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THESIS APPROVAL

The abstract and thesis of Yoon S. Choi for the Master of Science degree in Chemistry was presented August 4, 1994 and accepted by the thesis committee and the department.

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ABSTRACT

An abstract of the thesis of Yoon S. Choi for the Master of Science in Chemistry presented August 4, 1994.

Title: Studies in Fluorine Chemistry: ^{13}C NMR
 Investigation of $\text{SF}_5/\text{SO}_2\text{F}$ Fluorinated Systems.

The purpose of this thesis was two fold:

- (i) The synthesis and characterization of SF_5 containing dienes.
- (ii) The characterization of hydro/fluorocarbon compounds containing $\text{SF}_5/\text{SO}_2\text{F}$ groups via their ^{13}C NMR spectra.

A new $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ was prepared and characterized as a precursor to new dielectric polymers. This new adduct was made from the reaction of pentafluorothio bromide with 1,1,2-trifluoro-1,4-pentadiene.

A SF_5 -diene was prepared from the reaction of pentafluorothio chloride with acetylene. This reaction involves a radical addition mechanism. The SF_5 group is bonded to the carbon atom carrying the most hydrogens. SF_5 -dienes are capable of undergoing different reactions, such as polymerization.

Fluorocarbon sulfonyl fluorides (RSO_2F), which have

been synthesized in our lab, were characterized by their ^{13}C NMR spectra. The ^{13}C NMR data of these sulfonyl fluorides show chemical shift values for the methyl and methylene groups next to a fluoroalkyl sulfonyl fluoride group in the 52.8-65.7 ppm range. The spectra showed that the inductive effect of electronegative substituents has a major influence on the $^1\text{J}_{\text{C-F}}$ and $^1\text{J}_{\text{C-H}}$ coupling.

Infrared, ^1H , ^{19}F and ^{13}C nuclear magnetic resonance and mass spectra are presented to support the assigned structure for the new compounds, $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ and $\text{SF}_5\text{CH}=\text{CHBrCH}_2\text{CF}=\text{CF}_2$.

STUDIES IN FLUORINE CHEMISTRY: ^{13}C NMR
INVESTIGATION OF $\text{SF}_5/\text{SO}_2\text{F}$ FLUORINATED SYSTEMS

by
YOON S. CHOI

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

MASTER OF SCIENCE
in
CHEMISTRY

Portland State University

1994

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Dr. Peyton and Clary Clish should be acknowledged for obtaining the ^{13}C spectra. Dr. Rolf W. Winter, of the Portland Veterans Hospital provided mass spectra.

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CHAPTER I

INTRODUCTION

In this chapter a review of the known literature covering the following will be discussed:

- (i) synthesis of carbon compounds containing the SF₅ group;
- (2i) Synthesis of SF₅Br--precursor to carbon compounds containing SF₅ group;
- (3i) Use and application of ¹³C NMR spectroscopy;
- (4i) Presentation of ¹³C NMR Data of known SF₅/SO₂F hydro/fluoro-carbons.

This discussion will be useful in analyzing and understanding the results of this study that appears in chapter III and IV.

THE SYNTHESIS OF PENTAFLUOROTHIO BROMIDE (SF₅Br)

Pentafluorothio bromide can be prepared by several routes.¹⁻³ In this study SF₅Br was obtained by reacting BrF with SF₄ in the presence of CsF; contaminant Br₂ may be removed by treatment with Hg.⁴

SF₅Br boils at 3.1°C at one atmosphere and has strong S-F IR bands at 891.3, 847.5 and 690.1 cm⁻¹.⁵ Its thermal¹ and hydrolytic properties² are given in the next two

equations:

THE ADDITION OF SF_5Br TO MULTIPLE CARBON-CARBON BONDS

SF_5X ($\text{X} = \text{Cl}, \text{Br}, \text{SF}_5$) adds across multiple bonds and forms adducts.⁹ Tetrafluorosulfur ylides ($\text{F}_4\text{S} = \text{CR}_1\text{R}_2$) add HF to form SF_5 -compounds, too; however, as most of these ylides are formed from SF_5 -compounds, this method is only of limited value.⁶ The simple organic derivatives can undergo further reactions; in particular, the primary addition products of SF_5X and alkenes or alkynes can be dehydrohalogenated to yield alkenes or alkynes.

Many SF_5 -Carbon derivatives were synthesized in the last thirty years. The high thermal, radiative and chemical stability of the pentafluorothio group makes these compounds attractive as replacements for compounds that contain a trifluoromethyl group.

It is, however, more difficult to introduce an SF_5 group into a molecule than a CF_3 -group, and also rather more expensive. It is envisioned that SF_5 -compounds could be useful dielectrics, replacements for fluorochloro hydrocarbons, very stable polymers, fuel cell electrolytes with advantageous properties, blood substitutes, surfactants, high energy materials (explosive and rocket

fuels) or pesticides.⁷ These expectations have been fulfilled in several cases.⁸

The addition of SF_5X to a multiple bond, which can be induced by light, heat or free-radical initiators, is a radical reaction. This involves the first step of cleavage of SF_5X to $\text{SF}_5\cdot$ and $\text{X}\cdot$, followed by addition to the multiple bond.⁹

The mechanism for this radical addition pathway is proposed as follows⁹:

Only initiation reaction (II) will lead to propagation step. The initiation reaction (I) will compete with (II) in this propagation step to give $\text{F}_5\text{S}-\text{C}-\text{C}-\text{X}$.¹⁰

The addition of SF_5X ($\text{X} = \text{Br}, \text{Cl}$) to olefins leads only to compounds which have an SF_5 -group attached to a CH_2 group:

The reversibility of SF_5 addition reaction is a consideration, particularly in photochemical reactions, where complicated product mixtures of S_2F_{10} , SF_4 and

fluorinated products may be formed.¹¹ The existence of SF_5 -radicals was confirmed through their observation at low temperature by either electron spin resonance or infrared spectroscopy. The radicals were generated by ultraviolet irradiation of SF_5X ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) or concomitant matrix deposition of SF_4 and fluorine that had passed through a microwave discharge.¹²

SF_5 -Alkenes are obtained mostly through SF_5X addition to alkenes, followed by dehydrohalogenation. Usually, the addition is uni-directional, with one product being formed in excess. Mixtures are obtained, exemplarily, with perfluoropropylene and trifluorochloroethene⁹ or trifluoroethylene¹³ or 1,1-difluoro-2-chloroethene.¹⁴

It was found that SF_5Cl will add to trifluoroethylene (CCl_4 , benzoyl peroxide, 150°C) to give a 95:5 mixture of $\text{SF}_5\text{CHFCF}_2\text{Cl}$ and $\text{SF}_5\text{CF}_2\text{CHFCl}$.¹³ It was also found that SF_5Br will add to β -acetoxy ethyl acrylate to give a mixture of α -bromo- β - SF_5 - β -acetoxy propionate and α - SF_5 - β -bromo- β -acetoxy propionate, with the latter being in excess.¹⁴

The reaction of SF_5X to alkenes has often been moderated by working in the gas phase (ethylene and SF_5Br), at low temperature and in high dilution in an inert solvent (SF_5Br and vinyl acetate in CCl_3F , -110°C)¹⁴, or at low temperature in the gas phase with irradiation (isobutylene and SF_5Cl).¹⁵ These reaction conditions are necessary because XF might be added instead of SF_5X , accompanied by

SF₄ expulsion, and polymerization of the olefin or both.

The requirements for the SF₅ addition to olefins are not severe because electron-poor double bonds will not react; maleic anhydride is completely inert to SF₅Br at 100°C. Electron-rich double bonds (1,3-butadiene, vinyl acetate, β,β-bis-ethoxy ethyl acrylate) are so reactive that it is difficult to obtain any SF₅X adducts (instead XF addition products are formed).^{9, 14} Addition reactions of SF₅X that illustrate these observations are given below:

Dehydrohalogenation of the adducts by treating with base (usually aqueous KOH) yields the SF₅-Olefins.^{3, 9}

Some exceptional cases were reported^{23, 24}

^{13}C NMR OF SF_5 COMPOUNDS AND SULFONYL FLUORIDES

History of ^{13}C NMR

The first great breakthrough in experimental ^{13}C NMR, wideband proton decoupling, was available as early as 1965, but the advancement of ^{13}C NMR spectroscopy to the status of a practical analytical research tool for chemists required several instrumental and technical developments that are now generally available in the 1970's.³¹

^{13}C NMR Spectral Characteristics

^{13}C NMR has greater potential than ^1H NMR for the study of the structure of compounds. Carbon resonances of compounds are found over a chemical shift range of ~200 ppm, compared with under 20 ppm for proton nuclei. With modern instrumental methods, it is also possible to have simpler resonance lines in ^{13}C NMR than for ^1H NMR spectra. ^1H spectra are extensively spin-coupled, leading to complicated multiplet resonance bands for most protons. However, in ^{13}C NMR the situation is more easily controlled and ^{13}C - ^{13}C spin-spin splitting is not usually detected.

In ^1H NMR, the three types of spectral information--chemical shifts, coupling constants, and peak area measurements, are of nearly comparable value in structure determinations. In ^{13}C NMR, chemical shifts generally are the most useful parameters.

Experimentally it has been found that the effects of

substituents on ^{13}C chemical shifts are largely additive; thus predictions of ^{13}C NMR shifts by semi-empirical methods are usually successful. The largest variation in shifts for carbon nuclei occurs with direct substitution by nuclei with electron-withdrawing characteristics (electronegative elements) or heavy atoms (e.g., iodine). Remote substituents also affect ^{13}C chemical shifts, but in a more complex manner.

Hybridization at carbon affects shifts significantly; sp^3 hybridized carbons occur at high fields, sp^2 carbons at low fields, and with sp carbon the shifts are intermediate. One very useful remote substituent effect in ^{13}C NMR is the steric compression shift.³¹ Carbon atoms that are sterically crowded appear at higher field than similar carbons that are not.

Despite the high degree of regularity for ^{13}C NMR chemical shifts, subtle differences may be important. A nearby center of molecular asymmetry can induce magnetic nonequivalence of otherwise equivalent carbons.²⁶

A correlation of bond angle and ^{13}C NMR chemical shifts has been found.²⁷

Coupling

The magnitude of the coupling between ^{13}C atoms and the attached protons, $^1J_{\text{CH}}$, is sensitive to the structure of the molecule and the local environment of the carbon atom.

There is considerable variation of $^1J_{\text{CH}}$ with angular

distortion in hydrocarbons.^{28,29} Whether this dependence is a result of changes in s-character of the orbitals involved or due to C-H bond shortening resulting from lower repulsive interactions of other bonds in the distorted molecule (which would also lead to an increase in the C-H coupling constant) is the subject of some question. Nevertheless, the correlation of bond deformation with $^1J_{CH}$ is well established.

Substitution by electronegative groups also leads to considerable increase in $^1J_{CH}$.³⁰ For example, $^1J_{C-H}$ for H-CH₃ is 125 Hz, while $^1J_{C-H}$ for H-CH₂F and H-HCF₂ are 147.9 and 184.5 Hz, respectively.³¹

Carbon-Carbon NMR coupling constants also play an important role in signal assignment and structural elucidation.

The $^1J_{C-C}$ values of compounds containing electronegative substituents, e.g. CF₃C, are exceptionally large. The inductive effect of the electronegative substituents has a major influence on the $^1J_{C-C}$ coupling.³²

The coupling constants between ^{19}F and directly bonded ^{13}C tend to decrease with increasing fluorine chemical shifts as shown in Table I.⁴²

TABLE I

CHEMICAL SHIFTS AND FLUORINE-CARBON-13
COUPLING CONSTANTS⁴²

Compound	ϕ^* (ppm)	$J_{F^{13}C}$ (Hz)
$Br_2C=CFBr$	58.1	323.6
$Cl_2C=CClF$	79.3	303.1
$Br_2C=CF_2$	79.2	289.9
$Cl_2C=CF_2$	88.5	288.9
cis- $BrFC=CBrF$	95.3	+324.7
cis- $ClFC=CClF$	105.1	+299.3
trans- $BrFC=CBrF$	113.0	+355.0
trans- $ClFC=CClF$	119.6	+289.6

An extensive study of ^{13}C splitting in fluorine NMR spectra by Muller and Carr³³ led to the conclusion that large J_{F-C} values and decreased fluorine magnetic shielding are due to the increased C-F double bond character.

In hydrocarbons, for example, $^1J_{C-H}$ has been related to the amount of s character on the carbon atom. Thus sp^3 hybridized carbons have the lowest one-bond C-H coupling constants ($^1J_{C-H} \sim 125$ Hz), whereas $^1J_{C-H}$ for sp hybridized carbons is highest (~ 250 Hz). Substitution on carbon by electronegative atoms increases $^1J_{C-H}$ significantly. Therefore, $^1J_{CH}$ shows the twin dependence on carbon

hybridization and substitution by electronegative atoms.

To date the ^{13}C NMR spectral data of some SF_5 containing adducts and some sulfonyl fluorides have been reported.^{34,35,36,37,38}

The analyses of the ^{13}C NMR spectra of some β -fluorosultones are listed in Table III.³⁹ If $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ is chosen as a reference, the effect of various substituents can be estimated; the corresponding increments are listed in Table II with regard to changes at the α carbon. The strongest shielding is found when H replaces F or when the $\text{F}_4\text{S=}$ group replaces two F atoms; weaker shielding values for CF_3- , CF_3OCF_2- , and $\text{ClCH}_2\text{CHClCH}_2-$ were also found. The deshielding behavior shown by the SF_5 and SF_4Cl groups suggest high electronegativity values for these groups; respective values in Pauling units of 3.62 and 3.48 were found. All β effects were reported to be very weak.³⁸

In general, the ^{13}C - ^{19}F coupling values for fluorosultones vary within the range of $\approx 270 - 330$ Hz. These values are in good agreement with values reported for other cyclic system; for $c\text{-C}_4\text{F}_8$ and $c\text{-C}_4\text{F}_4\text{Cl}$, the corresponding values are 298 and 300 Hz, respectively.³³ A large coupling constant ($^1J_{\text{C-F}}$) increase is observed under the influence of increasing electron withdrawal in going from $\text{ClCH}_2\text{ClCHCH}_2\overline{\text{CFCF}_2\text{OSO}_2}$ or $\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$ to $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$ or $\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$ ³⁸

TABLE II

SUBSTITUTION EFFECT ON THE ^{13}C NMR CHEMICAL SHIFTS OF

Sultone	$\text{X}(\overline{\text{XCFCF}_2\text{OSO}_2})$	Chemical shifts (ppm)	
		XCF	CF_2
$\text{CF}_3\overline{\text{CHCF}_2\text{OSO}_2}$	H	≈ -30	≈ 0
$\text{CF}_3\overline{\text{CFCF}_2\text{OSO}_2}$	CF_3	-13.5	-3.0
$\text{SF}_5\overline{\text{CHCF}_2\text{OSO}_2}$	H	≈ -30	≈ 0
$\text{SF}_5\overline{\text{CFCF}_2\text{OSO}_2}$	SF_5	+2.3	0
$\text{SF}_4\text{Cl}\overline{\text{CHCF}_2\text{OSO}_2}$	SF_4Cl	$\approx +13$	≈ 0
$\text{CF}_3\text{OCF}_2\overline{\text{CFCF}_2\text{OSO}_2}$	CF_3OCF_2	-15.1	-1.2
$\text{CH}_2\text{ClCHClCH}_2\overline{\text{CFCF}_2\text{OSO}_2}$	$\text{CH}_2\text{ClCHClCH}_2$	-7.2	+0.3
$\text{SF}_4 = \overline{\text{CCF}_2\text{OSO}_2}$	$=\text{SF}_4$	-45.3	+1

TABLE III

 ^{13}C NMR DATA OF SOME β -FLUOROSULTONES

Sultone	Chemical Shifts (ppm)	Coupling Constant (Hz)	Ref.
$\text{FSF}_4\text{CHC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CH 99.6 (d,p,m) CF ₂ 112 (br,p)	$J_{1,2} = 293.0$	34
$\text{SF}_4\text{ClCHC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CH 108.8 (d,m) CF ₂ 113.4 (t)	$J_{1,2} = 294.0$	36
$\text{SF}_4=\text{CC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	=C 80.7 ($\approx$ p,t) CF ₂ 114.5 (t,p)	$J_{1,2} = 282.4$	36
$\text{CF}_2\text{C}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CF ₂ 126 (t,t) CF ₂ O 113.5 (t,t)	$J_{1,2} = 294.3$	38
$\text{CF}_3\text{CFC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CF ₃ 117.2 (q,d,m) CF 112.5 (d,m) CF ₂ 110.5 (t,d)	$J_{1,2} = 293.6$	38
$\text{CF}_3\text{CHC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CF ₃ 118.4 (q) CH 79.3 (q,d,d) CF ₂ 111.2 (t,q)	$J_{1,2} = 291.0$	38
$\text{FSF}_4\text{CFC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CF 128.3 (d,m) CF ₂ 113.5 (t,p)	$J_{1,2} = 298.0$	38
$\text{CF}_3\text{OCF}_2\text{CFC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CF ₃ 119.2 (q,m) OCF ₂ 114.7 (m) CF ₂ 112.3 (d,d,m) CF 110.9 (d,m)	$J_{1,2} = 294.0$	38
$\text{CH}_2\text{ClCHClCH}_2\text{CFC}_{(2)}\text{F}_{2(1)}\text{OSO}_2$	CF ₂ 113.8 (d,d,d) CF 118.9 (d,d,d) CH ₂ 32.4 (d) CH 51.7 (s) CH ₂ 46.8 (s)	$J_{1,2} = 290.0$	37

TABLE IV

 ^{13}C NMR DATA FOR $\text{SF}_5\text{C}_\alpha\text{C}_\beta$ COMPOUNDS²³

$\text{SF}_5\text{CHFCF}_2\text{Br}^2$ $\text{F}^{\text{A}}\text{F}_4^{\text{B}}\text{SC}_\alpha\text{HFC}_\beta\text{F}_2\text{Br}$	$\delta_\alpha = 108.15$ (d-d-d-p) $\delta_\beta = 114.87$ (d-d-d)	$J_{\text{F}_\alpha\text{C}_\alpha} = 249.0$ $J_{\text{BC}_\alpha} = 23.3$ $J_{\text{F}_{\beta_1}\text{C}_\alpha} = 36.0$ (27.0) $J_{\text{F}_{\beta_2}\text{C}_\alpha} = 27.0$ (36.0) $J_{\text{F}_{\beta_1}\text{C}_\beta} = 315.4$ (307.8) $J_{\text{F}_{\beta_2}\text{C}_\beta} = 307.8$ (315.4) $J_{\text{F}_\alpha\text{C}_\beta} = 30.2$
$\text{F}_5\text{SC}^{\text{A}}(\text{SO}_2\text{F}) = \text{C}^{\text{B}} = \text{O}$	$\delta_\alpha = 86.28$ (d-p) $\delta_\beta = 174.81$ ($\approx$ pentet) (ill-resolved)	$J_{\text{SO}_2\text{F}-\alpha} = 39.70$ $J_{\text{B}-\alpha} = 32.46$ $J_{\text{B}-\beta} \approx 3.3$
$\text{SF}_5\text{CF}_2\text{CF}_2\text{I}^2$ $\text{F}^{\text{A}}\text{F}_4^{\text{B}}\text{SC}_\alpha\text{F}_2\text{C}_\beta\text{F}_2\text{I}$	$\delta_\alpha = 119.72$ (t,p) $\delta_\beta = 91.30$ (t,t)	$J_{\text{BC}_\alpha} = 25.9$ $J_{\text{F}_\alpha\text{C}_\alpha} = 305.5$ $J_{\text{F}_\beta\text{C}_\alpha} = 34.5$ $J_{\text{F}_\beta\text{C}_\beta} = 323.0$ $J_{\text{F}_\alpha\text{C}_\beta} = 41.0$
$\text{SF}_5\text{C}(\text{SO}_2\text{F})\text{CFO}^-\text{Cs}^{+1}$ $\text{SF}_5\text{CH}(\text{SO}_2\text{F})\text{COF}^2$ $\text{SF}_5\text{C}(\text{SO}_2\text{F}) = \text{C} = \text{O}^2$ $\text{SF}_5\text{C}(\text{SO}_2\text{F})=\text{CHOSi}(\text{CH}_3)_3$	$\delta_\alpha = 104.33$ $\delta_\alpha = 88.5$ $\delta_\alpha = 86.28$ $\delta_\alpha = 126.95$	$\delta_\beta = 157.5$ $\delta_\beta = 146.8$ $\delta_\beta = 174.81$ $\delta_\beta = 159.36$
1. in CD_3CN ; 2. in CDCl_3		

TABLE V

 ^{13}C NMR DATA FOR SF_5 - EPOXIDES²³

$ \begin{array}{c} \text{F}^{\text{A}}\text{F}_4^{\text{B}}\text{S} \\ \\ \text{C}_\alpha \text{---} \text{C}_\beta \\ \quad \diagup \quad \diagdown \\ \text{X} \quad \text{O} \quad \text{F}^2 \end{array} $ <p style="text-align: right;">X = H or F</p>		
$ \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{F}_5\text{SC}_\alpha\text{F} \text{---} \text{C}_\beta\text{F}_2 \end{array} $	$\delta_\alpha = 107.4 \text{ (d,m)}$ $\delta_\beta = 107.73 \text{ (t,d)}$	$J_{\text{BC}_\alpha} = -$ $J_{\text{F}_\alpha\text{C}_\alpha} \approx 337$ $J_{\text{F}_\beta\text{C}_\alpha} = -$ $J_{\text{F}_\beta\text{C}_\beta} = 344.6$ $J_{\text{F}_\alpha\text{C}_\beta} = 18.0$
$ \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{F}_5\text{SC}_\alpha\text{F} \text{---} \text{C}_\beta\text{F}_2 \end{array} $	$\delta_\alpha = 81.45 \text{ (d,p)}^*$ $\delta_\beta = 108.40 \text{ (t)}$	$J_{\text{BC}_\alpha} = 29$ $J_{\text{HC}_\alpha} = 205.7$ $J_{\text{F}_\beta\text{C}_\alpha} = -$ $J_{\text{F}_\beta\text{C}_\beta} = 295.6$ $J_{\text{HC}_\beta} = 0.0$
X ^{13}C spectra are run in CDCl_3 solution.		
* The individual bands show further structure, but they are only ill-resolved.		

TABLE VI

¹³C NMR DATA FOR SF₅-ETHANE SULFONIC ACIDS¹ (40)

I. $ \begin{array}{c} \text{H}_\alpha \quad \text{Y}_{\beta_2} \\ \quad \\ \text{F}^{\text{A}}\text{F}_4^{\text{B}} - \text{C}_\alpha - \text{C}_\beta - \text{SO}_3\text{H} \\ \quad \\ \text{X}_\alpha \quad \text{Y}_{\beta_1} \end{array} \quad \text{X, Y = H, F} $			
SF ₅ CH ₂ CH ₂ SO ₃ H	$\delta_\alpha = 65.4 \text{ (p)}$ $\delta_\beta = 46.9 \text{ (p)}$	$J_{\text{BC}_\alpha} = 15.9$ $J_{\text{BC}_\beta} = 4.7$	
SF ₅ CH ₂ CH ₂ SO ₃ Na	$\delta_\alpha = 65.4 \text{ (p)}$ $\delta_\beta = 46.9 \text{ (p)}$	$J_{\text{BC}_\alpha} = 15.9$ $J_{\text{BC}_\beta} = 4.7$	
SF ₅ CH ₂ CH ₂ SO ₃ Li (41)	$\delta_\alpha = 67.2 \text{ (p)}$ $\delta_\beta = 48.2 \text{ (p)}$	$J_{\text{BC}_\alpha} = 15.2$ $J_{\text{BC}_\beta} = 4.5$ $J_{\text{HC}_\beta} = 140$	

$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Li}$ (41)	$\delta_\alpha = 67.2$ (p) $\delta_\beta = 116.9$	$J_{\text{BC}_\alpha} = 17.4$ $J_{\text{CF}_2\text{C}_\alpha} = 20.9$ $J_{\text{HC}_\alpha} = 144.24$ $J_{\text{BC}_\beta} = 0$ $J_{\text{CF}_2\text{C}_\beta} = 281.0$	
$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	$\delta_\alpha = 66.5$ (t,p) $\delta_\beta = 117.4$ (t,p)	$J_{\text{BC}_\alpha} = 17.2$ $J_{\text{BC}_\beta} = 2.1$	$J_{\text{C}_\alpha\text{CF}_2} = 20.2$ $J_{\text{C}_\beta\text{CF}_2} = 281.5$
$\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	$\delta_\alpha = 105.6$ (d,d,d,p) $\delta_\beta = 114.7$ (d,d,d)	$J_{\text{BC}_\alpha} = 22.4$ $J_{\text{BC}_\beta} = 0.0$	$J_{\text{F}_\alpha\text{C}_\alpha} = 241.9$ $J_{\text{F}_{\beta_1}\text{C}_\alpha} = 22.2$ (36.6) $J_{\text{F}_{\beta_2}\text{C}_\alpha} = 36.6$ (22.2) $J_{\text{F}_\alpha\text{C}_\beta} = 28.0$ $J_{\text{F}_{\beta_1}\text{C}_\beta} = 294.8$ (282.0) $J_{\text{F}_{\beta_2}\text{C}_\beta} = 282.0$ (294.8)
$\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Li}$ (41)	$\delta_\alpha = 106.5$ $\delta_\beta = 114.7$		$J_{\text{F}_\alpha\text{C}_\beta} = 24.2$ $J_{\text{F}_{\beta_1}\text{C}_\beta} = 291.0$ (278.6) $J_{\text{F}_{\beta_2}\text{C}_\beta} = 278.6$ (291.0)

In the ^{13}C spectra of pentafluorothioalkyl sulfonic acids, the chemical shift sequence of $\text{C}_\alpha\text{C}_\beta$ in $\text{SF}_5\text{C}_\alpha\text{C}_\beta$ is inverted in going from $\text{F}_5\text{SCH}_2\text{CH}_2\text{SO}_3\text{H}$ to the two fluorinated acids. The two carbons appear as a pentet and are readily identified by the magnitude of the CB_4 coupling: $J_{\text{C}_\alpha\text{B}_4} = 14\text{--}23$ Hz and $J_{\text{C}_\beta\text{B}_4} = 0\text{--}7$ Hz, as established by measuring the ^{13}C spectra of SF_5 and SF_4X compounds.

In no case was coupling of the axial fluorine of the SF_5 group to either C_α or C_β observed.

TABLE VII

^{13}C NMR DATA FOR SF_5 -METHANE SULFONIC ACIDS² (14)

II. $\text{F}^{\text{A}}\text{F}_4^{\text{B}}\text{S} - \text{C}_\alpha\text{F}_2\text{SO}_3\text{H}$		
$\text{SF}_5\text{CH}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	$\delta_\alpha = 77.6$ (m)	
$\text{SF}_5\text{CHFSO}_3\text{H}$	$\delta_\alpha = 112.4$ (d,p,d)	$J_{\text{AC}_\alpha} = 6.0$ $J_{\text{BC}_\alpha} = 18.1$ $J_{\text{F}_\alpha\text{C}_\alpha} = 267.1$
$\text{SF}_5\text{CF}_2\text{SO}_3\text{H} \cdot 2.5 \text{ H}_2\text{O}$	$\delta_\alpha = 127.2$ (t,p,d)	$J_{\text{F}_\alpha\text{C}_\alpha} = 336.3$ $J_{\text{BC}_\alpha} = 18.8$ $J_{\text{AC}_\alpha} = 2.5$
<u>Notes</u> 1. The solvent was D_2O . For (I) and (II) compounds all chemical shifts are relative to TMS. 2. The solvent for $\text{SF}_5\text{CH}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ was CDCl_3 and for $\text{SF}_5\text{CF}_2\text{SO}_3\text{H} \cdot 2.5 \text{ H}_2\text{O}$ was CD_3CN .		

TABLE VIII

¹³C NMR DATA FOR PENTAFLUOROTHIO SULTONE* (34)

$\begin{array}{c} \text{F}^{\text{A}}\text{F}_3^{\text{B}}\text{S}-\text{C}_{\alpha}\text{HC}_{\beta}\text{F}_2 \text{ (I)} \\ \quad \\ \text{O}_2\text{S}-\text{O} \end{array}$	$\delta_{\alpha} = 99.6 \text{ (d,p,m)}$ $J_{\text{B}\cdot\text{C}_{\alpha}} = 23$	$\delta_{\beta} = 112.0 \text{ (br.p)}$ $J_{\text{BC}_{\beta}} = 3.8$ $J_{\text{F}_{\beta}\text{C}_{\beta}} = 293$
$\begin{array}{c} \text{F}^{\text{A}}\text{F}_3^{\text{B}}\text{S}-\text{C}_{\alpha}\text{H}-\text{C}_{\beta}\text{OF} \text{ (II)} \\ \\ \text{SO}_2\text{F} \end{array}$	$\delta_{\alpha} = 88.5 \text{ (d,d,p,d)}$ $J_{\text{B}\cdot\text{C}_{\alpha}} = 21.6$	$\delta_{\beta} = 146.8 \text{ (d,p)}$ $J_{\text{BC}_{\beta}} = 2.9$ $J_{\text{F}_{\beta}\text{C}_{\beta}} = 363.5$
$\text{F}^{\text{A}}\text{F}_3^{\text{B}}\text{SC}_{\alpha}\text{H}_2\text{SO}_2\text{F} \text{ (III)}$	$\delta_{\alpha} = 77.6 \text{ (m)}$	
$\text{F}^{\text{A}}\text{F}_3^{\text{B}}\text{S}-\text{C}_{\alpha}\text{H}_2-\text{SO}_3\text{H}\cdot\text{H}_2\text{O} \text{ (V)}$	$\delta_{\alpha} = 82.8 \text{ (br.s)}$	
* Solvent CDCl ₃ : chemical shifts in ppm relative to TMS and coupling constants in Hz. Abbreviations: s = singlet, d=doublet, t=triplet, p=pentet, br=broadened, m=multiplet.		

Chemical shift values for the carbon next to an SF₅ group, C_α, range from 77.6 to 99.6 ppm; for C_β in I and II the values are 112.0 and 146.8 ppm, respectively. Compound V has only a broadened singlet at 77.6 ppm while III has a band center of a complex multiplet at 82.8 ppm.

TABLE IX

¹³C NMR DATA FOR SULFONYL FLUORIDES $\overset{\text{a}}{\text{CXY}}(\overset{\text{b}}{\text{OCF}_2}\overset{\text{c}}{\text{CF}_2}\text{SO}_2\text{F})_2^*$
 AND
 $\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na})_2$ (43)

CXY	OCF ₂	CF ₂ S
$\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (1) $\delta = 85.3$ (p) $J_{\text{F}_{\text{b-a}}} = 5.3$	$\delta = 116.8$ (t,t,d) $J_{\text{F}_{\text{b-b}}} = 280.8$ $J_{\text{F}_{\text{c-b}}} = 28.7$ $J_{\text{SO}_2\text{F-b}} = 3.4$	$\delta = 114.0$ (t,t,d) $J_{\text{F}_{\text{c-c}}} = 301.3$ $J_{\text{F}_{\text{b-c}}} = 41.0$ $J_{\text{SO}_2\text{F-c}} = 36.0$
$\text{CHF}(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (2) $\delta = 107.4$ (d,p) $J_{\text{F}_{\text{a-a}}} = 264.4$ $J_{\text{F}_{\text{b-a}}} = 4.9$	$\delta = 114.8$ (t,t,d,d) $J_{\text{F}_{\text{b-b}}} = 285.3$ $J_{\text{F}_{\text{c-b}}} = 29.8$ $J_{\text{SO}_2\text{F-b}} = 2.6$ $J_{\text{F}_{\text{a-b}}} = 2.6$	$\delta = 112.6$ (t,t,d) $J_{\text{F}_{\text{c-c}}} = 302.4$ $J_{\text{F}_{\text{b-c}}} = 38.6$ $J_{\text{SO}_2\text{F-c}} = 38.6$
$\text{CF}_2(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (3) $\delta = 118.0$ (t) $J_{\text{F}_{\text{a-a}}} = 278.9$	$\delta = 113.7$ (t,t,d,d) $J_{\text{F}_{\text{b-b}}} = 290.4$ $J_{\text{F}_{\text{c-b}}} = 30.1$ $J_{\text{F}_{\text{a-b}}} = 1.5$ $J_{\text{SO}_2\text{F-b}} = 3.0$	$\delta = 111.8$ (t,t,d,t) $J_{\text{F}_{\text{c-c}}} = 302.5$ $J_{\text{F}_{\text{b-c}}} = 38.5$ $J_{\text{SO}_2\text{F-c}} = 38.5$ $J_{\text{F}_{\text{a-c}}} = 1.2$
$\text{CH}_2(\text{OCF}_2\text{CF}_2\text{SO}_3\text{Na})_2$ (6) $\delta = 83.8$	$\delta = 118.2$ (t,t) $J_{\text{F}_{\text{b-b}}} = 276.2$ $J_{\text{F}_{\text{c-b}}} = 32.0$ $J_{\text{F}_{\text{b-a}}} = 5.8$	$\delta = 113.0$ (t,t) $J_{\text{F}_{\text{c-c}}} = 286.3$ $J_{\text{F}_{\text{b-c}}} = 35.6$

* Chemical shifts in ppm, coupling constants in Hz. Splitting patterns of **1**, **2** and **6** listed for the proton-decoupled spectra. In the proton-coupled spectra, the splitting patterns and couplings found were: **1**, CH₂ (t,p), OCF₂ (t,t,d,t) and J_{Hb} = 5.3, J_{Ha} = 178.8 Hz; **2**, CHF (d,d,p), OCF₂ (t,t,d,d) and J_{Hb} = 2.6, J_{Ha} = 214.8 Hz; **6**, CH₂ (t,p), OCF₂ (t,t,t) and J_{Hb} = 5.0.

The ¹³C NMR proton decoupled spectra of compounds **1**, **2**, and **3** show variations in the coupling between the carbon a and the OCF₂ fluorines; values of 5.3 and 4.9 Hz were obtained for compounds **1** and **2**, respectively whereas with compound **3** no similar type coupling was observed. Also, coupling was observed between the OCF₂ carbon b and the F_a fluorines; values of 2.6 and 1.5 Hz were found for compounds **2** and **3**, respectively. The ¹³C NMR proton-coupled spectrum of the CH₂ group in compound **1** and **6** was found to have the expected triple-pentet pattern with a coupling of 178.8 and 177.4 Hz, respectively; for compound **2** the CHF group exhibited a d,d,p pattern with a hydrogen coupling of 214.8 Hz.

TABLE X

 ^{13}C NMR DATA FOR $\text{R}^1\text{CH}_2\text{CH}(\text{R}^2)\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (44)

Compound	R^1	R^2	a R^1CH_2	b CHR^2	c CH_2O	d CF_2	e CF_2S
(2) $\text{HOCH}_2\text{CH}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	HO	$\text{C}_6\text{H}_5\text{CH}_2$ benzylic 73.9 aromatic 129.2 128.6 128.5 128.4	$\delta=62.9$ $J_{\text{H}_{\text{a-a}}}=142.9$	$\delta=70.0$ $J_{\text{H}_{\text{b-b}}}=142.9$	$\delta=68.8$ $J_{\text{F}_{\text{e-c}}}=4.0$	$\delta=116.9$ $J_{\text{F}_{\text{d-d}}}=271.3$ $J_{\text{F}_{\text{e-e}}}=27.5$ $J_{\text{SO}_2\text{F-d}}=3.5$	$\delta=114.5$ $J_{\text{F}_{\text{e-e}}}=291.7$ $J_{\text{F}_{\text{e-e}}}=42.8$ $J_{\text{SO}_2\text{F-e}}=30.2$
(3) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	$\text{C}_6\text{H}_5\text{CH}_2$ benzylic 72.8 aromatic same as (2)	HO	$\delta=71.7$ $J_{\text{H}_{\text{a-a}}}=142.9$	$\delta=68.5$ $J_{\text{H}_{\text{b-b}}}=142.9$	$\delta=68.9$ $J_{\text{F}_{\text{e-c}}}=4.5$	Same as (2)	Same as (2)
(4) $\text{ClCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	Cl	HO	$\delta=44.9$ $J_{\text{H}_{\text{a-a}}}=151.5$	$\delta=68.9$ $J_{\text{H}_{\text{b-b}}}=141.4$	$\delta=66.6$ $J_{\text{F}_{\text{e-c}}}=4.2$	$\delta=116.0$ $J_{\text{F}_{\text{d-d}}}=275.9$ $J_{\text{F}_{\text{e-d}}}=28.0$ $J_{\text{SO}_2\text{F-d}}=3.8$	$\delta=113.7$ $J_{\text{F}_{\text{e-e}}}=301.8$ $J_{\text{F}_{\text{e-e}}}=41.6$ $J_{\text{SO}_2\text{F-e}}=34.4$
(5) $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$	HO	HO	$\delta=63.0$ $J_{\text{H}_{\text{a-a}}}=142.3$	$\delta=70.1$ $J_{\text{H}_{\text{b-b}}}=143.3$	$\delta=68.7$ $J_{\text{F}_{\text{e-c}}}=4.1$	$\delta=116.9$ $J_{\text{F}_{\text{d-d}}}=273.4$ $J_{\text{F}_{\text{e-d}}}=27.9$ $J_{\text{SO}_2\text{F-d}}=3.7$	$\delta=114.6$ $J_{\text{F}_{\text{e-e}}}=300.5$ $J_{\text{F}_{\text{e-e}}}=42.7$ $J_{\text{SO}_2\text{F-e}}=34.3$

* Chemical Shifts in ppm, coupling constants in Hz

^{13}C -NMR spectral data for these fluorocarbon sulfonyl fluorides containing aromatic primary and secondary alcohols, chlorohydrin and diol groups were similar in that the methylene groups nearest the fluoroalkyl groups had chemical shifts ranging from 66.6 to 68.9 ppm and exhibited $J_{\text{F}_{\text{e-c}}}$ coupling of 4.0-4.5 Hz. The methine carbons, recognized as the only doublets in the ^1H -coupled spectra, were found in the range of 68.5 to 70.1 ppm and showed similar $J_{\text{H}_{\text{b-b}}}$ coupling of 141.4 to 143.3 Hz. The $\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ portions of the spectra are all quite similar and agree with published results.⁴³

TABLE XI

¹³C NMR DATA FOR NEW SULFONYL FLUORIDES⁴⁵

$\text{SO}_2(\text{CF}_2\text{SO}_2\text{F})_2$	$\delta_{\text{CF}_2} = 119.7$ $^1J_{\text{FA}} = 347.0$ $^1J_{\text{FB}} = 349.0$ $^2J_{\text{C-SF}} = 38.3$ $^3J_{\text{C-F}_2} = 2.1$	
$\text{CF}_2(\text{SO}_2\text{F})_2$	$\delta_{\text{CF}_2} = 116.5 \text{ (t,t)}$ $^1J = 334.2$ $^2J = 40.6$	
$^1\text{CF}_3\text{SO}_2^2\text{CF}_2\text{SO}_2^3\text{CF}_2\text{SO}_2\text{F}$	$\delta_{1\text{C}} = 119.1 \text{ (q,t)}$ $^1J_{1\text{C}} = 332.1$ $^3J_{1\text{C}} = 0.6$ $\delta_{3\text{C}} = 119.6 \text{ (t,d)}$ $^1J_{3\text{C}} = 346.0$ $^2J_{3\text{C}} = 37.75$	$\delta_{2\text{C}} = 121.4 \text{ (t,q,d)}$ $^1J_{2\text{C}} = 354.2$ $^3J_{1\text{CF}_3} = 3.15$ $^4J_{2\text{C}} = 2.2$

* Chemical shifts in ppm, coupling constants in Hz.

CHAPTER II

EXPERIMENTAL

APPARATUS

Vacuum Line

The vacuum system used in this work consisted of a manifold evacuated by means of a Welch Duo-Seal rotary vacuum pump operating in conjunction with a liquid nitrogen cooled trap. The manifold was made of 25 mm inside diameter Pyrex tubing fitted with four taps. Each tap had an Eck and Krebs 2 mm high vacuum stopcock, to which a Pyrex 10/30 outer glass joint was attached. The Frederick Company Televac thermocouple gauge was used to monitor the pressure in the 1-100 micron range, while a mercury manometer or Heise-Bourdon gauge was used to measure pressures in the 1-760 mm Hg range. All joints and stopcocks were lubricated with Fisher Scientific Fluorolube GR-290 or Arthur Thomas' Lubriseal grease; connections requiring a wax seal were obtained using Haolocarbon Corporation's Halocarbon wax.

Reaction Vessels

1. Pyrex-Glass Reaction Vessels

For measuring SF_5Br , 3-liter Pyrex glass vessels were used. The vessel had 2 mm high vacuum Teflon stopcock, and

was tipped with Pyrex 10/30 standard taper ground glass inner joint for attaching to the vacuum line. Heavy wall Pyrex-glass Carius tubes (130 mL) were also used. For distillation, either at reduced or atmospheric pressure, a "Bantam Ware" Kontes Pyrex-glass distillation apparatus with 14-20 or 19-22 ground joints were used. The unit was connected to the atmosphere via a trap cooled to -78°C or to the vacuum line via a trap cooled to -196°C .

2. Metal High Pressure Vessel

Pentafluorothio bromide was prepared in a 150 mL Monel vessel equipped with a Whitey stainless steel valve and tipped with a brass 10/30 inner joint.

3. Dry Box

For the manipulation of moisture sensitive materials a Vacuum Atmospheres Corporation Dri-Lab HE-43-42 was used. Nitrogen gas, dried over heated molecular sieve, was used as the dry box atmosphere. The atmosphere inside the box was dried with phosphorous pentoxide (P_4O_{10}). Moisture was kept below 10 ppm, the point at which titanium tetrachloride begins to fume in moist air.⁴⁶

PHYSICAL METHODS

Infrared Spectra

The infrared spectra from $4600\text{--}400\text{ cm}^{-1}$ were obtained as capillary films on potassium bromide plates for liquid

samples using a PERKIN-ELMER 1600. The gaseous samples were run in a cell with KBr windows; the cell path length was 10 cm.

Nuclear Magnetic Resonance Spectra

The ^1H and ^{19}F nuclear magnetic resonance spectra were recorded with a Varian EM-390 spectrometer operating at 90.0 MHz for proton and at 84.67 MHz for fluorine resonances. A Bruker AMX-400 instrument operating at 400 MHz for ^1H , 376.8 MHz for ^{19}F was employed as well.

TMS (CCH_3) $_4\text{Si}$) and CFCl_3 were used as internal standards for ^1H resonance and ^{19}F resonance, respectively. In ^{19}F spectra, chemical shifts upfield from CFCl_3 are assigned negative values.

The ^{13}C NMR spectra were obtained using a Bruker AMX-400 spectrometer operating at 100.6 MHz. TMS was used as an internal standard for ^{13}C resonance.

Mass Spectra

The mass spectra were obtained using a Hewlett-Packard HP5890 Series II gas chromatograph with a 5970 mass selective detector utilizing a 25 meter DB-5 column, operating at 70 eV. These analyses were performed at the Portland Veterans Hospital.

Sublimation

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

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

Melting point

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

REAGENTS

Br₂: Analytical reagent bromine was purchased from Mallinckrodt and was used without further purification.

BrF₃: The BrF₃ was purchased from Ozark-Mahoning-Pennwalt.

SF₄: The SF₄ was purchased from Ozark-Mahoning-Pennwalt.

CsF: The CsF was purchased from Peninsular Chemical Research Corporation (PCR).

1,1,2-trifluoro-1,4-pentadiene; ($\text{CH}_2=\text{CHCH}_2\text{CF}=\text{CF}_2$)

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

Tetramethyl silane; (TMS)

(CH_3)₄Si was purchased from Baker and was used without further purification.

Mercury

Hg (analytical reagent grade) was purchased from

American Scientific & Chemicals.

Benzoyl Peroxide

$(C_6H_5CO)_2O_2$ was purchased from Aldrich and was used without further purification.

Composition of Solutions for ^{13}C Studies

$SF_5CH_2CHBrCH_2CF=CF_2$ (0.19 g)	$CDCl_3$ (0.43 g)
$SF_5CH=CHCH=CHCl$ (0.52 g)	$CDCl_3$ (0.47 g)
$CH_3OCF_2CF_2SO_2F$ (0.48 g)	$CDCl_3$ (0.45 g)
$CH_3CH_2CF_2CF_2OCF_2CF_2SO_2F$ (0.38g)	$CDCl_3$ (0.30 g)
$BrCH_2CH_2OCF_2CF_2SO_2F$ (0.11 g)	$CDCl_3$ (0.10 g)
$(CF_3)_2CFCH_2CH_2OCF_2CF_2SO_2F$ (0.37 g)	$CDCl_3$ (0.26 g)
$CH_2=CHCF_2CF_2OCF_2CF_2SO_2F$ (0.36 g)	$CDCl_3$ (0.29 g)
$C_6H_5CH_2OCF_2CF_2SO_2F$ (0.04 g)	$CDCl_3$ (0.24 g)
$C_6F_5CH_2OCF_2CF_2SO_2F$ (0.15 g)	$CDCl_3$ (0.46 g)
$C_6H_5CH_2OCF_2CF(CF_3)SO_2F$ (0.778 g)	$CDCl_3$ (0.312 g)

CHAPTER III

SYNTHESIS OF NEW SF_5 -OLEFIN: $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$

Introduction

A new SF_5 -olefin was made by addition of pentafluorothio bromide to a fluorinated diene. The addition of pentafluorothio chloride to acetylene also gave an SF_5 containing diene⁵⁰ which was previously prepared but only characterized partially.

It is known that the incorporation of pentafluorothio groups (SF_5) (pentafluoro- λ^6 -sulfanyl) into molecular systems can bring about significant changes in their physical, chemical and biological properties. These properties are useful for various applications, such as solvents for polymers, perfluorinated blood substitutes, surface-active agents (surfactants), fumigants, and as thermally and chemically stable compounds.⁸

The syntheses of these compounds are the subjects of ongoing studies.⁴⁰ One compound of particular interest is $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, which could be a precursor to new cyclic and polymeric products.

The reaction of pentafluorothio bromide with fluorinated diene is a good pathway for preparation of new fluorinated monomers and polymers containing the

pentafluorothio group (SF_5); thus the reaction of 1,1,2-trifluoro-1,4-pentadiene with pentafluorothio bromide was studied in order to obtain $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$.

The new product was a clear colorless liquid that boils at $51 \pm 3^\circ\text{C}/15 \text{ mm Hg}$.

The by-product from the addition reaction of pentafluorothio chloride to acetylene, $\text{SH}_5\text{CH}=\text{CHCH}=\text{CHCl}$ was characterized using NMR, mass, and IR spectroscopies.⁵⁵ This molecule was also found to be polymerized by radical initiator like benzoyl peroxide to give a brownish oily polymer, with a yield of 12%. In addition, the residual unsaturation should allow for cross-linking if so desired.⁶²

EXPERIMENTAL

Preparation of SF_5Br

Dried CsF (20g, 130.67 mmol) was charged into a 150 ml stainless steel vessel. Bromine trifluoride (31.9g, 232.8 mmol) was added to the vessel by vacuum transfer, then bromine (46.7 g, 291.8 mmol) was added. The reaction mixture was kept at room temperature for one week. Then SF_4

(75.4 g, 698.2 mmol) was added in two portions. First, 40.0 g were added, then after two weeks 35.4 g were added. The crude SF_5Br (176.6 g) was transferred from the stainless steel vessel at -78°C by vacuum distillation during a 4 hour period. SF_6 and SF_4 were major by-products. The crude SF_5Br was shaken with mercury (20-30 g for 170 g of crude SF_5Br) at room temperature until the bromine color was gone resulting in a greenish yellow. This had to be repeated several times.

Reaction of SF_5Br with $\text{CH}_2=\text{CHCH}_2\text{CF}=\text{CF}_2$

Into an evacuated 75 mL Hoke stainless steel vessel equipped with a Whitey stainless steel valve, SF_5Br (16.15g, 78.0 mmol) and $\text{CH}_2=\text{CHCH}_2\text{CF}=\text{CF}_2$ (8.97g, 73.5 mmol) were condensed at -196°C . The mixture was slowly warmed to and held at room temperature for 1 day, then heated to 50°C with occasional shaking over 1 week. The pure product, $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ (5.6 g, 17.1 mmol), was obtained by distillation of the liquid product in a Kontes (19/22) all glass apparatus at 15 mm Hg (b.p. $51 \pm 3^\circ\text{C}$). This procedure gave a yield of 23.2% of $\text{CH}_2=\text{CHCH}_2\text{CF}=\text{CF}_2$.

Infrared Spectra

The infrared spectrum of the SF_5 -olefin had the following bands (cm^{-1}) listed in Table XII and exhibit the features of the SF_5 -olefin. The presence of the highly electronegative fluorine as part of the olefinic bond leads

to a high frequency for the C=C stretching frequency. This characteristic C=C stretching frequency occurs with medium intensity at 1802 cm^{-1} for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$. A dominant feature of the spectrum is the absorption band due to the SF_5 group. These bands are centered about 850 cm^{-1} and can be directly related to the vibrational mode of the SF_5 group. Cross and coworkers⁴⁷ found that the SF_5 group should have the most intense bands in the $850\text{--}920\text{ cm}^{-1}$ region due to S-F stretching modes and in the 600 cm^{-1} region due to the S-F deformation modes. Therefore, the band at 845 cm^{-1} for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ is assigned to S-F stretching mode. The S-F deformation mode is located at 603 cm^{-1} for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$.

For compounds containing the C-F group, the C-F stretching absorption band is usually located in $1000\text{--}1100\text{ cm}^{-1}$ region while for CF_2 group, the band is in $1050\text{--}1250\text{ cm}^{-1}$ region⁴⁸. Therefore, the band at 1027 cm^{-1} is assigned to C-F stretch and the bands in $1103\text{--}1302\text{ cm}^{-1}$ region would be assigned to CF_2 stretching mode.

The C-H stretching mode was observed at 2976 cm^{-1} . The C-Br stretching mode was found at 571 cm^{-1} .

TABLE XII

IR DATA FOR $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ (LIQUID)

2976 (w)
1802 (s)
1425 (w-m)
1302 (s)
1273 (m)
1243 (m)
1174 (w-m)
1103 (s)
1027 (w)
845 (vs)
785 (w)
603 (w)
571 (m)

Mass Spectra (M/e) (EI⁺)

The (EI)⁺ mass spectrum listed in the Table XIII were supportive of the assigned structure. The molecular ion peaks were found at 328 [(M-1)⁺, 3.46], 330 [(M+1)⁺, 3.39]. $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ gave a base peak of M/e = 95 assigned to $\text{CF}_2\text{CFCH}_2^+$. Other main fragments were observed at M/e = 127 (SF_5^+), M/e = 108 (SF_4^+), M/e = 89 (SF_3^+), M/e = 70 (SF_2^+) and M/e = 51 (SF^+).

Bromine isotopic peaks due to ^{79}Br and ^{81}Br were found in the mass spectra, as well as sulfur isotopic peaks. Bromine is 50.54% ^{79}Br and 49.46% ^{81}Br , so a peak with M/e =

N should have a companion peak at $M/e = N+2$ with 100% of its relative intensity. Sulfur is 95.0% ^{32}S and 4.22% ^{34}S , so a peak with $M/e = N'$ should have a companion peak at $M/e = N'+2$ with 4.44% of its relative intensity.

For the $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, the $M/e = 136.9$ assigned to $\text{SC}_2\text{H}_2\text{Br}^+$ (relative intensity 5.48) has a companion peak at 138.9 (relative intensity 5.95), and the $M/e = 180.9$ assigned to $\text{SFCH}_2\text{CHBrCC}$ (relative intensity 2.36) has a companion peak at 182.9 (relative intensity 2.26).

Consequently an interesting phenomenon can be observed for ions containing both bromine and sulfur; a run of four peaks is generated due to the presence of four isotope combinations...a (^{79}Br , ^{32}S), a (^{81}Br , ^{32}S), a (^{79}Br , ^{34}S) and a (^{81}Br , ^{34}S) peak. The assigned peaks for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ analyzed were consistent with the structure as written above.

TABLE XIII

MASS SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$

M/e	Rel. Int.	Type
26.1	5.15	C_2H_2^+
27.1	20.71	C_2H_3^+
31.1	8.83	CF^+
33.1	2.02	CH_2F^+
38.1	3.61	C_3H_2^+
39.1	17.44	C_3H_3^+
40.1	1.72	C_3H_4^+
41.1	6.88	C_3H_5^+
45.0	10.18	$\text{C}_2\text{H}_2\text{F}^+$
46.1	5.71	$\text{C}_2\text{H}_3\text{F}^+$
50.1	6.53	CF_2^+
51.0	26.43	$^{32}\text{SF}^+$
52.1	3.38	SFH^+
53.1	6.32	$^{32}\text{SFH}_2^+$, $^{34}\text{SF}^+$
56.0	2.09	C_2S^+ , C_3HF^+
57.0	9.40	C_2HS^+ , CFCH_2C^+ ($=\text{C}_3\text{H}_2\text{F}^+$)
58.1	1.46	$\text{C}_2\text{H}_2\text{S}^+$, $\text{C}_3\text{H}_3\text{F}^+$
59.0	4.56	$\text{C}_2\text{H}_3\text{S}^+$, $\text{C}_3\text{H}_4\text{F}^+$ (CH_2CFCH_2)
64.1	1.69	SFCH^+
65.0	2.32	SFCH_2^+
69.0	54.22	CF_3^+
70.0	11.37	$^{32}\text{SF}_2^+$
71.0	10.23	$\text{C}_4\text{H}_4\text{F}^+$ ($\text{CFCH}_2\text{CHCH}^+$)
72.0	12.05	$^{34}\text{SF}_2^+$, $\text{C}_4\text{H}_5\text{F}^+$
75.0	13.37	$\text{CF}_2\cdot\text{CCH}^+$
76.0	2.87	$\text{CF}_2\text{CCH}_2^+$
77.0	38.09	$\text{CF}_2\cdot\text{CCH}_3^+$
78.9	1.31	$^{79}\text{Br}^+$
80.95	2.19	$^{81}\text{Br}^+$, C_2F_3^+

82.0	2.1	CFC_4H_3^+
89.0	23.63	$^{32}\text{SF}_3^+$
90.0	2.14	SF_3H^+
91.0	7.06	$\text{CBr}^+, ^{34}\text{SF}_3^+$
93.0	2.35	$\text{C}_3\text{F}_3^+ (\text{CF}_2=\text{CFC}^+)$
95.0	100.00	$\text{C}_3\text{F}_3\text{H}_2^+ (\text{CF}_2=\text{CFCH}_2^+)$
96.0	5.57	SF_2CHCH^+
99.0	1.57	$\text{C}_4\text{FS}^+ (^{32}\text{SFC}_4)$
101.0	44.95	$^{34}\text{SFC}_4^+, \text{SF}_3\text{C}^+$
102.0	7.14	SF_3CH^+
104.9	4.29	$\text{C}_2\text{H}_2^{79}\text{Br}^+$
105.9	9.47	$\text{C}_2\text{H}_3^{79}\text{Br}^+$
106.9	5.28	$\text{C}_2\text{H}_2^{81}\text{Br}^+, \text{C}_2\text{H}_4^{79}\text{Br}^+$
107.9	9.95	$\text{SF}_4^+, \text{C}_2\text{H}_3^{81}\text{Br}^+, \text{C}_4\text{H}_3\text{F}_3^+$
113.0	10.56	SF_3C_2^+
119.0	3.48	$\text{C}_5\text{H}_2\text{F}_3^+ (\text{CF}_2=\text{CFCH}_2\text{C}\cdot\text{C})$
120.0	2.65	$\text{C}_5\text{H}_3\text{F}_3^+$
121.0	51.08	$\text{C}_5\text{H}_4\text{F}_3^+, (\text{CF}_2=\text{CFCH}_2\text{CHCH})$
122.0	10.09	$\text{C}_5\text{H}_5\text{F}_3^+, (\text{CF}_2=\text{CFCH}_2\text{CHCH}_2)$
124.9	3.51	$^{32}\text{SF}_3\text{C}_3^+$
126.9	17.84	$^{32}\text{SF}_5^+, ^{34}\text{SF}_3\text{C}_3^+$
128.9	1.60	$^{34}\text{SF}_5^+$
136.9	5.48	$^{32}\text{SC}_2\text{H}_2^{79}\text{Br}^+,$
138.9	5.95	$^{32}\text{SC}_2\text{H}_2^{81}\text{Br}^+, ^{34}\text{SC}_2\text{H}_2^{79}\text{Br}^+, \text{SF}_5\text{C}^+$
140.0	16.17	$^{32}\text{SC}_2\text{H}_3^{79}\text{Br}^+, ^{32}\text{SF}_5\text{CH}^+$
141.0	52.13	SF_5CH_2^+
142.0	2.9	$^{34}\text{SC}_2\text{H}_3^{79}\text{Br}^+, ^{32}\text{SC}_2\text{H}_3^{81}\text{Br}^+, ^{34}\text{SF}_5\text{CH}^+$
154.9	2.30	$^{32}\text{SFC}_2\text{H}_2^{79}\text{Br}^+$
155.9	8.71	$\text{SFC}_2\text{H}_3^{79}\text{Br}^+$
156.9	2.51	$^{32}\text{SFC}_2\text{H}_2^{81}\text{Br}^+, ^{34}\text{SFC}_2\text{H}_2^{79}\text{Br}^+$
157.9	8.12	$\text{SFC}_2\text{H}_3^{81}\text{Br}^+$
180.9	2.36	$\text{C}_5\text{H}_5\text{F}_2^{79}\text{Br}^+ (\text{CFCFCH}_2\text{CHBrCH})$
182.9	2.26	$\text{C}_5\text{H}_5\text{F}_2^{81}\text{Br}^+$
327.8	3.46	$\text{SF}_5\text{CH}_2\text{CH}^{79}\text{BrCHCF}=\text{CF}_2$

329.9	3.39	$\text{SF}_5\text{CH}_2\text{CH}^{\delta 1}\text{BrCHCF}=\text{CF}_2$
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$\alpha \quad \beta \quad \gamma \quad \delta \quad \epsilon$

Nuclear Magnetic Resonance $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$

^1H , ^{19}F and ^{13}C nuclear magnetic resonance spectra of the $\alpha \quad \beta \quad \gamma \quad \delta \quad \epsilon$ $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ were run to help characterize this compound.

For the pentafluorothio compound, the SF_5 group is of major importance in explaining its NMR spectra. The fluorines of the SF_5 group are not all equivalent; the one axial fluorine (A) behaves differently from the four equatorial fluorines (B_4). The SF_5 group is identified as an AB_4 configuration in Pople notation.⁴⁹⁻⁵² The ^{19}F NMR spectrum of the SF_5 group shows a nine line pattern for the axial fluorine, and a twelve line pattern for the equatorial fluorines due to the complex interactions between these two kinds of fluorine.^{50,52,53} Under the conditions for this spectrum, the equatorial and axial pattern appear as a doublet of a multiplet (the B-resonance) and a 9-line pattern, which is actually the superposition of a singlet, a triplet and a quintet.⁵⁰ These SF_5 fluorines influence the ^1H , ^{19}F and ^{13}C NMR spectra through coupling. The equatorial fluorines are prominent in this regard, creating pentet patterns throughout the spectra. Notation for SF_5 compound would be given as follows: " α " and " β " refer to the carbon bonded to, and the carbon next to the carbon bonded to the

SF₅ group respectively. These letters can therefore be used to denote the hydrogens or fluorines bonded to these carbons. From the Pople notation for the configuration of the SF₅ group, AB₄, one can use "A" for "the axial fluorine" and "B" for "the equatorial fluorines" of the SF₅ group. The subscripts "1" and "2" are sometimes needed when two atoms, like hydrogen or fluorine bound to a single carbon, are not magnetically equivalent.

SF₅CH₂CHBrCH₂CF=CF₂ can be predicted to give complex NMR spectra. The β carbon is asymmetric, causing the hydrogens on the α, γ carbon and fluorines on the ε carbon to be non-equivalent.⁵⁴

In the ¹H NMR spectra, three signal groups were found: 13-line group and 8-line group downfield, and a complex multiplet upfield. The large number of peaks shows that this 13-line pattern arises from the coupling of the α carbon hydrogens with the β carbon hydrogens and the four equatorial fluorines of SF₅ group, and a full explanation of this pattern is not simple. If the SF₅Br addition had occurred at the CF=CF₂ end, the α carbon hydrogens would have a simpler splitting pattern, because of no coupling by four equatorial fluorines. The proton spectrum of the β carbon hydrogen gives a complex multiplet. The γ carbon hydrogens couple with δ and ε carbon fluorines and β carbon hydrogen to give a complex multiplet.

The ¹⁹F spectrum shows 5 sets of peaks; 2 sets of peaks

attributable to the SF_5 group and the other three peaks from δ and ϵ carbon fluorines. The axial and equatorial fluorines of the SF_5 group give the characteristic patterns described above. The magnetically inequivalent ϵ carbon fluorines give very different chemical shifts (-102.4 and -121.2 ppm), and split each other into doublets. The coupling value is $J_{F_{\epsilon_1}F_{\epsilon_2}} = 82.0$ Hz. The δ carbon fluorine splits this signal into a doublet of doublets.

The δ carbon fluorine appears as a doublet of doublets of triplets due to the nonequivalent ϵ carbon fluorines and the γ carbon hydrogens. The β carbon hydrogen seems to split this signal into a doublet of doublets of triplets of doublets with coupling of the order of 1.0 Hz or less.

The ^{13}C NMR spectra show five carbons in the molecule, the δ and the ϵ carbon signals downfield and the β and the γ carbon signals upfield, with the α carbon signal intermediate.

The proton decoupled spectra show the α carbon signal as a pentet due to the four equatorial fluorines of the SF_5 group. The β carbon has its signal coupled with the δ fluorine or axial fluorine of SF_5 to give a doublet; weak coupling to the SF_4 group is present. The γ carbon has its signal coupled with the δ fluorine; the δ fluorine splits this signal into a doublet. The δ carbon has its signal coupled with three kinds of fluorines; the nonequivalent ϵ fluorines split this signal into a doublet of doublets, and

the δ fluorine splits this signal into a doublet of doublets of doublets. The ϵ carbon has its signal coupled with three kinds of fluorines, too; δ fluorine splits this signal into a doublet and nonequivalent ϵ fluorines split this into a doublet of doublets of doublets.

The proton coupled ^{13}C NMR spectrum shows the α carbon as a triplet of pentets of doublets ($\alpha\text{-H}$, SF_4 , $\beta\text{-H}$ coupling). The β carbon has its signal coupled with its hydrogen and δ fluorine to give a doublet of doublets; weak coupling to the SF_4 group is present. The γ carbon has its signal coupled with two kinds of hydrogen and the δ fluorine; the β hydrogen splits this signal into a doublet, the δ fluorine splits this into a doublet of doublets and the γ hydrogens split this into a triplet of doublets of doublets. Part of the γ carbon signal was overlapped with an impurity showing a complex multiplet.

The proton coupled ^{13}C NMR subspectrum of carbon δ shows its signal as a complex multiplet. The proton coupled ^{13}C NMR subspectrum of carbon ϵ shows doublet-doublet-doublet-triplet pattern as expected, although part of the spectrum appears to be contaminated with an impurity.

TABLE XIV

$\alpha \quad \beta \quad \gamma$
 $^1\text{H NMR DATA FOR SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF=CF}_2$

$\delta_\alpha = 4.24$	$\delta_\beta = 3.52$	$\delta_\gamma = 4.08$
Integral Ratios $\alpha:\beta:\gamma = 2:1:1.7$		

TABLE XV

$^{19}\text{F NMR DATA FOR SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF=CF}_2$

$\begin{array}{c} \text{F}_{(1)} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{F}_{(2)} \end{array} = \begin{array}{c} \text{C} \\ \diagup \\ \text{F}_{(3)} \\ \diagdown \\ \text{CH}_2(4) \end{array}$			
$\phi_A = +81.6 \text{ (m)}$	$\phi_B = +65.6$ (complex d,t)	$J_{AB}=154.5 \text{ Hz}$	
$\phi_{F(1)} = -102.4$ (d,d)	$\phi_{F(2)} = -121.2$ (d,d)	$\phi_{F(3)} = -174.6$ (d,d,t)	
$J_{(1)(2)} = 82$	$J_{(1)(3)} = 33$	$J_{(2)(3)} = 114$	$J_{(3)(4)} = 20.2$
* Chemical shifts in ppm, coupling constants in Hz.			

TABLE XVI

$AB_4\alpha \quad \beta \quad \gamma \quad \delta \quad \epsilon$
 ^{13}C NMR DATA FOR $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$

α SF_5CH_2	β CHBr	γ CH_2	δ CF	ϵ CF_2
(t,p,d)	(d,d)	(t,d,d)	(d,d,d,m)	(d,d,d,t)
δ 76.2	40.5	35.0	126.0	154.5
$J_{\text{H}\alpha-\alpha} = 144.9$	$J_{\text{H}\beta-\beta} = 157.7$	$J_{\text{H}\gamma-\gamma} = 131.8$	$J_{\text{F}\delta-\delta} = 234.7$	$J_{\text{F}\epsilon_1-\epsilon} = 288.1$ (288.6)
$J_{\text{B}-\alpha} = 14.0$	$J_{\text{F}\delta-\beta} = 2.7$	$J_{\text{F}\delta-\gamma} = 21.3$	$J_{\text{F}\epsilon_1-\delta} = 53.0$ (53.1)	$J_{\text{F}\epsilon_2-\epsilon} = 288.6$ (288.1)
$J_{\text{H}\beta-\alpha} = 3.2$		$J_{\text{H}\beta-\gamma} < 1$	$J_{\text{F}\epsilon_2-\delta} = 53.1$ (53.0)	$J_{\text{F}\delta-\epsilon} = 45.0$
			$J_{\text{H}\gamma-\delta} = 4.1$	$J_{\text{H}\gamma-\epsilon} = 2.9$
* Chemical shifts in ppm, coupling constants in Hz.				

Preparation of $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$

This diene was prepared according to published procedures⁵⁵. For example, a mixture of 12 g of acetylene and 150 g of SF_5Cl was heated in a 400 mL stainless steel pressure vessel for 1 h. at 160°C and 4 hr. at 175°C. Distillation of the liquid product (69 g) gave 33 g (35%) of $\text{SF}_5\text{CH}=\text{CHCl}$, b.p. 65-67°C, 8 g of $\text{SF}_5\text{HC}=\text{CHCl}=\text{CHCl}$ and 28 g of a higher boiling residue. The boiling point of $\text{SF}_5\text{CH}=\text{CHCl}=\text{CHCl}$ was determined in our laboratory and found to be 56-56.5°C/26mm Hg.

Infrared Spectra

The infrared spectrum of the liquid had the following bands (cm^{-1}) listed in Table XVI. An important feature of the spectrum of this new compound is the bands due to the SF_5 group. Cross and coworkers ⁴⁷ found the SF_5 group to have the most intense bands in the $850\text{--}920\text{ cm}^{-1}$ region due to S-F stretch modes and in the 600 cm^{-1} region due to S-F deformation modes. Therefore, the bands at 842 and 904 cm^{-1} are assigned to S-F stretching mode. The S-F deformation modes are found at 599 cm^{-1} . The IR spectra of $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ contain the characteristic absorption band of the olefinic C=C stretching vibration at 1630 and 1583 cm^{-1} . The bands at 1630 cm^{-1} and 1583 cm^{-1} are for C=C stretching vibration in $\text{SF}_5\text{CH}=\text{CH-}$ and $-\text{CH}=\text{CHCl}$, respectively. The C-H stretching vibrations for this compound is located at 3087 cm^{-1} . The C-Cl stretching bands are found at 743 and 767 cm^{-1} .

TABLE XVII

INFRARED DATA FOR $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$

3087 (s)
1630 (s)
1583 (s)
1445 (w)
1344 (m)
1298 (m)
1254 (m)
1196 (m)
1100 (w-m)
969 (s)
904 (vs)
842 (vs)
767 (s)
743 (s)
651 (s)
599 (s)
572 (s)
503 (m)

Mass Spectra (m/e) (EI⁺)

The mass spectrum of $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ (70 eV) had the following m/e peaks:

TABLE XVIII

MASS SPECTRUM OF $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$

M/e	Type
26	C_2H_2^+
51	SF^+
70	SF_2^+
89	SF_3^+
108	SF_4^+
179	$\text{SF}_5\text{CH}=\text{CHCH}=\text{CH}^+$
214	$\text{SF}_5\text{CH}=\text{CHCH}=\text{CH}^{35}\text{Cl}^+$
216	$\text{SF}_5\text{CH}=\text{CHCH}=\text{CH}^{37}\text{Cl}^+$

The molecular ion peaks were found at 214 [M^+], 216 [$(\text{M}+2)^+$]. Other main fragments were observed at $\text{M/e} = 127$ (SF_5^+), $\text{M/e} = 108$ (SF_4^+), $\text{M/e} = 89$ (SF_3^+), $\text{M/e} = 70$ (SF_2^+), and $\text{M/e} = 51$ (SF^+). $\text{SF}_5\text{HC}=\text{CHCH}=\text{CHCl}$ gave a base peak of $\text{M/e} = 51$ assigned to SF^+ .

Chlorine isotopic peaks due to ^{35}Cl and ^{37}Cl were found in the mass spectra as well as sulfur isotopic peaks. Natural chlorine is 75.53% ^{35}Cl and 24.47% ^{37}Cl , so a peak with $\text{M/e} = \text{N}$ should have a companion peak at $\text{M/e} = \text{N}+2$ with 33% of its relative intensity.

For $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, the $M/e = 214$ assigned to molecular peak has a companion peak at 216 with 33% of its relative intensity.

The assigned peaks for $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ analyzed are consistent with the structure assigned.

Nuclear Magnetic Resonance

^1H , ^{19}F , ^{13}C nuclear magnetic resonance spectra of $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ were run to help characterize this compound. As with the $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, the SF_5 group is of major importance in explaining its NMR spectra. See page 37 for a discussion of this group.

In the ^1H NMR spectra, it was observed that the chemical shifts of the α protons were in the region expected for SF_5 hydrocarbons, ~ 4 ppm. However, the pattern for $\text{SF}_5\text{CH}_2=\text{CHCH}=\text{CHCl}$ was a complex second order affair and was ill resolved.

The ^{19}F NMR spectrum shows two AB_4 patterns. The chemical shift values were $\phi_A = 82.6$ and 83.0 ppm with $\phi_B = 63$ ppm.

The ^{13}C NMR spectrum shows four carbons in the molecule; α and β carbon signals downfield and γ and δ carbon signals upfield relatively.

The proton decoupled ^{13}C spectrum shows the α and β carbon signals as a pentet due to the four equatorial fluorines of the SF_5 group. The magnitude of the coupling constant for the α carbon (21.1 Hz) is the same as it is for

the β carbon. γ carbon has its signal coupled with four equatorial fluorine of SF_5 group, though the magnitude of the coupling constant is much less (6.9 Hz). The subspectrum of δ carbon shows a δ carbon signal as a singlet.

The proton coupled ^{13}C spectrum shows α carbon signal as a doublet of pentets of doublets of doublets. α carbon has its signal coupled with three kinds of hydrogen and four equatorial fluorines of SF_5 group. The γ carbon hydrogen splits this signal into a doublet; β carbon hydrogen splits this into a doublet of doublets; four equatorial fluorines of SF_5 group split this into a pentet of doublets of doublets and the α carbon hydrogen splits this into a doublet of pentets of doublets of doublets. β carbon has its signal coupled with three kinds of hydrogen and four equatorial fluorines of SF_5 group. The four equatorial fluorines split this into a pentet and the β carbon hydrogen splits this into a doublet of pentets. However, part of β carbon signal is overlapped with α carbon signal. The splitting of β carbon by γ and α carbon hydrogen is too weak and complex with coupling of the order of 1.5 Hz or less.

The γ carbon subspectrum shows γ carbon signal as a doublet of doublets of triplets. γ carbon has its signal coupled with three kinds of hydrogens and four equatorial fluorines. α and δ hydrogens split this into a triplet; β carbon hydrogen splits this into a doublet of triplets and γ

carbon hydrogen splits this into a doublet of doublets of triplets. The magnitude of the coupling by equatorial fluorine (6.9 Hz) is smaller than that of α , β and δ carbon hydrogen (7.0~7.1 Hz) that the coupling by four equatorial fluorines could not appear in the proton coupled spectrum.

The δ carbon subspectrum shows δ carbon signal as a doublet of doublets of doublets. δ carbon has its signal coupled with three kinds of hydrogen. β carbon hydrogen splits this into a doublet; γ carbon hydrogen splits this into a doublet of doublets and δ carbon hydrogen splits this into a doublet of doublets of doublets.

TABLE XIX

^{19}F NMR DATA FOR $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$

$\phi_A = +82.6, +83.0$ (9 lines pattern)
$\phi_B = +63$ (complex doublet)
$J_{AB} \approx 155.1$ Hz

TABLE XX

α β γ δ
 ^{13}C NMR DATA FOR $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$

SF_5CH	CH	CH	CH
$\delta = 144.2$ (d,p,d,d)	$\delta = 142.0$ (d,p,m)	$\delta = 133.1$ (d,d,t)	$\delta = 124.9$ (d,d,d)
$J_{\text{H}\alpha-\alpha} = 180.1$	$J_{\text{H}\beta-\beta} = 187.4$	$J_{\text{H}\gamma-\gamma} = 159.9$	$J_{\text{H}\delta-\delta} = 162.8$
$J_{\text{B}-\alpha} = 21.1$	$J_{\text{B}-\beta} = 21.1$	$J_{\text{B}-\gamma} = 6.9$	$J_{\text{H}\gamma-\delta} = 6.2$
$J_{\text{H}\beta-\alpha} = 4.9$		$J_{\text{H}\beta-\gamma} = 7.1$	$J_{\text{H}\beta-\delta} = 6.0$
$J_{\text{H}\gamma-\alpha} = 4.9$		$J_{\text{H}\alpha-\gamma} = 7.0$	
		$J_{\text{H}\delta-\gamma} = 7.0$	

Preparation of SF_5 -Polymer

A mixture of 0.68 g (3.18 mmol) of $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ and 0.0032 g (0.02 mmol) of AIBN (Azobis isobutyronitrile) was heated to 56°C for 3 d. No polymer was made from this reaction. Then, a mixture of a 0.52 g (2.43 mmol) of $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ and 0.0141 g (0.06 mmol) of benzoyl peroxide was heated to 72°C for 23 h., 92°C for 4 h and 100°C for 1 h. This reaction gave brownish oily polymer (yield, 11.5%) after evaporation for 1 d. The sample ($\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$) was irradiated with 450 Hanovia UV lamps for 3.6 h. This irradiation caused decomposition, as evident by charring.

IR Spectra

Compared with the IR spectrum of monomeric SF_5 -diene, ($\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$), the disappearance of the band at 1583 cm^{-1} , which was the C=C stretching frequency of $\text{CH}=\text{CHCl}$ portion, shows the polymerization of the monomer occurred through the $-\text{CH}=\text{CHCl}$ end. It is also of interest that a new C-H band appeared at 2995 cm^{-1} .

TABLE XXI

IR DATA FOR SF₅-POLYMER

3081 (w)
2995 (w)
1738 (m)
1453 (w)
1257 (s)
1085 (m)
1066 (m)
967 (m)
838 (vs)
734 (m)
710 (m)
650 (m)
601 (m)
571 (w)

Treatment of SF₅CH₂CHBrCH₂CF=CF₂ with K₂CO₃ in acetone failed to produce the expected diene SF₅CH=CHCHCF=CF₂. Additional work is needed to find a suitable pathway to this interesting SF₅ containing diene.

Discussion/Summary

It has been observed that when SF_5Br is added to fluorinated olefins, the SF_5 group is attached to the carbon with the most hydrogens. The addition of pentafluorothio bromide to 1,1,2-trifluoro-1,4-pentadiene gave $\text{SF}_5\text{CH}_2\text{CHBrCF}=\text{CF}_2$, where the SF_5 group also attached itself to the carbon with the most hydrogens.

The addition of pentafluorothio chloride to acetylene gave $\text{SF}_5\text{CH}=\text{CHCl}$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$.

The SF_5 -diene $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, was polymerized by free radical initiator, such as Bz_2O_2 to give an oily polymer. The yields were low for preparing both $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$; these pathways seem not to be useful methods for preparing four and five carbon- SF_5 containing olefins.

The NMR spectra of $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ were in agreement with the proposed structures:

In the ^1H NMR spectra, it was observed that the chemical shifts of the protons were in the region expected for SF_5 hydrocarbons. The couplings of the equatorial fluorines (SF_4) and the aliphatic fluorines to the α , β and γ protons

of $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ could not be determined due to the complex second order splitting. The patterns for $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ protons were a complex second order affair.

In the ^{19}F NMR spectra, the SF_5 group was observed as an AB_4 system. The chemical shift values were $\phi_A = 81.6, 82.6$ ppm and $\phi_B = 65.6, 63$ ppm for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, respectively. These results are in accord with the literature.^{56,57} The coupling constants observed for the SF_5 group (J_{AB}), 154.5 and 155.1 Hz for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, respectively were in line with the expected values⁵⁷.

For $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, nonequivalent CF_2 fluorines result in different chemical shifts. The coupling value between these two fluorines was 82.0 Hz. In the ^{13}C NMR spectra of $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, four equatorial fluorines affect α carbon and through coupling create a pentet; the coupling with β carbon is too weak to be observed. Nonequivalent ϵ fluorines result in doublet-doublet-doublet patterns for both δ and ϵ carbons.

In ^{13}C NMR spectra for $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, the coupling constants between α carbon and α carbon hydrogen, β carbon and β carbon hydrogen were much greater than those of γ and δ carbon, and show the inductive effect of electronegative substituents.

The most prominent feature of the infrared spectra of the $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ is the high frequency for $\text{C}=\text{C}$

stretching frequency in the region 1802 cm^{-1} due to the electronegative fluorines. For $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, the $\text{C}=\text{C}$ stretching frequency was observed in the region 1630 cm^{-1} for $\text{SF}_5\text{CH}=\text{CH}$ and 1583 cm^{-1} for $\text{CH}=\text{CHCl}$. The other major bands were consistent with the assigned structures, with the SF stretching and deformation modes in the region 845 cm^{-1} and 603 cm^{-1} for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, 842.0 , 904 cm^{-1} and 599.7 cm^{-1} for $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$, 838 cm^{-1} and 601 cm^{-1} for SF_5 -polymer.

The CF stretching mode for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ appeared at 1026 cm^{-1} , which is consistent with the previous work. The CF_2 stretching modes were observed at slightly higher frequencies, between 1103 - 1302 cm^{-1} .

The C-H stretching vibrations for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ were located at 2976 cm^{-1} and 3087 cm^{-1} , respectively. The C-Br stretching band for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ was found at 571 cm^{-1} . The C-Cl stretching bands for $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ would be found at 744 and 768 cm^{-1} . For the SF_5 -polymer, the disappearance of the band at 1583 cm^{-1} shows that the polymerization occurred at the $\text{CH}=\text{CHCl}$ portion.

The mass spectrum was supportive of the assigned structures. M/e values of 127 (SF_5^+), 108 (SF_4^+), 89 (SF_3^+), 70 (SF_2^+), and 51 (SF^+) provide evidence for the presence of the SF_5 group in the new adducts. For, $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, M/e values of 121 ($\text{CF}_2=\text{CFCH}_2\text{CHCH}^+$) and 122 ($\text{CF}_2=\text{CFCH}_2\text{CHCH}_2^+$)

provide evidence for the presence of $\text{CF}_2=\text{CFCH}_2\text{CHCH}_2$ group in the new adduct.

The $\text{CF}_2\text{CFCH}_2^+$ and SF^+ fragments were the base peak for $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ respectively. The remainder of the fragmentation patterns were consistent with the assigned structures.

CHAPTER IV

^{13}C NMR STUDIES OF $\text{SF}_5/\text{SO}_2\text{F}$ FLUORINATED SYSTEMS

INTRODUCTION

$\text{SF}_5/\text{SO}_2\text{F}$

SF_5 compounds show a wide range of useful and interesting properties. With the introduction of a SF_5 group, molecules change in their physical, chemical and biological properties. These properties are useful in various applications requiring thermally and chemically stable systems, including solvents for polymers, perfluorinated blood substitutes, surface-active agents, and fumigants.^{8,19} Fluoroalkyl sulfonyl fluorides (RSO_2F) have been of interest because of their utilization as an ion exchange resins, surface active agents and strong sulfonic acids.⁵⁸⁻⁶¹

In this study, some ^{13}C NMR data (chemical shifts and coupling constants) for SF_5 -diene and various kinds of sulfonyl fluorides will be presented.

EXPERIMENTAL

(These compounds were synthesized by L.F. Chen and N.N. Hamel in the Lab of Dr. G. L. Gard.)

Preparation of $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ ⁶³

Into a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve and a Teflon stirring bar were added 4.20 g (33.0 mmol) of dried silver fluoride, 7.0 mL of diglyme and 7.70 g (42.7 mmol) of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$. The reaction mixture was stirred at room temperature for 5 h, followed by the addition of 6.00 g (30.00 mmol) of $\text{BrCH}=\text{CHCH}_2\text{Br}$. The mixture was maintained at 0°C for 1.5 h and at 35-37°C for 24 h. The mixture was filtered to remove the AgBr. The filtrate was washed three times with water to give 7.0 g of a crude product, which was dried over P_4O_{10} and distilled to give 0.40 g (6.2% yield) of $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$; b.p. 45-46°C/143 mm Hg, and 5.2 g (16.3 mmol) of $\text{BrCH}=\text{CHCH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (trans 60%, cis 40%) in 54% yield; b.p. 119-122°C/143 mm Hg.

Preparation of $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ ⁶⁴

Into a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve and a Teflon stirring bar were added 15.0 g (35.2 mmol) of $\text{ICF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, 0.45g (1.8 mmol) of benzoyl peroxide and 93.2 mmol of $\text{CH}_2=\text{CH}_2$. The reaction mixture was heated at 150°C for 28 h, then at 200-250°C for 12 h; a liquid (3.5 g) was decanted from the

black solid in the vessel. The black solid was extracted three times with diethyl ether and washed twice with an aqueous NaHSO_3 solution. The ether extracts along with the 3.5 g of liquid were dried (Na_2SO_4) overnight and distilled to give 4.7 g of $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ b.p. $120\sim121^\circ\text{C}$.

Preparation of $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ ⁶³

Into a 125 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 3.3 g (26.2 mmol) of dried silver fluoride, 10.0 mL of diglyme, 5.2 g (28.8 mmol) of $\text{CF}_2\text{CF}_2\text{OSO}_2$, 3.2 g (17.0 mmol) of 1,2-dibromoethane. The reaction mixture was heated at $35\sim37^\circ\text{C}$ for 26 h. AgBr was removed and the filtrate was decanted into 20mL water. The oily layer which formed was isolated, washed three times with water and dried over P_4O_{10} . Distillation gave 3.0 g (9.8 mmol) of $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (5.7.5% yield), b.p. $74\sim77^\circ\text{C}/22$ mm Hg and 1.4 g (3.3 mmol) of $(\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})_2$ (19.4% yield), b.p. $106\sim107^\circ\text{C}/25$ mm Hg.

Preparation of $(\text{CF}_3)_2\text{CF}(\text{CH}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$ ⁶³

Into a 125 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 3.50 g (27.5 mmol) of dried silver fluoride, 5.0 mL of diglyme and 6.80g (37.8 mmol) of $\text{CF}_2\text{CF}_2\text{OSO}_2$. The reaction mixture was kept at room temperature for 24 h to give a homogenous clear solution of $\text{AgOCF}_2\text{CF}_2\text{SO}_2\text{F}$ and diglyme. The mixture was cooled and 8.0 g (24.7 mmol) of $(\text{CF}_3)_2\text{CFCH}_2\text{CH}_2\text{I}$

was added. The reaction mixture was warmed and maintained at room temperature for 3 d. The products were transferred under vacuum and washed with water. 8.10 g of an oily material was collected, dried over P_4O_{10} and distilled to give 5.1 g (12.9 mmol) of product in 52.1% yield; b.p. 150-152°C.

Preparation of $CH_2=CH(CF_2)_2O(CF_2)_2SO_2F$ ⁶⁴

Into four 5 ml glass tubes were added 2.00 g (4.40 mmol) of $ICF_2CF_2OCF_2CF_2SO_2F$, 0.54 g (5.3 mmol) of triethylamine. The tubes were sealed and heated at 80-85°C (20 h). To each of four glass tubes 2.5 mL of water was added; the oily layer was separated, dried over Na_2SO_4 , vacuum transferred and distilled; 1.10 g (3.38 mmol) of product $CH_2=CH(CF_2)_2SO_2F$ was obtained (76.7% yield), b.p. 115-116°C.

Preparation of $C_6H_5CH_2OCF_2CF_2SO_2F$ ⁶⁵

Into a 125 mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 4.70 g (37.0 mmol) of dried silver fluoride and 7.0 mL of diglyme. The β -sultone, $\overline{CF_2CF_2OSO_2}$ (7.70g, 42.8 mmol), was transferred under vacuum into the reaction vessel cooled to -196°C. The reaction mixture was warmed to room temperature and stirred for 3 h at 35-40°C. At -196°C, 5.50 g (32.2 mmol) of benzyl bromide was transferred into vessel, and the reaction was maintained at 35-38°C for 64 h. At -196°C, 1.30g of

volatile materials (mixture of SO_2F_2 and $\text{FC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$) were collected. The rest of the reaction mixture was filtered in order to remove AgBr and the filtrate was washed three times with water (25 mL). The oily crude product was separated, dried over P_4O_{10} and distilled to give 5.30 g of product (56.9% yield), b.p. $95-96^\circ\text{C}/14$ mm Hg.

Preparation of $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ ⁶⁵

Into a 125 mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 5.40 g (42.5 mmol) of dried silver fluoride, 8.0 mL of diglyme and 10.0 g (55.6 mmol) of $\overline{\text{CF}_2\text{CF}_2\text{OSO}_2}$. The reaction was stirred at 35°C for 3 h, after which 9.00 (34.5 mmol) of $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$ was transferred in vacuo into the reactor at -196°C . The reaction mixture was heated at 35°C for 3 d. At -196°C , 1.50 g of volatile materials (SO_2F_2 and $\text{FC}(\text{O})\text{CF}_2\text{SO}_2\text{F}$) were collected. The reaction mixture was filtered in order to remove AgBr . The filtrate was washed three times with water (25 mL). The oily crude product was dried over P_4O_{10} and distilled to give 8.5 g of product, 64.9% yield, b.p. $104-105^\circ\text{C}/20$ mm Hg.

Preparation of $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$ ⁶⁵

Into a 125 ml Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 6.00 g (47.2 mmol) of dried silver fluoride, 7.0 mL of diglyme and 10.0 g (43.5 mmol) of $\text{CF}_3\overline{\text{CFCF}_2}\text{SO}_2$. The reaction was stirred

at 35°C for 2 h, after which 8.60 g (33.0 mmol) of $C_6F_5CH_2Br$ was transferred in vacuo into the reactor cooled to -196°C. The reaction mixture was heated at 35--37°C for 3 d. At -196°C, 1.00 g of volatile materials (SO_2F_2 , $CF(O)CF(CF_3)SO_2F$) were collected. The reaction mixture was filtered in order to remove AgBr. The filtrate was washed three times with water (25 mL). The oily crude product was dried over P_4O_{10} ; distillation gave 10.8 g of the product, 76.1% yield, b.p. 99-100°C/10 mm Hg.

TABLE XXII

 ^{13}C NMR DATA FOR SULFONYL FLUORIDES

a b c $CH_3OCF_2CF_2SO_2F$ (1)		
a CH_3	b OCF_2	c CF_2S
(q,t)	(t,t,d)	(t,t,d)
δ (ppm) 52.8	116.9	114.3
$J_{H_a-a} = 149.7$	$J_{F_b-b} = 270.7$	$J_{F_c-c} = 297.2$
$J_{F_b-a} = 6.1$	$J_{F_c-b} = 28.0$	$J_{F_b-c} = 42$
	$J_{F_{SO_2F}-b} = 3.8$	$J_{F_{SO_2F}-c} = 34.6$

a b c d e f $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (2)					
a CH_3	b CH_2	c CF_2	d CF_2	e OCF_2	f CF_2S
(q, t, t)	(t, t, q)	(t, t)	(t, t)	(t, t, d)	(t, t, d)
δ (ppm) 4.7	24.8	117.1	118.5	115.8	113.7
$J_{\text{H}_{a-a}} = 130.8$	$J_{\text{H}_{b-b}} = 129.6$	$J_{\text{F}_{c-c}} = 252.9$	$J_{\text{F}_{d-d}} = 288.1$	$J_{\text{F}_{e-e}} = 288.1$	$J_{\text{F}_{f-f}} = 301.5$
$J_{\text{F}_{c-a}} = 4.7$	$J_{\text{F}_{c-b}} = 22.9$	$J_{\text{F}_{d-c}} = 26.8$	$J_{\text{F}_{c-d}} = 35.9$	$J_{\text{F}_{f-e}} = 30.2$	$J_{\text{F}_{e-f}} = 38.2$
$J_{\text{H}_{b-a}} < 1.5$	$J_{\text{H}_{a-b}} = 4.6$	$J_{\text{H}_{b-c}} < 1.5$ $J_{\text{H}_{a-c}} < 1.5$		$J_{\text{F}_{\text{SO}_2\text{F-e}}} = 2.7$	$J_{\text{F}_{\text{SO}_2\text{F-f}}} = 37.5$

a b c d $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (3)			
a CH_2	b CH_2	c OCF_2	d CF_2S
(t, t, t)	(t, t, t)	(t, t, d)	(t, t, d)
δ (ppm) 26.6	65.7	115.8	113.5
$J_{\text{H}_{a-a}} = 153.3$	$J_{\text{H}_{b-b}} = 152.3$	$J_{\text{F}_{c-c}} = 276.2$	$J_{\text{F}_{d-d}} = 301.6$
$J_{\text{H}_{b-a}} = 2.1$	$J_{\text{F}_{c-b}} = 4.7$	$J_{\text{F}_{d-c}} = 28.1$	$J_{\text{F}_{c-d}} = 41.5$
$J_{\text{F}_{c-a}} = 4.2$	$J_{\text{H}_{a-b}} = 2.5$	$J_{\text{SO}_2\text{F-c}} = 3.5$	$J_{\text{SO}_2\text{F-d}} = 34.8$

$ \begin{array}{c} \text{a} \\ \text{CF}_3 \\ \text{g} \\ \text{CF}_3 \end{array} \begin{array}{c} \text{b c d e f} \\ >\text{CFCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \\ \text{CF}_3 \end{array} \quad (4) $					
ag CF ₃	b CF	c CH ₂	d CH ₂	e OCF ₂	f CF ₂ S
(q, d)	(d, sept, t)	(t, d)	(t)	(t, t, d)	(t, t, d)
δ (ppm) 121.8	91.2	29.0	59.8	117.1	114.3
J _{F_{a-a}} = 285.6 (J _{F_{g-g}} = 285.6)		J _{H_{c-c}} = 132.9	J _{H_{d-d}} = 152.5	J _{F_{e-e}} = 276.5	J _{F_{f-t}} = 301.9
J _{F_{b-a}} = 27.3 (J _{F_{b-g}} = 27.3)		J _{F_{b-c}} = 20.0		J _{F_{t-e}} = 28.5	J _{F_{e-t}} = 41.3
				J _{SO₂F-e} = 3.7	J _{SO₂F-t} = 35.2
				J _{H_{d-e}} < 1.5	
	J _{F_{b-b}} = 205.3				
	J _{F_{a,g-b}} = 32.9				
	J _{H_{c-b}} = 2.8				
	J _{H_{d-b}} < 1.5				

$ \begin{array}{c} \text{a b c d e f} \\ \text{CH}_2=\text{CHCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \\ \text{CF}_3 \end{array} \quad (5) $					
a CH ₂	b CH	c CF ₂	d CF ₂	e OCF ₂	f CF ₂ S
(t, t, d)	(d, t, d)	(t, t)	(t, t)	(t, t, d)	(t, t, d)
δ (ppm) 126.6	124.9	112.8	118.3	115.6	113.3
J _{H_{a-a}} = 164.1	J _{H_{b-b}} = 170.7	J _{F_{c-c}} = 251.3	J _{F_{d-d}} = 288.9	J _{F_{e-e}} = 287.4	J _{F_{t-t}} = 302.1
J _{F_{c-a}} = 9.3	J _{F_{c-b}} = 23.9	J _{F_{d-c}} = 33.5	J _{F_{c-d}} = 36.9	J _{F_{t-e}} = 29.5	J _{F_{e-t}} = 40.5
J _{H_{b-a}} = 4.9	J _{H_{a-b}} = 6.6	J _{H_{a-c}} < 2.8		J _{SO₂F-e} = 3	J _{SO₂F-t} = 40.5
		J _{H_{b-c}} < 2.8			

a b c C ₆ H ₅ CH ₂ OCF ₂ CF ₂ SO ₂ F (6)		
a C ₆ H ₅ CH ₂	b OCF ₂	c CF ₂ S
benzylic (t,t)	(t,t,d)	(t,t,d)
δ (ppm) 68.3	116.1	113.7
J _{H_a-a} = 149.5	J _{F_b-b} = 275.9	J _{F_c-c} = 301.8
J _{F_b-a} = 5.1	J _{F_c-b} = 27.9	J _{F_b-c} = 41.9
	J _{SO₂F-b} = 3.3	J _{SO₂F-c} = 34.1
Aromatic (4) 129.2 (3) 128.9 (2) 128.2		

a b c C ₆ F ₅ CH ₂ OCF ₂ CF ₂ SO ₂ F (7)		
a C ₆ F ₅ CH ₂	b OCF ₂	c CF ₂ S
benzylic (t)	(t,t,d)	(t,t,d)
δ (ppm) 55.1	116.0	113.3
J _{H_a-a} = 159.2	J _{F_b-b} = 277.6	J _{F_c-c} = 301.8
	J _{F_c-b} = 28.4	J _{F_b-c} = 41.0
	J _{SO₂F-b} = 3.6	J _{SO₂F-c} = 35.2
Aromatic (4) 145.9 (3) 142.8 (2) 137.7		

a b c $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CFSO}_2\text{F}$ (8) $^d\text{CF}_3$			
a $\text{C}_6\text{F}_5\text{CH}_2$	b OCF_2	c CFS	d CF_3
benzylic (t)	(t,d)	(d,t,q,d)	(q,d)
δ (ppm) 55.1	117.1	98.8	118
$J_{\text{H}_{\text{a-a}}}$ = 154.5	$J_{\text{F}_{\text{b-b}}}$ = 278.7	$J_{\text{F}_{\text{c-c}}}$ = 257.1	$J_{\text{F}_{\text{d-d}}}$ = 288.7
	$J_{\text{F}_{\text{c-b}}}$ = 23.7	$J_{\text{F}_{\text{b-c}}}$ = 35.1	$J_{\text{F}_{\text{c-d}}}$ = 26.0
		$J_{\text{F}_{\text{d-c}}}$ = 35.0	$J_{\text{SO}_2\text{F-d}}$ < 1 Hz
		$J_{\text{SO}_2\text{F-c}}$ = 9.1	
Aromatic (4) 145.9 (3) 142.8 (2) 137.8			

a b c
 $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

The ^{13}C spectra reveal three carbons in the molecule, the **b** carbon and the **c** carbon signals downfield, and the **a** carbon signal upfield. The proton decoupled spectra show the **a** carbon signal to be a triplet, split by the **b** carbon fluorines, and carbon **c** has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits carbon **c** into a doublet; the **b** carbon fluorines split this into a triplet of doublets, and the **c** carbon fluorines split this into a triplet of triplets of doublets. Also, the **b** carbon has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits this signal into a doublet; the

c carbon fluorines split this into a triplet of doublets, and the **b** carbon fluorines split this into a triplet of triplets of doublets.

In the proton coupled spectra the **a** carbon signal was found to have the expected a quartet of triplets with a coupling of $J_{H_{a-a}} = 149.7$ Hz due to its own hydrogens, as well as from the **b** carbon fluorines ($J_{F_{b-a}} = 6.1$ Hz).

The **b** carbon has its signal coupled with the **a** carbon hydrogens, but this coupling could not be resolved with coupling of the order of 1.8 Hz or less.

The ^{13}C spectra reveal six carbons in the molecule, **c**, **d**, **e** and **f** carbon signals downfield and the **a** and **b** carbon signals upfield. The proton decoupled spectrum shows the **a** carbon signal as a triplet, split by the two **c** carbon fluorines. The **b** carbon subspectrum shows the **b** carbon signal as a triplet, split by the two **c** carbon fluorines. The **c** carbon has its signal coupled with two kinds of fluorines. The two **d** carbon fluorines split this into a triplet, and the **c** carbon fluorines split this into a triplet of triplets. The **d** carbon has its signal coupled with two kinds of fluorines, too. The **c** carbon fluorines split this into a triplet, and the **d** carbon fluorines split this into a triplet of triplets. No coupling between the **d** carbon and the **e** carbon fluorines was observed. The **e**

carbon has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits this into a doublet, the **f** carbon fluorines split this into a triplet of doublets, and the **e** carbon fluorines split this into a triplet of triplets of doublets. The coupling of the **d** carbon fluorines with the **e** carbon was not found either. The **f** carbon has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits this into a doublet, the **e** carbon fluorines split this into a triplet of doublets, and the **f** carbon fluorines split this into a triplet of triplets of doublets.

The proton coupled spectrum shows the **a** carbon signal as a quartet of triplets of triplets. The **a** carbon has its signal coupled with two kinds of hydrogens and the **c** carbon fluorines. The **b** carbon hydrogens split this signal into a triplet, the **c** carbon fluorines split this into a triplet of triplets, and the **a** carbon hydrogens split this into a quartet of triplets of triplets. The splitting by the **b** carbon hydrogen is too weak and complex to be observed, with coupling of the order of 1.5 Hz or less. The **b** carbon has its signal coupled with two kinds of hydrogens and the **c** carbon fluorines. The **a** carbon hydrogens split this into a quartet, the **c** carbon fluorines split this into a triplet of quartets, and the **b** carbon hydrogens split this into a triplet of triplets of quartets. The **c** carbon has its signal coupled with two kinds of fluorines, in addition to the **a** and **b** carbon hydrogens. The coupling of **c** carbon with

a and **b** carbon hydrogens could not be resolved, with coupling of the order of 1.5 Hz or less.

The ¹³C spectra reveal four carbons in the molecule, the **c** and **d** carbon signals downfield, and the **a** and **b** carbon signals upfield. The proton decoupled spectra show the **a** carbon signal as a singlet and the **b** carbon signal as a triplet, split by the two **c** carbon fluorines. The **c** carbon fluorines split the **a** carbon with coupling of the order of 4.2 Hz or less.

The **d** carbon has its signal coupled with three kinds of fluorines. The one SO₂F fluorine splits this signal into a doublet, the **c** carbon fluorines split this into a triplet of doublets, and the **d** carbon fluorines split this into a triplet of triplets of doublets. The **c** carbon has its signal coupled with three kinds of fluorines, too. The one SO₂F fluorine splits this signal into a doublet, the **d** carbon fluorines split this into a triplet of doublets, and the **c** carbon fluorines split this into a triplet of triplets of doublets.

The proton coupled spectrum shows the **a** carbon signal as a triplet of triplets of triplets, split by **a** and **b** carbon hydrogens and the **c** carbon fluorines, although the coupling of **a** carbon with **c** carbon fluorines and **b** carbon hydrogens could not be resolved, with coupling of the order

of 2.1 Hz or less.

The **b** carbon has its signal coupled with two kinds of hydrogens, and the **c** carbon fluorines. The **a** carbon hydrogens split this into a triplet, the **c** carbon fluorines split this into a triplet of triplets, and the **b** carbon hydrogens split this into a triplet of triplets of triplets.

The **c** carbon seems to be coupled with **b** carbon hydrogens, but this coupling could not be resolved, with coupling of the order of 1.5 Hz or less.

The ^{13}C spectrum reveals seven carbons in the molecule. **a** and **g** carbon signals are most downfield and **c** and **d** carbon signals are most upfield. The proton decoupled spectrum shows a **c** carbon signal as doublet, split by the **b** carbon fluorine. The **d** carbon signal appears as a singlet, and the **e** carbon fluorines seem not to be coupled to the **d** carbon. The **b** carbon has its signal coupled with two kinds of fluorines. The **a** and **g** carbon fluorines split this signal into a septet, and the **b** carbon fluorine splits this into a doublet of septets. The **f** carbon has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits this signal into a doublet, the **e** carbon fluorines split this into a triplet of doublets and the **f** carbon fluorines split this into a triplet of triplets of doublets. The **e**

carbon has its signal coupled with three kinds of fluorines, too. The one SO_2F fluorine splits this signal into a doublet, the **f** carbon fluorines split this into a triplet of doublets, and the **e** carbon fluorines split this into a triplet of triplets of doublets. The **a** and **g** carbons have their signal coupled with two kinds of fluorines. The **b** carbon fluorine splits these into a doublet, and either **a** or **g** carbon fluorines split these into a quartet of doublets.

The proton coupled spectrum shows the **c** carbon signal as a triplet of doublets. The **b** carbon fluorine splits the **c** carbon into a doublet, and the **c** carbon hydrogens split this into a triplet of doublets. No splitting by the **d** carbon hydrogens is observed. **d** carbon has its signal coupled with its own hydrogens to give a triplet. No splitting by **c** carbon hydrogens are observed to the **d** carbon, either. The **b** carbon has its signal coupled with two kinds of fluorines, the **c** and **d** hydrogens. The **c** carbon hydrogen would split this into a triplet, the **a** and **g** carbon fluorines split this into a septet, and the **b** carbon fluorine splits this into a doublet of septets of triplets. However, the coupling of the **d** carbon hydrogens with the **b** carbon is so complex that one cannot measure the coupling constant. The **e** carbon seems to be split by the **d** carbon hydrogens, but this coupling could not be resolved, with coupling of the order of 1.5 Hz or less.

The ^{13}C spectra reveal six carbons in the molecule, with the **a** and **b** carbon signals most downfield. The proton decoupled spectra show the **a** carbon signal as a triplet, split into three by the two **c** carbon fluorines. The **b** carbon subspectrum shows **b** carbon signal as a triplet split by the **c** carbon fluorines. The magnitude of the coupling by **c** carbon fluorines for the **b** carbon ($J_{\text{F}_{\text{c-b}}} = 23.9 \text{ Hz}$) is greater than it is for the **a** carbon ($J_{\text{F}_{\text{c-a}}} = 9.3 \text{ Hz}$)

The **d** carbon has its signal coupled with two kinds of fluorines. The **c** carbon fluorines split this signal into a triplet, and the **d** carbon fluorines split this into a triplet of triplets. The **e** carbon has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits this into a doublet, the **f** carbon fluorines split this into a triplet of doublets, and the **e** carbon fluorines split this into a triplet of triplets of doublets. It is noteworthy that the **d** carbon fluorines do not give a measurable coupling with **e** carbon. The **f** carbon has its signal coupled with three kinds of fluorines. The one SO_2F fluorine splits this into a doublet, the **e** carbon fluorines split this into a triplet of doublets, and the **f** carbon fluorines split this into a triplet of triplets of doublets. The **c** carbon has its signal coupled with two kinds of fluorines. The **d** carbon fluorines split this into a triplet, and the **c** carbon

fluorines split this into a triplet of triples. The proton coupled spectrum shows the **a** carbon signal as a triplet of triplets of doublets, split into two by **b** carbon hydrogen, and then split into three by the two **c** carbon fluorines to give a triplet of doublets, while the **a** carbon hydrogens split this into a triplet of triplets of doublets. The **b** carbon has its signal coupled with two kinds of hydrogens, in addition to the **c** carbon fluorines. The **a** carbon hydrogens couple with the **b** carbon, with the different J. values. But with asymmetric **b** carbon, one **a** carbon hydrogen is so positioned that it can couple more strongly with the **b** carbon, while the other **a** carbon hydrogen couples less strongly.

So, one **a** carbon hydrogen split **b** carbon into a doublet; the **c** carbon fluorines split this into a triplet of doublets and the **b** carbon hydrogen splits this into a doublet of triplets of doublets.

The **c** carbon has its signal coupled with two kinds of fluorines and two kinds of hydrogens. However, the coupling of the **c** carbon with the **a** and **b** carbon hydrogens could not be resolved, with coupling of the order of 2.8 Hz or less.

The proton coupled ^{13}C spectra reveal **a** carbon as a triplet of triplets. The **b** carbon fluorines split the **b** carbon signal into a triplet and the **a** carbon hydrogens split this into a triplet of triplets.

The **b** carbon has its signal coupled with three kinds of fluorines. The one SO₂F fluorine splits this into a doublet; the **c** carbon fluorines split this into a triplet of doublets, and the **b** carbon fluorines split this into a triplet of triplets of doublets.

The **c** carbon has its signal coupled with three kinds of fluorines, too. The one SO₂F fluorine splits carbon **c** into a doublet; the **b** carbon fluorines split this into a triplet of doublets, and the **c** carbon fluorines split this into a triplet of triplets of doublets. The subspectrum of aromatic carbons shows symmetry between those carbons.

The proton coupled ¹³C spectra reveal the **a** carbon as a triplet. The **a** carbon has its signal coupled with its own hydrogens. The coupling between **b** carbon fluorines was not resolved due to large line widths. The coupling constant between **a** carbon and attached hydrogen was greater than that of compound (6), which shows the more electronegative environment of the **a** carbon of compound (7) than that of compound (6). The substitution of hydrogen by fluorine of aromatic carbon led to the increase in chemical shifts; the chemical shifts of aromatic carbons change from 128.2-129.2 ppm to 137.7-145.9 ppm.

The OCF₂CF₂SO₂F portion of the spectra were quite similar to compound (6).

The substitution of one of two **c** carbon fluorines of compound (7) by CF_3 group led to the decrease in both chemical shift and coupling constant, $J_{\text{F}_{\text{c-c}}}$; the chemical shift decreased from 113.3 ppm to 98.8 ppm, and the coupling constant decreased from 301.8 Hz to 257.1 Hz. The rest of the spectra are quite similar to compound (7).

Discussion

$\begin{array}{ccc} \text{a} & \text{b} & \text{c} \end{array}$
For $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, the chemical shift assignment to carbon **b** and carbon **c** was critical. So, in order to determine which one is the more deshielded one, coupling constants of either carbon with SO_2F group was compared. The coupling information allows peak assignment.

$\begin{array}{cccccc} \text{a} & \text{b} & \text{c} & \text{d} & \text{e} & \text{f} \end{array}$
For $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, the subspectra of carbon **c, d, e, and f** were so close together that chemical shift assignments to these carbons were not simple. By studying both proton coupled and decoupled spectrum of this compound, coupling information was obtained to allow peak assignment.

peaks were overlapped with carbon **e** and **f** peaks, so that it was not simple to assign chemical shifts. Coupling

constants between these carbons and fluorines were compared to determine the chemical shift.

a b c d e f

In the $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ spectrum, chemical shift assignment to carbon **a** and carbon **b** is critical. In order to determine the more deshielded one, a proton coupled spectrum was compared with a proton decoupled spectrum. The splitting pattern due to the hydrogens made it possible to assign chemical shifts. For $\text{C}_6\text{H}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (6),

a b c a b c d
 $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (7), $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$ (8),

carbon 1 ( ) peak was too weak to find due to the

fact that it has neither hydrogen nor fluorine. The subspectrum of carbon 2 and 3 shows that it is symmetric to carbon 2' and 3', respectively. For compound **7**, the coupling constant of $J_{\text{H}_a-\text{a}}$ is greater than that of compound **6** and **8**, which shows its more electronegative environment of the coupling carbon. Due to the effect of replacing aromatic H by F, chemical shift values for aromatic carbons change from 128.2-129.2 ppm to 137.7-145.9 ppm. The ^{13}C NMR proton-coupled spectra for compound **7** and **8** show no coupling between aromatic carbon and benzylic hydrogen, although for compound **6** this coupling was observed. The OCF_2 carbon was not split by benzylic hydrogen in all the compounds.

The compound (8), $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}(\text{CF}_3)\text{SO}_2\text{F}$, shows the effect of electronegative substituent on the chemical shift

and the coupling constant. The substitution of one fluorine of two fluorines of **c** carbon of $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ by CF_3 group led to the decrease in both chemical shift and coupling constant. This shows the less electronegative value of CF_3 group than that of fluorine.

The ^{13}C NMR data for these sulfonyl fluorides show chemical shift values for the methyl and methylene groups next to fluoroalkyl sulfonyl fluoride group ranging from 52.8 to 68.3 ppm. The effect of replacing H by F is so large that the spectra show chemical shift values of 118.5 and 118.3 ppm for compound **2** and **5**.

The coupling of the carbon **a** of compound **1** and **6**, carbon **b** of compound **3**, with OCF_2 fluorine show values of 6.1, 5.1 and 4.7 Hz, respectively, while with compound **2**, **4**, **5**, **7** and **8** the similar coupling was not observed--perhaps due to larger line widths.

No coupling was observed between CF_2O fluorines and OCF_2 carbon and between CF_2O carbon and OCF_2 fluorines, neither. $^1J_{\text{CF}}$ values varied within the range of ~253-302 Hz according to the electronic environment of the coupling carbon. The coupling constants increased under the increasing influence of electron withdrawal, which is in agreement with the literature.⁶⁶

The ^{13}C NMR proton-coupled spectra show variations in $^1J_{\text{CH}}$; values range from 129.6 and 167.8 Hz according to the electronic environment of the coupling carbon. The

$\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ portions of the spectra are quite similar and agree with published results⁴³. Therefore, it can be said that chemical shifts of polyfluorinated carbons are not highly sensitive to environmental changes.

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APPENDIX

^{13}C , ^{19}F , ^1H NMR SPECTRA

FIGURE 1: ^1H NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$

FIGURE 2: ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
AXIAL FLUORINE

FIGURE 3: ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
EQUATORIAL FLUORINE

FIGURE 4: ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 ϵ_1 FLUORINE

FIGURE 5: ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 ϵ_2 FLUORINE

FIGURE 6: ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 δ FLUORINE

α β
FIGURE 7: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 α CARBON, PROTON DECOUPLED

α β

FIGURE 8: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 α CARBON, PROTON COUPLED
(CDCl_3 PEAK AT $\delta = 77.2$)

FIGURE 9: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 α β
 β CARBON, PROTON DECOUPLED

FIGURE 10: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\overset{\alpha}{\text{CH}}\text{Br}\overset{\beta}{\text{CH}_2}\text{CF}=\text{CF}_2$ -
 β CARBON, PROTON COUPLED

FIGURE 11: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 γ CARBON, PROTON DECOUPLED

FIGURE 12: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 γ CARBON, PROTON COUPLED

FIGURE 13:

α β γ δ ϵ
 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 δ CARBON, PROTON DECOUPLED

FIGURE 14:

α β γ δ ϵ
 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 δ CARBON, PROTON COUPLED

FIGURE 15:

$\alpha \quad \beta \quad \gamma \quad \delta \quad \epsilon$
 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 ϵ CARBON, PROTON DECOUPLED

FIGURE 16:

^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ -
 ϵ CARBON, PROTON COUPLED

α β γ δ ϵ

FIGURE 17: ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$

FIGURE 18: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}=\text{CH}=\text{CHCl}$ - α , β CARBON, PROTON DECOUPLED

FIGURE 19:

α β γ δ
 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ -
 α , β CARBON, PROTON COUPLED

FIGURE 20: ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CH}=\text{CHCH}=\text{CHCl}$ -
 α β γ δ
 γ , δ CARBON, PROTON COUPLED

FIGURE 21: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON DECOUPLED

FIGURE 22: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON COUPLED

FIGURE 23: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b, c CARBON, PROTON COUPLED

FIGURE 24: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON DECOUPLED

FIGURE 25: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON COUPLED

FIGURE 26:

a b c d e f
 ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b CARBON, PROTON DECOUPLED

FIGURE 27: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b CARBON, PROTON COUPLED

FIGURE 28: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
c, d, e f CARBON, PROTON COUPLED

FIGURE 29: ^{13}C NMR SPECTRUM OF $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
 c, d, e f CARBON, PROTON DECOUPLED

FIGURE 30: ^{13}C NMR SPECTRUM OF $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON DECOUPLED

FIGURE 31: ^{13}C NMR SPECTRUM OF $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON COUPLED

FIGURE 32: ^{13}C NMR SPECTRUM OF $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b CARBON, PROTON DECOUPLED

FIGURE 33: ^{13}C NMR SPECTRUM OF $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b CARBON, PROTON COUPLED

FIGURE 34: ^{13}C NMR SPECTRUM OF $\text{BrCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
c, d CARBON, PROTON COUPLED

FIGURE 35: ^{13}C NMR SPECTRUM OF

c CARBON, PROTON DECOUPLED

FIGURE 36: ^{13}C NMR SPECTRUM OF $\begin{matrix} \text{a} \\ \text{CF}_3 \\ \text{g} \end{matrix} \begin{matrix} \text{b} & \text{c} & \text{d} & \text{e} & \text{f} \\ >\text{CFCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \end{matrix}$

c CARBON, PROTON COUPLED

FIGURE 37: ^{13}C NMR SPECTRUM OF $\begin{matrix} \text{a} \\ \text{CF}_3 \\ \text{g} \\ \text{CF}_3 \end{matrix} > \text{CFCH}_2\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ $\begin{matrix} \text{b} & \text{c} & \text{d} & \text{e} & \text{f} \end{matrix}$

d CARBON, PROTON DECOUPLED

FIGURE 38: ^{13}C NMR SPECTRUM OF

d CARBON, PROTON COUPLED

FIGURE 40:

^{13}C NMR SPECTRUM OF

b CARBON, PROTON COUPLED

FIGURE 41:

 ^{13}C NMR SPECTRUM OF

a, g, e, f CARBON, PROTON COUPLED

FIGURE 42: ^{13}C NMR SPECTRUM OF $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a, b CARBON, PROTON DECOUPLED

FIGURE 43:

a b
 ^{13}C NMR SPECTRUM OF $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
 a, b CARBON, PROTON COUPLED

FIGURE 44: ^{13}C NMR SPECTRUM OF $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{OE}_2\text{CF}_2\text{SO}_2\text{F}$ -
 c, d, e, f CARBON, PROTON COUPLED

FIGURE 45: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{H}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON COUPLED

FIGURE 46:

^{13}C NMR SPECTRUM OF $\text{C}_6\text{H}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b, c CARBON, PROTON COUPLED

FIGURE 47: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{H}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
AROMATIC CARBON, PROTON COUPLED

FIGURE 48: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
a CARBON, PROTON COUPLED

FIGURE 49:

^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
b, c CARBON, PROTON DECOUPLED

FIGURE 50:

^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ -
AROMATIC CARBON, PROTON COUPLED

FIGURE 51: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\overset{\text{a}}{\underset{\text{dCF}_3}{\underset{\text{b}}{\text{C}}}}\overset{\text{c}}{\text{F}}\text{SO}_2\text{F}$ -
a CARBON, PROTON COUPLED

FIGURE 52: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{C}^{\text{a}}\text{F}^{\text{b}}(\text{CF}_3)^{\text{c}}\text{SO}_2\text{F}$ -
 c CARBON, PROTON COUPLED

FIGURE 53: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{C}^{\text{a}}\text{F}^{\text{b}}\text{SO}_2\text{F} - \text{c}$
 dCF_3
b, d CARBON, PROTON COUPLED

FIGURE 54: ^{13}C NMR SPECTRUM OF $\text{C}_6\text{F}_5\text{CH}_2\text{OCF}_2\text{C}(\text{CF}_3)\text{SO}_2\text{F}$ -
AROMATIC CARBON, PROTON COUPLED