacting the sultone or acid with an appropriate base:

\[
2\text{SF₅CHCF₂OSO₂} + 5\text{Ca(OH)}_2(aq) \rightarrow \text{Ca(SF₅CH₂SO₃)}_2 + 2\text{CaCO}_3 + 2\text{CaF}_2 + 4\text{H}_2\text{O} \quad (7)
\]

In addition to preparing the SF₅ containing sultone, its rearranged product, and eventually a new SF₅ sulfinic acid, we have found that interaction of SF₅ containing sultones, SF₅CXCF₂OSO₂ (X = F, H) with fluoroalcohols produces new SF₅ containing sulfonyl fluoride esters:

\[
\text{SF₅CXCF₂OSO₂} + R_f\text{OH} + \text{NaF} \rightarrow \text{SF₅CX(SO₂F)C(O)OR_f} + \text{NaHF₂} \quad (8)
\]

\[R_f = \text{CF₃CH}_2, \quad X = \text{H (VI), } X = \text{F (VIII);}
\]
\[(\text{CF₃})_2\text{CH}, \quad X = \text{H (VII), } X = \text{F (IX)}\]
With a fluorinated bis alcohol, the following diester is produced:

$$2\text{SF}_5\text{CF}_2\text{OSO}_2 + \text{ROCH}_2(\text{CF}_2)_3\text{CH}_2\text{OH} \rightarrow \left[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C(O)}\text{OCH}_2\text{CF}_2\right]_2\text{CF}_2 + 2\text{NaHF}_2 \quad (9)$$

The new SF$_5$ containing sulfonyl fluoride esters are clear colorless liquids which are stable upon heating. Mechanistically, in ester formation, the sodium fluoride and/or the alcohol serves as a catalyst for the rearrangement of the sultone:20,21

$$\text{F}^- + \text{SF}_5\text{CX}-\text{CF}_2 \rightarrow \text{SF}_5\text{CX}-\text{C}-\text{F} \rightarrow \text{SF}_5\text{CX}-\text{C}-\text{F} + \text{F}^- \quad (10)$$

$$\text{R}_f\text{OH} + \text{SF}_5\text{CX}-\text{CF}_2 \rightarrow \text{SF}_5\text{CX}-\text{C}-\text{O}^- \rightarrow \text{SF}_5\text{CX} - \text{C} - \text{F} + \text{R}_f\text{OH} \quad (11)$$

$$\text{SF}_5\text{CX}-\text{C}-\text{F} + \text{ROH} + \text{NaF} \rightarrow \text{SF}_5\text{CX}(\text{SO}_2\text{F})\text{C(O)}\text{OR}_f + \text{NaHF}_2 \quad (12)$$

**Figure 3.** Mechanism for Ester Preparation.

The resulting acid fluoride reacts with alcohols, in the presence of NaF, forming the corresponding ester and NaHF$_2$.

These routes to the stable ester products are strongly
supported by the following isomerization of β-sultones with different nucleophiles to the acyclic isomer: \[ \text{XCFCF}_2\text{OSO}_2 \rightarrow \text{FSO}_2\text{CFXC(O)F} \] \( \text{a} \)

\[ X = \text{F}, \text{CF}_3 \]

\[ a = \text{F}^-, \text{Et}_3\text{N}, \text{H}_2\text{O} \text{ or dioxane} \]

Additional support for the rearrangement mechanism is found by examining reaction mixtures prior to final work-up. In these reaction mixtures, it was found via infrared spectral studies that the sultone had rearranged during the course of the reaction to \( \text{SF}_5\text{CX(SO}_2\text{F)C(O)F} \), \((X = \text{H}, \text{F})\).

The infrared spectra for all new compounds have in common the characteristic absorption bands of the SF5-group. Cross and coworkers\(^6^2\) reported that the most intense band for compounds containing the SF5 grouping should appear in the region 850-920 cm\(^{-1}\) (SF stretching modes) and in the region of 600 cm\(^{-1}\) (S-F deformation modes). For the new compounds reported in this paper, absorption bands in the 816 to 930 cm\(^{-1}\) region are found with the new SF5 esters having absorptions in the higher part of this range. The SF5 deformation modes are located in the 597-620 cm\(^{-1}\) range.

For compounds containing C-F and CF3 groups, the C-F stretching vibration is usually located in the 1000-1100 cm\(^{-1}\) region\(^6^3\) while marked absorption in the range 1360-1300 cm\(^{-1}\) can be correlated with the CF3 group\(^6^3\). In the compound, SF5CFHCF3, the C-F stretching vibration was assigned
to the 1161 cm⁻¹ absorption band. For the new esters, the stretching vibration for the CF group appears to be located in the 1100-1200 cm⁻¹ region while the CF₃ group is located in the 1230-1390 cm⁻¹ region. The CF₃ deformation band is located in the 737-760 cm⁻¹ region.

Compounds containing the -SO₂⁻ functional group exhibit a strong asymmetric stretching band in the 1419-1469 cm⁻¹ region and a strong symmetric stretching band in the 1200-1259 cm⁻¹ range. This assignment is complicated in some cases by the appearance of strong carbon-fluorine absorption bands in the 1110-1300 cm⁻¹ region but, in any case, the above assignment agrees closely with the found for CF₃SO₂F and other fluorosulfonyl derivatives. For the sulfonyl fluoride group, the strong S-F absorption band is located near 786 cm⁻¹ and is in the region found for other sulfonyl fluorides. This band disappears when the acid/salts are formed from SF₅CH₂SO₂F. The asymmetric and symmetric stretching SO₃ bands for the sulfonic acid monohydrate, SF₅CH₂SO₃H•H₂O, and calcium salt are found in the 1223-1244 cm⁻¹ and 1033-1064 cm⁻¹ region, respectively; for salts containing the CF₃SO₃⁻ group the respective regions are 1266-1279 and 1025-1042 cm⁻¹. The carbonyl stretching frequency is characteristically found in the 1790-1834 cm⁻¹ range for esters prepared from SF₅CFCF₂OSO₂ and in the 1750-1820 cm⁻¹ range for the esters prepared from SF₅CHCF₂OSO₂; the carbonyl frequencies for the esters prepared from the
perfluorinated sultone are significantly higher and are in line with the expected inductive effect. The C-H absorption bands are located near 3000 cm⁻¹ (for SF₅CFHCF₃ the C-H stretching frequency was found at 3007 cm⁻¹). The acid, SF₅CH₂SO₃H•H₂O, gave a broad OH absorption band centered at 3308 cm⁻¹.

The major mass spectral peaks for these compounds are listed in the experimental section. The molecular ion peaks were not observed for any of the compounds listed, however, many did show (M-X)⁺ peaks such as (M-F)⁺, (M-HF)⁺, (M-H₂O)⁺; for the sultone I the (M-H)⁻ peak was found. Prominent peaks (m/e) at 89 (SF₃⁺) and 127 (SF₅⁺) were observed for all compounds and 89 (CF₃⁺) occurred in all esters except [SF₅CF(SO₂F)C(O)OCH₂CF₂]₂CF₂. Appropriate fragments were found for cleavages at the -C(O)O- functional group in the esters.

The nmr spectra generally consist of complex multiplets (see Table VIII for chemical shift values). Some of the first order coupling constants were determined and are reported in Table IX. In most cases the SF₅ fluorine resonances consist of the AB₄ multiplet with B₄ equatorial fluorines split into a doublet and the A part into a nine-line pattern. In compounds I, III, VI and VII the AB₄ pattern is overlapping, therefore the chemical shifts and/or coupling constants could only be approximated. The AB₄ pattern in SF₅CH(SO₂F)COF is reversed with the A axial
fluorine pattern occurring upfield from the B4 doublet. Compounds I, VI and VII also show overlap and reversal of the AB4 pattern compared to other SF5 systems. This reversal of the AB4 pattern has also been noted for SF5NCO and SF5C=CH.67,68 The chemical shift values for the SF5 group in all compounds fall within the expected range.60,69 It is interesting to note that the collapse and reversal of the SF5 pattern occurs only for derivatives of sultone I and not for derivatives of SF5CF2OSO2. The acid SF5CFHSO3H gives SF(ax) at $\delta$ 72.3 ppm and SF4(eq) at $\delta$ 53.5 ppm,19 while compound V gives SF(ax) at $\delta$ 81.4 ppm and SF4(eq) at $\delta$ 68.1 ppm. The axial and equatorial fluorine chemical shifts of the SF5 group in SF5CH2CHFBr are $\delta$ 79.9 ppm and 66.4 ppm, respectively.60 For the compound, SF5CHCF2\cdot2SO3, the expected AB4 pattern is not observed for the SF5 group; instead a complex series of multiplets extending from $\delta$ 94.6 to $\delta$ 49.2 ppm is found.

The $^{19}$F nmr resonance for the fluorosulfonyl group is found in the range $\delta$ 48.9 to 58.5 ppm. The splitting pattern of the CF2 group for the new sultone I consists of a doublet of doublets exhibiting the weak-strong-strong-weak pattern reported for other fluorinated sultones.6,18,19 The $^1$H nmr spectra for all compounds were self consistent with respect to the expected chemical shifts for CH and CH2 groups.
In general, we find that replacing a hydrogen with fluorine on carbon adjacent to an SF₅ group results in greater shielding (shift to high field) for all fluorogroups present; for example, in going from SF₅CH₂SO₂F to SF₅CHFSO₂F the SF(ax), SF₄(eq), and SO₂F groups are more shielded by 0, 16, and 7 ppm, respectively. Also, in going from SF₅CH(SO₂F)R to SF₅CF(SO₂F)R where R = C(O)F, C(O)OR', greater shielding for the SF(ax), SF₄(eq), SO₂F and C(O)F groups is found. While it is impossible to rule out anisotropic effects produced upon replacing a hydrogen with fluorine, it is suggested that, inductively, replacement by fluorine allows for electron donation from that fluorine to other fluorogroups thereby causing a general increase in shielding. Correspondingly, the CF resonance is deshielded in molecular systems in which SF₅, SO₂F, C(O)F and C(O)OR groups are present.

Coupling constants for the SF(ax) to SF₄(eq) fluorines in the new compounds vary from approximately 100 Hz to 149 Hz. The coupling constants for J₁,2 could not be determined for compound III. It is interesting to note that the lower values for J₁,2 occur in compounds derived from sultone I, and go as low as 100 Hz in ester IV. The sultone, SF₅CFCF₂OSO₂, and its derivatives have an AB₄ coupling in the range J = 141 to 157 Hz; one exception is found for SF₅CF(SO₂F)COF with J₁,2 = 100.1 Hz.¹⁹ Esters derived from this sultone and reported here have coupling constants J₁,2
in the 136-141 Hz range; by comparison, the ester SF₅CF(CF₃)COOCH₃ has a \( J_{1,2} = 144 \) Hz. The compounds containing the sulfonyl fluoride-grouping vicinal to the SF₄(ax) have values ranging from \( J_{2,4} = 9.2 \) to 12.8 Hz.

The new sulfonyl fluoride esters contain fluorine-fluorine and fluorine-proton coupling constants which are self consistent. In esters VIII, IX and X and \( J_{1,2} \) and \( J_{2,3} \) values are the same, 3.0 Hz. The coupling constant, \( J_{4,5} = 103 \) Hz in \( \beta \)-sultone I is approximately the same as in SF₅CFCF₂O₃O₂ where \( J_{4,5} = 104 \) Hz. The coupling \( J_{2,3} \) in compounds I, II and V vary considerably; \( J = 4.8, 3.0 \) and 7.5 Hz, respectively. These values reflect the differences in structure with different group attachments to the SF₅CH moiety. Due to the complexity of the spectrum, no coupling constants could be determined for compound III.

The \(^{13}\text{C} \) nmr spectral data for compounds I, II, III and V are given in Table X. Chemical shift values for the carbon next to an SF₅ group, C(A), range from \( \delta 77.6 \) to 99.6 ppm; for C(B) in I and II the values are \( \delta 112.0 \) and 146.8 ppm, respectively. Compound V has only a broadened singlet at \( \delta 77.6 \) ppm while III has a band center of a complex multiplet at \( \delta 82.8 \) ppm. The coupling constant for I (\( J_{B,4} \)) is in good agreement with values reported for other cyclic systems; for c-C₄F₈ and c-C₄F₄Cl₄ the \( J_{CF} \) values are 298 and 300 Hz, respectively. The large \( J_{CF} \) coupling (\( J_{B,5} \)) value
of 363.5 Hz for II is in good agreement with other acyl fluorides.\textsuperscript{70}
<table>
<thead>
<tr>
<th>Compound</th>
<th>SF\textsubscript{4}(ax)</th>
<th>SF\textsubscript{4}(eq)</th>
<th>CF\textsubscript{3}</th>
<th>CF\textsubscript{2}</th>
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<tbody>
<tr>
<td>SF\textsubscript{5}CHCF\textsubscript{2}OSO\textsubscript{2} (\text{I}) in F-11</td>
<td>69.4(m)</td>
<td>-</td>
<td>-72.8(d)</td>
<td>-79.7(d)</td>
</tr>
<tr>
<td>SF\textsubscript{5}CH(SO\textsubscript{2}F)COF (\text{II})\textsuperscript{b}</td>
<td>66(9-ln) 72.2(d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF\textsubscript{5}CH\textsubscript{2}SO\textsubscript{2}F (\text{III})</td>
<td>71.4(m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(SF\textsubscript{5}CH\textsubscript{2}SO\textsubscript{3})\textsubscript{2}Ca (\text{IV})</td>
<td>76.7(9-ln) 64.3(d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF\textsubscript{5}CH\textsubscript{2}SO\textsubscript{3}H\cdot\textsubscript{H}\textsubscript{2}O (\text{V})\textsuperscript{c} in CD\textsubscript{3}CN</td>
<td>81.4(9-ln) 68.1(d)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF\textsubscript{5}CH(SO\textsubscript{2}F)COOC\textsubscript{H}\textsubscript{2}CF\textsubscript{3} (\text{VI})</td>
<td>70.0(m)</td>
<td>-76.4(t)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF\textsubscript{5}CH(SO\textsubscript{2}F)COOC\textsubscript{H}(CF\textsubscript{3})\textsubscript{2} (\text{VII})</td>
<td>70.5(m)</td>
<td>-75.4(d)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF\textsubscript{5}CF(SO\textsubscript{2}F)COOC\textsubscript{H}\textsubscript{2}CF\textsubscript{3} (\text{VIII})</td>
<td>62.3(9-ln) 56.5(d)</td>
<td>-76.2(t)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF\textsubscript{5}CF(SO\textsubscript{2}F)COOC\textsubscript{H}(CF\textsubscript{3})\textsubscript{2} (\text{IX})</td>
<td>61.5(9-ln) 57.2(d)</td>
<td>-75.2(d)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[SF\textsubscript{5}CF(SO\textsubscript{2}F)COO-CH\textsubscript{2}CF\textsubscript{2}]\textsubscript{2}CF\textsubscript{2} (\text{x})</td>
<td>62.6(9-ln) 56.7(d)</td>
<td>-</td>
<td>-121.3(br.t)</td>
<td>-127(br.s)</td>
</tr>
</tbody>
</table>
### TABLE VIII

19F AND 1H NMR CHEMICAL SHIFTS FOR SF5CHCF2OSO2,

DERIVATIVES AND ESTERS OF SF5CFCF2OSO2<sup>a,c</sup>

(continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CF</th>
<th>SO₂F</th>
<th>CH</th>
<th>CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₅CHCF₂O₅SO₂ (I) in F-11</td>
<td>-</td>
<td>-</td>
<td>6.58 (m)</td>
<td>-</td>
</tr>
<tr>
<td>SF₅CH(SO₂F)COF (II)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>58.4</td>
<td>6.18 (d, p)</td>
<td>-</td>
</tr>
<tr>
<td>SF₅CH₂SO₂F (III)</td>
<td>-</td>
<td>58.5 (m)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>5.33 (m)</td>
</tr>
<tr>
<td>(SF₅CH₂SO₃)₂Ca (IV)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.0 (p)</td>
</tr>
<tr>
<td>SF₅CH₂SO₃H·H₂O (V)&lt;sup&gt;f&lt;/sup&gt; in CD₃CN</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.13 (p)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>SF₅CH(SO₂F)COOCH₂CF₃ (VI)</td>
<td>-</td>
<td>57.0 (p)</td>
<td>6.23 (d, p)</td>
<td>4.83 (b.r.q)</td>
</tr>
<tr>
<td>SF₅CH(SO₂F)COOCH(CF₃)₂ (VII)</td>
<td>-</td>
<td>58.5 (p)</td>
<td>6.20 (p)</td>
<td>-</td>
</tr>
<tr>
<td>SF₅CF(SO₂F)COOCH₂CF₃ (VIII)</td>
<td>-123.5 (d, p)</td>
<td>48.9 (p)</td>
<td>-</td>
<td>4.97 (q)</td>
</tr>
<tr>
<td>SF₅CF(SO₂F)COOCH(CF₃)₂ (IX)</td>
<td>-119.0 (d, p)</td>
<td>49.6 (p)</td>
<td>6.25 (sept.)</td>
<td>-</td>
</tr>
<tr>
<td>[SF₅CF(SO₂F)COO-CH₂CF₂]₂CF₂ (X) (br.p)</td>
<td>-123.4</td>
<td>49.1 (p)</td>
<td>-</td>
<td>5.22 (b.r.t)</td>
</tr>
</tbody>
</table>

**a.** Fluorine chemical shifts in ppm from CFCl₃ and proton chemical shifts in ppm downfield from TMS.

**b.** Chemical shift for the COF fluorine is ϴ 46.5 ppm (m); it is found at ϴ 30.4 ppm in SF₅CF(SO₂F)COF.<sup>19</sup>

**c.** s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept. = septet, 9-ln = nine-line, br. = broadened, m = multiplet.

**d.** For SF₅CHFSO₂F and CF₃CH₂SO₂F the chemical shifts are: ϴ +51.3 and +64.75 ppm, respectively.<sup>6,69</sup>

**e.** ¹H chemical shifts for SF₅CHFSO₂F and CF₃CH₂SO₂F are 6.31 and 4.10 ppm, respectively.<sup>6,69</sup>

**f.** The chemical shift value for the proton on -SO₃H is 10.22 ppm.
<table>
<thead>
<tr>
<th>Compound</th>
<th>19F and 1H NMR Coupling Constants, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)-SF4(2)-C — C — F(5) (I)</td>
<td>J1,2 = 130  J2,3 = 4.6  J4,5 = 103</td>
</tr>
<tr>
<td>F(1)-SF4(2)-C — C — F(5) (II)</td>
<td>J1,2 = 148.9  J3,5 = 4.9  J2,3 = 3.0  J2,4 = 12.0  J4,5 = 12.0  J2,5 = 8.7</td>
</tr>
<tr>
<td>SF4(2)CH2(3)SO2F(4) (III)</td>
<td>—</td>
</tr>
<tr>
<td>(F(1)SF4(2)CH2(3)SO3)2Ca (IV)</td>
<td>J1,2 = 141.1  J2,3 = 7.5</td>
</tr>
<tr>
<td>F(1)SF4(2)CH2(3)SO3H•H2O (V)</td>
<td>J1,2 = 141.1  J2,3 = 7.5</td>
</tr>
<tr>
<td>F(1)SF4(2)C — OCH2(5)CF3(6) (VI)</td>
<td>J1,2 = 100  J2,4 = 12.8  J1,3 = 2.25  J5,6 = 5.4  J2,3 = 4.5</td>
</tr>
<tr>
<td>F(1)SF4(2)C — OCH(5)(CF3)2(6) (VII)</td>
<td>J1,2 = 122  J2,4 = 11.8  J2,3 = 4.5  J5,6 = 7.4</td>
</tr>
</tbody>
</table>
TABLE IX

$^{19}$F AND $^1$H NMR COUPLING CONSTANTS FOR SF$_5$CHCF$_2$OSO$_2$, DERIVATIVES AND ESTERS OF SF$_5$CFCEOSO$_2$$^{a,c}$
(continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coupling Constants, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F(3)}\text{O}$</td>
<td></td>
</tr>
</tbody>
</table>
| $\text{F(1)SF}_4(2)\text{C} - \text{C-OCH}_2(5)\text{CF}_3(6)$ (VIII) | $J_{1,2} = 141$  $J_{2,4} = 9.4$
| | $J_{1,3} = 4.5$  $J_{5,6} = 7.4$
| | $J_{2,3} = 3.0$

| $\text{F(3)}\text{O}$ | |
| $\text{F(1)SF}_4(2)\text{C} - \text{C-OCH}_5(\text{CF}_3)_2(6)$ (XI) | $J_{1,2} = 136$  $J_{2,4} = 10.1$
| | $J_{1,2} = 3.0$  $J_{5,6} = 5.6$
| | $J_{2,3} = 3.0$

| $\text{F(3)}\text{O}$ | |
| $\text{[F(1)SF}_4(2)\text{C} - \text{C-OCH}_2(5)\text{CF}_2(6)]\text{CF}_2(7)$ (X) | $J_{1,2} = 136$  $J_{2,4} = 9.2$
| | $J_{1,3} = 3.0$  $J_{5,6} = 12$
| | $J_{2,3} = 3.0$
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shifts and Coupling Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)SF₄(2)CH₃CF₂(4)O₂S⁻⁻⁻⁰</td>
<td>δₐ = 99.6</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1)SF₄(2)CH₃COF⁻⁻⁻ SO₂F</td>
<td>δₐ = 88.5</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1)SF₄(2)CH₂(3)SO₂F⁻⁻⁻⁻</td>
<td>δₐ = 77.6 (m)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>F(1)SF₄(2)CH₂(3)SO₃H•H₂O</td>
<td>δₐ = 82.8 (br.s)</td>
</tr>
</tbody>
</table>

* Solvent CDC1₃, chemical shifts in ppm relative to TMS.  
  s = singlet; d = doublet; t = triplet; p = pentet; br. =  
  broadened; m = multiplet
POLYMER ESTERS CONTAINING SO₂F

We have found that the following fluorosultones, CF₂CF₂OSO₂, CF₃CFCF₂OSO₂, SF₅CFCF₂OSO₂ and SF₅CHCF₂OSO₂ react with allyl alcohol according to the following equation:

$$\text{CF}_2\text{CF}_2\text{OSO}_2 + \text{CH}_2=\text{CHCH}_2\text{OH} + \text{NaF} \rightarrow \text{FSO}_2\text{CF}_2\text{C(O)OCH}_2\text{CH}=\text{CH}_2 + \text{NaF}\cdot\text{HF}$$

(14)

$$\text{CF}_3\text{CFCF}_2\text{OSO}_2 + \text{CH}_2=\text{CHCH}_2\text{OH} + \text{NaF} \rightarrow \text{CF}_3\text{CF(}\text{SO}_2\text{F})\text{C(O)OCH}_2\text{CH}=\text{CH}_2 + \text{NaF}\cdot\text{HF}$$

(15)

$$\text{SF}_5\text{CXCF}_2\text{OSO}_2 + \text{CH}_2=\text{CHCH}_2\text{OH} + \text{NaF} \rightarrow \text{SF}_5\text{CX(}\text{SO}_2\text{F})\text{C(O)OCH}_2\text{CH}=\text{CH}_2 + \text{NaF}\cdot\text{HF}$$

(16)

$$X = \text{F}, \text{H}$$

The new fluorosulfonyl allyl esters are stable water clear liquids.

While a number of non-fluorinated and fluorinated polyesters exist⁷¹,⁷², there are no systems in which the SO₂F group and SF₅ group are incorporated into the polyester framework. Our group has found new ways to incorporate these groups into a polyester. One way involves UV irradiation of the new allyl monomers in CFCl₃:

$$\text{CF}_3\text{CF(}\text{SO}_2\text{F})\text{C(O)OCH}_2\text{CH}=\text{CH}_2 \xrightarrow{\text{UV}} (\text{CF}_3\text{CF(}\text{SO}_2\text{F})\text{C(O)OCH}_2\text{CH}=\text{CH}_2)_n$$

(17)
The decomposition and solubility characteristics are summarized in Table XI; fluorosulfonyl polyesters appear to have limited thermal stability.

The infrared spectra of the polymers are similar to the results reported for the corresponding monomers with one notable exception; the C=C stretching frequency near 1650 cm\(^{-1}\) is absent in all polymers.

The infrared spectra of the allyl sulfonyl fluoride monomeric esters have several common features. The carbonyl stretching frequency is found in the 1764-1792 cm\(^{-1}\) region; the carbonyl bands for these esters agree closely with those found for perfluoro/polyfluoro esters. The asymmetric and symmetric \(-\text{SO}_2\)- bands can be tentatively assigned to the regions 1440-1455 and 1222-1237 cm\(^{-1}\), respectively. The assignment is complicated by the appearance of strong carbon-fluorine absorption bands usually found in the 1100-1300 cm\(^{-1}\) region, but in any case the above assignment for the \(\text{SO}_2\) group agrees closely with that found for \(\text{CF}_3\text{SO}_2\text{F}\) and other fluorosulfuryl derivatives. For the fluorosulfonyl group, the intense S-F absorption band is located in the 801-808 cm\(^{-1}\) region and is in the region found for other sulfonyl fluorides. The C-H absorption bands for
the hydrogen containing esters are located in the 2699-3100 cm\(^{-1}\) region. The C=C stretching frequency is located near 1650 cm\(^{-1}\). The two SF\(_5\) containing esters have as a common feature the SF\(_5\) group and its characteristic infrared absorptions. As stated earlier, Cross and coworkers\(^{62}\) reported that for compounds containing the SF\(_5\) group, the most intense bands should occur in the region of 850-920 cm\(^{-1}\) (S-F) stretching modes, and in the region of 600 cm\(^{-1}\) (S-F) deformation modes. For the SF\(_5\) containing esters reported in this paper, absorption bands in the 850-934 cm\(^{-1}\) region are assigned to the S-F stretching vibrations. The S-F deformation modes are found near 600 cm\(^{-1}\). For compounds containing a C-F group and a CF\(_2\) group, the C-F stretching vibration is usually located in the 1000-1100 cm\(^{-1}\) region while marked absorption in the range 1050-1250 cm\(^{-1}\) can be correlated with the CF\(_2\) group.\(^{63}\)

The \(^1\)H nmr data (chemical shifts and coupling constants) for the monomer and corresponding new polymer esters are reported in Table XII. The chemical shifts and coupling constants for the -CH\(_2\)CH=CH\(_2\) moiety are in agreement with values reported for allyl alcohol and FO\(_2\)S(CF\(_2\))\(_2\)O(CF\(_2\))\(_2\)OCH\(_2\)CH=CH\(_2\).\(^{38,75}\) The CH proton chemical shift in SF\(_5\)CH(SO\(_2\)F)C(O)OC\(_3\)H\(_5\) was located at \(\delta\) 6.24 ppm; in SF\(_5\)CFHSO\(_2\)F the corresponding shift was reported at \(\delta\) 6.31 ppm.\(^{19}\) The proton chemical shifts for polymeric materials
obtained with ultraviolet irradiation showed, in general, broad peaks for the CH and CH$_2$ groups.

The fluorine chemical shifts for polymeric materials obtained from ultraviolet irradiation were, in general, in agreement with values found for the corresponding monomers; as expected the peaks were significantly broadened.

The $^{19}$F nmr spectral data are reported in Table XIII. The $^{19}$F nmr spectra for the SF$_5$ group of SF$_5$CF(SO$_2$F)C(O)O-C$_3$H$_5$ consisted of the expected AB$_4$ pattern with the B$_4$ equatorial fluorines split into a complex doublet and the axial fluorine, A, into a nine-line pattern. The chemical shifts for the AB$_4$ pattern in SF$_5$CF(SO$_2$F)C(O)OC$_3$H$_5$ were located at $\delta$ 64.3(A) and $\delta$ 56.3(B) ppm. In SF$_5$CH(SO$_2$F)-C(O)OC$_3$H$_5$, the expected AB$_4$ pattern is not observed but instead a complex multiplet centered at $\delta$ 70.7 ppm is found. The CF chemical shift in SF$_5$CF(SO$_2$F)C(O)OC$_3$H$_5$ was found at $\delta$ -121.9 ppm; in SF$_5$CF(SO$_2$F)COF the corresponding chemical shift was reported as $\delta$ -122 ppm. The $^{19}$F nmr spectrum of the allyl ester, prepared from CF$_2$CF$_2$OSO$_2$, contained the CF$_2$ resonance at $\delta$ -104.9 ppm which is the region expected for a CF$_2$ group; for example, in FSO$_2$CF$_2$C(O)OCH$_2$CF$_3$ the CF$_2$ resonance was found at $\delta$ -106.4 ppm. In all allyl esters, the resonance bands for the FSO$_2$ are located in the region $\delta$ 39.9-58.5 ppm; in a number of sulfonyl fluoride derivatives CF$_3$CFHSO$_2$F, SF$_5$CFHSO$_2$F, FSO$_2$CF$_2$C(O)OCH$_2$CF$_3$ the corresponding resonance band was located in the $\delta$ 40-52 ppm range.
TABLE XI
PROPERTIES OF FLUOROSULFONYL FLUOROESTERS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decomp. (°C)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CF₃CF(SO₂F)C(O)OCH₂CHCH₂⁻)ₙ</td>
<td>164</td>
<td>H₂O ins. acetone sl. sol. CFCl₃ ins.</td>
</tr>
<tr>
<td>(SF₅CF(SO₂F)C(O)OCH₂CHCH₂⁻)ₙ</td>
<td>150</td>
<td>H₂O ins. acetone sol. CFCl₃ ins.</td>
</tr>
<tr>
<td>(SF₅CH(SO₂F)C(O)OCH₂CHCH₂⁻)ₙ</td>
<td>170</td>
<td>H₂O ins. acetone sol. CFCl₃ ins.</td>
</tr>
</tbody>
</table>

Note: Viscous polymers prepared from allyl esters were soluble in acetone and CFCl₃.
<table>
<thead>
<tr>
<th>Chemical Shifts (ppm)</th>
<th>Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rf (monomers)</strong></td>
<td></td>
</tr>
<tr>
<td>SF5CF(SO2F)CO2</td>
<td>5.07  6.12  5.82  5.58</td>
</tr>
<tr>
<td>SF5CH'(SO2F)CO2*</td>
<td>4.90  6.04  5.72  5.54</td>
</tr>
<tr>
<td>CF3CF(SO2F)CO2</td>
<td>4.95  5.96  5.66  5.42</td>
</tr>
<tr>
<td><strong>Rf (polymers)</strong></td>
<td></td>
</tr>
<tr>
<td>SF5CF(SO2F)CO2</td>
<td>4.8  1.0 - 3.5</td>
</tr>
<tr>
<td>SF5CH'(SO2F)CO2*</td>
<td>4.4  1.2 - 3.3</td>
</tr>
<tr>
<td>CF3CF(SO2F)CO2</td>
<td>4.8  1.2 - 3.8</td>
</tr>
</tbody>
</table>

* The CH' proton occurs at \(66.24\) ppm (multiplet, \(J_{SF_4CH} = 10.2\) Hz), in the polymer the CH' proton occurs at \(\delta 7.24\) ppm and is broadened. All chemical shifts relative to TMS.

** In the monomers \(H_d\) is a doublet, \(H_c\) is a doublet of triplets, \(H_b\) is a doublet of doublets and \(H_a\) is a doublet of doublets. For the polymers \(H_d\) is a broadened singlet and \(H_c, H_b,\) and \(H_a\) are broadened multiplets.
**TABLE XIII**

$^{19}$F NMR DATA FOR MONOMER AND CORRESPONDING POLYMER ESTERS*

$$\text{RgCH}_2\text{CH}=\text{CH}_2$$

<table>
<thead>
<tr>
<th>$\text{Rg}$ (monomers)</th>
<th>Chemical Shifts (ppm)</th>
<th>Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}(a)\text{SF}_4(b)\text{CF}(c)\text{CO}_2$</td>
<td>a: 64.3 b: 56.3 c: -121.9 d: 48.6</td>
<td>$J_{a,b} = 141, J_{a,c} = 3.1, J_{b,c} = 3.1, J_{c,d} &lt; 1, J_{b,d} = 11.6$</td>
</tr>
<tr>
<td>$\text{F}(a)\text{SF}_4(b)\text{CH}(c)\text{CO}_2$</td>
<td>a: 70.7 (m)</td>
<td>$J_{b,c} = 4.5, J_{b,d} = 11.6$</td>
</tr>
<tr>
<td>$\text{CF}_3(a)\text{CF}(b)\text{CO}_2$</td>
<td>a: -73.3 b: -161.8 c: 50.1 d: -</td>
<td>$J_{a,b} = 8.3, J_{a,c} = 9.6, J_{b,c} = 4.2$</td>
</tr>
</tbody>
</table>

| $\text{Rg}$ (polymers, no coupling constants were obtained) |
|------------------------|-----------------------|
| $\text{F}(a)\text{SF}_4(b)\text{CF}(c)\text{CO}_2$ | a: 65.2 b: 57.4 c: -121.5 d: 48.8 |
| $\text{F}(a)\text{SF}_4(b)\text{CH}(c)\text{CO}_2$ | a: 71.3 (m) |
| $\text{CF}_3(a)\text{CF}(b)\text{CO}_2$ | a: -73.3 b: -161.8 c: 50.1 |

* Fluorine chemical shifts in ppm from external CFCl$_3$, d = doublet, t = triplet, q = quartet, p = pentet, s = sextet, m = multiplet, br. = broadened.

* Complex multiplet observed in place of expected AB$_4$ (FSF$_4$) coupling.
SILVER SALT AND ESTER DERIVATIVES

We have found that difluoro(fluorosulfonyl)acetic acid, FSO₂CF₂C(Ο)OH, reacts with silver oxide in diethyl ether according to the following equation:

\[
\text{Et}_2\text{O} \hspace{1cm} 2\text{FSO}_2\text{CF}_2\text{C(Ο)OH} + \text{Ag}_2\text{O} \rightarrow 2\text{FSO}_2\text{CF}_2\text{C(Ο)OAg} + \text{H}_2\text{O} \hspace{1cm} (19)
\]

The silver difluoro(fluorosulfonyl)acetate is a white solid sensitive to light and heat; it is soluble in water and slightly soluble in diethyl ether at room temperature.

The silver salt can be used with alkyliodides/bromides to provide a route for preparing new sulfonyl fluoride esters:

\[
\text{FSO}_2\text{CF}_2\text{C(Ο)OAg} + \text{RBr} \rightarrow \text{FSO}_2\text{CF}_2\text{C(Ο)OR} + \text{AgBr} \hspace{1cm} (20) \\
\text{R} = \text{BrCH}_2\text{CH}_2, \text{CH}_3\text{CH}_2\text{OC(Ο)CH}_2, \text{CH}_2=\text{CHCH}_2
\]

\[
\text{FSO}_2\text{CF}_2\text{C(Ο)OAg} + \text{RI} \rightarrow \text{FSO}_2\text{CF}_2\text{C(Ο)OR} + \text{AgI} \hspace{1cm} (21) \\
\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2, (\text{CH}_3)_3\text{Si}
\]

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

\[
2\text{FSO}_2\text{CF}_2\text{C(Ο)OAg} + \text{CH}_2\text{I}_2 \rightarrow (\text{FSO}_2\text{CF}_2\text{C(Ο)O})_2\text{CH}_2 + 2\text{AgI} \hspace{1cm} (22)
\]

Interestingly, reaction of \(\text{FSO}_2\text{CF}_2\text{CO}_2\text{Ag}\) with \(\text{HOCH}_2\text{CH}_2\text{I}\) gave the disubstituted ester product:

\[
\text{FSO}_2\text{CF}_2\text{C(Ο)OAg} + \text{HOCH}_2\text{CH}_2\text{I} \rightarrow (\text{FSO}_2\text{CF}_2\text{C(Ο)OCH}_2)_2 + \text{AgI/AgOH} \hspace{1cm} (23)
\]
The esters prepared in this work are all stable high boiling colorless liquids. In all cases, reaction was observed by noting the appearance of the yellow silver halide.

A suggested mechanism for the reaction of HOCH₂CH₂I with FSO₂CF₂CO₂Ag is given in Figure 4.

\[
\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{O}^- + \text{HOCH}_2\text{CH}_2\text{I} \rightleftharpoons \text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OH} + \text{I}^- \quad (24)
\]

\[
(\text{Ag}^+) \quad \text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{O}^- + \text{HOCH}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F} \rightleftharpoons \text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OH} + \text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F} \quad (25)
\]

\[
\text{FSO}_2\text{CF}_2\text{(O)OH} + \text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F} \rightleftharpoons (\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2)_2 + \text{OH}^- \quad (26)
\]

\[
\text{Ag}^+ + \text{I}^-/\text{OH}^- \rightleftharpoons \text{AgI}/\text{AgOH} \quad (27)
\]

*Figure 4.* Mechanism for the reaction of FSO₂CF₂CO(O)Ag with HOCH₂CH₂I

In equation (24), the carboxylate ion displaces I⁻ from HOCH₂CH₂I to form the monosubstituted alcohol intermediate. Then, in equation (25) equilibrium is established between the intermediate alcohol and the alkoxide anion, \(\text{-OCH}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}\), which, in a subsequent reaction via nucleophilic attack on the carboxylic acid, produces the diester.

The infrared spectra of the sulfonyl fluoride esters have several common features. The stretching frequency for the carbonyl group adjacent to CF₂ is found in the 1785-1813
cm⁻¹ region; for the carbonyl group next to CH₂ the corresponding frequency is located at 1757 cm⁻¹. The carbonyl bands next to the fluorinated carbon agree closely with those found for other fluorinated esters. 21,58,73 In the silver salt, FSO₂CF₂C(O)OAg, the carbonyl stretching frequency is found at 1708 cm⁻¹; in AgCF₃COO, the carbonyl stretching frequency is located at 1720 cm⁻¹.77

In all esters, as well as the silver salt, the asymmetric and symmetric SO₂ stretching frequencies are assigned to the 1448-1462 cm⁻¹ region and the 1223-1243 cm⁻¹ region, respectively. These values correspond to the SO₂ frequencies reported for other sulfonyl fluoride compounds.20,21,58 The carbon-fluoride absorption bands occur at 1166 to 1321 cm⁻¹. The S-F absorptions for the sulfonyl fluoride group occur in the 794 to 808 cm⁻¹ region as expected.20,21,58 The C-H absorptions in the esters range from 2854 to 2979 cm⁻¹.

In the mass spectrum, a molecular ion peak was found for FSO₂CF₂C(O)OSi(CH₃)₃; however, MH⁺ ions were found for FSO₂CF₂C(O)OCH₂C(O)OC₂H₅, FSO₂CF₂C(O)OSi(CH₃)₃, [FSO₂CF₂C(O)OCH₂]₂ and FSO₂CF₂C(O)OCH₃. In all cases appropriate fragmentation peaks are found indicating cleavage at the ester linkage. Bromine isotopes were detected in the compound FSO₂CF₂C(O)OC₂H₄Br.

The ¹⁹F nmr spectra for all new esters and the silver salt, FSO₂CF₂C(O)OAg, exhibit common features and are given
The chemical shifts for FSO₂ group (triplet) range from Ø 37.9 to Ø 40.4 ppm while for the CF₂ group (doublet) occur at Ø -97.2 to Ø -109.0 ppm. The chemical shifts are consistent with those of other reported esters prepared from the sultone, CF₂CF₂OSO₂.²⁰,²¹,⁵⁸ For the new esters the coupling constants, JCF₂,SO₂F range in value from J = 5.3 to 5.64 Hz; except for FSO₂CF₂C(O)OSi(CH₃)₃ and the salt, FSO₂CF₂C(O)OAg which are J = 4.6 Hz and J = 3.5 Hz, respectively.

For monosubstituted esters, the ¹H nmr spectra (see Table XV) gave splitting patterns similar to the starting alkyl bromide or iodide; with HOCH₂CH₂I and CH₂I₂ a singlet at δ 5.03 and δ 6.53 ppm, respectively, were found. The spectrum of FSO₂CF₂C(O)OCH₂CH₂Br contains triplets at δ 3.98 ppm (CH₂Br) and δ 5.13 ppm (OCH₂); the JCH₂CH₂ = 6.0 Hz.

¹⁹F/¹H nmr data for the ester prepared from BrCH₂CH=CH₂ agreed with the literature values.⁷⁸ While the ester prepared from CH₃I has been previously synthesized, the no spectral data has been reported.

In order to determine more accurately proton couplings of the allyl group in previously reported allyl fluoroesters containing the sulfonyl fluoride grouping,⁷⁹,⁸⁰ the proton spectrum of FSO₂CF₂C(O)OCH₂(d)CH(c)=CH(a)H(b), was obtained at 300 MHz. It was possible to resolve all possible couplings in the allyl group; new coupling constants found were Jb,d = 1.2 Hz and Ja,d = 1.2 Hz. the values of Ja,c,
<table>
<thead>
<tr>
<th>R</th>
<th>[FSO₂CF₂(C(O)O)₂-R₁]</th>
<th>SO₂F (ppm)</th>
<th>CF₂ (ppm)</th>
<th>J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (I)</td>
<td>38.0</td>
<td>-100.9</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>CH₂C(O)OC₂H₅ (II)</td>
<td>40.5</td>
<td>-105.5</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>CH₂CH₂Br (III)</td>
<td>38.3</td>
<td>-109.0</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>CH₂CH₂CH₃ (IV)</td>
<td>39.7</td>
<td>-105.4</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Si(CH₃)₃ (V)</td>
<td>37.8</td>
<td>-97.2</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>CH₃ (VI)</td>
<td>39.1</td>
<td>-105.5</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>CH₂CH=CH₂ (VII)</td>
<td>39.9</td>
<td>-104.9</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>[FSO₂CF₂C(O)O]₂-R₁</td>
<td>SO₂F (ppm)</td>
<td>CF₂ (ppm)</td>
<td>J (Hz)</td>
</tr>
<tr>
<td>CH₂ (VIII)</td>
<td>39.2</td>
<td>-105.6</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>CH₂CH₂ (IX)</td>
<td>40.4</td>
<td>-105.0</td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

* Chemical shifts reported in ppm relative to CFCl₃. All SO₂F peaks are triplets, and CF₂ peaks are doublets.

Jₜ,c and Jc,d were in good agreement with the literature; the Jₜ,a,b value found was 1.2 Hz. The earlier reports found for a series of allyl esters the Jₜ,a,b coupling of the allyl group to be in the range of 3-5 Hz; it is expected, based on this study, that this range should be 1-2 Hz.
TABLE XV

$^1$H NMR OF FSO$_2$CF$_2$C(O)OAg AND DERIVATIVES*

<table>
<thead>
<tr>
<th>R (FSO$_2$CF$_2$C(O)O-R)</th>
<th>CH$_2'$ (ppm)</th>
<th>CH$_2$ (ppm)</th>
<th>CH$_3$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$'C(O)OCH$_2$CH$_3$ (II)</td>
<td>5.12 (s)</td>
<td>4.40 (q)</td>
<td>1.40 (q)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{J}_{\text{CH}_2,\text{CH}_3} = 7.2 \text{ Hz}$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$'CH$_2$Br (III)</td>
<td>5.13 (s)</td>
<td>3.98 (t)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$J = 6.0 \text{ Hz}$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$'CH$_2$CH$_3$ (IV)</td>
<td>4.19 (t)</td>
<td>1.50 (6-ln)</td>
<td>0.68 (t)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{J}_{\text{CH}_2,\text{CH}<em>3} = 7.2 \text{ Hz}, \text{J}</em>{\text{CH}_3,\text{CH}_3} = 6.6 \text{ Hz}$</td>
<td></td>
</tr>
<tr>
<td>Si(CH$_3$)$_3$ (V)</td>
<td></td>
<td>0.40 (s)</td>
<td></td>
</tr>
<tr>
<td>CH$_3$ (VI)</td>
<td></td>
<td>4.17 (s)</td>
<td></td>
</tr>
<tr>
<td>CH$_2$'CH=CH$_2$** (VII)</td>
<td></td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R (FSO$_2$CF$_2$C(O)O)</th>
<th>CH$_2$ (VIII)</th>
<th>CH$_2$CH$_2$ (IX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$</td>
<td>5.03 (s)</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CH$_2$</td>
<td>6.53 (s)</td>
<td></td>
</tr>
</tbody>
</table>

* Chemical shifts reported in ppm relative to TMS; s = singlet, t = triplet, q = quartet, 6-ln = six line pattern.

** Chemical Shifts (ppm)

```
    H(c)       H(a)
    C = C
    CH$_2$(d)   H(b)
```

<table>
<thead>
<tr>
<th>H$_d$</th>
<th>H$_c$</th>
<th>H$_b$</th>
<th>H$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.95</td>
<td>6.02</td>
<td>5.72</td>
<td>5.43</td>
</tr>
</tbody>
</table>

Coupling Constants (Hz)

$J_{a,b} = 1.2$, $J_{a,c} = 10.8$, $J_{a,d} = 1.2$, $J_{b,c} = 17.2$, $J_{b,d} = 1.2$, $J_{c,d} = 6.0$
**EXPERIMENTAL**

**SF₅CH=CF₂ with SO₃**

Into a 130mL Pyrex glass Carius tube equipped with a Kontes Teflon value were added 52.3 mmol of SO₃ and 57.05 mmol of SF₅CH=CF₂. The mixture was heated for 24 h at 95±5°C. Distillation gave 30.33 mmol of a white solid, SF₅CHCF₂OSO₂, in 58% yield; b.p. 108-111°C/600mm, mp 47-48°C.

The infrared spectrum of SF₅CHCF₂OSO₂ had the following bands (cm⁻¹): 3002 (wm), 1419(s), 1315(s), 1271(s), 1203(vs), 1106(s), 1078(s), 965(m), 916(vw), 878, 845, 819(vs,b), 750(vs), 684(s), 669(w), 656(ms), 612(ms), 575(m,sh. at 565), 525(s), 444(m), 403(m).

The ¹⁹F nmr spectrum ð gave the following relative peak areas: SF₅ (4.94), CF₂ (1+1). The negative ion (Cl⁻) mass spectrum (m/e, species, %): 269, M-H⁻, 11.1; 142, C₂F₂SO₃⁻, 13.5; 138, SC₂SO₃H₂⁻, 17.1; 136, SC₂SO₃⁻, 21.2; 127, SF₅⁻ or FSCSO₂⁻, 100; 123, C₂FSO₃⁻, 9.5; 83, SF₂CH⁻ or SO₂F⁻, 34.5; 81, SO₃H⁻, 30.7; 79, CHCF₂O⁻, 29.6.

**Anal.** Calcd. for C₂HF₇O₃S₂: C, 8.89; H, 0.37; S, 23.74; F, 49.2. Found: C, 9.05; H, 0.51; S, 23.63; F, 48.9.

The pot residue from the above distillation was redistilled to give a pale yellow liquid, SF₅CHCF₂·2SO₃, in 14.5% yield; b.p. 102-103°C/100mm. In another run 49.6 mmol
of SO₃ was reacted with 25.5 mmol of SF₅CH=CF₂ to give 13.8 mmol of SF₅CHCF₂OSO₂ (54% yield) and 9.68 mmol of SF₅CHCF₂•2SO₃ (19.5% yield).

The infrared spectrum of SF₅CHCF₂•2SO₃ had the following bands (cm⁻¹): 3001(wm), 1491(s), 1431(s), 1325(ms), 1281(s), 1253(s), 1222(s), 1175(wm), 1144(wm), 1103(vw), 1075(ms), 1062(ms), 975(ms), 894(vs,b), 850(s), 800(wm), 759(ms), 737(ms), 691(w, sh at 681), 656(w), 625(vw), 612(vw), 603(w), 587(w), 575(m), 537(ms), 519(vw), 506(vw), 481(m), 450(w), 444(wv), 434(vw), 422(vw).

The ¹⁹F nmr of SF₅CHCF₂•2SO₃ gave the following chemical shifts: 0 94.6 ppm (multiplet), 0 76.2 ppm (triplet of multiplets), 0 65.0 ppm (multiplet), 0 49.2 ppm (multiplet), and a series of multiplets at 0 -68.6, -70.7, and -72.5 ppm. Relative peak areas were 1:1:2:1:3 respectively. The ¹H nmr gave multiplets at δ 6.85 and 4.5-4.6 ppm in a ratio of 1:4. Interpretation and assignment of the nmr spectra was not accomplished.

Anal. calcd. for C₂HF₇S₃O₆: C, 6.80; H, 0.28; F, 38.0; S, 27.43. Found: C, 6.78; H, 0.30; F, 38.5; S, 27.35.

SF₅CHCF₂OSO₂ with NaF

Into a 50 ml Pyrex-glass round bottom flask equipped with a Teflon stir bar were added 29 mmol of dried NaF and 12.4 mmol of SF₅CHCF₂OSO₂. The reaction vessel was connected to a reflux condenser and dry ice trap which was
attached to a drying tube. The mixture was heated at 60°C with stirring for four days. Distillation gave a clear liquid in 58% yield, b.p. 115-117°C.

The infrared spectrum had absorption bands at (cm⁻¹):
3037(vw), 2980(w), 1856(m), 1448(ins), 1387(vw), 1291(wm), 1222(m), 1181(w), 1116(w), 1078(vw), 872(vs, b, sh at 850, 834, 816, 803), 772(wm), 681(w), 656(w), 609(wm), 578(m), 572(m), 559(ms), 487(w), 450(w), 419(w), 413(w).

The ¹⁹F nmr spectrum gave the following relative band areas: SF (1.1); SF₄ (4.8); SO₂F (1.1); COF (1.0).

**SF₅CH(CF₂)SO₂ with H₂O**

Into a 40 mL Kel-F vessel equipped with a Teflon stirring bar was added 17.74 mmol of SF₅CH(CF₂)SO₂. The reaction vessel was cooled to 0°C and 88 mmol of H₂O was added slowly with stirring over a period of four hours. The mixture was allowed to stand at room temperature overnight after which the lower layer was separated, washed with water and dried over MgSO₄. Distillation gave 9.03 mmol of SF₅CH₂SO₂F in 51% yield; b.p. 110-111°C.

The infrared spectrum had the following bands (cm⁻¹):
3037(m), 2980(m), 1478(w), 1441(s), 1384(m), 1356(w), 1291(ms), 1222(s), 1181(m), 1150(w), 1075(w), 1028(w), 894, 872(vs,b), 847(s), 831(s,sh. at 816), 791(m), 769(m), 709(wm), 656(ms), 613(m), 578(s), 559(s), 487(m), 450(m), 406(m).
The $^{19}$F nmr spectrum gave the following relative peak areas: SF$_5$ (5.0) and SO$_2$F (1.0). EI$^+$ mass spectrum (m/e, species, %): 204, (M-F)$^+$, 2.23; 129, FSCH$_2$SO$_2$$^+$, 6.92; 127, SF$_5$$^+$ or FSCSO$_2$$^+$, 100; 97, CH$_2$SO$_2$F$^+$ or FSCH$_2$S$^+$, 25.71; 89, SF$_3$$^+$, 42.59; 78, CHSO$_2$$^+$ or SCF$_2$S$^+$, 8.25; 67, SOF$^+$, 53.44.

Anal. Calcd. for CH$_2$F$_6$O$_2$S$_2$: C, 5.36; H, 0.90; S, 28.61; F, 50.9. Found: C, 5.48; H, 0.90; S, 28.59; F, 50.8.

**SF$_5$CH$_2$SO$_2$F/SF$_5$CH$_2$SO$_3$Na with HCl**

Into a 50 mL Pyrex-glass round bottom flask equipped with a Kontes Teflon valve and a Teflon stirring bar were added 20 mL (1389 mmol) of H$_2$O and 78.5 mmol of NaOH. To this solution, cooled to 0°C, 27.8 mmol of SF$_5$CH$_2$SO$_2$F was slowly added over two days. The mixture was heated to 50°C for 42 hours under reflux. Hydrogen chloride was slowly bubbled into this solution at room temperature for one hour. The mixture was filtered; excess water was evaporated away. The crude product, SF$_5$CH$_2$SO$_3$H•H$_2$O, was purified by sublimation; 6 mmol of SF$_5$CH$_2$SO$_3$H•H$_2$O; yield 22%, m.p. 97±1°C.

The infrared spectrum had the following bands (cm$^{-1}$): 3308(s,b), 3051(w), 2987(w), 1718(m,b), 1400(vw), 1242(vs), 1223(vs), 1177(m), 1064(m), 1029(m), 900(m), 892(m), 876(ms), 862(m), 829(m), 821(ms), 810(s), 772(w), 695(w),
649(w), 524(wm), 589(ms), 564(wm), 528 (m, sh. at 517), 438(vw).

The $^{19}$F nmr spectrum (Ø) gave the following relative peak areas: SF (1.0) and SF$_4$ (3.8). EI$^+$ mass spectrum (m/e, species, %): 223, (M+H-H$_2$O)$^+$, 0.73; 202, SF$_4$CH$_2$SO$_3$$^+$, 32.05; 149, SF$_2$CH$_2$SO$_2$$^+$, 8.06; 127, SF$_5$$^+$ or FSCS$_2$$^+$, 25.46; 122, SF$_4$CH$^+$, 71.88; 97 SCH$_3$$^+$, 12.27; 95, CH$_2$SO$_3$$^+$, 36.24; 89, SF$_3$$^+$, 100; 81, SO$_3$$^+$, 15.57; 80, SO$_3$$^+$, 4.77; 70, SF$_2$$^+$, 9.48; 67, SOP$^+$, 15.37; 65, FSCH$_2$$^+$, 54.5; 64, FSCH$^+$ or SO$_2$$^+$, 18.55; 48, SO$^+$, 17.03; 44, CS$^+$, 8.22.

Anal. Calcd. for CH$_5$F$_5$O$_4$S: C, 5.00; H, 2.10; S, 26.70; F, 39.5. Found: C, 5.30; H, 1.93; S, 26.55; F, 39.1.

**SF$_5$CHCF$_2$OSO$_2$ with CaO**

To a Pyrex-glass round bottom flask was added 11.6 mmol SF$_5$CHCF$_2$OSO$_2$, 26.8 mmol CaO and 14.7 g H$_2$O. The mixture was heated at 50+5°C for a period of 1.1 days. CO$_2$ gas was bubbled vigorously through the mixture (~15 min). It was then filtered and the salt dried under vacuum giving 3.15 mmol of Ca(SF$_5$CH$_2$SO$_3$)$_2$ in 54.3% yield: decomposes at 340°C.

The infrared spectrum had the following bands (cm$^{-1}$): 3051(vw), 2987(vw), 1391(w), 1286(m), 1244(s), 1223(s), 1173(ms) 1103(m, sh. at 1082), 1033·m), 885(ms), 871(ms), 815(ms), 779(m), 702(w), 653(m), 618(w), 597(m), 562(wm), 534(w), 512(m).
The $^{19}\text{F}$ nmr spectrum gave the following relative peak areas: SF (1.0) and SF$_4$ (4.0).

SF$_5$CHCF$_2$O$_2$S with CF$_3$CH$_2$OH

Into a 100 ml Pyrex-glass reaction vessel equipped with a Teflon stir bar and a Kontes Teflon valve, were added 60 mmol dried NaF, 19.05 mmol SF$_5$CHCF$_2$O$_2$S and 20.6 mmol CF$_3$CH$_2$OH. The mixture was heated with stirring at 60°C for four days. Distillation under vacuum gave 13.38 mmol of SF$_5$CH(SO$_2$F)C(O)OCH$_2$CF$_3$ in 70% yield; b.p. 103°C/100 mm.

The infrared spectrum of SF$_5$CH(SO$_2$F)C(O)OCH$_2$CF$_3$ had the following bands (cm$^{-1}$): 2987(wm), 1785(s), 1448(s), 1412(m), 1315(s), 1293(s), 1272(s), 1223(s), 1187(s), 1147(s), 1050(w), 1033(vw), 984(ms), 875(vs,b,sh. at 920), 803(ms), 775(wm), 750(wm), 694(wm), 666(wm), 612(m), 569(s), 553(m), 491(m), 459(w), 444(w), 434(w), 419(w), 403(w).

The $^{19}\text{F}$ nmr spectrum ($\delta$) gave the following relative peak areas: SF$_5$ (5.3), SO$_2$F (1.0) and CF$_3$ (3.0); the $^1\text{H}$ nmr spectrum ($\delta$) gave: CH (1.0) and CH$_2$ (2.2). EI$^+$ mass spectrum (m/e, species, %): 331, (M-F)$^+$, 0.93; 330, (M-HF)$^+$, 5.06; 251, SF$_5$CHSO$_2$FCO$^+$, 30.54; 231, SF$_5$CSO$_2$CO$^+$, 20.62; 209, SF$_3$C$_2$SO$_4$$^+$, 9.06; 127, SF$_5^+$ or CF$_3$CH$_2$O$^+$ or FSCSO$_2$$^+$, 44.79; 105, CHSO$_2$CO$^+$, 6.26; 89, SF$_3^+$, 67.29; 83, CH$_2$CF$_3^+$ or SO$_2$F$^+$, 100 + 3.08; 69, CF$_3^+$, 9.90; 67, SOF$^+$, 26.2; 51, SF$^+$, 4.07; 44, CS$^+$, 6.19.
Anal. Calcd. for C₄H₄F₁₀O₄S₂: C, 13.72; H, 0.8635; S, 18.31; F, 48.8. Found: C, 13.86; H, 0.85; S, 18.24; F, 48.5.

SF₅CHCF₂OSO₂ with (CF₃)₂CHOH

Into a 100 mL Pyrex-glass reaction vessel equipped with a Teflon stir bar and a Kontes Teflon valve, were added 75.5 mmol dried NaF, 17.73 mmol SF₅CHCF₂OSO₂ and 17.92 mmol (CF₃)₂CHOH. The mixture was heated with stirring for 7 days at 45±5°C. Distillation under vacuum gave 14.18 mmol of liquid SF₅CH(SO₂F)C(O)OCH(CF₃)₂ in 80% yield; b.p. 98-100°C/100 mm.

The infrared spectrum had the following bands (cm⁻¹):
2987 (wm), 1799 (ms), 1453 (ms), 1384 (ms), 1366 (ms),
1287 (ms, sh. at 1303), 1269 (ms), 1237 (s), 1212 (s), 1118 (s),
1081 (wm), 1066 (wm), 969 (wm), 956 (wm), 897 (s), 875 (vs),
806 (wm), 784 (wm), 775 (wm), 756 (wm), 722 (wm), 691 (ms),
647 (w), 613 (ms, sh. at 603), 569 (ms), 525 (w), 491 (w), 469 (w),
456 (wm), 419 (vw), 409 (w).

The ¹⁹F nmr spectrum (Ø) gave the following relative peak areas: SF₅ (5.3), SO₂F (1.0) and CF₃ (5.4). EI⁺ mass spectrum (m/e, species, %): 401, (M-H₂O)⁺, 0.28; 400, (M-F)⁺, 0.77; 399, (M-HF)⁺, 4.32; 398, (M-H₂F)⁺, 6.65; 251, SF₅CS₂O₂CO⁺, 61.95; 231, SF₅CS₂O₂⁺, 25.72; 195, CO₂CH(CF₃)₂⁺, 44.12; 151, CH(CF₃)₂⁺, 37.38; 143, F₂SCHSCO⁺, 8.31; 127, SF₅⁺ or FSCSO₂⁺, 79.96; 105, HCS₂O₂CO⁺, 8.54; 89,
SF$_3^+$, 88.64; 83, SO$_2$F$^+$, 6.31; 69, CF$_3^+$, 100; 67, SOF$^+$, 40.57; 51, SF$^+$, 16.68; 48, SO$^+$, 5.6; 44, CO$_2^+$ or CS$^+$, 3.58.

**Anal.** Calcd. for C$_5$H$_3$F$_{13}$O$_4$S$_2$: C, 14.36; H, 0.48; S, 15.34; F, 54.5. Found: C, 14.45; H, 0.53; S, 15.36; F, 54.2.

**Polymerization of CF$_3$CF(SO$_2$F)C(O)OCH$_2$CH=CH$_2$ Olefin**

In a 80 mL quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 1.75 g (6.53 mmol) CF$_3$CF(SO$_2$F)C(O)OCH$_2$CH=CH$_2$ olefin in 7.77 g (56.5 mmol) of trichlorofluoromethane was irradiated with an ultraviolet light from a 100 watt Hanovia lamp for 72 hours. The resulting light yellow solution was filtered through a sintered funnel to remove discolored solid material. Removal of all volatile material left behind a viscous tan oil, 0.856 g of [CF$_3$CF(SO$_2$F)C(O)OCH$_2$CHCH$_2$]$_n$ in 49% yield.

The infrared spectrum of the viscous liquid has bands (cm$^{-1}$): 2945 (w), 2875 (vw), 1792 (s), 1454 (s), 1393 (vw), 1300 (s), 1250 (vs), 1166 (s), 1068 (w), 1018 (m), 983 (w), 835 (s, b with sh at 824), 744 (m), 688 (m), 603 (s), 547 (w), 484 (w), 456 (w).

The $^{19}$F nmr spectrum contained a broadened singlet at $\delta$ 50.5 ppm (SO$_2$F), a broadened singlet at $\delta$ -73.5 ppm (CF$_3$), and a broadened singlet at $\delta$ -161.4 ppm (CF). The relative
band areas for SO₂F, CF₃, and CF were 1.0:3.2:1.0; theor. 1.0:3.0:1.0.

The proton nmr spectrum contained a broad singlet centered at δ4.8 ppm (CH₂O) and a series of peaks in the δ 1.2-3.8 ppm range (CH₂, CH).

Anal. Calcd. for C₆H₅F₅SO₄: C, 26.87; H, 1.88; F, 35.4; S, 11.96. Found: C, 26.79; H, 1.94; F, 35.6; S, 11.85.

In another run, 3.96 g (14.8 mmol) of CF₃CF(SO₂F)C(O)OCH₂CH=CH₂ was placed in a quartz reaction vessel with 1.99 g (14.5 mmol) of CFCl₃ and irradiated for 56 hours. The liquid was drained from the reaction vessel, and the CFCl₃ removed under vacuum to give a brown highly viscous liquid, 3.19 g, in 80% yield. Left behind in the reaction vessel was a tan waxy solid, 0.376 g, formed in 9.4% yield. The waxy solid did not soften and melt prior to decomposition at 164°C.

The infrared and nmr spectra for both products agreed with that found in the previous run.

Polymerization of SF₅CF(SO₂F)C(O)OCH₂=CH₂ Olefin

In a 80mL quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, 2.07 g (6.30 mmol) of SF₅CF(SO₂F)C(O)OCH₂CH=CH₂ in 7.77 g (56.5 mmol) of trichlorofluoromethane was irradiated with a 100 watt ultraviolet Hanovia lamp for 78 hours. The fraction soluble
in F-11 was transferred from the reaction flask; the F-11 was removed under vacuo yielding a brownish viscous oil of 0.917 g \(\text{SF}_5\text{CF(SO}_2\text{F)C(O)OCH}_2\text{CHCH}_2\text{H}_n\), 44% yield.

The infrared spectrum of the viscous liquid had bands (cm\(^{-1}\)): 2973(w,b), 1792(s), 1454(s), 1384(w), 1365(w), 1278(s), 1228(s), 1171(s), 1090(vw), 1018(w), 990(w), 934(w), 882(vs), 856(w), 812(s), 784(s), 678(m), 618(s), 587(s), 575(s), 487(m), 453(w).

The proton nmr spectrum contained a broad singlet centered at \(\delta 4.8\) ppm (CH\(_2\text{O}\)) and a series of peaks in the range of \(\delta 1.0-3.5\) ppm (CH\(_2\), CH).

The \(^{19}\text{F}\) nmr spectrum contained a broadened multiplet at \(\delta 65.2\) ppm (axial SF), a broadened doublet at \(\delta 57.4\) ppm (SF\(_4\)), a broadened singlet at \(\delta 48.8\) ppm (SO\(_2\)F), and a broadened singlet at \(\delta -121.5\) ppm (CF). The relative band areas for SF:SF\(_4\):CF:SO\(_2\)F were: 1.4:4.0:1.0:1.0.

\textbf{Anal.} Calculated for C\(_5\)H\(_5\)F\(_7\)S\(_2\)O\(_4\): C, 18.41; H, 1.54; F, 40.8; S, 19.66. Found: C, 18.86; H, 1.50; F, 40.0; S, 19.30.

In another run, 0.602 g (1.84 mmol) of \(\text{SF}_5\text{CF(SO}_2\text{F)C(O)OCH}_2\text{CH=CH}_2\) was placed in a quartz reaction vessel with 2.45 g (17.8 mmol) of CFCl\(_3\) and was irradiated for 39 hours. The CFCl\(_3\) was removed under vacuum leaving a light tan waxy solid with some viscous oil on the sides of the vessel; \(\text{SF}_5\text{CF(SO}_2\text{F)C(O)OCH}_2\text{CHCH}_2\text{H}_n\) was formed in 95% yield. The softening temperature of the solid was \(-52^\circ\text{C}\). The IR and
nmr spectra agreed with that found for the viscous oil reported in the first run.

**Polymerization of SF₅CH(SO₂F)C(O)OCH₂CH=CH₂ Olefin**

In a 80 mL quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, 1.89 g (6.10 mmol) of SF₅CH(SO₂F)C(O)OCH₂CH=CH₂ in 6.21 g (45.2 mmol) of trichlorofluoromethane was irradiated with a 100 watt ultraviolet Hanovia lamp for 26 hours. After this time period, an insoluble oil had formed on the walls of the quartz vessel. The trichlorofluoromethane solution was decanted and the remaining oil was extracted with acetone. The acetone soluble solution was evaporated in vacuo to yield a viscous clear dark brown oil of 0.9523 g (3.09 mmol) \([SF₅CH(SO₂F)C(O)OCH₂CHCH₂]_n\), 51% yield.

The infrared spectrum of the viscous liquid had bands (cm⁻¹): 2973(w), 1764(s), 1440(s with sh at 1384), 1293(s), 1222(s), 1159(s), 1068(w), 990(w), 871(vs,b), 800(s), 772(m), 750(m), 690(m), 644(m), 612(m), 569(s), 489(m), 457(m), 415(w).

The proton nmr spectrum contained a broad singlet at δ 7.24 ppm (SF₅CH), a broad singlet at δ 4.4 ppm (CH₂O) and a series of peaks in the range of δ 1.2-3.3 ppm (CH₂, CH).

The ¹⁹F spectrum contained a broadened singlet at Ø 71.3 ppm (SF₅), and a broadened singlet at Ø 58.5 ppm (SO₂F).
Anal. Calcd. for C₅H₆F₆S₂O₄: C, 19.48; H, 1.96; F, 37.0; S, 20.80. Found: C, 19.76; H, 2.09; F, 36.4; S, 20.54.

In another run, 0.440 g (1.43 mmol) of SF₅CH(SO₂F)C(O)OCH₂CH=CH₂ was placed in the 80 mL quartz vessel with 1.39 g (10.1 mmol) CFCl₃ and irradiated for 26 hours. The CFCl₃ was removed under vacuum leaving a tan waxy solid along with some viscous oil; [SF₅CH(SO₂F)C(O)OCH₂CHCH₂]ₙ was formed in 100% yield. The softening temperature of the solid was ~45°C.

The above product exhibited the same infrared and nmr spectra as previously reported.

FSO₂CF₂C(O)OH with Ag₂O

To a 200 mL Pyrex-glass three neck reaction vessel equipped with a reflux condenser and containing a Teflon stirring bar, were added 48.3 mmol of Ag₂O and 60 mL diethyl ether. The acid FSO₂FSC₂C(O)OH, 94.6 mmol, was added slowly with stirring over a period of ~2 hours and then allowed to react overnight. The mixture was filtered and the ether was partially removed by evaporation. The salt, FSO₂CF₂CO₂Ag (81.4 mmol), was dried with intermittent heating at 80°C; the yield was 86%.

The infrared spectrum had the following bands (cm⁻¹): 1708 (s), 1687 (s), 1427 (s), 1384 (m), 1230 (m), 1180 (ms, w, sh at 1138), 998 (m, sh. at 955), 899 (w), 843 (m),
The $^{19}\text{F}$ nmr spectrum contained a triplet at $0 \text{ ppm} (\text{SO}_2\text{F})$ and a doublet at $0 -100.9 \text{ ppm} (\text{CF}_2)$ with a coupling constant, $J = 3.52 \text{ Hz}$. The relative band area for $\text{FSO}_2$ to $\text{CF}_2$ was $1.0:2.0$, theor. $1.0:2.0$.

**General Procedure for Ester Preparation from the Silversalt, $\text{FSO}_2\text{CF}_2\text{COOAg}$**

To a 90 to 150 mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve and under a nitrogen atmosphere, was added $\text{FSO}_2\text{CF}_2\text{C(O)OAg}$. The iodo- or bromo-containing compounds were either condensed via vacuum transfer or directly added, in a dry box, into the reaction vessel and cooled to $-196^\circ\text{C}$. The reaction mixtures were protected from light and allowed to warm slowly to room temperature ($\sim 24$ hours).

**$\text{FSO}_2\text{CF}_2\text{C(O)OAg}$ with $\text{CH}_3\text{I}$**

To the reaction vessel previously described 2.40 mmol $\text{FSO}_2\text{CF}_2\text{C(O)OAg}$ and 3.17 mmol $\text{CH}_3\text{I}$ were added. The mixture was protected from light and warmed slowly to room temperature for 24 hours. Trap-to-trap distillation gave 1.51 mmol of the ester $\text{FSO}_2\text{CF}_2\text{C(O)OCH}_3$ ($\sim 40^\circ\text{C}$ trap) in 63% yield.

The infrared spectrum had the following bands (cm$^{-1}$): 2973 (mw), 1806 (s), 1462 (vs), 1321 (s), 1243 (s), 1209
The $^{19}$F nmr spectrum contained a triplet at $\delta$ 39.1 ppm (SO$_2$F) and a doublet at $\delta$ -105.5 ppm (CF$_2$) with a coupling constant $J = 5.64$ Hz. The relative band area was 1.0:1.9 (theor. 1.0:2.0). The $^1$H nmr spectrum contained a singlet at $\delta$ 4.17 ppm.

The positive ion mass spectrum CI$^+$ gave peaks (m/e, species, %): 193, MH$^+$, 1.6; 124, CH$_2$COOCF$_2$S$^+$, 5.2 109, (M-SO$_2$F)$^+$, 55.9; 79, CSOF$^+$, 8.6; 67, SOF$^+$, 19.1; 65, SO$_2$H$^+$, 23.6; 59, CH$_3$CO$_2$+ , 100; 51, SF$^+$, 4.7.

Anal. Calcd for C$_3$H$_3$F$_3$SO$_4$: C, 18.76; H, 1.57; F, 29.8; S, 16.69. Found: C, 18.80; H, 1.65; F, 29.5; S, 16.69.

**FSO$_2$CF$_2$(O)OAg with CH$_3$CH$_2$CH$_2$I**

To the reaction vessel previously described were added 15.11 mmol FSO$_2$CF$_2$(O)OAg and 14.18 mmol of CH$_3$CH$_2$CH$_2$I. After reaction, the volatile liquid mixture was washed with H$_2$O, dried over MgSO$_4$ and distilled. The fraction boiling at 142-143° was further purified by gas chromatography giving 1.54 mmol of FSO$_2$CF$_2$(O)OCH$_2$CH$_2$CH$_3$ in 11% yield.

The infrared spectrum had the following bands (cm$^{-1}$): 2980 (m), 2945 (w), 2889 (w), 1792 (s), 1448 (s), 1398 (w), 1356 (w), 1313 (s), 1237 (s), 1193 (s), 1166 (s), 1152 (s), 1103 (vw), 1082 (vw), 1054 (wm), 1012 (m), 927 (w), 899 (w),
829 (m), 801 (ms), 723 (vw), 646 (m), 604 (m), 576 (m), 484 (vw), 463 (vw).

The $^{19}$F nmr spectrum of $\text{FSO}_2\text{CF}_2\text{C(O)OCH}_2\text{CH}_2\text{CH}_3$ contained
a triplet at $\delta$ 39.7 ppm ($\text{SO}_2\text{F}$) and a doublet at $\delta$ 105.4 ppm
($\text{CF}_2$) with a coupling constant $J = 5.3$ Hz. The relative
band area for $\text{FSO}_2:\text{CF}_2$ was 1.0:1.8 (theor. 1.0:2.0). The $^1\text{H}$
nmr spectrum contained a triplet at $\delta$ 0.68 ppm ($\text{CH}_3$), a
sextet at $\delta$ 1.50 ppm ($\text{CH}_2$) and a triplet at 4.19 ppm ($\text{CH}_2$).
$J_{\text{CH}_3-\text{CH}_2} = 7.2$ Hz and $J_{\text{CH}_2-\text{CH}_2} = 6.6$ Hz. The relative band
area for $-\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_3$ was 2.0:2.0:3.1 (theor. 2.0:2.0:3.0).

The positive ion mass spectrum, $\text{Cl}^+$, gave peaks (m/e, 
species, %): 205, ($\text{M-CH}_3)^+$ or ($\text{MH-O})^+$, 2.32; 149,
$\text{SC}_2\text{COC}_3\text{H}_3^+$, 12.49; 119, $\text{SCFCOC}_2\text{H}_4^+$, 6.18; 109, $\text{SC}_5\text{HO}^+$,
23.63; 107, $\text{FSO}_2\text{C}_2^+$ or $\text{CF}_2\text{CO}_2\text{CH}^+$, 24.87; 97, $\text{SC}_4\text{HO}^+$, 16.55;
95, $\text{FSO}_2\text{C}^+$, 12.36; 91, $\text{SCFCO}^+$, 5.10; 83, $\text{SO}_2\text{F}^+$, 9.92; 81,
$\text{C}_4\text{O}_2\text{H}^+$, 6.92; 79, $\text{FSCO}^+$, 5.23; 73 $\text{CFCOCH}_2^+$, 12.29; 70,
$\text{COC}_3\text{H}_6^+$, 6.03; 69, $\text{COC}_3\text{H}_5$, 26.62; 67, $\text{SOF}^+$ or $\text{COC}_3\text{H}_3^+$,
12.79; 65, $\text{COC}_3\text{H}^+$, 100; 59, $\text{CFCO}^+$, 18.53; 57, $\text{CO}_2\text{CH}^+$, 33.55;
56, $\text{C}_2\text{O}_2^+$ or $\text{SC}_2^+$, 7.68; 55, $\text{COC}_2\text{H}_3^+$, 33.06; 53, $\text{C}_2\text{OCH}^+$,
5.98; 51, $\text{SF}^+$, 13.48.

**Anal.** Calcd. for $\text{C}_5\text{H}_7\text{F}_3\text{SO}_4$: C, 27.28; H, 3.21; F,
25.9; S, 14.56. Found: C, 27.29; H, 3.22; F, 26.1; S,
14.57.
To the reaction vessel previously described, were added 20.9 mmol of \(\text{FSO}_2\text{CF}_2\text{C(O)}\text{OAg}\) and 19.55 mmol \(\text{HOCH}_2\text{CH}_2\text{I}\). Distillation gave 2.38 mmol of \([\text{FSO}_2\text{CF}_2\text{C(O)}\text{OCH}_2]^2\) in 23% yield, b.p. 96°C/70μ.

The infrared spectrum had the following bands (cm\(^{-1}\)): 2987 (vw), 1792 (s), 1448 (s), 1372 (w), 1307 (ms), 1237 (s), 1208 (ms), 1159 (s), 1124 (wm), 1047 (wm), 1019 (w), 871 (wm), 808 (ms, br), 723 (vw), 646 (ms), 604 (m), 569 (m), 484 (w), 463 (vw).

The \(^{19}\text{F}\) nmr spectrum contained a triplet at \(\delta 40.4\) ppm (SO\(_2\)F) and a doublet at \(\delta -105.0\) ppm with a coupling constant \(J = 5.64\) Hz. The integration ratio was 1.0:1.9 (theor. 1.0:2.0). The \(^1\text{H}\) nmr contained a singlet at \(\delta 5.03\) ppm.

The positive ion mass spectrum, \(\text{Cl}^+\), gives peaks (m/e, species, %): 229, (M-SO\(_2\)F)\(^+\), 1.06; 207, \(\text{C}_6\text{O}_4\text{F}_2\text{SH}^+\), 17.17; 206, \(\text{C}_6\text{O}_4\text{F}_2\text{S}^+\), 15.33; 205, \(\text{FSO}_2\text{CF}_2\text{CO}_2\text{C}_2\text{H}_4^+\), 100; 155, \(\text{FSCF}_2\text{COC}_2\text{H}_2^+\), 17.02; 141, \(\text{FSCF}_2\text{COC}^+\), 24.45; 123, \(\text{SCF}_2\text{COCH}^+\), 5.92; 122, \(\text{SCF}_2\text{COC}^+\), 7.70; 119, \(\text{SFCOC}_2\text{H}_4^+\), 24.37; 113, \(\text{FSCF}_2\text{C}^+\), 6.74; 111, \(\text{C}_5\text{O}_3\text{H}_3^+\), 7.66; 97, \(\text{SC}_4\text{H}_9^+\), 5.52; 91 \(\text{SCFCO}^+\), 7.73; 79, \(\text{FSOC}^+\), 13.39; 78, \(\text{CF}_2\text{CO}^+\), 7.36; 69, \(\text{C}_3\text{O}_2\text{H}^+\), 8.22; 67, \(\text{FSO}^+\), 44.13; 65, \(\text{C}_4\text{H}_9^+\), 50.33; 51, \(\text{SF}^+\), 13.36.
Anal. Calcd. for C₆H₄F₆S₂O₉: C, 18.85; H, 1.05; F, 29.8; S, 16.78. Found: C, 19.32; H, 1.01; F, 28.9; S, 15.91.

**FSO₂CF₂C(O)₁₄Ag with (CH₃)₃SiI**

To the reaction vessel previously described, was added 13.46 mmol of (CH₃)₃SiI and 13.30 mmol of FSO₂CF₂C(O)OAg. Distillation of the liquid product gave 3.84 mmol FSO₂CF₂C(O)OSi(CH₃)₃ in 29% yield, b.p. 86°C/46 mm.

The infrared spectrum had the following bands (cm⁻¹): 2959 (w, sh at 2924 and 2903), 1785 (s), 1448 (s, sh at 1427), 1328 (m), 1258 (m, sh at 1279), 1230 (m), 1195 (m), 1152 (s), 1012 (m, sh at 1047), 913 (vw), 850 (s, b, sh at 878), 801 (s, b), 759 (w), 730 (vw), 639 (m, sh at 667).

The ¹⁹F nmr spectrum contained a triplet at 0.37 ppm (SO₂F) and a doublet at 0.97 ppm (CF₂) with a coupling constant J = 4.65 Hz. The relative band area for FSO₂ to CF₂ was 1.0:2.0, (theor. 1.0:2.0). The ¹H nmr spectrum contained a singlet at 0.4 ppm.

The positive ion mass spectrum, CI⁺, gave peaks (m/e, species, %): 251, MH⁺, 1.53; 250, M⁺, 1.73; 149, (M-H)⁺, 13.81; 199, SCF₂CO₂SiC₃H₅⁺, 5.83; 91, SCFCO⁺, 4.34; 88, OSiC₂H₈⁺, 9.42; 87, OSiC₃H₇⁺, 100; 74, OSiC₂H₆⁺, 4.23; 73, SiC₃H₉⁺, 45.92; 65, SiC₃H₇⁺, 9.29; 63, SCF⁺, 7.73; 59, CFCO⁺, 39.97; 57, SiC₂H₅⁺, 6.53; 55, SiC₂H₅⁺, 7.88.
Anal. Calcd. for C$_5$H$_9$F$_3$SO$_4$Si:  F, 22.8;  S, 12.81.

Found:  F, 22.3;  S, 11.26.
CHAPTER V

RELATED REACTIONS

Recently, workers\textsuperscript{81} have reported on a synthetic pathway that we have found useful in preparing several SF\textsubscript{5}-containing fluoroethers. This pathway involves the addition of reactive trifluoromethyl hypochlorite to substituted olefins:

\[
\text{F}_3\text{COCl} + \text{C} = \text{C} \rightarrow \text{F}_3\text{COCCl}
\]  

(1)

In order to evaluate this pathway for preparing pentafluorothio (SF\textsubscript{5}) derivatives, the reactions of CF\textsubscript{3}OCl with a number of SF\textsubscript{5} olefins, were studied. Reactions of SF\textsubscript{5}CH=CF\textsubscript{2} with Cl\textsubscript{F}, SF\textsubscript{5}CH=CF\textsubscript{2} with Cl\textsubscript{2} and SF\textsubscript{5}CF=CF\textsubscript{2} with CF\textsubscript{3}OCl and reported here were prepared in conjunction with Dr. Roger M. Sheets.\textsuperscript{92}

In our continuing studies of pentafluorothiocarbon systems, we have found that upon reacting SF\textsubscript{5}Br with fluoroolefins not only monomeric liquids but polymeric solids are produced under proper conditions of heat and pressure. The polymer SF\textsubscript{5}(CHFCF\textsubscript{2})\textsubscript{30}Br\textsubscript{0.30} has been previously reported but is included here for comparison.\textsuperscript{82} It is possible that the SF\textsubscript{5} grouping may serve as a precursor to an SO\textsubscript{2}F grouping; work is ongoing in our laboratories.
TRIFLUOROMETHYL HYPOCHLORITE/CHLORINE MONOFUORIDE REACTIONS

The reaction of CF₃OCl with SF₅CH=CH₂ proceeded smoothly at room temperature:

$$\text{SF}_5\text{CH}=\text{CH}_2 + \text{CF}_3\text{OCl} \rightarrow \text{SF}_5\text{CHClCH}_2\text{OCF}_3$$  (2)

The new SF₅ fluoroether boils at 93±1 °C and is a water-white liquid.

When trifluoromethyl hypochlorite was reacted with SF₅CF=CF₂ at 110 °C, the following reaction occurred to give essentially one product (69%) that boiled at 72-73 °C:

$$\text{SF}_5\text{CF}=\text{CF}_2 + \text{CF}_3\text{OCl} \rightarrow \text{SF}_5\text{CFClCF}_2\text{OCF}_3$$  (3)

With hexafluoropropene the following isomers, CF₃OCF₂CFClCF₃ (71.5%) and CF₃OCF(CF₃)CF₂Cl (28.5%), were produced.²

It was interesting to find that while SF₅CH=CH₂ and SF₅CF=CF₂ added only CF₃OCl, this behavior did not extend to SF₅CH=CF₂. With this olefin, ClF addition was the major reaction pathway:

$$\text{SF}_5\text{CH}=\text{CF}_2 + \text{CF}_3\text{OCl} \rightarrow \text{SF}_5\text{CHClCF}_3 + \text{COF}_2$$  (4)

In separate reactions to confirm reaction (4), the straightforward addition of ClF to SF₅CH=CF₂ was carried out to give identical product.

$$\text{SF}_5\text{CH}=\text{CF}_2 + \text{ClF} \rightarrow \text{SF}_5\text{CHClCF}_3$$  (5)

It was found also that Cl₂ added directly to SF₅CH=CF₂ in high yield:

$$\text{SF}_5\text{CH}=\text{CF}_2 + \text{Cl}_2 \rightarrow \text{SF}_5\text{CHClCF}_2\text{Cl}$$  (6)
The reaction which occurred between SF$_5$CCl=CH$_2$ and CF$_3$OCl gave rise to one major product, SF$_5$CCl$_2$CH$_2$CH$_2$CCl$_2$SF$_5$. This sort of dimerization has not been observed previously in these systems.

It is unusual that ClF instead of CF$_3$OCl addition occurred with the above olefin but not with SF$_5$CH=CH$_2$, SF$_5$CF=CF$_2$, or CF$_3$CH=CH$_2$. Other olefinic systems in which significant ClF addition occurred using CF$_3$OCl included the unsymmetrical olefins CH$_2$=CF$_2$, CF$_2$=CHBr, and CH$_2$=CHF.

In order to prepare new olefinic systems containing an SF$_5$ group, the addition products obtained in eq. (2) and eq. (4) were treated with potassium hydroxide:

$$\text{SF}_5\text{CHClCH}_2\text{OCF}_3 + \text{KOH} \rightarrow \text{SF}_5\text{CCl=CH}_2$$  \hspace{1cm} (7)

$$\text{SF}_5\text{CHClCF}_3 + \text{KOH} \rightarrow \text{SF}_5\text{CCl=CF}_2$$  \hspace{1cm} (8)

The two olefins formed above are new compounds. The loss of [CF$_3$OH] in eq. (7), while unusual, has been observed previously when the reacting ether was CF$_3$OCH(CF$_3$)CH$_2$Cl which resulted in the formation of CF$_3$CH=CHCl.

As reported earlier, Cross and coworkers observed that for compounds in which the SF$_5$ group is bound to an aliphatic hydrocarbon a very intense, usually broad band centered at about 870 cm$^{-1}$ and a less intense but sharp band at or near 600 cm$^{-1}$ are always found. They assigned the former to the S-F stretching mode and the latter to the S-F
deformation mode. For the compounds reported here, the S-F stretching modes and the S-F deformation mode are located in the regions at 840-913 cm\(^{-1}\) and at 590-613 cm\(^{-1}\), respectively. It is known that for compounds with C-F, CF\(_2\), or CF\(_3\) strong C-F stretching vibrations are usually located in the 1000-1280 cm\(^{-1}\) region. These appropriate carbon-fluorine absorption bands are found for the new compounds. The absorption band near 3000 cm\(^{-1}\) is assigned to the C-H stretching mode. The C=C stretching vibrations for SF\(_5\)CCl=CH\(_2\) and SF\(_5\)CCl=CF\(_2\) are found at 1616 and 1721 cm\(^{-1}\), respectively.

The major mass spectral peaks for these compounds are listed in the experimental section. In all compounds, the mass spectra contained prominent peaks (m/e) at 89(SF\(_3^+\)) and 127(SF\(_5^+\)). The compounds SF\(_5\)CCl=CF\(_2\) and SF\(_5\)CCl=CH\(_2\) exhibited parent ions.

The nmr spectra generally consists of complex multiplets (Table XVI). However, with most compounds first-order coupling constants could be determined and these are given. The nmr pattern for the SF\(_5\) group consisted of the expected AB\(_4\) pattern with the B\(_4\) equatorial fluorine atoms split into a doublet and the A part into a nine-line pattern. Analysis of the chemical shifts confirms the proposed structures. For example, the proton chemical shift of a CHX group next to an SF\(_5\) group is consistent from one SF\(_5\) fluoroalkyl derivative to another. In our compounds the proton chemical
shift values for SF₅CHClCH₂OCl, SF₅CHClCF₃, and SF₅CHClCF₂Cl are 5.62, 5.46 and 6.10 ppm, respectively. For other SF₅ systems, such as SF₅CHFCF₃, SF₅CHFCF₂Br, SF₅CHFCHClBr, SF₅CHFCFCBr, and SF₅CHClCF₂Br, the values are 5.41, 5.58, 5.85, 5.68 and 5.5 ppm, respectively. Also, the proton chemical shift of a CH₂ group one carbon away from an SF₅ is also consistent from one SF₅ fluoroalkyl derivative to another. In SF₅CHClCH₂OCl and (SF₅CCl₂CH₂)₂ the proton chemical shifts were found at 5.55/4.80 and 4.81 ppm, respectively. In SF₅CBr₂CH₂Br the proton chemical shift was found at 5.83 ppm. The proton chemical shift values for the olefin SF₅CCl=CH₂ are due to the following structure.

The Hₐ (doublet) pattern is located at 6.20 ppm while for Hₐ (multiplet) the band center is found at 5.95 ppm. These values are in close agreement with the corresponding bromo derivative (5.64 and 5.9 ppm). Determination of the protons Hₐ and Hₐ is based on the fact that a proton trans to the SF₅ group interacts more strongly than the proton in the cis position.

For a number of systems it is found that CF₃OC₁ adds in a Markovnikov fashion producing syn addition products. However, we have found, as have others, that in some
olefinic systems, COF₂ elimination occurred either in place of CF₃OC1 addition or with CF₃OC1 addition. It is difficult to account for these observations unless one invokes a radical ion reaction mechanism. For CF₃OC1 addition, the following sequence is possible.

\[
\begin{align*}
\text{C} + \text{CF₃OC1} & \xrightarrow{\text{e}^-, \text{transfer}} \text{C} + \text{CF₃OC1}^- \\
\text{[CF₃OC1]}^- & \xrightarrow{\text{[CF₃O}^\cdot \text{Cl}^-]}
\end{align*}
\]

Figure 5. Free radical mechanism for CF₃OC1 addition
This mechanism would explain that carbon (b) containing the less electronegative substituents is observed to combine with chlorine while carbon (a) with the more electronegative element substituents adds F via F· abstraction or CF₃O· via recombination. It is possible that a secondary oxidation-reduction step occurs prior to (4i) or (5i), viz.,

The trifluoromethoxide ion could recombine to give the desired ether or undergo COF₂ elimination with the resulting F⁻ adding to the carbocation. It is anticipated that unsymmetrical hydrogen-containing olefins would be more susceptible to F/F⁻ abstractions with concomitant formation of COF₂ than more symmetrical systems.
<table>
<thead>
<tr>
<th>Compound</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(a)SF₄(b)CH(c)ClCHH'(d)OCF₃(e)</td>
<td>73.3(n)</td>
<td>53.2(m)</td>
<td>5.62(m)</td>
<td>4.55(m)</td>
<td>-63.6(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.80(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ja,b = 144, Jb,c = 4.5, Jb,d = 0.9, Jb,d' =1.2, Jc,d = 4.8, Jc,d' = 6.9, Jd,d' = 17.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(a)SF₄(b)CF(c)ClCF₂(d)OCF₃(e)</td>
<td>63.3(n,d)</td>
<td>46.3(d,m)</td>
<td>-98.2(m)</td>
<td>-82.3(m)</td>
<td>-57.3(t)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ja,b = 143, Ja,c = 4.4, Jb,d = 9.9, Jc,d = 21.2, Jd,e = 9.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(a)SF₄(b)CH(c)ClCF₃(d)</td>
<td>68.7(n)</td>
<td>57.7(d,m)</td>
<td>5.61(m)</td>
<td>-73.0(p,d) -</td>
<td></td>
</tr>
<tr>
<td>[F(a)SF₄(b)CCL₂CH₂(c)]₂</td>
<td>71.2(n)</td>
<td>47.1(d,m)</td>
<td>4.81(m)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ja,b = 134, Jb,c = 1.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F(a)SF₄(b)CH(c)ClCF₂(d)Cl</td>
<td>70.0(n)</td>
<td>58.8(d,m)</td>
<td>6.10(m)</td>
<td>-64.8(d) -</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ja,b = 141, Jc,d = 5.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>H(d)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.8(n)</td>
<td>55.2(d,m)</td>
<td>6.2(d)</td>
<td>5.95(m) -</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ja,b = 152, Jb,c = 3.3, Jc,d = 3.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* ¹⁹F chemical shifts (ppm) relative to CFCl₃; ¹H chemical shifts (ppm) relative to TMS; s = singlet, d = doublet, t = triplet, p = pentet, n = 9-line, m = multiplet. Coupling constants in Hz.
SF$_5$Br WITH FLUOROOLEFINS TO FORM POLYMERS

We have found that SF$_5$Br reacts with fluoroethylenes to form polymers incorporating the SF$_5$-group according to the following equations:

\[
\begin{align*}
SF_5Br + xS CH_2=CHF & \rightarrow SF_5(CH_2CHF)_{10}Br \quad (9) \\
SF_5Br + xS CH_2=CF_2 & \rightarrow SF_5(CH_2CF_2)_8Br \quad (10) \\
SF_5Br + xS CFH=CF_2 & \rightarrow SF_5(CFHCFCF_2)_{30}Br_{0.7} \quad (11) \\
SF_5Br + xS CF_2=CF_2 & \rightarrow SF_5(CF_2CF_2)_{16}Br_{0.3} \quad (12)
\end{align*}
\]

With ethylene, essentially no polymer was formed. In addition to the above polymers (eqns. 9-12), the adducts SF$_5$RBr (R is CH$_2$CHF, CH$_2$CH$_2$, CHFCF$_2$, CF$_2$CF$_2$) are formed. The monomeric adducts with the exception of SF$_5$CF$_2$CF$_2$Br have been previously reported as has the polymer in (11).$^{60,88}$

The key factor in this preparative route seems to be high pressure along with a $90\pm5^\circ$C temperature; calculated pressures can possibly go as high as 90 atmospheres for reactions reported here.

All of the polymers are waxy and become whiter as the number of fluorines in the structure increases. Other trends also coincide with the increasing number of fluorines in the structure and include: i) an increase in melting point, 2i) an increase in stability, and 3i) a decrease in solubility. These findings are summarized in Table XVII. Additional qualitative tests with the SF$_5$(CFHCFCF$_2$)$_{30}$Br$_{0.7}$ and SF$_5$(CF$_2$CF$_2$)$_{16}$Br$_{0.3}$ polymers found that they were not soluble
or reactive with a variety of concentrated acids (HCl, HNO₃, H₂SO₄) or base (6N, NaOH) at temperatures up to 100°C.

The empirical formulas of the polymers are given in Table XVIII and are based upon elemental analyses. As with other polymer systems, we would expect a variety of chain lengths and end groupings depending upon the nature of the termination in each case; possibilities for termination include coupling of two chains with end groups (SF₅, SF₅) or termination with SF₅· or Br· radicals resulting in end groups of (SF₅, SF₅) or (SF₅, Br). Chain termination, either by coupling or reaction with SF₅ radicals would result in a lower bromine content in the polymer.

As previously mentioned,⁶² for compounds in which the SF₅ group is bound to an aliphatic hydrocarbon, a very intense infrared band centered on or about 870 cm⁻¹ and a less intense but sharp band at or near 600 cm⁻¹ are always found. For the polymers reported in this paper, we find the S-F stretching mode and one of the S-F deformation modes are located in the region 845-899 cm⁻¹ and 606-600 cm⁻¹, respectively; for SF₅CF₂CF₂Br the corresponding modes were located at 903 and 609 cm⁻¹, respectively. It is known that for monomeric compounds with C-F and -CF₂- groupings, strong C-F stretching vibrations are usually located in the 1000-1250 cm⁻¹ region of the infrared; appropriate carbon fluorine absorption bands are found for these new compounds. The absorption bands in the 2941-3010 cm⁻¹ region are
attributed to C-H stretching modes. The C-Br stretching bands for fluoroalkyl bromides are reported to be in the 740-770 cm\(^{-1}\) region, while for alkylbromides the range is 515-680 cm\(^{-1}\). For the new compounds described in this paper, the bands in the 766-705 cm\(^{-1}\) region may well be due to the C-Br stretching mode.

The mass spectrum for SF\(_5\)CF\(_2\)CF\(_2\)Br did not contain a molecular ion peak but other appropriate fragment peaks were found: (C\(_2\)F\(_4\)Br\(^+\)), (C\(_2\)F\(_3\)Br\(^+\)), (CF\(_2\)Br\(^+\)), (SF\(_5\))\(^+\)), (SF\(_4\)C\(^+\)), (CF\(_3\)Br\(^+\)), (SF\(_4\))^+, (C\(_2\)F\(_4\))^+, (SF\(_3\))^+, and Br\(^+\).

The nmr spectra for all the polymers except SF\(_5\)(CF\(_2\)CF\(_2\))\(_{16}\)Br\(_{0.3}\) consist of complex multiplets from which representative chemical shift values were found (Table XIX). The \(^{19}\)F nmr pattern for the SF\(_5\) group consisted of the expected AB\(_4\) pattern with the B\(_4\) equatorial fluorines split into a complex doublet and the axial fluorine, A, into a nine-line pattern. The chemical shift values for the equatorial fluorine are found in a range of \(\delta\) 54 to 66 ppm while for monomeric adducts the corresponding values range from \(\delta\) 44 to 67 ppm. The axial fluorine values range from \(\delta\) 71 to 83 ppm for polymers and \(\delta\) 61 to 80 ppm for the respective monomeric adduct. In the trifluoroethylene polymer, two types of SF\(_5\) groups were present. For the SF\(_5\)(CF\(_2\)CHF)\(_{10}\)Br and SF((CHFCF\(_2\))\(_3\)Br\(_{0.7}\) polymers, the \(^{19}\)F resonances for C-F are found at \(\delta\) -183 ppm and \(\delta\) -211 ppm, respectively. By comparison, the \(^{19}\)F chemical shift values
for C-F in polyvinylfluoride are located at $\delta$ -178 to -185 ppm (broad peaks); chemical shifts at $\delta$ -190 to -200 ppm represent inversion defects in the chain. The $^{19}$F chemical shift values for the CF$_2$ group vary from $\delta$ -93 to -130 ppm. Wilson and Santee report regions of CF$_2$ shifts in polyvinylidene fluoride of $\delta$ -91.6, -94.8, -113.6 and -115.6 ppm depending on the relationship of the CF$_2$ to other CH$_2$ and CF$_2$ groups in the chain.

The new monomeric adduct, F(a)SF$_4$(b)CF$_2$(c)CF$_2$(d)Br, has $^{19}$F chemical shift values for CF$_2$ groups in the characteristic region and contains the AB$_4$ pattern for the SF$_5$ group. The equatorial fluorines are split into the typical doublet and the axial fluorine into a nine-line pattern with $\delta$ 44.3 ppm and $\delta$ 61.5 ppm, respectively. The coupling constant $J_{a,b} = 146.6$ Hz. For the CF$_2$ groups, the fluorines (c) and (d) are assigned at $\delta$ -93.5 ppm and $\delta$ -66.5 ppm, respectively with $J_{b,c} = 14.4$ Hz, $J_{a,c} = 4.23$ Hz, $J_{b,d} = 11.3$ Hz and $J_{c,d}$ estimated at 4.5 Hz. The chemical shifts are consistent with other monomeric adducts.

The $^1$H nmr spectra for the polymers are complex multiplets in which characteristic chemical shift values are found. For SF$_5$(CHFCF$_2$)$_{30}$Br$_{0.7}$, the $^1$H chemical shifts occur at $\delta$ 1.3 to 3 ppm and $\delta$ 5.5 ppm corresponding to the CH in the chain and the CH next to the SF$_5$, respectively. The monomer adduct has a CH value of $\delta$ 5.58 ppm next to the SF$_5$. In the SF$_5$(CH$_2$CHF)$_{10}$Br the CH chemical shift is assigned to the
band at δ 4.74 ppm and overlaps with the CH$_2$ resonances when the CH$_2$ is attached to the SF$_5$ group; in the corresponding monomeric adduct, the CH$_2$ value is found at δ 4.27 ppm. The chemical shift of the CH$_2$ group located in the chain is found at δ 1.8 ppm. By comparison, it is reported that for polyvinyl chloride, the chemical shift values, in the δ 1.9-2.3 ppm region, are attributed to the B protons (CH$_2$) and the values at δ 4.2-4.5 to the (CH) protons. In the polymer SF$_5$(CH$_2$CF$_2$)$_8$Br, $^1$H chemical shift values are found at δ 2.8 and δ 4.5 ppm corresponding to the chain CH$_2$ groups and the CH$_2$ next to the SF$_5$, respectively. The monomeric adduct has a CH$_2$ chemical shift of δ 4.46 ppm.

In general, we find that for SF$_5$ containing fluoropolymers, when the SF$_5$ group is attached to a CH$_2$ group in the chain, the proton chemical shift is found near δ 4.5 ppm; for the rest of the CH$_2$ in the chain, the chemical shift values are located in the δ 1.8-2.8 ppm region. We find the chemical shift at δ 5.15 ppm for the C-H group when attached to SF$_5$, while for the rest of the CH groups in the chain, chemical shift values are located in the range of δ 1.3-3.0 ppm.
### TABLE XVII

**PROPERTIES OF SF₅-CONTAINING FLUOROPOLYMERS**

<table>
<thead>
<tr>
<th>Compound*</th>
<th>Melting Range (°C)</th>
<th>Decomp. (°C)</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₅(CH₂CHF)₁₀Br</td>
<td>100-110</td>
<td>190</td>
<td>ins. sol.</td>
</tr>
<tr>
<td>SF₅(CH₂CF₂)₈Br</td>
<td>118-150</td>
<td>330</td>
<td>ins. sol.</td>
</tr>
<tr>
<td>SF₅(CHFCF₂)₃₀Br₀.₇</td>
<td>130-160</td>
<td>460</td>
<td>ins. sl. sol.</td>
</tr>
<tr>
<td>SF₅(CF₂CF₂)₁₆Br₀.₃</td>
<td>310-318</td>
<td>&gt;510</td>
<td>ins. insol.</td>
</tr>
</tbody>
</table>

* Empirical composition based on elemental analysis.

### TABLE XVIII

**ANALYSIS OF SF₅-CONTAINING FLUOROPOLYMERS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc. Found</th>
<th>C</th>
<th>H</th>
<th>F</th>
<th>S</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₅(CH₂CHF)₁₀Br</td>
<td>35.98</td>
<td>4.54</td>
<td>42.7</td>
<td>4.80</td>
<td>11.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.79</td>
<td>4.39</td>
<td>43.0</td>
<td>4.86</td>
<td>11.95</td>
<td></td>
</tr>
<tr>
<td>SF₅(CH₂CF₂)₈Br</td>
<td>26.70</td>
<td>2.22</td>
<td>55.4</td>
<td>4.46</td>
<td>11.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26.83</td>
<td>2.33</td>
<td>54.2</td>
<td>4.54</td>
<td>10.91</td>
<td></td>
</tr>
<tr>
<td>SF₅(CHFCF₂)₃₀Br₀.₇</td>
<td>27.42</td>
<td>1.14</td>
<td>68.1</td>
<td>1.21</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.34</td>
<td>1.19</td>
<td>68.2</td>
<td>1.44</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>SF₅(CF₂CF₂)₁₆Br₀.₃</td>
<td>21.95</td>
<td>-</td>
<td>74.9</td>
<td>1.83</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21.42</td>
<td>-</td>
<td>72.8</td>
<td>1.89</td>
<td>1.38</td>
<td></td>
</tr>
</tbody>
</table>
TABLE XVII

$^{19}$F AND $^1$H NMR DATA FOR SF5-CONTAINING FLUOROMONOMERS/POLYMERS*

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Chemical Shifts (ppm)</th>
<th>SF</th>
<th>SF4</th>
<th>CF</th>
<th>CF2</th>
<th>CH2</th>
<th>CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSF$_4$CH$_2$CHFBr$^b$</td>
<td>79.9 66.4 -139.2 -</td>
<td>4.27</td>
<td>6.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FSF$_4$CH$_2$CF$_2$Br$^b$</td>
<td>77.3 70.5 - -51.5 4.46 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FSF$_4$CHFCF$_2$Br$^b$</td>
<td>70.0 53.7 -163.5 -63.1 -</td>
<td>5.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FSF$_4$CF$_2$CF$_2'Br$</td>
<td>61.5(n,t) 44.3(d,m) - -93.5(p,m) -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[coupling constants for F(a)SF$_4$(b)CF$_2$(c)CF$_2$(d)Br (Hz): $J_a,b = 146.6$, $J_a,c = 4.23$, $J_b,c = 14.4$, $J_b,d = 11.3$, $J_c,d = -4.5$]

<table>
<thead>
<tr>
<th>Polymers$^c$</th>
<th>SF</th>
<th>SF4</th>
<th>CF</th>
<th>CH2</th>
<th>CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSF$_4$(CH$<em>2$CHF)$</em>{10}$Br</td>
<td>83</td>
<td>65.5</td>
<td>-183</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>FSF$_4$(CH$_2$CF$_2$)$_8$Br</td>
<td>81</td>
<td>71.2</td>
<td>-</td>
<td>-93</td>
<td>2.8,4.5</td>
</tr>
<tr>
<td>FSF$_4$(CHFCF$<em>2$)$</em>{30}$Br$^b$</td>
<td>71</td>
<td>56,54</td>
<td>-211</td>
<td>-120,-122</td>
<td>2.8,4.5</td>
</tr>
</tbody>
</table>

FSF$_4$(CF$_2$CF$_2'$)$_{16}$Br$^c$ (not determined)

a. Chemical shifts given relative to CFCl$_3$ for $^{19}$F and TMS for $^1$H; d = doublet, t = triplet, p = pentet, n = 9-line, and m = multiplet.

b. Previously reported monomers.$^60$ Previously reported polymer.$^88$

c. All peaks are broadened; no coupling constants could be determined.
EXPERIMENTAL

SF$_5$CH=CH$_2$ with CF$_3$OCl to form SF$_5$CHClCH$_2$OCF$_3$

Into a 1.0 L Pyrex glass vessel equipped with a Kontes Teflon valve were added 34.5 mmol of SF$_5$CH=CH$_2$ and 30.8 mmol of CF$_3$OCl. The mixture was warmed to room temperature for one hour; with shaking for 1.5 hours. The product, 20.8 mmol of SF$_5$CHClCH$_2$OCF$_3$, is formed in 67% yield; bp=94-96 °C.

The infrared spectrum of the liquid had bands (cm$^{-1}$): 3009(vw), 1469(w), 1412(w), 1279(vs), 1223(vs), 1194(s), 1159(vs), 1089(w), 1061(w), 1012(w), 850(vs, b), 780(w), 759(m), 723(w), 667(w), 611(w), 590(m), 576(w), 555(w), 512(w), and 491(w).

The $^{19}$F nmr spectrum for F(a)SF$_4$(b)CH(c)ClCH(d)H(d')OCF$_3$(e) contained a singlet at $\delta$ -63.6 (F$_e$) and two multiplets at $\delta$ 53.2 (F$_b$) (doublet of multiplets) and $\delta$ 73.3 (F$_a$) (nine line pattern). Relative band areas are 2.9:1.0:4.1, respectively (theor. 3.0:1.0:4.0), $J_{a,b} = 144$ Hz. The $^1$H nmr spectrum contained multiplets centered at $\delta$ 4.55 (H$_d$), 4.80 (H$_d'$), and 5.62 (H$_c$) ppm. Relative band areas ($\delta$ 4.55 and 4.80 combined) are 2.0:1.0, respectively (theor. 2.0:1.0). Coupling constants are $J_{b,c} = 4.5$, $J_{b,d} = 0.9$, $J_{b,d'} = 1.2$, $J_{c,d} = 4.8$, $J_{c,d'} = 6.9$, and $J_{d,d'} = 17.7$ Hz.

The positive mass spectrum, CI$^+$ gives peaks, (m/e, species, %): 189, (M-OCF$_3$)$^+$, 17.9; 147, C$_3$H$_3$F$_3$ClO$^+$, 25.1; 127,
\[ \text{SF}_5^+, 2.9; 99, \text{C}_2\text{H}_2\text{F}_3\text{O}^+, 30.2; 89, \text{SF}_3^+, 24; 81, \text{SCH}_2\text{Cl}^+, 100; 69 \text{CF}_3^+, 61.2. \]

**Anal.** Calcd. for \( \text{C}_3\text{H}_3\text{F}_8\text{SOCl} \): C, 13.12; H, 1.10; S, 11.68; Cl, 12.91. Found: C, 13.05; H, 1.10; S, 11.45; Cl, 12.92.

**SF\(_5\)CF=CF\(_2\) with CF\(_3\)OCl to form SF\(_5\)CFClCF\(_2\)OCF\(_3\)**

Into a 75 mL Hoke stainless steel vessel equipped with a Whitey stainless steel valve were added 17.6 mmol of \( \text{SF}_5\text{CF}=\text{CF}_2 \) and 22.7 mmol of \( \text{CF}_3\text{OCl} \). The mixture was heated at 110 °C for 24 hours. The product, 12.2 mmol of \( \text{SF}_5\text{CFClCF}_2\text{OCF}_3 \), was obtained in 69% yield; bp 72–73 °C.

The infrared spectrum of the liquid gave bands (cm\(^{-1}\)):

- 1314(s), 1251(vs), 1166(s), 1152(s), 1054(w), 969(w), 941(m), 900(vs), 878(m), 857(s), 800(s), 688(w), 663(vw), 603(s), and 584(w).

The \(^{19}\text{F} \) nmr spectrum for \( \text{F(a)SF}_4\text{(b)CF(c)ClCF}_2\text{(d)OCF}_3\text{(e)} \) contained a multiplet at 0 63.3 (F\(_a\)) (nine-line pattern of doublets), a doublet of multiplets at 0 46.3 (F\(_b\)), a triplet at 0 -57.3 (F\(_e\)), a nine-line multiplet at 0 -82.3 (F\(_d\)), and a multiplet at 0 -98.2 ppm (F\(_c\)); \( J_{a,b} = 143, J_{a,c} = 4.4, J_{b,d} = 9.9, J_{c,d} = 21.2 \) and \( J_{d,e} = 9.1 \) Hz. The positive mass spectrum, CI\(^+\) gives peaks, (m/e, species, %): 201, (M-SF\(_5\))^+, 9.9; 135, C\(_2\)F\(_5\)O^+, 100; 127, SF\(_5\)^+, 4.9; 119, C\(_2\)F\(_5\)^+, 5.1; 89 SF\(_3\)^+, 14.9; 69, CF\(_3\)^+, 83.2.

SF$_5$CCl=CH$_2$ with CF$_3$OCl to form (SF$_5$CCl$_2$CH$_2$)$_2$

Into a 100 mL Pyrex glass vessel equipped with a Kontes Teflon stopcock were added 3.15 mmol of SF$_5$CCl=CH$_2$ and 2.98 mmol of CF$_3$OCl. The mixture was warmed to room temperature (~ 14 h) and heated at 47-49 °C for three hours. The nonvolatile product (SF$_5$CCl$_2$CH$_2$)$_2$ remaining in the reaction vessel (1.56 mmol) was obtained in 52% yield.

The infrared spectrum of the liquid had bands (cm$^{-1}$): 2938(w), 2882(w), 1799(w), 1462(w), 1363(w), 1279(w), 1237(w), 1152(s), 1089(w), 1033(w), 977(w), 941(vw), 830(vs, b), 772(m), 745(m), 702(m), 674(w), 590(s), 576(m), and 520 (w).

The $^{19}$F nmr spectrum for [F(a)SF$_4$(b)CCl$_2$CH$_2$(c)]$_2$ contained a nine-line multiplet at $\delta$ 71.2 ppm (F$_a$) and a doublet of multiplets at $\delta$ 47.1 ppm (F$_b$), $J_{a,b} = 134$ Hz. Relative band areas were 1.0:4.1, respectively (theor. 1.0:4.0). The $^1$H nmr spectrum contained a multiplet at $\delta$ 4.81 ppm (distorted pentet), $J_{b,c} = 1.92$ Hz. The positive mass spectrum, CI$^+$ gives peaks, (m/e, species, %): 336, C$_4$H$_2$F$_8$S$_2$Cl$_2^+$, 3.1; 203, C$_2$HF$_4$SCl$_2^+$, 10.6; 147, C$_2$H$_2$FSCl$_2^+$, 15.4; 127, SF$_5^+$, 23.7; 117, CF$_2$SCl$^+$, 63.2; 115, C$_2$H$_2$F$_3$S$^+$, 100; 89, SF$_3^+$, 36.7.
Anal. Calcd. for C₄H₄F₁₀S₂Cl₄:  C, 10.72; H, 0.90; S, 14.31; Cl, 31.65. Found: C, 10.77; H, 0.79; S, 13.31; Cl, 32.32.

**SF₅CH=CF₂ with ClF to form SF₅CHClCF₃**

Into a 75 ml Hoke stainless steel vessel equipped with a Whitey stainless steel valve were added 2.0 mmol of SF₅CH=CF₂ and 2.0 mmol of ClF. The mixture was allowed to warm to room temperature for 13 hours. The volatile materials were removed at -98 °C. The product, 1.8 mmol SF₅CHClCF₃ was obtained in 98% yield. The infrared and nmr spectra agreed with those reported for the product obtained from SF₅CH=CF₂ and CF₃OC₁.⁹²

The infrared spectrum of the liquid had bands (cm⁻¹): 3022(w), 1321(s), 1271(vs), 1250(s), 1201(vs), 1152(vs), 913(vs), 885(vs,b), 835(vs), 702(w), 674(s), 610(s), 573(m), and 523(w).

The ¹⁹F nmr spectrum for F(a)SF₄(b)CH(c)ClCF₃(d) consisted of a multiplet at δ 68.7 ppm (Fa, nine-line pattern), δ 57.7 ppm (Fb, doublet of multiplets), and δ -73.0 ppm (Fd, pentet of doublets); Jₐ,b = 151, Jₐ,c = 5.6, Jₖ,b = 11.2 and Jₖ,d = 6.3 Hz. The ¹H nmr spectrum contained a multiplet at δ 5.61 ppm.
**SF\(_5\)CH=CF\(_2\) with Cl\(_2\) to form SF\(_5\)CHClCF\(_2\)Cl**

Into a 100 mL Pyrex glass vessel equipped with a Kontes Teflon stopcock were added 3.28 mmol of SF\(_5\)CH=CF\(_2\) and 3.75 mmol of Cl\(_2\). The mixture was warmed to room temperature (\(~\sim 20\) h) and was irradiated with a G. E. sunlamp for 4.5 hours. The volatile materials were removed at -98 °C. The product, 3.03 mmol SF\(_5\)CHClCF\(_2\)Cl, was obtained in 92% yield.

The infrared spectrum of the liquid contained bands (cm\(^{-1}\)): 3148(vw), 3016(vw), 1243(w), 1138(m), 1050(m), 991(m), 934(vs), 885(vs), 822(vs), 668(w), 660(vw), 597(m), 576(w) and 541(s).

The \(^{19}\)F nmr spectrum for F(a)SF\(_4\)(b)CH(c)ClCF\(_2\)(d)Cl contained multiplets at \(\sim 70\) ppm (Fa, nine-line pattern), \(\sim 58.8\) ppm (Fb, doublet of multiplets), and a doublet at \(\sim -64.8\) ppm (Fd), \(J_{a,b} = 141\) Hz. The relative band areas for SF\(_4\) to CF\(_2\) are 1.8 to 1.0; theor. 2.0 to 1.0. The \(^1\)H nmr spectrum contains a multiplet at \(\sim 6.10\) ppm, \(J_{c,d} = 5.6\) Hz.

**SF\(_5\)CHClCH\(_2\)OCF\(_3\) with KOH to form SF\(_5\)CCl=CH\(_2\)**

Into a 100 mL Carius tube equipped with a Kontes Teflon stopcock and two stirring bars were added 116 mmol KOH and 8.74 mmol SF\(_5\)CHClCH\(_2\)OArCF\(_3\). The mixture was shaken while warming to room temperature until no additional heat of reaction was evolved. The volatile materials were transferred into a storage tube. A second run using 230 mmol KOH and 13.7 mmol of the adduct was treated as above.
The product, 9.43 mmol of SF₅CCl=CH₂, was formed in 42% yield; bp 64 °C; molecular weight calcd: 188.5; found 190.0.

The infrared spectrum of the liquid had bands (cm⁻¹): 3149 (vw), 1616 (m), 1405 (m), 1356 (w), 1293 (w), 1180 (w), 1124 (m), 1083 (w), 919 (s with sh at 912, vs, broad), 778 (vs), 684 (m), 612 (m), 594 (m), 512 (m), and 481 (m).

The ¹⁹F nmr spectrum for F(a)SF₄(b)CClCH(c)H(d) contained a multiplet (nine-line pattern) at $\delta$ 74.8 ppm (Fa) and a doublet of multiplets at $\delta$ 55.2 ppm (Fb) with relative peak areas 1.0:4.0 (theor. 1.0:4.0); $J_{a,b} = 152$. The ¹H nmr spectrum contained a doublet at $\delta$ 6.20 ppm (Hc) and a complex multiplet at $\delta$ 5.95 ppm (Hd); $J_{b,c} = 3.3$ and $J_{c,d} = 3.9$ Hz.

The positive mass spectrum, CI⁺ gives peaks, (m/e, species, %): 188, M⁺, 29.9; 127, SF₅⁺, 20.9; 89, SF₃⁺, 24.3; 61, C₂H₂Cl⁺, 100.

Anal. Calcd. for C₂H₂F₃SCl: C, 12.74; H, 1.07. Found: C, 12.81; H, 1.05.

CF₂=CF₂ with SF₅Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 64 mmol of SF₅Br and 75 mmol of CF₂=CF₂. The mixture was heated for 5.8 days at 90±5 °C. The volatile materials were transferred out leaving behind 6.44g of a white solid.
The melting range for the white solid is 310-318 °C with no decomposition observed up to 510 °C.

The infrared spectrum of the solid has bands (cm⁻¹): 1216(s, with sh at 1244), 1152(s), 899(ms, with sh at 866), 847(w), 825(w), 781(w), 741(w), 719(w), 688(w), 640(m,), 625(m), 606(wm), 556(m), 503(s,b).

**Anal. calcd. for SF₅(CF₂CF₂)₁₆Br₀.₃:** C, 21.95; S, 1.83; F, 74.87; Br, 1.35. **Found:** C, 21.42; S, 1.89; F, 72.8; Br, 1.38.

In a second run, 61.0 mmol of CF₂=CF₂ and 62.2 mmol of SF₅Br were heated at 90±5 °C (2d). Distillation of the volatile material gave 3.71 mmol of SF₅CF₂CF₂Br, bp. 60-62 °C, leaving behind 8.91 grams of solid polymer. The molecular weight of SF₅CF₂CF₂Br (calc. 307.0, found 303.6).

The infrared spectrum of the liquid had the following bands (cm⁻¹): 1216(ms), 1194(m), 1173(w), 1152(s), 1061(m), 1047(w), 934(m), 903(vs,b), 859(vw), 831(m), 766(vs), 684(w), 609(ms,), 591(w), 578(w).

The ¹⁹F nmr spectrum contained a multiplet at Ø 61.5 ppm (nine-line pattern of triplets), a doublet of multiplets at Ø 44.3 ppm, a pentet of multiplets at Ø -93.5 and -66.5 ppm (relative band areas for SF to SF₄ was 1.0:3.9, theor. 1.0:4.0 and for CF₂Br to SF₅CF₂ was 1.0:1.0). Coupling constants for F(a)SF₄(a)CF₂(c)CF₂(d)Br were Jₐ,b = 146.6, Jₐ,c = 4.23, Jₐ,b,c = 14.4, Jₐ,b,d = 11.3, Jₓ-d ~ 4.5 Hz.
A molecular ion was not observed but other fragment ions were found: 179,181 (C₂F₄Br)⁺; 160,162 (C₂F₃Br)⁺; 129,131 (CF₂Br)⁺; 127 (SF₅)⁺; 120 (SF₄C)⁺; 110,112 (CFBr)⁺; 108 (SF₄)⁺; 101 (SF₃C)⁺; 100 (C₂F₄)⁺; 89 (SF₃)⁺; 79,81 (Br)⁺; 70 (SF₂)⁺; 69 (CF₃)⁺; 63 (SFC)⁺; 51 (SF)⁺; 50 (CF₂)⁺; 44 (SC)⁺.

Anal. Calcd. for C₂F₉SBr: C, 7.82; F, 55.7; S, 10.44; Br, 26.03. Found: C, 7.83; F, 55.40; S, 10.59; Br, 25.98%.

CFH=CF₂ with SF₅Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 93 mmol of SF₅Br and 100 mmol of CF₂=CFH; after heating this mixture at 90±5 °C for four days, an additional 52 mmol of SF₅Br and 64 mmol of CF₂CFH were added. The reaction mixture was heated at 90±5 °C for three days. The volatile materials at room temperature (58 mmol of SF₅CFHCF₂Br) were removed leaving behind 9.0 grams of a white waxy solid.

In an additional run, 58.8 mmol of SF₅Br and 75.8 mmol of CFH=CF₂ were heated at 90±5 °C for four days. To this reaction mixture an additional 69.7 mmol of CF₂=CFH was added and heated at 90±5 °C (3d); in this run 10.9 grams of the same white waxy solid was formed. The melting range of this polymer was 130-160 °C with decomposition at 460 °C.

The infrared spectrum of this solid had the following bands (cm⁻¹): 2994(w), 1394(m), 1350(m), 1281(ms),
The $^{19}$F nmr spectrum contained a complex doublet of doublets at $\delta$ 56 and 54 ppm (SF$_4$) and a multiplet at $\delta$ 71 ppm (SF); multiplets at $\delta$ -120, -122, -125, -129 ppm (CF$_2$) and at -211 (CF) ppm are present. The $^1$H nmr spectrum has two broad multiplets centered at $\delta$ 5.5 ppm and a series of peaks in the range of $\delta$ 1.3 - 3.0 ppm.

Anal. calcd for SF$_5$(CHFCH$_2$)$_3$OBr$_{0.7}$: C, 27.42; H, 1.14; F, 68.1; S, 1.21; Br, 2.11. Found: C, 27.34; H, 1.19; S, 1.44; F, 68.2; Br, 2.01.

CF$_2$=CH$_2$ with SF$_5$Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 96.2 mmol of SF$_5$Br and 118.3 mmol of CF$_2$=CH$_2$. The reaction mixture was maintained at 90±5 °C for 12 hours, at room temperature for 5 hours, and 90±5 °C for 3 days. The products, 69.4 mmol of SF$_5$CH$_2$CF$_2$Br (bp 86-87 °C) and 3.0 grams of a waxy solid were formed. The waxy solid (slightly discolored) melted in 118-150 °C range and decomposed at 330 °C.

The infrared spectrum of the solid had the following bands (cm$^{-1}$): 3010 (w), 2984 (w), 1422 (m), 1399 (m), 1384 (m), 1270 (m), 1209 (s), 1183 (s), 1158 (s), 1077 (m), 1012 (w), 975 (m), 941 (m), 871 (s), 838 (s), 796 (m), 762 (m), 727 (w),
The $^{19}$F nmr spectrum contained a complex doublet at $\delta$ 71 ppm ($SF_4$) and a multiplet at $\delta$ 81 ppm ($SF$); multiplets at $\delta$ -93 and $\delta$ -98 ppm ($CF_2$) were present. The $^1$H nmr spectrum contained broad complex multiplets with the bands centered at $\delta$ 2.8 and $\delta$ 4.5 ppm.

**Anal.** for $SF_5(CH_2CF_2)_8$Br, Calcd: C, 26.70; H, 2.22; F, 55.4; S, 4.46; Br, 11.10. Found: C, 26.83; H, 2.33; F, 54.2; S, 4.54; Br, 10.91.

**CFH=CH$_2$ with $SF_5$Br**

The reactants, $SF_5$Br (84 mmol) and CFH=CH$_2$ (102.9 mmol) were condensed into the 75 mL reaction vessel. The reaction mixture was heated at 90±5 °C for three days and at 60 °C for one day. The volatile materials, containing $SF_5CH_2CHFBr$ were removed leaving behind 1.68 g of a waxy solid (slightly discolored). The waxy solid melted in the 100-110 °C range and decomposed at 190 °C.

The infrared spectrum of this solid had the following bands (cm$^{-1}$): 2970(s), 2941(s), 1446(m), 1426(s), 1411(s), 1370(ms), 1257(m), 1067(s with sh. at 1087), 845(s), 830(s), 824(s), 720(m), 705(m), 642(m), 601(m), 565(m), and 457(m).

The $^{19}$F nmr spectrum contained a complex doublet at $\delta$ 66 ppm ($SF_4$) and a multiplet at $\delta$ 83 ppm ($SF$); $J_{SF-SF_4} = 155$ Hz, the CF resonance was a complex multiplet centered at
$\delta -183$ ppm. The $^1$H nmr spectrum contained two broad multiplets centered at $\delta 1.8$ (CH$_2$) and $\sim \delta 4.7$ (CH) ppm; relative band areas 2.1:1.0 (theor. 2.0:1.0).

**Anal.** for SF$_5$(CH$_2$CFH)$_{10}$Br, Calcd: C, 35.98; H, 4.54; S, 4.80; F, 42.7; Br, 11.97. Found: C, 35.79; H, 4.39; S, 4.86; F, 43.0; Br, 11.95.

**CH$_2$=CH$_2$ with SF$_5$Br**

To the 75 mL reactor described earlier, 99 mmol of SF$_5$Br and 136 mmol of CH$_2$=CH$_2$ were added. The reaction mixture was warmed to room temperature (16 hours), heated at 55±2 °C for 2 days and at 90±5 °C for 3 days. The volatile materials were removed leaving behind 1.1 g of charred material. Distillation of the volatile materials gave a fraction boiling at 74-77 °C (3.77 g). The molecular weight of this fraction (137 g/mole), its characteristic infrared and nmr spectra confirmed the material to be a mixture of FCH$_2$CH$_2$Br (91%) and SF$_5$CH$_2$CH$_2$Br (9%).

In a second run, under mild conditions, 84.3 mmol of SF$_5$Br and 109.2 mmol of CH$_2$=CH$_2$ were used. The reaction mixture was warmed to room temperature for 16 h. Again, a volatile fraction boiling at 74-77 °C (3.06 g) and a small amount <1 g of charred material was formed.
REFERENCES

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2. G. L. Gard, unpublished reports to Gas Research Institute.


85. Thank-you to Dr. Carl Wamser for helpful discussions.
APPENDIX

INFRARED AND NMR SPECTRA
Figure 6. Infrared Spectrum for SF₅CHCF₂OSO₂.
Figure 7. Infrared Spectrum for SF$_5$CHCF$_2$·SO$_3$. 
Figure 8. Infrared Spectrum for SF₅CH(SO₂F)COF.
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Figure 11. Infrared Spectrum for SF₅CH₂SO₃H·H₂O.
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Figure 13. Infrared Spectrum for SF₅CH(SO₂F)C(O)OCH(CF₃)₂.
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Figure 16. Infrared Spectrum for
[SF\textsubscript{5}CH(SO\textsubscript{2}F)C(O)OCH\textsubscript{2}CHCH\textsubscript{2}-]n.
Figure 17. Infrared Spectrum for FSO₂CF₂C(0)OAg.
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Figure 46. $^1$H and $^{19}$F nmr for $\text{[SF}_5\text{CH(SO}_2\text{F)}\text{C(O)O-CH}_2\text{CHCH}_2\text{-}_n}$ (sw = 10 for $^1$H and 50 for $^{19}$F).
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Figure 59. $^1$H and $^{19}$F nmr for SF$_5$(CH$_2$CHF)$_{10}$Br.