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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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AN ABSTRACT OF THE DISSERTATION OF Robin J. Terjeson for the
Doctor of Philosophy in Environmental Science and Resources:
Chemistry presented April 28, 1989.

Title: The Chemistry of Sulfonyl Fluorides: SF_5 and/or
 SO_2F Containing Compounds as Precursors to Sulfonic
Acids

APPROVED BY MEMBERS OF THE DISSERTATION COMMITTEE:

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Larry H. Crawshaw

Sulfonyl fluoride systems and their derivatives, RSO_2F , where R represents hydrocarbon/fluorocarbon moieties continue to be of considerable interest. The incorporation of the sulfonyl fluoride group (SO_2F) 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 SF_5 containing sulfonyl fluorides led to the synthesis of the β -sultone, $\text{SF}_5\text{CHCF}_2\text{OSO}_2$, and its rearranged product. Hydrolysis of the sultone gave $\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$ which led to the sulfonic acid and salt, $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ and $(\text{SF}_5\text{CH}_2\text{SO}_3)_2\text{Ca}$. Esters of the sultone were prepared by reaction of the sultone with fluorinated alcohols in the presence of NaF to give $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OR}$ where $\text{R} = \text{CH}_2\text{CF}_3$ and $\text{CH}(\text{CF}_3)_2$.

Polymeric $\text{SF}_5/\text{SO}_2\text{F}$ containing esters were prepared by reaction of allyl esters, $\text{RCX}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$, in ultraviolet light where $\text{R} = \text{CF}_3$ or SF_5 and $\text{X} = \text{H}$ or F .

Fluorinated silver carboxylate salts have been useful in preparing fluoroesters from alkyl iodides. Therefore, a new silver salt, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ was prepared and characterized; its reaction with $(\text{CH}_3)_3\text{SiI}$, $\text{HOCH}_2\text{CH}_2\text{I}$ and alkyl bromides and iodides are reported.

In addition, new SF_5 containing fluoropolymers were synthesized via reaction of fluorinated olefins with SF_5Br . Reactions of SF_5 containing olefins with CF_3OCl , ClF and Cl_2

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}C nmr and ^{19}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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CHAPTER I

INTRODUCTION AND SIGNIFICANCE

FUEL CELLS

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

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 ($\text{R}=\text{SF}_5\text{CH}_2$, SF_5CHF , CH_3 , CF_3CF_2 , etc., $\text{X}=\text{F}$, 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:²

- (1) Acid strength for acids that depend on the amount and position of fluorine in the fluorocarbon "tail". ($\text{CF}_3\text{SO}_3\text{H}$ is a stronger acid than $\text{CH}_3\text{SO}_3\text{H}$)
- (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 $\text{CF}_3\text{SO}_2\text{X}$, $\text{X}=\text{Cl}, \text{F}$, is comparable to phosphoric acid as an electrolyte for fuel cells. Preliminary testing of $\text{SF}_5\text{CHFSO}_3\text{H}$ prepared in our laboratory also showed potential as an electrolyte.

Preparation of sulfonyl fluorides and their conversion to sulfonic acids have been reported previously.³⁻⁶ 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 SF_5 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.⁷ 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 (SO_2F) 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_5Br 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.⁸ Fluoroalkyl ethers are useful as monomers for polymerization as well as for their own physical properties.⁹

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.¹⁰

CHAPTER II

REVIEW OF SULFONYL FLUORIDE SYSTEMS

Fluorinated sulfonyl fluoride (SO_2F) 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_2F 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_2F moiety are of interest for the same reason.

Fluorinated polymeric solids and viscous oils with the SO_2F group also incur growing interest as potential ion exchange resins, as precursors to polymeric sulfonic acids similar to NafionTM, and as copolymers. (See Table V) In this chapter we will review a variety of methods used for preparing SO_2F 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:^{4,11,12}

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

Reactions of $\text{ClSO}_2\text{F}/\text{SO}_2\text{F}_2$ with Olefins

Addition of ClSO_2F or SO_2F_2 to olefins has been used to prepare some SO_2F containing compounds in reactions such as:¹³

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

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 (SO_3) 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:

$\text{XFC}-\text{CYZ}$ where X may be F, H, CF_3 , Cl or other
 $\begin{array}{c} | \quad | \\ \text{O}_2\text{S}-\text{O} \end{array}$ 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

With tetrafluoroethylene in addition to the β -sultone $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$, 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 β -sultones undergo hydrolysis via the following reaction to give a sulfonyl fluoride compound:

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

With tetrafluoroethylene β -sultone, the carboxylic acid, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OH}$, 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 β -sultones are given in Table I. A review by Knunyants and Sokolskii done in 1972 gives a variety of reactions possible with fluorinated β -sultones, many of which produce fluorinated sulfonyl fluorides. The reactions of the interesting disultone gives fluorosulfate/sulfonyl fluoride products:¹⁷

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.^{18,19}

In addition to the expected hydrolysis and rearrangement products, the sulfonic acid, $\text{SF}_5\text{CHFSO}_3\text{H}$, prepared from the sultone, $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ (2-hydroxy-1-(pentafluoro- λ^6 -sulfanyl)-1,2,2-trifluoroethanesulfonic acid sultone), is currently under evaluation as a potential fuel cell electrolyte. The products of the reaction of $\text{CF}_3\overline{\text{CHCF}_2\text{OSO}_2}$ with alcohols give esters which have been shown to have a labile proton as observed via nmr by stabilization with base (eqn. 14):¹⁸

In a number of cases it is possible to replace the proton in the esters $\text{CF}_3\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{R}$ to form the derivatives

$\text{CF}_3\text{CBr}(\text{SO}_2\text{F})\text{COOR}$ and $\text{CF}_3\text{CCl}(\text{SO}_2\text{F})\text{COOR}$; and in one reaction,

$\text{CF}_3\text{CCl}_2\text{SO}_2\text{F}$ (also obtained by chlorination of $\text{CF}_3\text{CH}_2\text{SO}_2\text{F}$ in a proposed two step process).¹⁸ Other studies by the same

group show the CH acidity of α -hydro containing sulfonyl fluorides to fall in the following order: $\text{CF}_3\text{CHFSO}_2\text{F} <$

$\text{CF}_3\text{CH}_2\text{SO}_2\text{F} < \text{CF}_3\text{CHClSO}_2\text{F} = \text{CF}_3\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OR}$. Based upon

proton nmr data, the CH acidity of some SF_5 -containing

sulfonyl fluoride systems occurs in the following order:

$\text{SF}_5\text{CH}_2\text{SO}_2\text{F} < \text{SF}_5\text{CHFSO}_2\text{F} = \text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OR}$ (Table VIII).¹⁹

Esters/Ethers Prepared via Reaction of Sultones with Alcohols

An early study found that 2-hydroxy-tetrafluoroethane- β -sultone, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ (I), or its acid, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OH}$ (II), when reacted with alcohols under mild conditions (0 to 10°C) produced the corresponding esters, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OR}$ ($\text{R} = \text{C}_3\text{H}_7$, C_8H_{17} , $\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{CHCH}_2$, and $\text{H}(\text{CF}_2)_4\text{CH}_2$ and the diester $(\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F})_2$.⁶ Similar reactions produce $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_3$, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$, and $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$.¹⁵ Reaction of 2-hydroxy-1-trifluoromethyl-1,2,2-trifluoroethanesulfonic acid sultone, $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$, with the alcohols $\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{CHCH}_2\text{OH}$, CH_3OH , and $(\text{CH}_3)_2\text{CHOH}$ also gave esters.^{6,16} In more recent studies, the β -sultones, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ and $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$, when reacted with fluorinated and nonfluorinated alcohols produce the sulfonyl fluoride (SO_2F) containing esters; with appropriate alkane diols, triols, or tetraols the corresponding di, tri, and tetraesters are formed.^{20,21} (See Table II)

Direct reaction of a number of the SO_2F containing esters with SF_4 acting as a fluorinating agent and a large excess of anhydrous HF has been shown to produce the corresponding ether derivatives.²²

$\text{R}_f = \text{CF}_3\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2$, CH_3CH_2 , $\text{C}(\text{CF}_3)_2\text{H}$, $\text{CF}_3\text{CH}(\text{CF}_3)$, $\text{CH}_3\text{C}(\text{CF}_2)_2$, $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2$, and $\text{C}(\text{CH}_2\text{O})_4$

TABLE I
PRODUCTS/DERIVATIVES OF SULTONE REARRANGEMENT
AND HYDROLYSIS REACTIONS

<u>Sultone</u>	<u>Product</u>	<u>Reference</u>
CF ₂ CF ₂ OSO ₂ (I)	FSO ₂ CF ₂ C(O)OH (II)	6, 15, 16
	FSO ₂ CF ₂ C(O)F	6
	FSO ₂ CF ₂ C(O)Cl (from II)	16
CHFCF ₂ OSO ₂ (III)	FSO ₂ CHFC(O)F	6
CF ₃ CFCF ₂ OSO ₂ (IV)	CF ₃ CF(SO ₂ F)C(O)F	6
	CF ₃ CHFSO ₂ F	6
CF ₂ CFC1OSO ₂ (V)	ClSO ₂ CF ₂ C(O)F	6
CFC1CF ₂ OSO ₂ (VI)	FSO ₂ CF ₂ C(O)F	6

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

<u>Esters of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$²⁰</u>	<u>Esters of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$²¹</u>
$\text{CF}_3\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	$\text{CF}_3\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$
$\text{CF}_3\text{CF}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	$(\text{CF}_3)_3\text{COC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	$\text{C}_6\text{F}_5\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$
$(\text{CF}_3)_2\text{C}(\text{CH}_3)\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	
$\text{CF}_3\text{CH}(\text{CH}_3)\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	<u>Esters of $\overline{\text{CF}_3\text{CFCF}_2\text{OSO}_2}$²¹</u>
$(\text{CF}_3)_2\text{CHOC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	$[\text{FSO}_2\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{OCH}_2]_2$
$\text{C}_7\text{F}_{15}\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	$(\text{CF}_3)_2\text{CHOC}(\text{O})\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$
$\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$	$\text{C}_6\text{F}_5\text{OC}(\text{O})\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$
$\text{CH}_3\text{C}[\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}]_3$	$\text{CF}_3\text{CH}_2\text{OC}(\text{O})\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$
$[\text{FSO}_2\text{CF}_2(\text{O})\text{COCH}_2]_2$	
$\text{C}[\text{CH}_2\text{OC}(\text{O})\text{CF}_2\text{SO}_2\text{F}]_4$	

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

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 SO_3 to give both the mono- β -sultone with olefin functionality and bis- β -sultones which produce products containing two SO_2F groupings. The monosultone is predominately produced when the ratio of olefin to SO_3 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 SO_2F containing compounds similar to those listed here for the mono and bis- β -sultone prepared from 1,7-octadiene.^{24,25}

Perfluoroethenesulfonyl fluoride, $\text{CF}_2=\text{CFSO}_2\text{F}$, is prepared by heating $\text{CF}_3\text{CHFSO}_2\text{F}$ to 500°C via a radical reaction:¹⁶

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

Pentafluoro-1-propene-1-sulfonyl fluoride, $\text{CF}_3\text{CF}=\text{C}(\text{SO}_2\text{F})\text{F}$, 2,2-difluoroethenesulfonyl fluoride, $\text{FSO}_2\text{CH}=\text{CF}_2$, and pentafluoropropene-2-sulfonyl fluoride, $\text{CF}_2=\text{C}(\text{SO}_2\text{F})\text{CF}_3$, 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.^{26,27,28} Examples of these reactions are (See Table III for additional compounds):²⁶

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 SO_3 and subsequent rearrangement gives an acyl fluoride with two SO_2F groups; ketenes were also produced.³¹

Synthesis of the ketene containing SO_2F compound, $\text{FSO}_2\text{C}(\text{CF}_3)=\text{C}=\text{O}$, 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:³³

Another route involves treating the rearranged product with the boron trifluoride-triethylamine complex.³³

TABLE III

LISTING OF DERIVATIVES OF SULFONYL FLUORIDES
CONTAINING A DOUBLE BOND

Derivatives of $\begin{array}{c} \text{CF}_3 \\ \diagdown \\ \text{C} = \text{C} \diagup \text{F} \\ \diagup \text{F} \quad \diagdown \text{SO}_2\text{F} \end{array}$; reference 26

$\text{CF}_3\text{C}(\text{O})\text{CHFSO}_2\text{F}$ $\text{CF}_3\text{CFC1CHFSO}_2\text{F}$ $\text{FSO}_2\text{CFHCF}(\text{OCH}_3)\text{CF}_3$
(isomers)

$\text{CF}_3\text{C}(\text{NEt}_3)=\text{CF}(\text{SO}_2\text{F})$ (isomers)

Derivatives of $\text{CF}_2=\text{C}(\text{CF}_3)\text{SO}_2\text{F}$; reference 28

$\text{ROCF}_2\text{CH}(\text{CF}_3)\text{SO}_2\text{F}$ ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{CH}(\text{CF}_2)_4\text{H},$
 $\text{CH}_2\text{CF}_2\text{NO}_2, \text{CH}_3\text{CH}_2\text{CF}_2\text{NO}_2$)

$\text{C}_4\text{H}_9\text{SCF}_2\text{CH}(\text{CF}_3)\text{SO}_2\text{F}$

$(\text{C}_2\text{H}_5)_2\text{NC}(\text{F})=\text{C}(\text{CF}_3)\text{SO}_2\text{F}$ (isomers)

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

$\text{XCF}_2\text{CH}(\text{CF}_3)\text{SO}_2\text{F}$ ($\text{X}=\text{Cl}, \text{Br}$) $\text{CF}_2=\text{C}(\text{CF}_2\text{Cl})\text{SO}_2\text{F}$

$4\text{-CH}_3\text{OC}_6\text{H}_4\text{CF}=\text{C}(\text{CF}_3)\text{SO}_2\text{F}$ (isomers) $\text{CF}_2\text{ClCCl}(\text{CF}_3)\text{SO}_2\text{F}$

$\text{FSO}_2\text{OCF}_2\text{C}(\text{SO}_2\text{F})=\text{CF}_2$

TABLE III

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

Derivatives of $\text{FSO}_2\text{CH}=\text{CF}_2$; reference 29

$\text{FSO}_2\text{CH}_2\text{CF}_2\text{OR}$ ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$)	$\text{FSO}_2\text{CH}=\text{CFOCH}(\text{CH}_3)_2$ (trans)
$\text{FSO}_2\text{CH}_2\text{CF}_2\text{SC}_3\text{H}_7$	$\text{FSO}_2\text{CH}_2\text{C}(\text{O})\text{SC}_3\text{H}_7$
$\text{FSO}_2\text{CH}=\text{CFNR}_2$ ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$)	$\text{FSO}_2\text{CH}_2\text{CF}_2\text{Cl}$
$\text{FSO}_2\text{CHClCF}_2\text{Cl}$	$\text{FSO}_2\text{CH}=\text{CFCl}$ (trans)
$\text{FSO}_2\text{CCl}_2\text{CF}_2\text{Cl}$	

Others; reference 30

$\text{RC}(\text{Net}_2)=\text{C}(\text{SO}_2\text{F})\text{F}$ ($\text{R}=\text{CF}_2\text{H}, \text{C}_3\text{F}_7$)	$\text{RCF}=\text{CFSO}_2\text{F}$ ($\text{R}=\text{HCF}_2, \text{CF}_2\text{Cl}$)
$\text{RCFC1CHFSO}_2\text{F}$ ($\text{R}=\text{CF}_2\text{Cl}, \text{CF}_2\text{H}, \text{C}_3\text{F}_7$)	$\text{HCF}_2\text{CF}(\text{X})\text{CF}(\text{X})\text{SO}_2\text{F}$ (isomers, $\text{X}=\text{Cl}, \text{Br}$)

($\text{R}=\text{HCF}_2, \text{CF}_2\text{Cl}, \text{C}_3\text{F}_7$)

Preparation of Iodine Containing Sulfonyl Fluoride Systems and Derivatives Prepared From $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$

The Chinese group at the Shanghai Institute has synthesized sulfonyl fluoride containing ether systems from the β -sultone, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$, by reaction with ICl and C_2F_4 in the presence of fluoride ion:³⁴

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 $\text{CH}_2=\text{CH}_2$ and may undergo dehydroiodination to give $\text{CH}_2=\text{CH}(\text{CF}_2)_n\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$. In this study a variety of products containing chlorine and the SO_2F grouping are reported as well as the corresponding olefins.³⁵ 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 fluoroiodide compounds.³⁶

Sulfonyl Fluoride Containing Fluoropolymers

Preparation of fluoropolymers containing the SO_2F 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

Fluoropolymers containing SO_2F 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 IV
DERIVATIVES OF $\overline{\text{CF}_2\text{CF}_2\text{O}}\text{SO}_2$

Reference 37

$\text{CF}_3(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$	$\text{ClCF}_2(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$
$(\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{K})_2$	$\text{ClCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{BrCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{Cl}_2\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{BrCFC}_1\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{ICFC}_1\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{CF}_3\text{CFC}_1\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{CF}_3\text{CFBrOCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{ClCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{BrCH}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{Cl}_2\text{CFCFC}_1\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{Cl}(\text{CF}_2\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{Cl}(\text{CF}_2\text{CF}_2)_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{Cl}(\text{CF}_2\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$(\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2)_2$	$[\text{FSO}_2\text{CF}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2)_2]_2$
$[\text{FSO}_2\text{CF}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2)_3]_2$	$[\text{FSO}_2\text{CF}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2)_4]_2$
$\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{CH}_2=\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{CH}_3\text{OCF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{ICF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

Reference 38

$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$	$\text{Cl}_2\text{FCCF}_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$
$\text{Cl}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$	$\text{H}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{H}$
$[\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2]_2\text{O}$	$[\text{Cl}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2]_2\text{O}$
$[\text{Cl}_2\text{FCCF}_2\text{O}(\text{CF}_2)_2\text{SO}_2]_2\text{O}$	$[\text{H}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2]_2\text{O}$
$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{CH}_3$	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{CH}(\text{CH}_3)_2$
$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{CH}_2\text{CH}_2\text{Cl}$	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{CH}_2\text{CF}_3$
$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{CH}_2(\text{CF}_2)_4\text{H}$	$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{C}_6\text{F}_5$
$\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{C}_6\text{H}_3(\text{NO}_2)_2$	$\text{FO}_2\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CFO}$

TABLE IV
DERIVATIVES OF $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$
(continued)

$\text{FO}_2\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{H}$	$\text{HO}_3\text{S}(\text{CF}_2)_2\text{OOCF}_2\text{CO}_2\text{H}$
$[\text{FO}_2\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}]_2\text{O}$	$\text{HO}_3\text{SCF}_2\text{CO}_2\text{H}$
$\text{FO}_2\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{CH}_3$	$\text{FO}_2\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{CH}_2(\text{CF}_2)\text{H}$
$\text{H}(\text{CF}_2)_2\text{CH}_2\text{O}_3\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{CH}_3$	$\text{C}_6\text{H}_5\text{O}_3\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{CH}_3$
$\text{H}(\text{CF}_2)_2\text{CH}_2\text{O}_3\text{C}(\text{CF}_2)_2$ O $\text{H}(\text{CF}_2)_2\text{CH}_2\text{O}_2\text{C}-\text{CF}_2$	$\text{C}_6\text{H}_5\text{O}_3\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CO}_2\text{C}_6\text{H}_5$
	$\text{FO}_2\text{S}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{OCH}_3$
$\text{FO}_2\text{S}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{OCH}_2\text{CH}=\text{CH}_2$	$\text{FO}_2\text{S}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{OCH}_2\text{CO}_2\text{C}_2\text{H}_5$
$\text{C}_6\text{H}_5\text{COCF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	$\text{CCl}_2=\text{CFO}(\text{CF}_2)_2\text{SO}_2\text{F}$
$\text{p-CH}_3\text{OC}_6\text{H}_4\text{COCF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	$\text{p-CH}_3\text{C}_6\text{H}_4\text{COCF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$
	$\text{FO}_2\text{S}(\text{CF}_2)_2\text{OCF}_2\text{CClO}$

Reference 34

$\text{ICF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{I}(\text{CF}_2\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{I}(\text{CF}_2\text{CF}_2)_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{I}(\text{CF}_2\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{I}(\text{CF}_2\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{CF}_3(\text{CF}_2)_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{CF}_3(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{CF}_3(\text{CF}_2)_7\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$	$\text{CF}_3(\text{CF}_2)_9\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$
$\text{CF}_3(\text{CF}_2)_3\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$	$\text{CF}_3(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$
$\text{CF}_3(\text{CF}_2)_7\text{OCF}_2\text{CF}_2\text{SO}_3\text{K}$	$\text{CF}_3\text{CF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{NHC}_3\text{H}_7$
$\text{CF}_3(\text{CF}_2)_3\text{O}(\text{CF}_2)_2\text{SO}_2\text{NHC}_3\text{H}_7$	
$\text{CF}_2(\text{CF}_2)_3\text{O}(\text{CF}_2)_2\text{SO}_2\text{N}(\text{C}_3\text{H}_7)\text{C}_2\text{H}_5\text{OH}$	
$\text{CF}_2\text{CF}_2\text{O}(\text{CF}_2)\text{SO}_2\text{N}(\text{C}_3\text{H}_7)(\text{C}_2\text{H}_4)\text{OH}$	
$\text{CF}_3(\text{CF}_2)_3\text{O}(\text{CF}_2)_2\text{SO}_2\text{N}(\text{C}_3\text{H}_7)(\text{CH}_2)_4\text{H}$	
$\text{CF}_3\text{CF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{N}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2$	

TABLE IV
DERIVATIVES OF $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$
(continued)

Reference 39

Reference 40

TABLE V
FLUOROPOLYMERS CONTAINING SO₂F

<u>Compound/preparation/use</u>	<u>Reference</u>
C ₂ F ₄ + CF=CFOCF ₂ CF(CF ₃)OCF ₂ CF ₂ SO ₂ F and similar compounds including amine derivaives are used to form membranes for chlor-alkali cells.	42
CF ₂ =CFOCF ₂ CF(CF ₃)OCF ₂ CF ₂ SO ₂ F is copolymerized with tetrafluoroethylene and trifluoroethylene and hydrolyzed to give ion exchange materials.	43
CF ₂ =CFCF ₃ + SO ₃ (with BF ₃ or B ₂ O ₃)—————> CF ₂ -CFCF ₂ OSO ₂ F which rearranges to give $\begin{array}{c} \quad \\ \text{O} \text{---} \text{SO}_2 \end{array}$ FCOF(SO ₂ F)CF ₂ OSO ₂ F; CF ₂ =CFCF ₂ OSO ₂ F is copolymerized with CH ₂ =CF ₂ , CH ₂ =CHF and CF ₂ =CF ₂ . The polymers are useful in the preparation of ion exchangers and catalysts.	44
ClCF ₂ CClFOCF ₂ CF(CF ₃)OCF ₂ CF ₂ SO ₂ F, FSO ₂ CF ₂ CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)SO ₂ F and similar compounds are used as solvents for copolymers and membrane repair.	45
CF ₂ =CFCF ₂ OSO ₂ F + FSO ₂ CF ₂ COF (KF, diglyme, 25-28°C) —> CF ₂ =CFCF ₂ OCF ₂ CF ₂ CF ₂ SO ₂ F; this compound and similar ones are copolymerized	46

TABLE V
FLUOROPOLYMERS CONTAINING SO₂F
(continued)

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

CF ₂ XCFXO[CF ₂ CF(CF ₃)O] _n (CF ₂) _m Y where X = halogen; n = 0,1; m = 1,2,3; Y = CO ₂ Me, SO ₂ F; form compounds used in casting reverse osmosis membranes.	47
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(Nafion™ eq. wt. ~1200)SO ₃ H + HF + SF ₄ —→ (Nafion™ eq. wt. ~1200)SO ₂ F	48
--	----

Compounds like FSO ₂ CF ₂ OC(CF ₃)FOCF=CF ₂ are used as as intermediates for polymerization (CsF is a catalyst).	49
---	----

REACTIONS OF SULFONYL FLUORIDE SYSTEMS:
SULFENE, CARBENE AND CARBANION INTERMEDIATES

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 S_N2 or elimination/addition as are shown in this example:

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 S_N2 mechanism due to the stability of the SO₂F grouping. S_N2 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, $\text{CF}_3\text{C}(\text{O})\text{CF}(\text{SO}_2\text{F})\text{CF}_3$, by potassium fluoride in pyridine solution when the trifluoromethylfluorosulfene was detected in the form of the pyridine adduct; in air the complex is converted to $\text{CF}_3\text{CFHSO}_2\text{OH}\cdot\text{Py}$.⁵⁰ In the Wedekind-Staudinger reaction, the compound $\text{C}_3\text{F}_7\text{C}(\text{O})\text{CHFSO}_2\text{F}$ reacts to form the sulfene, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{CF}=\text{SO}_2$, and carbene, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{CF}:$, and give isomers of the episulfone 4,7-dioxoperfluoro-5-decene episulfone, $\text{C}_3\text{F}_7\text{C}(\text{O})\text{CF}-\text{CFC}(\text{O})\text{C}_3\text{F}_7$.⁵⁷

SO_2

The Chinese group at the Shanghai Institute of Organic Chemistry studied the reactions of difluoromethanesulfonyl fluoride, $\text{HCF}_2\text{SO}_2\text{F}$, and found that usually nucleophilic attack occurred at the sulfur atom of the SO_2F group. However, with reagents of stronger basicity, RO^- ($\text{R}=\text{H}$, C_2H_5 , $\text{HCF}_2\text{CF}_2\text{CH}_2$, C_6H_5 , 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 SO_2 and F^- producing compounds of the form ROCF_2H . In the latter scheme the carbene, $:\text{CF}_2$, acts as an intermediate. The formation of sulfonates does not involve a sulfene intermediate.⁵²

$\text{R} = \text{Et}, \text{Ph}, \text{HCF}_2\text{CF}_2\text{CH}_2$

Reaction with the α -hydro-containing fluorinated sulfonyl fluoride, $(\text{CF}_3)_2\text{CHSO}_2\text{F}$, and tertiary amines gives the carbanion complex, $[(\text{CF}_3)_2\text{CSO}_2\text{F}]^- \cdot [\text{HNR}_3]^+$ as determined by ^1H and ^{19}F 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, $(\text{CF}_3)_2\text{CHSO}_2\text{F}$, with nitriles and other esters were also studied.⁵³

TABLE VI
RATE CONSTANTS OF ALKALINE HYDROLYSIS K_c OF SULFONYL
FLUORIDES IN THE PRESCENCE OF POTASSIUM CHLORIDE
AT 25°C AND pH 10.0.

R-SO ₂ F	K_c
R	(l x mol ⁻¹ x s ⁻¹)
CF ₃ CFCl	3.3
C ₆ H ₅	8.2
CH ₂ =CH	18.3
H ₃ C	46.1
C ₆ H ₅ -CH ₂	912
F ₃ C-CHF	923

Source: Knunyants and Sokolskii, Angew. Chem. Int. Ed.¹⁷

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

Many of the sulfonyl fluoride containing olefins reported in Table III result from the stabilized carbanion intermediate:⁵⁵

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 $\text{SF}_5\overline{\text{CHCF}_2}\text{OSO}_2$, and ester formation; preparation of SO_2F containing polymer esters; and the preparation of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ and its ester derivatives. Compounds prepared and characterized are listed in Table VII.

Chapter V Related Reactions

Preparation of fluoroethers by reacting olefins, especially SF_5 -containing systems with trifluoromethyl hypochlorite $(\text{CF}_3\text{OCl})/\text{ClF}/\text{Cl}_2$ are reported. In some cases, new fluoroolefins are produced. New polymers containing the SF_5 group were prepared again utilizing fluoroolefins and reacting them with SF_5Br . Pertinent references for these

TABLE VII
NEW COMPOUNDS REPORTED

Chapter IV

$\text{SF}_5\overline{\text{CHCF}_2}\text{OSO}_2$	$[\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{1}{\text{CH}}\text{CH}_2-\text{I}]_n$
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$	$[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{1}{\text{CH}}\text{CH}_2-\text{I}]_n$
$\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$	$[\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{1}{\text{CH}}\text{CH}_2-\text{I}]_n$
$\text{SF}_5\text{CH}_2\text{SO}_3\text{Na/Ca}$	$\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$
$\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$	$\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_3$
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$	$\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$	$\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$
$[\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2]_2$	$\text{SF}_5\text{CH}=\text{CF}_2\cdot 2\text{SO}_3$

Chapter V

$\text{SF}_5\text{CHClCH}_2\text{OCF}_3$	$\text{SF}_5(\text{CH}_2\text{CHF})_{10}\text{Br}$
$\text{SF}_5\text{CFC}_1\text{CF}_2\text{OCF}_3$	$\text{SF}_5(\text{CH}_2\text{CF}_2)_8\text{Br}$
$\text{SF}_5\text{CHClCF}_3$	$\text{SF}_5(\text{CF}_2\text{CF}_2)_{16}\text{Br}_{0.3}$
$(\text{SF}_5\text{CCl}_2\text{CH}_2)_2$	$\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$ (adduct)
$\text{SF}_5\text{CHClCF}_2\text{Cl}$	
$\text{SF}_5\text{CCl}=\text{CH}_2$	

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 , $\text{BrCH}_2\text{CO}_2\text{C}_2\text{H}_5$, $\text{BrC}_2\text{H}_4\text{Br}$, $\text{BrCH}_2\text{CH}=\text{CH}_2$ (MCB); NaOH , $\text{Ca}(\text{OH})_2$, KOH (Baker); $(\text{CF}_3)_2\text{CHOH}$ (Eastman); HCl (Matheson); MgSO_4 , Ag_2O , CH_3OH , $(\text{C}_2\text{H}_5)_2\text{O}$ (Mallinckrodt); COF_2 , ClF (Pennwalt Chemicals); Cl_2 (Matheson); $\text{HOCH}_2\text{CH}_2\text{I}$, $\text{C}_3\text{H}_7\text{I}$, $(\text{CH}_3)_3\text{SiI}$ (Aldrich); CH_3I (Kodak); $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_2=\text{CF}_2$, $\text{CFH}=\text{CF}_2$, $\text{CH}_2=\text{CF}_2$, $\text{CHF}=\text{CH}_2$ and $\text{CH}_2=\text{CH}_2$ were obtained from SCM Specialty Chemicals. The above reagents were used without further purification. CF_3COCl , $\text{CF}_2(\text{SO}_2\text{F})\text{COOH}$, $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{CO}_2\text{CH}_2\text{CH}_2=\text{CH}_2$, $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$ were prepared according to literature methods^{56,57,58}. The olefins, $\text{SF}_5\text{CH}=\text{CH}_2$, $\text{SF}_5\text{CH}=\text{CF}_2$ and $\text{SF}_5\text{CF}=\text{CF}_2$, were prepared by the dehydrohalogenation of the appropriate fluoroalkyl

bromide^{59,60,61}. SF_5Br was prepared as previously reported⁶⁰ 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.

CHAPTER IV

SULFONYL FLUORIDE SYSTEMS

Compounds containing the SO_2F 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 sulfonyl fluoride compounds via several routes described earlier. We also include the preparation of SF_5 -containing monomeric and polymeric sulfonyl fluoride systems.

Included for comparison in the SF_5 sultone and derivatives discussion are esters prepared from the sultone $\text{SF}_5\text{CF}_2\text{OSO}_2$ by Javid Mohtasham.⁹⁴ The same is true for the silver salt and ester derivatives where several additional esters were prepared by Mr. Mohtasham.⁹⁵ The discussion section on the $-\text{SO}_2\text{F}-$ containing polymer esters includes data from the monomer esters. Preparation of the polymer esters was done in conjunction with Dr. Roger Sheets.⁹³

SF_5 SULTONE AND DERIVATIVES

The new pentafluorothio β -sultone, 2-hydroxyl-1-(pentafluoro- λ^6 -sulfanyl)-2,2-difluoroethanesulfonic acid sultone, $\text{SF}_5\text{CHCF}_2\text{OSO}_2$, was prepared via the reaction of

$\text{SF}_5\text{CH}=\text{CF}_2$ with monomeric sulfur trioxide in a Carius tube under autogeneous pressure at 100°C :

The $\text{SF}_5\text{CHCF}_2\text{OSO}_2$ product is a stable crystalline solid with a vapor pressure of 9 torr at 22°C ; it melts at $47-48^\circ\text{C}$. Interpretation of the ^1H and ^{19}F nmr for the interesting compound, $\text{SF}_5\text{CHCF}_2 \cdot 2\text{SO}_3$, was not accomplished. Elemental analysis confirmed the empirical formula. Possible structures include; $\text{SF}_5\text{CH} - \text{CF}_2$, the rearranged

product(s), or a mixture.

The SF_5 sultone undergoes rearrangement in the presence of NaX ($\text{X} = \text{I}, \text{F}$) giving the isomeric bifunctional fluoride, 2-(fluorosulfonyl)-2-(pentafluoro- λ^6 -sulfanyl) acetyl fluoride:

In the presence of water, $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ undergoes rearrangement, followed by a concerted hydrolysis decarboxylation reaction:

Attempts to isolate the acid intermediate prior to decomposition failed. The final SF_5 containing product,

$\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$, hydryl(pentafluoro- λ^6 -sulfanyl)methanesulfonyl fluoride is a stable, colorless liquid that boils at 110-111°C. Treatment of the SF_5 -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 SF_5 sulfonic acid:

The new SF_5 containing acid, hydryl(pentafluoro- λ^6 -sulfanyl)methanesulfonic acid monohydrate is isolated from solution and purified by sublimation; it is a white solid which melts at $97 \pm 1^\circ\text{C}$. The corresponding salt of this acid can be prepared by reacting the sultone or acid with an appropriate base:

In addition to preparing the SF_5 containing sultone, its rearranged product, and eventually a new SF_5 sulfonic acid, we have found that interaction of SF_5 containing sultones, $\text{SF}_5\overline{\text{CXCF}_2\text{OSO}_2}$ ($\text{X} = \text{F}, \text{H}$) with fluoroalcohols produces new SF_5 containing sulfonyl fluoride esters:

With a fluorinated bis alcohol, the following diester is produced:

The new SF₅ 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}

Figure 3. Mechanism for Ester Preparation.

The resulting acid fluoride reacts with alcohols, in the presence of NaF, forming the corresponding ester and NaHF₂. These routes to the stable ester products are strongly

supported by the following isomerization of β -sultones with different nucleophiles to the acyclic isomer:^{6,17,19,20,21}

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 $\text{SF}_5\text{CX}(\text{SO}_2\text{F})\text{C}(\text{O})\text{F}$, ($\text{X} = \text{H}, \text{F}$).

The infrared spectra for all new compounds have in common the characteristic absorption bands of the SF_5 -group. Cross and coworkers⁶² reported that the most intense band for compounds containing the SF_5 grouping should appear in the region $850\text{--}920 \text{ cm}^{-1}$ (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 SF_5 esters having absorptions in the higher part of this range. The SF_5 deformation modes are located in the $597\text{--}620 \text{ cm}^{-1}$ range.

For compounds containing C-F and CF_3 groups, the C-F stretching vibration is usually located in the $1000\text{--}1100 \text{ cm}^{-1}$ region⁶³ while marked absorption in the range $1360\text{--}1300 \text{ cm}^{-1}$ can be correlated with the CF_3 group⁶³. In the compound, $\text{SF}_5\text{CFHCF}_3$, the C-F stretching vibration was assigned

to the 1161 cm^{-1} absorption band⁶⁴. For the new esters, the stretching vibration for the CF group appears to be located in the $1100\text{--}1200\text{ cm}^{-1}$ region while the CF_3 group is located in the $1230\text{--}1390\text{ cm}^{-1}$ region. The CF_3 deformation band is located in the $737\text{--}760\text{ cm}^{-1}$ region.⁶³

Compounds containing the $\text{-SO}_2\text{-}$ functional group exhibit a strong asymmetric stretching band in the $1419\text{--}1469\text{ cm}^{-1}$ region and a strong symmetric stretching band in the $1200\text{--}1259\text{ cm}^{-1}$ range. This assignment is complicated in some cases by the appearance of strong carbon-fluorine absorption bands in the $1110\text{--}1300\text{ cm}^{-1}$ region but, in any case, the above assignment agrees closely with the found for $\text{CF}_3\text{SO}_2\text{F}$ and other fluorosulfonyl derivatives.⁶⁵ 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.⁶⁶ This band disappears when the acid/salts are formed from $\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$. The asymmetric and symmetric stretching SO_3 bands for the sulfonic acid monohydrate, $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, and calcium salt are found in the $1223\text{--}1244\text{ cm}^{-1}$ and $1033\text{--}1064\text{ cm}^{-1}$ region, respectively; for salts containing the $\text{CF}_3\text{SO}_3\text{-}$ group the respective regions are $1266\text{--}1279$ and $1025\text{--}1042\text{ cm}^{-1}$.⁶⁵ The carbonyl stretching frequency is characteristically found in the $1790\text{--}1834\text{ cm}^{-1}$ range for esters prepared from $\text{SF}_5\overline{\text{CFCF}_2}\text{OSO}_2$ and in the $1750\text{--}1820\text{ cm}^{-1}$ range for the esters prepared from $\text{SF}_5\overline{\text{CHCF}_2}\text{OSO}_2$; 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 $\text{SF}_5\text{CFHCF}_3$ the C-H stretching frequency was found at 3007 cm^{-1}).⁶⁴ The acid, $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, 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 $(\text{M-X})^+$ peaks such as $(\text{M-F})^+$, $(\text{M-HF})^+$, $(\text{M-H}_2\text{O})^+$; for the sultone I the $(\text{M-H})^-$ peak was found. Prominent peaks (m/e) at 89 (SF_3^+) and 127 (SF_5^+) were observed for all compounds and 89 (CF_3^+) occurred in all esters except $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_2]_2\text{CF}_2$. Appropriate fragments were found for cleavages at the $-\text{C}(\text{O})\text{O}-$ 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 SF_5 fluorine resonances consist of the AB_4 multiplet with B_4 equatorial fluorines split into a doublet and the A part into a nine-line pattern. In compounds I, III, VI and VII the AB_4 pattern is overlapping, therefore the chemical shifts and/or coupling constants could only be approximated. The AB_4 pattern in $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}$ 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 SF₅CFCF₂OSO₂. The acid SF₅CFHSO₃H gives SF_(ax) at δ 72.3 ppm and SF_{4(eq)} at δ 53.5 ppm,¹⁹ while compound V gives SF_(ax) at δ 81.4 ppm and SF_{4(eq)} at δ 68.1 ppm. The axial and equatorial fluorine chemical shifts of the SF₅ group in SF₅CH₂CHFBr are δ 79.9 ppm and 66.4 ppm, respectively.⁶⁰ For the compound, SF₅CHCF₂•2SO₃, the expected AB₄ pattern is not observed for the SF₅ group; instead a complex series of multiplets extending from δ 94.6 to δ 49.2 ppm is found.

The ¹⁹F nmr resonance for the fluorosulfonyl group is found in the range δ 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 ¹H 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 SF_5 group results in greater shielding (shift to high field) for all fluorogroups present; for example, in going from $\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$ to $\text{SF}_5\text{CHF}\text{SO}_2\text{F}$ the $\text{SF}_{(\text{ax})}$, $\text{SF}_{4(\text{eq})}$, and SO_2F groups are more shielded by 6, 16 and 7 ppm, respectively. Also, in going from $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{R}$ to $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{R}$ where $\text{R} = \text{C}(\text{O})\text{F}$, $\text{C}(\text{O})\text{OR}'$ greater shielding for the $\text{SF}_{(\text{ax})}$, $\text{SF}_{4(\text{eq})}$, SO_2F and $\text{C}(\text{O})\text{F}$ 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 SF_5 , SO_2F , $\text{C}(\text{O})\text{F}$ and $\text{C}(\text{O})\text{OR}$ groups are present.

Coupling constants for the $\text{SF}_{(\text{ax})}$ to $\text{SF}_{4(\text{eq})}$ fluorines in the new compounds vary from approximately 100 Hz to 149 Hz. The coupling constants for $J_{1,2}$ could not be determined for compound III. It is interesting to note that the lower values for $J_{1,2}$ occur in compounds derived from sultone I, and go as low as 100 Hz in ester IV. The sultone, $\text{SF}_5\text{CF}(\text{CF}_2\text{OSO}_2)$, and its derivatives have an AB_4 coupling in the range $J = 141$ to 157 Hz; one exception is found for $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COF}$ with $J_{1,2} = 100.1$ Hz.¹⁹ Esters derived from this sultone and reported here have coupling constants $J_{1,2}$

in the 136-141 Hz range; by comparison, the ester $\text{SF}_5\text{CF}(\text{CF}_3)\text{COOCH}_3$ has a $J_{1,2} = 144$ Hz.⁶⁰ The compounds containing the sulfonyl fluoride-grouping vicinal to the $\text{SF}_4(\text{ax})$ 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 β -sultone I is approximately the same as in $\text{SF}_5\overline{\text{CFCF}_2}\text{OSO}_2$ 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 SF_5CH moiety. Due to the complexity of the spectrum, no coupling constants could be determined for compound III.

The ^{13}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 SF_5 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 $\text{c-C}_4\text{F}_8$ and $\text{c-C}_4\text{F}_4\text{Cl}_4$ the J_{CF} values are 298 and 300 Hz, respectively.¹⁷ The large J_{CF} coupling ($J_{B,5}$) value

of 363.5 Hz for II is in good agreement with other acyl fluorides.⁷⁰

TABLE VIII

^{19}F AND ^1H NMR CHEMICAL SHIFTS FOR $\text{SF}_5\text{CHCF}_2\text{OSO}_2$,
DERIVATIVES AND ESTERS OF $\text{SF}_5\text{CFCF}_2\text{OSO}_2^{\text{a, c}}$

Compound	SF (ax)	SF ₄ (eq)	CF ₃	CF ₂
$\text{SF}_5\text{CHCF}_2\text{OSO}_2$ (I) in F-11	69.4 (m)		-	-72.8 (d) -79.7 (d)
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}$ (II) ^b	66 (9-1n)	72.2 (d)	-	-
$\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$ (III)	71.4 (m)		-	-
$(\text{SF}_5\text{CH}_2\text{SO}_3)_2\text{Ca}$ (IV)	76.7 (9-1n)	64.3 (d)	-	-
$\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (V) ^f in CD ₃ CN	81.4 (9-1n)	68.1 (d)	-	-
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COOCH}_2\text{CF}_3$ (VI)	70.0 (m)		-76.4 (t)	-
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COOCH}(\text{CF}_3)_2$ (VII)	70.5 (m)		-75.4 (d)	-
$\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COOCH}_2\text{CF}_3$ (VIII)	62.3 (9-1n)	56.5 (d)	-76.2 (t)	-
$\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COOCH}(\text{CF}_3)_2$ (IX)	61.5 (9-1n)	57.2 (d)	-75.2 (d)	-
$[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COO}-\text{CH}_2\text{CF}_2]_2\text{CF}_2$ (X)	62.6 (9-1n)	56.7 (d)	-	-121.3 (br.t) -127 (br.s)

TABLE VIII

^{19}F AND ^1H NMR CHEMICAL SHIFTS FOR $\text{SF}_5\text{CHCF}_2\text{OSO}_2$,
DERIVATIVES AND ESTERS OF $\text{SF}_5\text{CF}_2\text{OSO}_2^{\text{a, c}}$
(continued)

Compound	CF	SO ₂ F	CH	CH ₂
$\text{SF}_5\text{CHCF}_2\text{OSO}_2$ (I) in F-11	-	-	6.58 (m)	-
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}$ (II) ^b	-	58.4	6.18 (d,p)	-
$\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$ (III)	-	58.5 (m) ^d	-	5.33 (m)
$(\text{SF}_5\text{CH}_2\text{SO}_3)_2\text{Ca}$ (IV)	-	-	-	5.0 (p)
$\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (V) ^f in CD_3CN	-	-	-	5.13 (p) ^e
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COOCH}_2\text{CF}_3$ (VI)	-	57.0 (p)	6.23 (d,p)	4.83 (brq)
$\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COOCH}(\text{CF}_3)_2$ (VII)	-	58.5 (p)	6.20 (p) 6.07 (sept)	-
$\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COOCH}_2\text{CF}_3$ (VIII)	-123.5 (d,p)	48.9 (p)	-	4.97 (q)
$\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COOCH}(\text{CF}_3)_2$ (IX)	-119.0 (d,p)	49.6 (p)	6.25 (sept.)	-
$[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COO}-\text{CH}_2\text{CF}_2]_2\text{CF}_2$ (X)	-123.4 (br.p)	49.1 (p)	-	5.22 (br.t)

- a. Fluorine chemical shifts in ppm from CFCI_3 and proton chemical shifts in ppm downfield from TMS.
- b. Chemical shift for the COF fluorine is $\emptyset$ 46.5 ppm (m); it is found at $\emptyset$ 30.4 ppm in $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{COF}$.¹⁹
- c. s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept. = septet, 9-ln = nine-line, br. = broadened, m = multiplet.
- d. For $\text{SF}_5\text{CHFSO}_2\text{F}$ and $\text{CF}_3\text{CH}_2\text{SO}_2\text{F}$ the chemical shifts are: $\emptyset$ +51.3 and +64.75 ppm, respectively.^{6, 69}
- e. ^1H chemical shifts for $\text{SF}_5\text{CHFSO}_2\text{F}$ and $\text{CF}_3\text{CH}_2\text{SO}_2\text{F}$ are 6.31 and 4.10 ppm, respectively.^{6, 69}
- f. The chemical shift value for the proton on $-\text{SO}_3\text{H}$ is 10.22 ppm.

TABLE IX

^{19}F AND ^1H NMR COUPLING CONSTANTS FOR $\text{SF}_5\text{CHCF}_2\text{OSO}_2$,
DERIVATIVES AND ESTERS OF $\text{SF}_5\text{CFCF}_2\text{OSO}_2^{\text{a,c}}$

<u>Compound</u>	<u>Coupling Constants, Hz</u>
$\begin{array}{c} \text{H (3)} \quad \text{F (4)} \\ \quad \\ \text{F (1) - SF}_4 \text{ (2) - C} - \text{C} - \text{F (5)} \quad \text{(I)} \\ \quad \\ \text{O}_2\text{S} - \text{O} \end{array}$	$J_{1,2} \sim 130 \quad J_{2,3} = 4.6$ $J_{4,5} = 103$
$\begin{array}{c} \text{H (3)} \quad \text{O} \\ \quad \\ \text{F (1) - SF}_4 \text{ (2) - C} - \text{C} - \text{F (5)} \quad \text{(II)} \\ \quad \\ \text{SO}_2\text{F (4)} \end{array}$	$J_{1,2} = 148.9 \quad J_{3,5} = 4.9$ $J_{2,3} = 3.0$ $J_{2,4} = 12.0 \quad J_{4,5} = 12.0$ $J_{2,5} = 8.7$
$\text{SF}_4 \text{ (2) CH}_2 \text{ (3) SO}_2\text{F (4)} \quad \text{(III)}$	—
$(\text{F (1) SF}_4 \text{ (2) CH}_2 \text{ (3) SO}_3)_2\text{Ca} \quad \text{(IV)}$	$J_{1,2} = 141.1$ $J_{2,3} = 7.5$
$\text{F (1) SF}_4 \text{ (2) CH}_2 \text{ (3) SO}_3\text{H} \cdot \text{H}_2\text{O} \quad \text{(V)}$	$J_{1,2} = 141.1 \quad J_{2,3} = 7.5$
$\begin{array}{c} \text{H (3)} \quad \text{O} \\ \quad \\ \text{F (1) SF}_4 \text{ (2) C} - \text{C} - \text{OCH}_2 \text{ (5) CF}_3 \text{ (6)} \quad \text{(VI)} \\ \quad \\ \text{SO}_2\text{F (4)} \end{array}$	$J_{1,2} \sim 100 \quad J_{2,4} = 12.8$ $J_{1,3} = 2.25 \quad J_{5,6} = 5.4$ $J_{2,3} = 4.5$
$\begin{array}{c} \text{H (3)} \quad \text{O} \\ \quad \\ \text{F (1) SF}_4 \text{ (2) C} - \text{C} - \text{OCH (5) (CF}_3)_2 \text{ (6)} \quad \text{(VII)} \\ \quad \\ \text{SO}_2\text{F (4)} \end{array}$	$J_{1,2} \sim 122 \quad J_{2,4} = 11.8$ $J_{2,3} = 4.5 \quad J_{5,6} = 7.4$

TABLE IX

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

<u>Compound</u>	<u>Coupling Constants, Hz</u>
$\begin{array}{c} \text{F (3) O} \\ \quad \\ \text{F (1) SF}_4 \text{ (2) C} - \text{C-OCH}_2 \text{ (5) CF}_3 \text{ (6)} \quad \text{(VIII)} \\ \\ \text{SO}_2\text{F (4)} \end{array}$	$\begin{array}{ll} J_{1,2} = 141 & J_{2,4} = 9.4 \\ J_{1,3} = 4.5 & J_{5,6} = 7.4 \\ J_{2,3} = 3.0 & \end{array}$
$\begin{array}{c} \text{F (3) O} \\ \quad \\ \text{F (1) SF}_4 \text{ (2) C} - \text{C-OCH (5) (CF}_3)_2 \text{ (6)} \quad \text{(XI)} \\ \\ \text{SO}_2\text{F (4)} \end{array}$	$\begin{array}{ll} J_{1,2} = 136 & J_{2,4} = 10.1 \\ J_{1,2} = 3.0 & J_{5,6} = 5.6 \\ J_{2,3} = 3.0 & \end{array}$
$\begin{array}{c} \text{F (3) O} \\ \quad \\ [\text{F (1) SF}_4 \text{ (2) C} - \text{C-OCH}_2 \text{ (5) CF}_2 \text{ (6)}] \text{CF}_2 \text{ (7)} \\ \\ \text{SO}_2\text{F (4)} \quad \quad \quad \text{(X)} \end{array}$	$\begin{array}{ll} J_{1,2} = 136 & J_{2,4} = 9.2 \\ J_{1,3} = 3.0 & J_{5,6} = 12 \\ J_{2,3} = 3.0 & \end{array}$

TABLE X

 ^{13}C NMR SPECTRA FOR $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ AND SOME DERIVATIVES*

Compound	Chemical Shifts and Coupling Constants	
$\begin{array}{c} \text{A} \quad \text{B} \\ \text{F (1) SF}_4 \text{ (2) CH (3) - CF}_2 \text{ (4)} \\ \quad \\ \text{O}_2\text{S} \text{ --- } \text{O} \end{array}$	$\delta_{\text{A}} = 99.6$	$\delta_{\text{B}} = 112 \text{ (br.p)}$
	$J_{\text{A},2} = 23$	$J_{\text{B},2} = 3.8$ $J_{\text{B},4} = 293$
$\begin{array}{c} \text{A} \quad \text{B} \\ \text{F (1) SF}_4 \text{ (2) CH (3) COF} \\ \\ \text{SO}_2\text{F} \end{array}$	$\delta_{\text{A}} = 88.5$	$\delta_{\text{B}} = 146.8 \text{ (d,p)}$
	$J_{\text{A},2} = 21.6$	$J_{\text{B},2} = 2.9$ $J_{\text{B},5} = 363.5$
$\begin{array}{c} \text{A} \\ \text{F (1) SF}_4 \text{ (2) CH}_2 \text{ (3) SO}_2\text{F} \end{array}$	$\delta_{\text{A}} = 77.6 \text{ (m)}$	
$\begin{array}{c} \text{A} \\ \text{F (1) SF}_4 \text{ (2) CH}_2 \text{ (3) SO}_3\text{H} \cdot \text{H}_2\text{O} \end{array}$	$\delta_{\text{A}} = 82.8 \text{ (br.s)}$	

* Solvent CDCl_3 , 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, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$, $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$, $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$ and $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ react with allyl alcohol according to the following equation:²¹

The new fluorosulfonyl allyl esters are stable water clear liquids.

While a number of non-fluorinated and fluorinated polyesters exist^{71,72}, 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 CFC₁₃:

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.^{73,74} 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 SO_2 group agrees closely with that found for $\text{CF}_3\text{SO}_2\text{F}$ and other fluorosulfuryl derivatives.^{4,19,20} For the fluoro-sulfonyl 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.⁶⁶ 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 coworkers⁶² 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 ^1H 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 $-\text{CH}_2\text{CH}=\text{CH}_2$ moiety are in agreement with values reported for allyl alcohol and $\text{FO}_2\text{S}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{OCH}_2\text{CH}=\text{CH}_2$.^{38, 75} The CH proton chemical shift in $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OC}_3\text{H}_5$ was located at δ 6.24 ppm; in $\text{SF}_5\text{CFHSO}_2\text{F}$ the corresponding shift was reported at δ 6.31 ppm.¹⁹ The proton chemical shifts for polymeric materials

obtained with ultraviolet irradiation showed, in general, broad peaks for the CH and CH₂ 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 ¹⁹F nmr spectral data are reported in Table XIII. The ¹⁹F nmr spectra for the SF₅ group of SF₅CF(SO₂F)C(O)OC₃H₅ consisted of the expected AB₄ pattern with the B₄ equatorial fluorines split into a complex doublet and the axial fluorine, A, into a nine-line pattern. The chemical shifts for the AB₄ pattern in SF₅CF(SO₂F)C(O)OC₃H₅ were located at δ 64.3(A) and δ 56.3(B) ppm. In SF₅CH(SO₂F)-C(O)OC₃H₅, the expected AB₄ pattern is not observed but instead a complex multiplet centered at δ 70.7 ppm is found. The CF chemical shift in SF₅CF(SO₂F)C(O)OC₃H₅ was found at δ -121.9 ppm; in SF₅CF(SO₂F)COF the corresponding chemical shift was reported as δ -122 ppm.¹⁹ The ¹⁹F nmr spectrum of the allyl ester, prepared from $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$, contained the CF₂ resonance at δ -104.9 ppm which is the region expected for a CF₂ group; for example, in FSO₂CF₂C(O)OCH₂CF₃ the CF₂ resonance was found at δ -106.4 ppm.²² In all allyl esters, the resonance bands for the FSO₂ are located in the region δ 39.9-58.5 ppm; in a number of sulfonyl fluoride derivatives CF₃CFHSO₂F, SF₅CFHSO₂F, FSO₂CF₂C(O)OCH₂CF₃ the corresponding resonance band was located in the δ 40-52 ppm range.^{19,21,76}

TABLE XI
PROPERTIES OF FLUOROSULFONYL FLUOROESTERS

<u>Compound</u>	<u>Decomp. (°C)</u>	<u>Solubility</u>		
		H ₂ O	Acetone	CFCl ₃
$(\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{ }{\text{CH}}\text{CH}_2-)_n$	164	ins.	sl. sol.	ins.
$(\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{ }{\text{CH}}\text{CH}_2-)_n$	150	ins.	sol.	ins.
$(\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{ }{\text{CH}}\text{CH}_2-)_n$	170	ins.	sol.	ins.

Note: Viscous polymers prepared from allyl esters were soluble in acetone and CFCl₃.

TABLE XII

¹H NMR DATA FOR MONOMER AND CORRESPONDING POLYMER ESTERS

R _f (monomers)**	Chemical Shifts (ppm)				Coupling Constants (Hz)			
	H _d	H _c	H _b	H _a	J _{a,b}	J _{a,c}	J _{b,c}	J _{c,d}
SF ₅ CF(SO ₂ F)CO ₂	5.07	6.12	5.82	5.58	5.1	9.9	17.1	5.7
SF ₅ CH'(SO ₂ F)CO ₂ *	4.90	6.04	5.72	5.54	4.5	10.5	18.0	5.7
CF ₃ CF(SO ₂ F)CO ₂	4.95	5.96	5.66	5.42	4.8	10.5	17.1	5.4
R _f (polymers)**								
SF ₅ CF(SO ₂ F)CO ₂	4.8	— 1.0 - 3.5 —			(no coupling constants were			
SF ₅ CH'(SO ₂ F)CO ₂ *	4.4	— 1.2 - 3.3 —			determined for the polymers)			
CF ₃ CF(SO ₂ F)CO ₂	4.8	— 1.2 - 3.8 —						

* The CH' proton occurs at δ 6.24 ppm (multiplet, J_{SF₄CH} = 10.2 Hz), in the polymer the CH' proton occurs at δ 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* $\text{RfCH}_2\text{CH}=\text{CH}_2$

<u>Rf (monomers)</u>	<u>Chemical Shifts (ppm)</u>				<u>Coupling Constants (Hz)</u>
	a	b	c	d	
F (a) SF_4 (b) CF (c) (SO_2F (d)) CO_2	64.3 (9-line)	56.3 (d)	-121.9 (s)	48.6 (p)	$J_{a,b} = 141$, $J_{a,c} = 3.1$, $J_{b,c} = 3.1$, $J_{c,d} < 1$, $J_{b,d} = 11.6$
F (a) SF_4 (b) CH (c) (SO_2F (d)) CO_2 #		70.7 (m)	-	58.5 (m)	$J_{b,c} = 4.5$, $J_{b,d} = 11.6$
CF ₃ (a) CF (b) (SO_2F (c)) CO_2	-74.3 (d,d)	-161.8 (q,d)	50.1 (q,d)	-	$J_{a,b} = 8.3$, $J_{a,c} = 9.6$, $J_{b,c} = 4.2$
<u>Rf (polymers, no coupling constants were obtained)</u>					
F (a) SF_4 (b) CF (c) (SO_2F (d)) CO_2	65.2 (br.m)	57.4 (br.d)	-121.5 (br.s)	48.8 (br.s)	
F (a) SF_4 (b) CH (c) (SO_2F (d)) CO_2 #		71.3 (m)	-	58.5 (m)	
CF ₃ (a) CF (b) (SO_2F (c)) CO_2	-73.5 (br.s)	-161.4 (br.s)	50.5 (br.s)	-	

* 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 AB₄ (FSF_4) coupling.

SILVER SALT AND ESTER DERIVATIVES

We have found that difluoro(fluorosulfonyl)acetic acid, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OH}$, reacts with silver oxide in diethyl ether according to the following equation:

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 alkyl iodides/bromides to provide a route for preparing new sulfonyl fluoride esters:

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

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:

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 $\text{HOCH}_2\text{CH}_2\text{I}$ with $\text{FSO}_2\text{CF}_2\text{CO}_2\text{Ag}$ is given in Figure 4.

Figure 4. Mechanism for the reaction of $\text{FSO}_2\text{CF}_2\text{CO}(\text{O})\text{Ag}$ with $\text{HOCH}_2\text{CH}_2\text{I}$

In equation (24), the carboxylate ion displaces I^- from $\text{HOCH}_2\text{CH}_2\text{I}$ to form the monosubstituted alcohol intermediate. Then, in equation (25) equilibrium is established between the intermediate alcohol and the alkoxide anion, $\text{}^-\text{OCH}_2\text{CH}_2\text{O}-\text{C}(\text{O})\text{CF}_2\text{SO}_2\text{F}$, 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 CF_2 is found in the 1785-1813

cm^{-1} region; for the carbonyl group next to CH_2 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, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$, the carbonyl stretching frequency is found at 1708 cm^{-1} ; in AgCF_3COO , the carbonyl stretching frequency is located at 1720 cm^{-1} .⁷⁷

In all esters, as well as the silver salt, the asymmetric and symmetric SO_2 stretching frequencies are assigned to the $1448\text{--}1462 \text{ cm}^{-1}$ region and the $1223\text{--}1243 \text{ cm}^{-1}$ region, respectively. These values correspond to the SO_2 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 $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$; however, MH^+ ions were found for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OC}_2\text{H}_5$, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$, $[\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2]_2$ and $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_3$. In all cases appropriate fragmentation peaks are found indicating cleavage at the ester linkage. Bromine isotopes were detected in the compound $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OC}_2\text{H}_4\text{Br}$.

The ^{19}F nmr spectra for all new esters and the silver salt, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$, exhibit common features and are given

on Table XIV. The chemical shifts for FSO_2 group (triplet) range from δ 37.9 to δ 40.4 ppm while for the CF_2 group (doublet) occur at δ -97.2 to δ -109.0 ppm. The chemical shifts are consistent with those of other reported esters prepared from the sultone, $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$.^{20,21,58} For the new esters the coupling constants, $J_{\text{CF}_2, \text{SO}_2\text{F}}$ range in value from $J = 5.3$ to 5.64 Hz; except for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$ and the salt, $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ 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 $\text{HOCH}_2\text{CH}_2\text{I}$ and CH_2I_2 a singlet at δ 5.03 and δ 6.53 ppm, respectively, were found. The spectrum of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{Br}$ contains triplets at δ 3.98 ppm (CH_2Br) and δ 5.13 ppm (OCH_2); the $J_{\text{CH}_2\text{CH}_2} = 6.0$ Hz.

$^{19}\text{F}/^1\text{H}$ nmr data for the ester prepared from $\text{BrCH}_2\text{CH}=\text{CH}_2$ agreed with the literature values.⁷⁸ While the ester prepared from CH_3I has been previously synthesized,²⁰ 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 $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2(\text{d})\text{CH}(\text{c})=\text{CH}(\text{a})\text{H}(\text{b})$, was obtained at 300 MHz. It was possible to resolve all possible couplings in the allyl group; new coupling constants found were $J_{\text{b,d}} = 1.2$ Hz and $J_{\text{a,d}} = 1.2$ Hz. the values of $J_{\text{a,c}}$,

TABLE XIV

 ^{19}F NMR OF $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ AND DERIVATIVES*

<u>R [FSO₂CF₂C(O)O-R]</u>	<u>SO₂F (ppm)</u>	<u>CF₂ (ppm)</u>	<u>J (Hz)</u>
Ag (I)	38.0	-100.9	3.5
CH ₂ C(O)OC ₂ H ₅ (II)	40.5	-105.5	5.4
CH ₂ CH ₂ Br (III)	38.3	-109.0	5.5
CH ₂ CH ₂ CH ₃ (IV)	39.7	-105.4	5.3
Si(CH ₃) ₃ (V)	37.8	-97.2	4.6
CH ₃ (VI)	39.1	-105.5	5.7
CH ₂ CH=CH ₂ (VII)	39.9	-104.9	5.3
<u>R [(FSO₂CF₂C(O)O)₂-R]</u>			
CH ₂ (VIII)	39.2	-105.6	5.5
CH ₂ CH ₂ (IX)	40.4	-105.0	5.6

* Chemical shifts reported in ppm relative to CFCl_3 . All SO_2F peaks are triplets, and CF_2 peaks are doublets.

$J_{b,c'}$ and $J_{c,d}$ were in good agreement with the literature;⁸⁰ the $J_{a,b}$ value found was 1.2 Hz. The earlier reports^{79,81}, found for a series of allyl esters the $J_{a,b}$ 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

¹H NMR OF FSO₂CF₂C(O)OAg AND DERIVATIVES*

<u>R (FSO₂CF₂C(O)O-R)</u>	<u>CH₂' (ppm)</u>	<u>CH₂ (ppm)</u>	<u>CH₃ (ppm)</u>
CH ₂ 'C(O)OCH ₂ CH ₃ (II)	5.12 (s) J _{CH₂,CH₃} = 7.2 Hz	4.40 (q)	1.40 (q)
CH ₂ 'CH ₂ Br (III)	5.13 (s) J = 6.0 Hz	3.98 (t)	
CH ₂ 'CH ₂ CH ₃ (IV)	4.19 (t) J _{CH₂,CH₃} = 7.2 Hz, J _{CH₂',CH₂} = 6.6 Hz	1.50 (6-ln)	0.68 (t)
Si(CH ₃) ₃ (V)			0.40 (s)
CH ₃ (VI)			4.17 (s)
CH ₂ 'CH=CH ₂ ** (VII)			
<u>R { [FSO₂CF₂C(O)O]₂-R }</u>			
CH ₂ (VIII)		5.03 (s)	
CH ₂ CH ₂ (IX)		6.53 (s)	

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

**	$ \begin{array}{ccc} \text{H(c)} & & \text{H(a)} \\ & \diagdown & / \\ & \text{C} = \text{C} & \\ & / & \diagdown \\ \text{CH}_2\text{(d)} & & \text{H(b)} \end{array} $	Chemical Shifts (ppm)
		$ \begin{array}{cccc} \underline{\text{H}_d} & \underline{\text{H}_c} & \underline{\text{H}_b} & \underline{\text{H}_a} \\ 4.95 & 6.02 & 5.72 & 5.43 \end{array} $

Coupling Constants (Hz)

$$\begin{aligned}
 J_{a,b} &= 1.2, J_{a,c} = 10.8, J_{a,d} = 1.2, J_{b,c} = 17.2, \\
 J_{b,d} &= 1.2, J_{c,d} = 6.0
 \end{aligned}$$

EXPERIMENTAL

SF₅CH=CF₂ with SO₃

Into a 130mL Pyrex glass Carius tube equipped with a Kontes Teflon valve 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 Ø gave the following relative peak areas: SF₅ (4.94), CF₂ (1+1). The negative ion (CI⁻) 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 SO_3 was reacted with 25.5 mmol of $\text{SF}_5\text{CH}=\text{CF}_2$ to give 13.8 mmol of $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ (54% yield) and 9.68 mmol of $\text{SF}_5\text{CHCF}_2 \cdot 2\text{SO}_3$ (19.5% yield).

The infrared spectrum of $\text{SF}_5\text{CHCF}_2 \cdot 2\text{SO}_3$ 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(w), 434(vw), 422(vw).

The ^{19}F nmr of $\text{SF}_5\text{CHCF}_2 \cdot 2\text{SO}_3$ gave the following chemical shifts: δ 94.6 ppm (multiplet), δ 76.2 ppm (triplet of multiplets), δ 65.0 ppm (multiplet), δ 49.2 ppm (multiplet), and a series of multiplets at δ -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 $\text{C}_2\text{HF}_7\text{S}_3\text{O}_6$: 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.

$\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$ 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 $\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$. 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(ms), 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 ^{19}F nmr spectrum gave the following relative band areas: SF (1.1); SF₄ (4.8); SO₂F (1.1); COF (1.0).

SF₅CHCF₂OSO₂ with H₂O

Into a 40 mL Kel-F vessel equipped with a Teflon stirring bar was added 17.74 mmol of SF₅CHCF₂OSO₂. 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_2F (1.0). EI^+ mass spectrum (m/e , species, %): 204, $(\text{M}-\text{F})^+$, 2.23; 129, $\text{FSCH}_2\text{SO}_2^+$, 6.92; 127, SF_5^+ or FSCSO_2^+ , 100; 97, $\text{CH}_2\text{SO}_2\text{F}^+$ or FSCH_2S^+ , 25.71; 89, SF_3^+ , 42.59; 78, CHSO_2^+ or SCF_2S^+ , 8.25; 67, SOF^+ , 53.44.

Anal. Calcd. for $\text{CH}_2\text{F}_6\text{O}_2\text{S}_2$: 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.

$\text{SF}_5\text{CH}_2\text{SO}_2\text{F}/\text{SF}_5\text{CH}_2\text{SO}_3\text{Na}$ 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_2O and 78.5 mmol of NaOH . To this solution, cooled to 0°C , 27.8 mmol of $\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$ 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, $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, was purified by sublimation; 6 mmol of $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$; yield 22%, m.p. $97\pm 1^\circ\text{C}$.

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), 624(wm), 589(ms), 564(wm), 528 (m,sh. at 517), 438(vw).

The ^{19}F nmr spectrum ($\emptyset$) gave the following relative peak areas: SF (1.0) and SF_4 (3.8). EI^+ mass spectrum (m/e, species, %): 223, $(\text{M}+\text{H}-\text{H}_2\text{O})^+$, 0.73; 202, $\text{SF}_4\text{CH}_2\text{SO}_3^+$, 32.05; 149, $\text{SF}_2\text{CH}_2\text{SO}_2\text{H}^+$, 8.06; 127, SF_5^+ or FSCSO_2^+ , 25.46; 122, SF_4CH^+ , 71.88; 97 SCH_3S^+ , 12.27; 95, $\text{CH}_2\text{SO}_3\text{H}^+$, 36.24; 89, SF_3^+ , 100; 81, SO_3H^+ , 15.57; 80, SO_3^+ , 4.77; 70, SF_2^+ , 9.48; 67, SOF^+ , 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 $\text{CH}_5\text{F}_5\text{O}_4\text{S}$: 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.

$\text{SF}_5\text{CHCF}_2\text{OSO}_2$ with CaO

To a Pyrex-glass round bottom flask was added 11.6 mmol $\text{SF}_5\text{CHCF}_2\text{OSO}_2$, 26.8 mmol CaO and 14.7 g H_2O . The mixture was heated at $50\pm 5^\circ\text{C}$ 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 $\text{Ca}(\text{SF}_5\text{CH}_2\text{SO}_3)_2$ 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}F nmr spectrum gave the following relative peak areas: SF (1.0) and SF_4 (4.0).

$\text{SF}_5\text{CHCF}_2\text{OSO}_2$ with $\text{CF}_3\text{CH}_2\text{OH}$

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 $\text{SF}_5\text{CHCF}_2\text{OSO}_2$ and 20.6 mmol $\text{CF}_3\text{CH}_2\text{OH}$. The mixture was heated with stirring at 60°C for four days. Distillation under vacuum gave 13.38 mmol of $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ in 70% yield; b.p. $103^\circ\text{C}/100\text{ mm}$.

The infrared spectrum of $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ 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}F nmr spectrum ($\emptyset$) gave the following relative peak areas: SF_5 (5.3), SO_2F (1.0) and CF_3 (3.0); the ^1H nmr spectrum (δ) gave: CH (1.0) and CH_2 (2.2). EI^+ mass spectrum (m/e , species, %): 331, $(\text{M}-\text{F})^+$, 0.93; 330, $(\text{M}-\text{HF})^+$, 5.06; 251, $\text{SF}_5\text{CHSO}_2\text{FCO}^+$, 30.54; 231, $\text{SF}_5\text{CSO}_2\text{CO}^+$, 20.62; 209, $\text{SF}_3\text{C}_2\text{SO}_4^+$, 9.06; 127, SF_5^+ or $\text{CF}_3\text{CH}_2\text{O}^+$ or FSCSO_2^+ , 44.79; 105, CHSO_2CO^+ , 6.26; 89, SF_3^+ , 67.29; 83, CH_2CF_3^+ or SO_2F^+ , 100 + 3.08; 69, CF_3^+ , 9.90; 67, SOF^+ , 26.2; 51, SF^+ , 4.07; 44, CS^+ , 6.19.

Anal. Calcd. for $C_4H_4F_{10}O_4S_2$: 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.

$SF_5CHCF_2OSO_2$ with $(CF_3)_2CHOH$

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 $SF_5CHCF_2OSO_2$ and 17.92 mmol $(CF_3)_2CHOH$. The mixture was heated with stirring for 7 days at $45 \pm 5^\circ C$. Distillation under vacuum gave 14.18 mmol of liquid $SF_5CH(SO_2F)C(O)OCH(CF_3)_2$ in 80% yield; b.p. $98-100^\circ C/100$ 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 ^{19}F nmr spectrum ($\emptyset$) gave the following' relative peak areas: SF_5 (5.3), SO_2F (1.0) and CF_3 (5.4). EI^+ mass spectrum (m/e, species, %): 401, $(M-H_2O)^+$, 0.28; 400, $(M-F)^+$, 0.77; 399, $(M-HF)^+$, 4.32; 398, $(M-H_2F)^+$, 6.65; 251, $SF_5CSO_2FCO^+$, 61.95; 231, $SF_5CSO_2CO^+$, 25.72; 195, $CO_2CH(CF_3)_2^+$, 44.12; 151, $CH(CF_3)_2^+$, 37.38; 143, $F_2SCHSCO^+$, 8.31; 127, SF_5^+ or $FSCSO_2^+$, 79.96; 105, $HCSO_2CO^+$, 8.54; 89,

SF_3^+ , 88.64; 83, SO_2F^+ , 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 $\text{C}_5\text{H}_3\text{F}_{13}\text{O}_4\text{S}_2$: 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 $\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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) $\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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 $[\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2-\text{I}]_n$ 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 δ 50.5 ppm (SO_2F), a broadened singlet at δ -73.5 ppm (CF_3), and a broadened singlet at δ -161.4 ppm (CF). The relative

band areas for SO_2F , CF_3 , 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 δ 4.8 ppm (CH_2O) and a series of peaks in the δ 1.2-3.8 ppm range (CH_2 , CH).

Anal. Calcd. for $\text{C}_6\text{H}_5\text{F}_5\text{SO}_4$: 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 $\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ was placed in a quartz reaction vessel with 1.99 g (14.5 mmol) of CFCl_3 and irradiated for 56 hours. The liquid was drained from the reaction vessel, and the CFCl_3 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 $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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 $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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 $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2]_n$, 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 δ 4.8 ppm (CH_2O) and a series of peaks in the range of δ 1.0-3.5 ppm (CH_2 , CH).

The ^{19}F nmr spectrum contained a broadened multiplet at δ 65.2 ppm (axial SF), a broadened doublet at δ 57.4 ppm (SF_4), a broadened singlet at δ 48.8 ppm (SO_2F), and a broadened singlet at δ -121.5 ppm (CF). The relative band areas for SF: SF_4 :CF: SO_2F were: 1.4:4.0:1.0:1.0.

Anal. Calcd. for $\text{C}_5\text{H}_5\text{F}_7\text{S}_2\text{O}_4$: 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 $\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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; $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2]_n$ was formed in 95% yield. The softening temperature of the solid was $\sim 52^\circ\text{C}$. The IR and

nmr spectra agreed with that found for the viscous oil reported in the first run.

Polymerization of $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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 $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$ 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) $[\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2]_n$, 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 (SF_5CH), a broad singlet at δ 4.4 ppm (CH_2O) and a series of peaks in the range of δ 1.2–3.3 ppm (CH_2 , CH).

The ^{19}F spectrum contained a broadened singlet at δ 71.3 ppm (SF_5), and a broadened singlet at δ 58.5 ppm (SO_2F).

Anal. Calcd. for $C_5H_6F_6S_2O_4$: 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 $SF_5CH(SO_2F)C(O)OCH_2CH=CH_2$ was placed in the 80 mL quartz vessel with 1.39 g (10.1 mmol) $CFCl_3$ and irradiated for 26 hours. The $CFCl_3$ was removed under vacuum leaving a tan waxy solid along with some viscous oil; $[SF_5CH(SO_2F)C(O)OCH_2\overset{|}{CH}CH_2]_n$ was formed in 100% yield. The softening temperature of the solid was $\sim 45^\circ C$.

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

$FSO_2CF_2C(O)OH$ with Ag_2O

To a 200 mL Pyrex-glass three neck reaction vessel equipped with a reflux condenser and containing a Teflon stirring bar, were added 48.3 mmol of Ag_2O and 60 mL diethyl ether. The acid $FSO_2FSC_2C(O)OH$, 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, $FSO_2CF_2CO_2Ag$ (81.4 mmol), was dried with intermittent heating at $80^\circ C$; 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),

808 (m, sh. at 787 and 738), 738 (m), 716 (wm), 649 (m), 604 (m), 562 (w), 541 (w), 484 (wm), 456 (wm).

The ^{19}F nmr spectrum contained a triplet at δ 38.0 ppm (SO_2F) and a doublet at δ -100.9 ppm (CF_2) with a coupling constant, $J = 3.52$ Hz. The relative band area for FSO_2 to 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°C . The reaction mixtures were protected from light and allowed to warm slowly to room temperature (~24 hours).

$\text{FSO}_2\text{CF}_2\text{C(O)OAg}$ with CH_3I

To the reaction vessel previously described 2.40 mmol $\text{FSO}_2\text{CF}_2\text{C(O)OAg}$ and 3.17 mmol CH_3I 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 $\text{FSO}_2\text{CF}_2\text{C(O)OCH}_3$ (-40°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

(s), 1159 (s), 1061 (m), 1026 (m), 955 (w), 878 (w), 829 (ms), 801 (s), 730 (w), 646 (m), 583 (m).

The ^{19}F nmr spectrum contained a triplet at δ 39.1 ppm (SO_2F) and a doublet at δ -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 ^1H nmr spectrum contained a singlet at δ 4.17 ppm.

The positive ion mass spectrum CI^+ gave peaks (m/e, species, %): 193, MH^+ , 1.6; 124, $\text{CH}_2\text{COOCF}_2\text{S}^+$, 5.2; 109, $(\text{M}-\text{SO}_2\text{F})^+$, 55.9; 79, CSOF^+ , 8.6; 67, SOF^+ , 19.1; 65, SO_2H^+ , 23.6; 59, CH_3CO_2^+ , 100; 51, SF^+ , 4.7.

Anal. Calcd for $\text{C}_3\text{H}_3\text{F}_3\text{SO}_4$: 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.

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

To the reaction vessel previously described were added 15.11 mmol $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ and 14.18 mmol of $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$. After reaction, the volatile liquid mixture was washed with H_2O , dried over MgSO_4 and distilled. The fraction boiling at $142-143^\circ$ was further purified by gas chromatography giving 1.54 mmol of $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$ 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 $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$ contained a triplet at δ 39.7 ppm (SO_2F) and a doublet at δ 105.4 ppm (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 ^1H nmr spectrum contained a triplet at δ 0.68 ppm (CH_3), a sextet at δ 1.50 ppm (CH_2) and a triplet at 4.19 ppm (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, CI^+ , gave peaks (m/e, species, %): 205, $(\text{M}-\text{CH}_3)^+$ or $(\text{MH}-\text{O})^+$, 2.32; 149, $\text{SCF}_2\text{COC}_3\text{H}_3^+$, 12.49; 119, $\text{SCFCOC}_2\text{H}_4^+$, 6.18; 109, SC_5HO^+ , 23.63; 107, FSO_2C_2^+ or $\text{CF}_2\text{CO}_2\text{CH}^+$, 24.87; 97, SC_4HO^+ , 16.55; 95, FSO_2C^+ , 12.36; 91, SCFCO^+ , 5.10; 83, SO_2F^+ , 9.92; 81, $\text{C}_4\text{O}_2\text{H}^+$, 6.92; 79, FSCO^+ , 5.23; 73, CFCOCH_2^+ , 12.29; 70, COC_3H_6^+ , 6.03; 69, COC_3H_5 , 26.62; 67, SOF^+ or COC_3H_3^+ , 12.79; 65, COC_3H^+ , 100; 59, CFCO^+ , 18.53; 57, CO_2CH^+ , 33.55; 56, C_2O_2^+ or SC_2^+ , 7.68; 55, COC_2H_3^+ , 33.06; 53, C_2OCH^+ , 5.98; 51, 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.

FO₂SCF₂C(O)OAg with HOCH₂CH₂I

To the reaction vessel previously described, were added 20.9 mmol of FSO₂CF₂C(O)OAg and 19.55 mmol HOCH₂CH₂I. Distillation gave 2.38 mmol of [FSO₂CF₂C(O)OCH₂]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 ¹⁹F nmr spectrum contained a triplet at δ 40.4 ppm (SO₂F) and a doublet at δ -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 ¹H nmr contained a singlet at δ 5.03 ppm.

The positive ion mass spectrum, CI⁺, gives peaks (m/e, species, %): 229, (M-SO₂F)⁺, 1.06; 207, C₆O₄F₂SH⁺, 17.17; 206, C₆O₄F₂S⁺, 15.33; 205, FSO₂CF₂CO₂C₂H₄⁺, 100; 155, FSCF₂COC₂H₂⁺, 17.02; 141, FSCF₂COC⁺, 24.45; 123, SCF₂COCH⁺, 5.92; 122, SCF₂COC⁺, 7.70; 119, SFCOC₂H₄⁺, 24.37; 113, FSCF₂C⁺, 6.74; 111, C₅O₃H₃⁺, 7.66; 97, SC₄HO⁺, 5.52; 91, SCFCO⁺, 7.73; 79, FSOC⁺, 13.39; 78, CF₂CO⁺, 7.36; 69, C₃O₂H⁺, 8.22; 67, FSO⁺, 44.13; 65, C₄HO⁺, 50.33; 51, SF⁺, 13.36.

Anal. Calcd. for $C_6H_4F_6S_2O_8$: 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.

$FSO_2CF_2C(O)OAg$ with $(CH_3)_3SiI$

To the reaction vessel previously described, was added 13.46 mmol of $(CH_3)_3SiI$ and 13.30 mmol of $FSO_2CF_2C(O)OAg$. Distillation of the liquid product gave 3.84 mmol $FSO_2CF_2C(O)OSi(CH_3)_3$ in 29% yield, b.p. $86^\circ C/46$ 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), 702 (vw), 639 (m,sh at 667).

The ^{19}F nmr spectrum contained a triplet at δ 37.8 ppm (SO_2F) and a doublet at δ -97.2 ppm (CF_2) with a coupling constant $J = 4.65$ Hz. The relative band area for FSO_2 to CF_2 was 1.0:2.0, (theor. 1.0:2.0). The 1H nmr spectrum contained a singlet at δ 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, $SCF_2CO_2SiC_3H_9^+$, 5.83; 91, $SCFCO^+$, 4.34; 88, $OSiC_2H_8^+$, 9.42; 87, $OSiC_3H_7^+$, 100; 74, $OSiC_2H_6^+$, 4.23; 73, $SiC_3H_9^+$, 45.92; 65, SiC_3H^+ , 9.29; 63, SCF^+ , 7.73; 59, $CFCO^+$, 39.97; 57, $SiC_2H_5^+$, 6.53; 55, $SiC_2H_5^+$, 7.88.

Anal. Calcd. for $\text{C}_5\text{H}_9\text{F}_3\text{SO}_4\text{Si}$: F, 22.8; S, 12.81.

Found: F, 22.3; S, 11.26.

CHAPTER V

RELATED REACTIONS

Recently, workers⁸¹ have reported on a synthetic pathway that we have found useful in preparing several SF₅-containing fluoroethers. This pathway involves the addition of reactive trifluoromethyl hypochlorite to substituted olefins:

In order to evaluate this pathway for preparing pentafluorothio (SF₅) derivatives, the reactions of CF₃OCl with a number of SF₅ olefins, were studied. Reactions of SF₅CH=CF₂ with ClF, SF₅CH=CF₂ with Cl₂ and SF₅CF=CF₂ with CF₃OCl and reported here were prepared in conjunction with Dr. Roger M. Sheets.⁹²

In our continuing studies of pentafluorothiocarbon systems, we have found that upon reacting SF₅Br with fluoroolefins not only monomeric liquids but polymeric solids are produced under proper conditions of heat and pressure. The polymer SF₅(CHF₂CF₂)₃₀Br_{0.30} has been previously reported but is included here for comparison.⁸² It is possible that the SF₅ grouping may serve as a precursor to an SO₂F grouping; work is ongoing in our laboratories.

TRIFLUOROMETHYL HYPOCHLORITE/CHLORINE MONOFLUORIDE REACTIONS

The reaction of CF_3OCl with $\text{SF}_5\text{CH}=\text{CH}_2$ proceeded smoothly at room temperature:

The new SF_5 fluoroether boils at 93 ± 1 °C and is a water-white liquid.

When trifluoromethyl hypochlorite was reacted with $\text{SF}_5\text{CF}=\text{CF}_2$ at 110 °C, the following reaction occurred to give essentially one product (69%) that boiled at 72-73 °C:

With hexafluoropropene the following isomers, $\text{CF}_3\text{OCF}_2\text{CFC1CF}_3$ (71.5%) and $\text{CF}_3\text{OCF}(\text{CF}_3)\text{CF}_2\text{Cl}$ (28.5%), were produced.⁸²

It was interesting to find that while $\text{SF}_5\text{CH}=\text{CH}_2$ and $\text{SF}_5\text{CF}=\text{CF}_2$ added only CF_3OCl , this behavior did not extend to $\text{SF}_5\text{CH}=\text{CF}_2$. With this olefin, ClF addition was the major reaction pathway:

In separate reactions to confirm reaction (4), the straightforward addition of ClF to $\text{SF}_5\text{CH}=\text{CF}_2$ was carried out to give identical product.

It was found also that Cl_2 added directly to $\text{SF}_5\text{CH}=\text{CF}_2$ in high yield:

The reaction which occurred between $\text{SF}_5\text{CCl}=\text{CH}_2$ and CF_3OCl gave rise to one major product, $\text{SF}_5\text{CCl}_2\text{CH}_2\text{CH}_2\text{CCl}_2\text{SF}_5$. This sort of dimerization has not been observed previously in these systems.

It is unusual that ClF instead of CF_3OCl addition occurred with the above olefin but not with $\text{SF}_5\text{CH}=\text{CH}_2$, $\text{SF}_5\text{CF}=\text{CF}_2$, or $\text{CF}_3\text{CH}=\text{CH}_2$.⁸³ Other olefinic systems in which significant ClF addition occurred using CF_3OCl included the unsymmetrical olefins $\text{CH}_2=\text{CF}_2$, $\text{CF}_2=\text{CHBr}$, and $\text{CH}_2=\text{CHF}$.⁸²

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:

The two olefins formed above are new compounds. The loss of $[\text{CF}_3\text{OH}]$ in eq. (7), while unusual, has been observed previously when the reacting ether was $\text{CF}_3\text{OCH}(\text{CF}_3)\text{CH}_2\text{Cl}$ which resulted in the formation of $\text{CF}_3\text{CH}=\text{CHCl}$.⁸³

As reported earlier, Cross and coworkers⁶² 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 $\text{SF}_5\text{CCl}=\text{CH}_2$ and $\text{SF}_5\text{CCl}=\text{CF}_2$ 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 $\text{SF}_5\text{CCl}=\text{CF}_2$ and $\text{SF}_5\text{CCl}=\text{CH}_2$ 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 $\text{SF}_5\text{CHClCH}_2\text{OCF}_3$, $\text{SF}_5\text{CHClCF}_3$, and $\text{SF}_5\text{CHClCF}_2\text{Cl}$ are $\delta 5.62$, 5.46 and 6.10 ppm, respectively. For other SF_5 systems, such as $\text{SF}_5\text{CHFCF}_3$, $\text{SF}_5\text{CHFCF}_2\text{Br}$, $\text{SF}_5\text{CHFCHClBr}$, $\text{SF}_5\text{CHFCFClBr}$, and $\text{SF}_5\text{CHClCF}_2\text{Br}$, the values are $\delta 5.41$, 5.58 , 5.85 , 5.68 and 5.5 ppm, respectively.⁸⁴ Also, the proton chemical shift of a CH_2 group one carbon away from an SF_5 is also consistent from one SF_5 fluoroalkyl derivative to another. In $\text{SF}_5\text{CHClCH}_2\text{OCF}_3$ and $(\text{SF}_5\text{CCl}_2\text{CH}_2)_2$ the proton chemical shifts were found at $\delta 4.55/4.80$ and 4.81 ppm, respectively. In $\text{SF}_5\text{CBr}_2\text{CH}_2\text{Br}$ the proton chemical shift was found at $\delta 4.83$ ppm.⁷⁹ The proton chemical shift values for the olefin $\text{SF}_5\text{CCl}=\text{CH}_2$ are due to the following structure.

The H_a (doublet) pattern is located at $\delta 6.20$ ppm while for H_b (multiplet) the band center is found at $\delta 5.95$ ppm. These values are in close agreement with the corresponding bromo derivative ($\delta 6.4$ and 5.9 ppm).⁷⁹ Determination of the protons H_a and H_b is based on the fact that a proton trans to the SF_5 group interacts more strongly than the proton in the cis position.^{68,79}

For a number of systems it is found that CF_3OCl adds in a Markovnikov fashion producing syn addition products.^{82,83} However, we have found, as have others,^{82,83} that in some

olefinic systems, COF_2 elimination occurred either in place of CF_3OCl addition or with CF_3OCl addition. It is difficult to account for these observations unless one invokes a radical ion reaction mechanism.⁸⁰ For CF_3OCl addition, the following sequence is possible.⁸⁵

or

Figure 5. Free radical mechanism for CF_3COCl 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 $F\cdot$ abstraction or $CF_3O\cdot$ 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 COF_2 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 COF_2 than more symmetrical systems.

TABLE XVI
¹H AND ¹⁹F NMR DATA FOR HYPOCHLORITE/ClF/Cl₂ REACTIONS*

Compound	a	b	c	d	e
F (a) SF ₄ (b) CH (c) ClCHH' (d) OCF ₃ (e)	73.3 (n)	53.2 (m)	5.62 (m)	4.55 (m) 4.80 (m)	-63.6 (s)
	J _{a,b} = 144, 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, J _{d,d'} = 17.7				
F (a) SF ₄ (b) CF (c) ClCF ₂ (d) OCF ₃ (e)	63.3 (n,d)	46.3 (d,m)	-98.2 (m)	-82.3 (m)	-57.3 (t)
	J _{a,b} = 143, J _{a,c} = 4.4, J _{b,d} = 9.9, J _{c,d} = 21.2, J _{d,e} = 9.1				
F (a) SF ₄ (b) CH (c) ClCF ₃ (d)	68.7 (n)	57.7 (d,m)	5.61 (m)	-73.0 (p,d)	-
	J _{a,b} = 151, J _{b,c} = 5.6, J _{b,d} = 11.2, J _{b,d} = 6.3				
[F (a) SF ₄ (b) CCl ₂ CH ₂ (c)] ₂	71.2 (n)	47.1 (d,m)	4.81 (m)	-	-
	J _{a,b} = 134, J _{b,c} = 1.92				
F (a) SF ₄ (b) CH (c) ClCF ₂ (d) Cl	70.0 (n)	58.8 (d,m)	6.10 (m)	-64.8 (d)	-
	J _{a,b} = 141, J _{c,d} = 5.6				
	74.8 (n)	55.2 (d,m)	6.2 (d)	5.95 (m)	-
	J _{a,b} = 152, J _{b,c} = 3.3, J _{c,d} = 3.9

* 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.

SF₅Br WITH FLUOROOLEFINS TO FORM POLYMERS

We have found that SF₅Br reacts with fluoroethylenes to form polymers incorporating the SF₅-group according to the following equations:

With ethylene, essentially no polymer was formed. In addition to the above polymers (eqns. 9-12), the adducts SF₅RBr (R is CH₂CHF, CH₂CH₂, CHF₂CF₂, CF₂CF₂) are formed. The monomeric adducts with the exception of SF₅CF₂CF₂Br 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±5°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: 1) an increase in melting point, 2) an increase in stability, and 3) a decrease in solubility. These findings are summarized in Table XVII. Additional qualitative tests with the SF₅(CFHCF₂)₃₀Br_{0.7} and SF₅(CF₂CF₂)₁₆Br_{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 bromides⁸⁶ are reported to be in the 740-770 cm^{-1} region, while for alkylbromides⁸⁷ 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 $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$ did not contain a molecular ion peak but other appropriate fragment peaks were found: $(\text{C}_2\text{F}_4\text{Br})^+$, $(\text{C}_2\text{F}_3\text{Br})^+$, $(\text{CF}_2\text{Br})^+$, $(\text{SF}_5)^+$, $(\text{SF}_4\text{C})^+$, $(\text{CFBr})^+$, $(\text{SF}_4)^+$, $(\text{C}_2\text{F}_4)^+$, $(\text{SF}_3)^+$, and Br^+ .

The nmr spectra for all the polymers except $\text{SF}_5(\text{CF}_2\text{CF}_2)_{16}\text{Br}_{0.3}$ 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 δ 54 to 66 ppm while for monomeric adducts the corresponding values range from δ 44 to 67 ppm.⁶⁰ The axial fluorine values range from δ 71 to 83 ppm for polymers and δ 61 to 80 ppm for the respective monomeric adduct.⁶⁰ In the trifluoroethylene polymer, two types of SF_5 groups were present. For the $\text{SF}_5(\text{CF}_2\text{CHF})_{10}\text{Br}$ and $\text{SF}((\text{CHF}\text{CF}_2)_3)_3\text{Br}_{0.7}$ polymers, the ^{19}F resonances for C-F are found at δ -183 ppm and δ -211 ppm, respectively. By comparison, the ^{19}F chemical shift values

for C-F in polyvinylfluoride are located at δ -178 to -185 ppm (broad peaks); chemical shifts at δ -190 to -200 ppm represent inversion defects in the chain.⁸⁹ The ^{19}F chemical shift values for the CF_2 group vary from δ -93 to -130 ppm. Wilson and Santee report regions of CF_2 shifts in polyvinylidene fluoride of δ -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.⁹⁰

The new monomeric adduct, $\text{F(a)SF}_4\text{(b)CF}_2\text{(c)CF}_2\text{(d)Br}$, 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 δ 44.3 ppm and δ 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 δ -93.5 ppm and δ -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.^{60,84}

The ^1H nmr spectra for the polymers are complex multiplets in which characteristic chemical shift values are found. For $\text{SF}_5(\text{CHFCF}_2)_{30}\text{Br}_{0.7}$, the ^1H chemical shifts occur at δ 1.3 to 3 ppm and δ 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 δ 5.58 ppm next to the SF_5 .⁶⁰ In the $\text{SF}_5(\text{CH}_2\text{CHF})_{10}\text{Br}$ the CH chemical shift is assigned to the

band at $\delta 4.74$ 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 $\delta 4.27$ ppm.⁶⁰ The chemical shift of the CH_2 group located in the chain is found at $\delta 1.8$ ppm. By comparison, it is reported that for polyvinyl chloride, the chemical shift values, in the $\delta 1.9$ - 2.3 ppm region, are attributed to the β protons (CH_2) and the values at $\delta 4.2$ - 4.5 to the (CH) protons.⁹¹ In the polymer $\text{SF}_5(\text{CH}_2\text{CF}_2)_8\text{Br}$, ^1H chemical shift values are found at $\delta 2.8$ and $\delta 4.5$ 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 $\delta 4.46$ ppm.⁶⁰

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 $\delta 4.5$ ppm; for the rest of the CH_2 in the chain, the chemical shift values are located in the $\delta 1.8$ - 2.8 ppm region. We find the chemical shift at $\delta 5.15$ 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 $\delta 1.3$ - 3.0 ppm.

TABLE XVII

PROPERTIES OF SF₅-CONTAINING FLUOROPOLYMERS

<u>Compound*</u>	<u>Melting</u>	<u>Decomp. (°C)</u>	<u>Solubility</u>	
	<u>Range (°C)</u>		H ₂ O	Acetone
SF ₅ (CH ₂ CHF) ₁₀ Br	100-110	190	ins.	sol.
SF ₅ (CH ₂ CF ₂) ₈ Br	118-150	330	ins.	sol.
SF ₅ (CHF ₂ CF ₂) ₃₀ Br _{0.7}	130-160	460	ins.	sl. sol.
SF ₅ (CF ₂ CF ₂) ₁₆ Br _{0.3}	310-318	>510	ins.	insol.

* Empirical composition based on elemental analysis.

TABLE XVIII

ANALYSIS OF SF₅-CONTAINING FLUOROPOLYMERS

<u>Compound</u>	<u>Calc.</u> <u>Found</u>	<u>C</u>	<u>H</u>	<u>F</u>	<u>S</u>	<u>Br</u>
SF ₅ (CH ₂ CHF) ₁₀ Br		<u>35.98</u>	<u>4.54</u>	<u>42.7</u>	<u>4.80</u>	<u>11.97</u>
		35.79	4.39	43.0	4.86	11.95
SF ₅ (CH ₂ CF ₂) ₈ Br		<u>26.70</u>	<u>2.22</u>	<u>55.4</u>	<u>4.46</u>	<u>11.10</u>
		26.83	2.33	54.2	4.54	10.91
SF ₅ (CHF ₂ CF ₂) ₃₀ Br _{0.7}		<u>27.42</u>	<u>1.14</u>	<u>68.1</u>	<u>1.21</u>	<u>2.11</u>
		27.34	1.19	68.2	1.44	2.01
SF ₅ (CF ₂ CF ₂) ₁₆ Br _{0.3}		<u>21.95</u>	-	<u>74.9</u>	<u>1.83</u>	<u>1.35</u>
		21.42	-	72.8	1.89	1.38

TABLE XVII

 ^{19}F AND ^1H NMR DATA FOR SF_5 -CONTAINING FLUOROMONOMERS/POLYMERS*

Monomers	Chemical Shifts (ppm)					
	SE	SE ₄	CF	CF ₂	CH ₂	CH
FSF ₄ CH ₂ CHFBr ^b	79.9	66.4	-139.2	-	4.27	6.95
FSF ₄ CH ₂ CF ₂ Br ^b	77.3	70.5	-	-51.5	4.46	-
FSF ₄ CHFCF ₂ Br ^b	70.0	53.7	-163.5	-63.1	-	5.58
FSF ₄ CF ₂ CF ₂ 'Br	61.5(n,t)	44.3(d,m)	-	-93.5(p,m) -66.5(p,m)	-	-
	[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]					
Polymers ^c						
FSF ₄ (CH ₂ CHF) ₁₀ Br	83	65.5	-183	-	1.8	4.74
FSF ₄ (CH ₂ CF ₂) ₈ Br	81	71.2	-	-93	2.8,4.5	-
FSF ₄ (CHFCF ₂) ₃₀ Br0.7 ^b	71	56,54	-211	-120,-122 -125,-129	-	2.8,4.5
FSF ₄ (CF ₂ CF ₂ ') ₁₆ Br0.3	(not determined)					

a. Chemical shifts given relative to CFCl_3 for ^{19}F and TMS for ^1H ; 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

SF₅CH=CH₂ with CF₃OCl to form SF₅CHClCH₂OCF₃

Into a 1.0 L Pyrex glass vessel equipped with a Kontes Teflon valve were added 34.5 mmol of SF₅CH=CH₂ and 30.8 mmol of CF₃OCl. The mixture was warmed to room temperature for one hour; with shaking for 1.5 hours. The product, 20.8 mmol of SF₅CHClCH₂OCF₃, 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 ¹⁹F nmr spectrum for F(a)SF₄(b)CH(c)ClCH(d)H(d')-OCF₃(e) contained a singlet at δ -63.6 (F_e) and two multiplets at δ 53.2 (F_b) (doublet of multiplets) and δ 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 ¹H nmr spectrum contained multiplets centered at δ 4.55 (H_d), 4.80 (H_{d'}), and 5.62 (H_c) ppm. Relative band areas (δ 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-OCF₃)⁺, 17.9; 147, C₃H₃F₃ClO⁺, 25.1; 127,

SF_5^+ , 2.9; 99, $\text{C}_2\text{H}_2\text{F}_3\text{O}^+$, 30.2; 89, SF_3^+ , 24; 81, SCH_2Cl^+ , 100; 69 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.

$\text{SF}_5\text{CF}=\text{CF}_2$ with CF_3OCl to form $\text{SF}_5\text{CFC1CF}_2\text{OCF}_3$

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 CF_3OCl . The mixture was heated at 110 °C for 24 hours. The product, 12.2 mmol of $\text{SF}_5\text{CFC1CF}_2\text{OCF}_3$, 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}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 δ 63.3 (F_a) (nine-line pattern of doublets), a doublet of multiplets at δ 46.3 (F_b), a triplet at δ -57.3 (F_e), a nine-line multiplet at δ -82.3 (F_d), and a multiplet at δ -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, Cl^+ gives peaks, (m/e, species, %): 201, (M-SF_5) $^+$, 9.9; 135, $\text{C}_2\text{F}_5\text{O}^+$, 100; 127, SF_5^+ , 4.9; 119, C_2F_5^+ , 5.1; 89 SF_3^+ , 14.9; 69, CF_3^+ , 83.2.

Anal. Calcd. for $C_3F_{11}OSCl$: C, 10.97. Found: C, 10.87.

$SF_5CCl=CH_2$ with CF_3OCl to form $(SF_5CCl_2CH_2)_2$

Into a 100 mL Pyrex glass vessel equipped with a Kontes Teflon stopcock were added 3.15 mmol of $SF_5CCl=CH_2$ and 2.98 mmol of CF_3OCl . The mixture was warmed to room temperature (~ 14 h) and heated at 47–49 °C for three hours. The nonvolatile product $(SF_5CCl_2CH_2)_2$ 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 $[F(a)SF_4(b)CCl_2CH_2(c)]_2$ contained a nine-line multiplet at δ 71.2 ppm (F_a) and a doublet of multiplets at δ 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 1H nmr spectrum contained a multiplet at δ 4.81 ppm (distorted pentet), $J_{b,c} = 1.92$ Hz. The positive mass spectrum, CI^+ gives peaks, (m/e, species, %): 336, $C_4H_2F_8S_2Cl_2^+$, 3.1; 203, $C_2HF_4SCl_2^+$, 10.6; 147, $C_2H_2FSCl_2^+$, 15.4; 127, SF_5^+ , 23.7; 117, CF_2SCl^+ , 63.2; 115, $C_2H_2F_3S^+$, 100; 89, SF_3^+ , 36.7.

Anal. Calcd. for $C_4H_4F_{10}S_2Cl_4$: 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 (F_a, nine-line pattern), δ 57.7 ppm (F_b, doublet of multiplets), and δ -73.0 ppm (F_d, pentet of doublets); J_{a,b} = 151, J_{b,c} = 5.6, J_{b,d} = 11.2 and J_{c,d} = 6.3 Hz. The ¹H nmr spectrum contained a multiplet at δ 5.61 ppm.

SF₅CH=CF₂ with Cl₂ to form SF₅CHClCF₂Cl

Into a 100 mL Pyrex glass vessel equipped with a Kontes Teflon stopcock were added 3.28 mmol of SF₅CH=CF₂ and 3.75 mmol of Cl₂. The mixture was warmed to room temperature (~ 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 SF₅CHClCF₂Cl, 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 ¹⁹F nmr spectrum for F(a)SF₄(b)CH(c)ClCF₂(d)Cl contained multiplets at δ 70 ppm (F_a, nine-line pattern), δ 58.8 ppm (F_b, doublet of multiplets), and a doublet at δ -64.8 ppm (F_d), J_{a,b} = 141 Hz. The relative band areas for SF₄ to CF₂ are 1.8 to 1.0; theor. 2.0 to 1.0. The ¹H nmr spectrum contains a multiplet at δ 6.10 ppm, J_{c,d} = 5.6 Hz.

SF₅CHClCH₂OCF₃ with KOH to form SF₅CCl=CH₂

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 SF₅CHClCH₂OCF₃. 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 $\text{SF}_5\text{CCl}=\text{CH}_2$, 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,, 891-872 (vs, broad), 778(vs), 684(m), 612(m), 594(m), 512(m), and 481(m).

The ^{19}F nmr spectrum for $\text{F(a)SF}_4\text{(b)CClCH(c)H(d)}$ contained a multiplet (nine-line pattern) at δ 74.8 ppm (F_a) and a doublet of multiplets at δ 55.2 ppm (F_b) 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 δ 6.20 ppm (H_c) and a complex multiplet at δ 5.95 ppm (H_d); $J_{b,c} = 3.3$ and $J_{c,d} = 3.9$ Hz. The positive mass spectrum, CI^+ gives peaks, (m/e, species, %): 188, M^+ , 29.9; 127, SF_5^+ , 20.9; 89, SF_3^+ , 24.3; 61, $\text{C}_2\text{H}_2\text{Cl}^+$, 100.

Anal. Calcd. for $\text{C}_2\text{H}_2\text{F}_3\text{SCl}$: C, 12.74; H, 1.07. Found: C, 12.81; H, 1.05.

$\text{CF}_2=\text{CF}_2$ with SF_5Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 64 mmol of SF_5Br and 75 mmol of $\text{CF}_2=\text{CF}_2$. 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 $\text{SF}_5(\text{CF}_2\text{CF}_2)_{16}\text{Br}_{0.3}$: 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 $\text{CF}_2=\text{CF}_2$ and 62.2 mmol of SF_5Br were heated at 90 ± 5 °C (2d). Distillation of the volatile material gave 3.71 mmol of $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$, bp. 60-62 °C, leaving behind 8.91 grams of solid polymer. The molecular weight of $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$ (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 ^{19}F nmr spectrum contained a multiplet at δ 61.5 ppm (nine-line pattern of triplets), a doublet of multiplets at δ 44.3 ppm, a pentet of multiplets at δ -93.5 and -66.5 ppm (relative band areas for SF to SF_4 was 1.0:3.9, theor. 1.0:4.0 and for CF_2Br to SF_5CF_2 was 1.0:1.0). Coupling constants for $\text{F(a)SF}_4(\text{a})\text{CF}_2(\text{c})\text{CF}_2(\text{d})\text{Br}$ were $J_{\text{a,b}} = 146.6$, $J_{\text{a,c}} = 4.23$, $J_{\text{b,c}} = 14.4$, $J_{\text{b,d}} = 11.3$, $J_{\text{c-d}} \sim 4.5$ Hz.

A molecular ion was not observed but other fragment ions were found: 179,181 ($\text{C}_2\text{F}_4\text{Br}^+$); 160,162 ($\text{C}_2\text{F}_3\text{Br}^+$); 129,131 (CF_2Br^+); 127 (SF_5^+); 120 (SF_4C^+); 110,112 (CFBr^+); 108 (SF_4^+); 101 (SF_3C^+); 100 (C_2F_4^+); 89 (SF_3^+); 79,81 (Br^+); 70 (SF_2^+); 69 (CF_3^+); 63 (SFC^+); 51 (SF^+); 50 (CF_2^+); 44 (SC^+).

Anal. Calcd. for $\text{C}_2\text{F}_9\text{SBr}$: 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%.

$\text{CFH}=\text{CF}_2$ with SF_5Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 93 mmol of SF_5Br and 100 mmol of $\text{CF}_2=\text{CFH}$; after heating this mixture at $90 \pm 5^\circ\text{C}$ for four days, an additional 52 mmol of SF_5Br and 64 mmol of CF_2CFH were added. The reaction mixture was heated at $90 \pm 5^\circ\text{C}$ for three days. The volatile materials at room temperature (58 mmol of $\text{SF}_5\text{CFHCF}_2\text{Br}$) were removed leaving behind 9.0 grams of a white waxy solid.

In an additional run, 58.8 mmol of SF_5Br and 75.8 mmol of $\text{CFH}=\text{CF}_2$ were heated at $90 \pm 5^\circ\text{C}$ for four days. To this reaction mixture an additional 69.7 mmol of $\text{CF}_2=\text{CFH}$ was added and heated at $90 \pm 5^\circ\text{C}$ (3d); in this run 10.9 grams of the same white waxy solid was formed. The melting range of this polymer was $130\text{--}160^\circ\text{C}$ 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),

1244(ms), 1197(s), 1156(s), 1112(s), 991(w), 978(w), 875(ms with sh. at 922), 834(ms), 728(w), 669(w), 628(w), 606(wm), 547(wm) 509(wm), 466(w), 438(w).

The ^{19}F nmr spectrum contained a complex doublet of doublets at δ 56 and 54 ppm (SF_4) and a multiplet at δ 71 ppm (SF); multiplets at δ -120, -122, -125, -129 ppm (CF_2) and at -211 (CF) ppm are present. The ^1H nmr spectrum has two broad multiplets centered at δ 5.5 ppm and a series of peaks in the range of δ 1.3 -3.0 ppm.

Anal. calcd for $\text{SF}_5(\text{CHFCH}_2)_{30}\text{Br}_{0.7}$: 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.

$\text{CF}_2=\text{CH}_2$ with SF_5Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 96.2 mmol of SF_5Br and 118.3 mmol of $\text{CF}_2=\text{CH}_2$. 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 $\text{SF}_5\text{CH}_2\text{CF}_2\text{Br}$ (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),

657(wm), 600(wm), 576(w), 566(wm), 531(wm), 509(w) and 493(wm).

The ^{19}F nmr spectrum contained a complex doublet at δ 71 ppm (SF_4) and a multiplet at δ 81 ppm (SF); multiplets at δ -93 and δ -98 ppm (CF_2) were present. The ^1H nmr spectrum contained broad complex multiplets with the bands centered at δ 2.8 and δ 4.5 ppm.

Anal. for $\text{SF}_5(\text{CH}_2\text{CF}_2)_8\text{Br}$, 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.

$\text{CFH}=\text{CH}_2$ with SF_5Br

The reactants, SF_5Br (84 mmol) and $\text{CFH}=\text{CH}_2$ (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 $\text{SF}_5\text{CH}_2\text{CH}_2\text{F}$ 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 δ 66 ppm (SF_4) and a multiplet at δ 83 ppm (SF); $J_{\text{SF}-\text{SF}_4} = 155$ Hz, the CF resonance was a complex multiplet centered at

δ -183 ppm. The ^1H nmr spectrum contained two broad multiplets centered at δ 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 $\text{SF}_5(\text{CH}_2\text{CFH})_{10}\text{Br}$, 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.

$\text{CH}_2=\text{CH}_2$ with SF_5Br

To the 75 mL reactor described earlier, 99 mmol of SF_5Br and 136 mmol of $\text{CH}_2=\text{CH}_2$ 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 $\text{FCH}_2\text{CH}_2\text{Br}$ (91%) and $\text{SF}_5\text{CH}_2\text{CH}_2\text{Br}$ (9%).

In a second run, under mild conditions, 84.3 mmol of SF_5Br and 109.2 mmol of $\text{CH}_2=\text{CH}_2$ 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.

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APPENDIX

INFRARED AND NMR SPECTRA

Figure 6. Infrared Spectrum for $\text{SF}_5\text{CHCF}_2\text{OSO}_2$.

Figure 7. Infrared Spectrum for $\text{SF}_5\text{CHCF}_2 \cdot \text{SO}_3$.

Figure 8. Infrared Spectrum for $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}$.

Figure 9. Infrared Spectrum for SF₅CH₂SO₂F.

Figure 10. Infrared Spectrum for $\text{SF}_5\text{CH}_2\text{SO}_3\text{Na}$.

Figure 11. Infrared Spectrum for $\text{SF}_5\text{CH}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.

Figure 12. Infrared Spectrum for $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$.

Figure 13. Infrared Spectrum for
 $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$.

Figure 14. Infrared Spectrum for
 $[\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CHCH}_2-]_n$.

Figure 15. Infrared Spectrum for $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CHCH}_2-\text{I}]_n$.

Figure 16. Infrared Spectrum for
 $[\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CH}_2-]_n$.

Figure 17. Infrared Spectrum for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$.

Figure 18. Infrared Spectrum for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_3$.

Figure 19. Infrared Spectrum for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_3$.

Figure 20. Infrared Spectrum for $(\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OCH}_2)_2$.

Figure 21. Infrared Spectrum for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OSi}(\text{CH}_3)_3$.

Figure 22. Infrared Spectrum for $\text{SF}_5\text{CHClCH}_2\text{OCF}_3$.

Figure 23. Infrared Spectrum for $\text{SF}_5\text{CFC1CF}_2\text{OCF}_3$.

Figure 24. Infrared Spectrum for $\text{SF}_5\text{CHClCF}_3$.

Figure 25. Infrared Spectrum for $(\text{SF}_5\text{CCl}_2\text{CH}_2)_2$.

Figure 26. Infrared Spectrum for SF₅CHClCF₂Cl.

Figure 27. Infrared Spectrum for $\text{SF}_5\text{CHCl}=\text{CF}_2$.

Figure 28. Infrared Spectrum for SF₅CF₂CF₂Br.

Figure 29. Infrared Spectrum for $\text{SF}_5(\text{CF}_2\text{CF}_2)_{16}\text{Br}_{0.3}$.

Figure 30. Infrared Spectrum for $\text{SF}_5(\text{CH}_2\text{CF}_2)_8\text{Br}$.

Figure 31. Infrared Spectrum for $\text{SF}_5(\text{CH}_2\text{CHF})_{10}\text{Br}$.

Figure 32. ^1H and ^{19}F nmr for $\text{SF}_5\text{CHCF}_2\text{OSO}_2$.

Figure 33. ^{13}C nmr for $\text{SF}_5\text{CHCF}_2\text{OSO}_2$ (^1H decoupled).

Figure 34. ^{19}F nmr for SF₅CHCF₂·2SO₃
(SF₅ region, sw = 50).

Figure 35. ^1H and ^{19}F nmr for $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}$.

Figure 36. ^{13}C nmr for $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}$ (^1H decoupled).

Figure 37. ^1H and ^{19}F nmr for $\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$.

Figure 38. ^{13}C nmr for $\text{SF}_5\text{CH}_2\text{SO}_2\text{F}$ (^1H decoupled, triplet is CDCl_3).

Figure 39. ^1H nmr for $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (sw = 10).

Figure 40. ^{19}F nmr for $\text{SF}_5\text{CH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (sw = 50).

Figure 41. ^1H nmr for $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}_2\text{CF}_3$ (upper, sw = 10) and $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$ (lower, sw = 2).

SF₅ (sw = 20) SO₂F (sw = 20) CF₃ (sw = 10)

Figure 42. ¹⁹F nmr for SF₅CH(SO₂F)C(O)OCH₂CF₃.

Figure 43. ^{19}F nmr for $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{OCH}(\text{CF}_3)_2$
(sw = 50).

Figure 44. ^1H and ^{19}F nmr for $[\text{CF}_3\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CHCH}_2-\text{I}]_n$ (sw = 50 for ^{19}F).

Figure 45. ^1H and ^{19}F nmr for $[\text{SF}_5\text{CF}(\text{SO}_2\text{F})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CHCH}_2-]_n$ ($\text{sw} = 50$ for ^{19}F).

Figure 46. ^1H and ^{19}F nmr for $[\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{C}(\text{O})\text{O}-\text{CH}_2\text{CHCH}_2]_n$ (sw = 10 for ^1H and 50 for ^{19}F).

SO_2F

CF_2

Figure 47. ^{19}F nmr pattern for $\text{FSO}_2\text{CF}_2\text{C}(\text{O})\text{OAg}$ and derivatives (sw = 5).

Figure 48. ^{19}F nmr for $\text{SF}_5\text{CHClCH}_2\text{OCF}_3$ (sw = 50).

Figure 49. ^1H nmr for $\text{SF}_5\text{CHClCH}_2\text{OCF}_3$ (sw = 2).

Figure 50. ^{19}F nmr for $\text{SF}_5\text{CFC1CF}_2\text{OCF}_3$.

Figure 51. ^1H and ^{19}F nmr for $\text{SF}_5\text{CHClCF}_3$.

Figure 52. ^1H and ^{19}F nmr for $(\text{SF}_5\text{CCl}_2\text{CH}_2)_2$.

Figure 53. ^{19}F nmr for $\text{SF}_5\text{CHClCF}_2\text{Cl}$.

Figure 54. ^1H nmr for $\text{SF}_5\text{CHClCF}_2\text{Cl}$ (sw = 10).

CH (sw = 2)

SF (sw = 50)

SF₄

Figure 55. ^1H and ^{19}F nmr for $\text{SF}_5\text{CCl}=\text{CH}_2$.

Figure 56. ^{19}F nmr for $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$.

Figure 57. ^1H nmr for $\text{SF}_5(\text{CH}_2\text{CF}_2)_8\text{Br}$ (sw = 10).

Figure 58. ^{19}F nmr for $\text{SF}_5(\text{CH}_2\text{CF}_2)_8\text{Br}$.

CH (sw = 10)

SF

(sw = 50)

SF₄

CF (sw = 10)

Figure 59. ^1H and ^{19}F nmr for $\text{SF}_5(\text{CH}_2\text{CHF})_{10}\text{Br}$.