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Synthesis and Characterization of Novel SF₅ Containing Fluoroalkyl Iodides and Derivatives

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THESIS APPROVAL

The abstract and thesis of Julia Anne Renn for the Master of Science degree in Chemistry was presented November 20, 1996 and accepted by the thesis committee and the department.

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ABSTRACT

An abstract of the thesis of Julia Anne Renn for the Master of Science in Chemistry presented November 20, 1996.

Title: Synthesis and Characterization of Novel SF₅
Containing Fluoroalkyl Iodides and Derivatives

Preparation of four SF₅-containing fluoroalkyl iodides and derivatives thereof was accomplished beginning with a simplified synthesis of ICF₂CF₂I. Characterization of the products followed using a variety of spectroscopic and physical methods.

The simplified method for preparing ICF₂CF₂I from iodine and tetrafluoroethylene (TFE) involved a reaction temperature of approximately 54°C and pressures of less than two atmospheres for the TFE. The synthesized ICF₂CF₂I was reacted with S₂F₁₀ and tetrafluoroethylene to give SF₅CF₂CF₂I. The subsequent synthesis of the SF₅ containing fluoroalkyl iodides and derivatives were carried out using SF₅CF₂CF₂I as the starting material in a Carius tube reaction vessel. The synthesized SF₅ containing compounds were: SF₅CF₂CF₂CF₂CF₂I, SF₅CF₂CF₂CH₂CH₂OH, SF₅CF₂CF₂CH₂CHICH₂CF=CF₂, and

$\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. In addition, a derivative of the original starting material, $\text{ICF}_2\text{CF}_2\text{I}$, was prepared. This derivative was identified as $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$.

Techniques employed for the characterization of the products included infrared spectrometry, ^{13}C , ^{19}F and ^1H nuclear magnetic resonance spectrometry, gas chromatography-mass spectrometry and elemental analysis. Melting point determinations were also performed for solid samples; boiling points were determined and used to characterize liquid samples.

SYNTHESIS AND CHARACTERIZATION OF NOVEL SF₅ CONTAINING
FLUOROALKYL IODIDES AND DERIVATIVES

by

JULIA ANNE RENN

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

MASTER OF SCIENCE
in
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TABLE OF CONTENTS

	PAGE
ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vii
CHAPTER	
I. INTRODUCTION.....	1
LITERATURE REVIEW.....	3
CHARACTERISTICS AND POTENTIAL APPLICATIONS OF SF ₅ -CONTAINING FLUOROALKYL HALIDES.....	3
SYNTHESIS OF SF ₅ -CONTAINING FLUOROALKYL IODIDES.....	5
SYNTHESIS OF ICF ₂ CF ₂ I AND HIGHER TELOMERS.....	12
PROPOSED MECHANISM FOR THE ADDITION OF SF ₅ -CONTAINING ALKYL IODIDES TO CARBON- CARBON MULTIPLE BONDS.....	14
II. EXPERIMENTAL METHODS.....	19
APPARATUS.....	19
INSTRUMENTATION AND PHYSICAL METHODS...	22
REAGENTS.....	24
REACTIONS.....	25
GENERAL PROCEDURE FOR CARIUS TUBE REACTIONS.....	26
REACTION OF IODINE WITH TETRAFLUOROETHYLENE.....	27
SYNTHESIS OF ICH ₂ CH ₂ CF ₂ CF ₂ CH ₂ CH ₂ I.....	31

SYNTHESIS OF PRECURSORS.....	33
SYNTHESIS OF ADDUCTS OF SF ₅ CF ₂ CF ₂ I USING THE CARIUS TUBE METHODOLOGY.....	35
SYNTHESIS OF DERIVATIVES.....	37
III. RESULTS.....	42
IR SPECTROSCOPY.....	43
NMR SPECTROSCOPY.....	53
MASS SPECTROSCOPY.....	69
ELEMENTAL ANALYSIS.....	77
SUMMARY.....	84
REFERENCES.....	87
APPENDICES	
A INFRARED SPECTRA.....	92
B NMR SPECTRA.....	99

LIST OF TABLES

TABLE	PAGE
3.01 IR SPECTRUM OF $\text{ICF}_2\text{CF}_2\text{I}$	47
3.02 IR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	48
3.03 IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	49
3.04 IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	50
3.05 IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	51
3.06 IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	52
3.07 ^{19}F NMR SPECTRUM OF $\text{ICF}_2\text{CF}_2\text{I}$	60
3.08 ^{13}C NMR SPECTRUM OF $\text{ICF}_2\text{CF}_2\text{I}$	60
3.09 ^1H NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	61
3.10 ^{19}F NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	61
3.11 ^{13}C NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	61
3.12 ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	62
3.13 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	62
3.14 ^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	63
3.15 ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	63
3.16 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	64
3.17 ^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	65
3.18 ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	65
3.19 ^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	66
3.20 ^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	67
3.21 ^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	67

3.22	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	68
3.23	MASS SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	72
3.24	MASS SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	73
3.25	MASS SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	74
3.26	MASS SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	75
3.27	RELATIVE ABUNDANCE OF ISOTOPES.....	76
3.28	ELEMENTAL ANALYSIS OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	79
3.29	ELEMENTAL ANALYSIS OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	80
3.30	ELEMENTAL ANALYSIS OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	81
3.31	ELEMENTAL ANALYSIS OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$...	82
3.32	ELEMENTAL ANALYSIS OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	83

LIST OF FIGURES

FIGURE		PAGE
1	SYNTHETIC APPLICATIONS OF PER- AND POLY- FLUOROALKYL IODIDES.....	6
2	CARIUS REACTION TUBE.....	21
3	IR SPECTRUM OF $\text{ICF}_2\text{CF}_2\text{I}$	93
4	IR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	94
5	IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	95
6	IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	96
7	IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	97
8	IR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	98
9	NMR PEAK ASSIGNMENTS FOR $\text{ICF}_2\text{CF}_2\text{I}$	100
10	^{19}F NMR SPECTRUM OF $\text{ICF}_2\text{CF}_2\text{I}$	101
11	^{13}C NMR SPECTRUM of $\text{ICF}_2\text{CF}_2\text{I}$	102
12	NMR PEAK ASSIGNMENTS FOR $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	103
13	^1H NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	104
14	^1H NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ - PEAK b.....	105
15	^{19}F NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	106
16	^{13}C NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$	107
17	^{13}C NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ - PEAK β	108
18	^{13}C NMR SPECTRUM OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ - PEAK γ	109

19	NMR PEAK ASSIGNMENTS FOR $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	110
20	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	111
21	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK a.....	112
22	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK b.....	113
23	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK c.....	114
24	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK d.....	115
25	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK e.....	116
26	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK f.....	117
27	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$	118
28	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAKS α, β, γ	119
29	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - PEAK δ	120
30	NMR PEAK ASSIGNMENTS FOR $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	121
31	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	122
32	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - PEAK a.....	123
33	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - PEAK b.....	124
34	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - PEAK c.....	125
35	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - PEAK d.....	126

36	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	127
37	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - PEAK α	128
38	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - PEAK β	129
39	NMR PEAK ASSIGNMENTS FOR $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$	130
40	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$...	131
41	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAKS e, g.....	132
42	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK f.....	133
43	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$...	134
44	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK a.....	135
45	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK b.....	136
46	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK c.....	137
47	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAKS d, d'.....	138
48	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK h.....	139
49	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK i.....	140
50	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK j.....	141
51	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$...	142

52	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAKS α, β, ϕ	143
53	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAKS γ, ϵ	144
54	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - PEAK ϕ	145
55	NMR PEAK ASSIGNMENTS FOR $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$	146
56	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK e.....	147
57	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK f.....	148
58	^1H NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK g.....	149
59	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK a.....	150
60	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK b.....	151
61	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK c.....	152
62	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK d.....	153
63	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK h.....	154
64	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK i.....	155
65	^{19}F NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK j.....	156
66	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$...	157

67	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAKS α, β, ϕ	158
68	^{13}C NMR SPECTRUM OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - PEAK ϕ	159

CHAPTER ONE

INTRODUCTION

The purpose of this work was to synthesize novel SF_5 -containing fluoroalkyl iodides and derivatives thereof for future use in preparing fluoro-organic and fluoro-organometallic derivatives. There are several possible commercial applications for these compounds as surfactants, solvents for polymers, perfluorinated blood substitutes, surface active agents, fumigants, and as thermally and chemically stable systems¹. To this end, two novel SF_5 -containing fluoroalkyl iodides and two derivatives of SF_5 -containing fluoroalkyl iodides were synthesized and fully characterized. Another goal of this research was to find quick, simple, and convenient syntheses for these compounds using less hazardous conditions and lower reaction pressures than previously employed. Efforts were taken to maximize the yields for all reactions.

The synthesis of the SF_5 -containing fluoroalkyl iodides depended upon a continuing supply of the $\text{ICF}_2\text{CF}_2\text{I}$ starting material. A simplified synthesis of this compound was therefore investigated. A derivative of this starting material was also prepared using a method

incorporating lower pressures and temperatures than previously employed. This derivative has been identified as $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$.

Included in this thesis are the experimental methods used for preparing precursors and the subsequent novel SF_5 -containing fluoroalkyl iodides and derivatives. The results of the characterization for each new compound are also included. The newly synthesized compounds are:

- (i) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$,
- (ii) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$,
- (iii) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, and
- (iv) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

The simplified preparation of the $\text{ICF}_2\text{CF}_2\text{I}$ starting material and its derivative, $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, are also covered.

This thesis is divided into several parts. This chapter contains a literature review of SF_5 -containing fluoroalkyl iodides, their synthesis, and possible uses. Chapter 2 includes the experimental methods used in this study. Chapter 3 is a discussion of the experimental results. Copies of the NMR and IR spectra collected for each compound are included in the appendices.

LITERATURE REVIEW

The literature review in this chapter covers the following topics:

- (i) the potential characteristics and applications of SF₅-containing fluoroalkyl halides,
- (ii) the history of the synthesis of existing SF₅-containing fluoroalkyl iodides,
- (iii) the published methods for the synthesis of ICF₂CF₂I and derivatives,
- (iv) the proposed mechanism for the addition of SF₅-containing alkyl iodides to multiple carbon-carbon bonds.

CHARACTERISTICS AND POTENTIAL APPLICATIONS OF SF₅-CONTAINING FLUOROALKYL HALIDES

SF₅-containing fluoroalkyl halides acquire their physical and chemical characteristics from two separate moieties, the SF₅ group and the fluoroalkyl chain. The fluoroalkyl chain is a carbon backbone with the carbon atoms being connected by either single or multiple carbon-carbon bonds. The remaining valences of the

carbon atoms are filled with either fluorine atoms or a combination of fluorine and hydrogen atoms. The SF_5 functional group contains a six-coordinate sulfur atom with octahedral geometry, where the five fluorine atoms occupy the four equatorial positions and one axial position. The other axial position is occupied by the fluoroalkyl chain. The SF_5 group possesses the advantages of the SF_6 parent compound. These advantages include a high group electronegativity, large steric bulk, nonfunctional hexacoordinate stereochemistry and high thermal and hydrolytic stability¹. Due to the stability of the SF_5 group, it is often an attractive replacement for the CF_3 functional group in its traditional uses².

Long fluoroalkyl chains incorporated into an organic compound introduce thermal and chemical stability, water resistance, oil resistance, and surface tension reduction in both aqueous and nonaqueous systems³. These characteristics can generally be attributed to the strong electronegativity of the fluoroalkyl chain and its nonpolar stable fluorinated groups.

The potential applications of SF₅-containing fluoroalkyl halides are numerous due to the advantages offered by the SF₅ group and the fluoroalkyl chain. As mentioned above, these applications include their use as solvents for polymers, perfluorinated blood substitutes, surface active agents, fumigants, and as thermally and chemically stable systems¹. Fluoroalkyl iodides have also been used in preparing large numbers of useful fluoro-organic and fluoro-organometallic derivatives⁴. Some of the synthetic applications of fluoroalkyl iodides are shown in figure 1⁵. Fluoroalkyl iodides have been specifically used as intermediates for surfactants and surface-treatment agents for textiles, leather, papers, etc.³ Incorporating the SF₅ group into these molecules may increase the chemical inertness of these agents. Several of the possible applications have been realized⁶.

SYNTHESIS OF SF₅-CONTAINING FLUOROALKYL IODIDES

Incorporation of the SF₅ group into a system is generally accomplished by adding SF₅X (X = Cl, Br, SF₅) across multiple bonds⁷. There are numerous examples of the synthesis of SF₅-containing fluoroalkyl chlorides

Figure 1
Synthetic Applications of Per- and
Poly-Fluoroalkyl Iodides⁵

1 Cu, DMF, Δ

2 Cu, DMF, Δ /ArI

3 n C_2F_4

4 Mg, THF

5 Zn

6 $CH_2=CH_2$

7 base

8 MSH

9 NR_3

10 MOH

11 methacrylic acid

12 [O]

and bromides using SF_5Cl and SF_5Br as starting materials¹. SF_5I is unknown, however, thus the syntheses of SF_5 -containing fluoroalkyl iodides are not nearly as numerous nor straightforward. What follows in this section is a history of the syntheses of the SF_5 -containing fluoroalkyl iodides which have been reported in the past twenty-five years.

These syntheses have been accomplished using starting materials other than SF_5I and often contain several steps involving numerous and sometimes quite hazardous reagents.

In 1970, the synthesis of $\text{SF}_5\text{CF}_2\text{I}$ was completed by R. A. Bekker et al. using the following scheme⁸:

In 1971/72 the synthesis of two SF₅-containing fluoroalkyl iodides was reported⁹. They were prepared as shown:

* Although iodine monofluoride hasn't been isolated, it is believed to be formed *in situ*¹⁰:

J. Hutchinson reported the preparation of several telomers of "pentafluorosulphur iodide" in 1973/74¹¹. Telomers are short-chain polymers usually defined as *n* equals 2 to 6 repeating units¹². The compounds synthesized by Hutchinson have the general formula of SF₅(C₂F₄)_{*n*}I where *n* = 1, 2, 3. The telomers were formed using the following synthesis:

The value of *n* was found to be a function of the amount of tetrafluoroethylene which was injected. Limited information was given for the characterization of products with *n* = 2,3. For products *n* = 4 - 9, the only characterization provided was the observation of the

parent molecular ions in the mass spectrum of the residue.

In 1974, R. E. Banks, et al. reported the results of several reactions using perfluorovinylsulphur pentafluoride ($\text{SF}_5\text{CF}=\text{CF}_2$) as the starting material¹³.

One of the products synthesized contains iodine,

$\text{SF}_5\text{CFICF}_2\text{CF}_3$. The synthesis was completed as follows:

Other products of this reaction were $\text{CF}_3\text{CF}_2\text{CFI}_2$ (21%) and CF_3SF_5 .

Wessel et al. reported on derivatives of $\text{HC}\equiv\text{CSF}_5$ and $\text{SF}_5\text{C}\equiv\text{CSF}_5$ in 1986¹⁴. One of the derivatives synthesized contains iodine, $\text{SF}_5\text{C}\equiv\text{CI}$. The scheme used to prepare this compound was:

The first SF_5 -substituted iodoperfluoroalkene was reported in 1991¹⁵. The synthesis was completed as shown here:

An improved synthesis for this alkene was published in 1992¹⁶. The yield of the final product was increased from 24% in the above reaction to 65%. The scheme is shown below:

SF₅R_fI iodides and their ethylene adducts, SF₅R_fCH₂CH₂I (where R_f comprises at least three fully fluorinated carbon atoms) were reported in 1992 and 1994^{17,18,19}. Limited information is given regarding the preparation, identification, and properties of these compounds. Electrochemical methods using pentafluorosulfanyl-fluoroaliphatic carbonyl and sulfonyl fluorides were employed. The following schemes were given:

As mentioned earlier, incorporating the SF₅ group into carbon systems is often accomplished by adding SF₅X (X = Cl, Br, SF₅) across multiple bonds⁷. Since SF₅I is unknown, Dr. Gard's group at Portland State University has been studying the synthesis of SF₅-containing fluoroalkyl iodides using SF₅C₂F₄I as the starting material. This study has resulted in the preparation of a number of SF₅-containing fluoroalkyl iodides including: SF₅CF₂CF₂CH₂CH₂I, SF₅CF₂CF₂CF₂CF₂I, SF₅CF₂CF₂CH₂CH₂CH₂CH₂I, SF₅CF₂CF₂CH=CHI (isomers), and SF₅CF₂CF₂(CHFCH₂)I (isomers). In addition, the higher molecular weight SF₅-containing fluoroalkyl iodides,

$\text{SF}_5(\text{CF}_2)_6\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CHF}\text{CF}_2)_2\text{I}$ (isomers), and $\text{SF}_5\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_3\text{I}$, were identified using GC-MS²⁰. All of these compounds were prepared using a Carius tube technique which will be discussed in the experimental section of this thesis. The reactions for these derivatives follow. Each reaction was a separate experiment and resulted in a unique derivative:

The higher homologues mentioned above were found for the $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CHF}\text{CF}_2\text{I}$ adducts.

SYNTHESIS OF $\text{ICF}_2\text{CF}_2\text{I}$ AND HIGHER TELOMERS

Two published methods for the synthesis of tetrafluoro-1,2-diiodoethane were reported^{21,22}. The first was an experimental procedure reported by Coffman et al. in 1947²¹. This method involved the reaction of I_2 with tetrafluoroethylene (TFE) in a silver-lined shaker tube at pressures of 300-370 psi; ether was used

as the solvent. The reaction mixture was held at 60°C for 15 hr. The reported yield was 74% based on iodine. In 1953 Haszeldine and Leedham published an alternative synthesis using a stainless-steel autoclave²². This procedure used dry iodine, α -pinene stabilizer and TFE. Pressures of up to 30 atm. at 100°C were observed. The reaction time was 24 hr. at 150°C. Yield of the product was reported as 76%. The experimental procedure of Haszeldine and Leedham had been modified using a lower reaction temperature (100 - 120°C) by Rolf Winter in Dr. Gard's lab²³.

The telomerization of $\text{ICF}_2\text{CF}_2\text{I}$ to give α,ω -diiodoperfluoroalkanes was discussed by Haszeldine in 1951²⁴. Experimental details and product characterizations were not given, however, and subsequent attempts to repeat the work produced mixtures of the telomers at low yields²⁵. Other methodologies for this reaction have appeared in the literature^{26,27,28}, but use of these methods to prepare the telomers were unsatisfactory due to the details for the preparation being omitted, the synthesis requiring several steps, or poor yield of the product. In 1980, Bedford and Baum

reported the development of an improved method for the laboratory-scale telomerization of tetrafluoroethylene with iodine²⁹. The reactions were carried out in stainless-steel cylinders at 200-220°C and initial pressures of 20-27 atm. The results of their studies showed that higher ratios of TFE to iodine favored the conversion to higher telomers.

A patent was issued in 1962 for telomers from $\text{CH}_2=\text{CH}_2$ and $\text{ICF}_2\text{CF}_2\text{I}$ ³⁰. The invention was for the thermal addition of ethylene to tetrafluoro-1,2-di-iodoethane which resulted in products $\text{ICF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_n\text{I}$ and $\text{I}(\text{CH}_2\text{CH}_2)_m\text{CF}_2\text{CF}_2(\text{CH}_2\text{CH}_2)_n$ where m and n were integers from 1 to 5. The methodology involved heating $\text{ICF}_2\text{CF}_2\text{I}$ with ethylene at temperatures of 180-220°C and pressures from 1-700atm.

PROPOSED MECHANISM FOR THE ADDITION OF SF_5 -CONTAINING ALKYL IODIDES TO CARBON-CARBON MULTIPLE BONDS.

The addition of fluorinated units to carbon-carbon multiple bonds can be accomplished using fluorinated radicals as reactive intermediates. The fluorinated radicals are usually generated in one of the following ways¹²:

1. Addition of a radical species $X\bullet$ to an unsaturated fluorinated unit:

2. Abstraction of a radical species $X\bullet$ from a saturated fluorocarbon:

3. Decomposition of fluoroalkyl iodides by heat or light:

The radicals which are formed can give the reactions commonly associated with radicals¹². These reactions include addition, chain transfer, substitution, coupling, rearrangement, fragmentation, and disproportionation. The synthetic reactions with radicals will generally involve more than one type of reaction.

The addition of both iodoperfluoroalkanes (R_fI) and S_2F_{10} to multiple carbon-carbon bonds is important in the research presented in this thesis. A discussion of free radical mechanisms for the addition of R_fI and S_2F_{10} to olefins follows.

The commonly assumed mechanism for the free radical addition of iodoperfluoroalkanes to olefins comprises three steps³¹:

In some cases, termination and transfer reactions are also involved. Some authors also include a recombination step where two radical species combine to give a product.

Two examples of free radical mechanisms involving the addition of R_fI to multiple carbon-carbon bonds are shown here. Haszeldine suggested the following mechanism for the addition of CF_3I to ethylene³²:

Although an ionic mechanism involving a trifluoromethyl anion would explain the nature of the products of this reaction, it was considered unlikely that a heterolytic bond fission would occur in the vapor-phase reactions.

Manseri et al. have suggested the following scheme for the thermal behavior of tetrafluoro-1,2-diiodoethane in the formation of higher telomers³³:

1. $\text{ICF}_2\text{CF}_2\text{I} \rightarrow \text{I}_2 + \text{CF}_2=\text{CF}_2$ (β -elimination)
2. $\text{ICF}_2\text{CF}_2\text{I} \rightarrow \text{ICF}_2\text{CF}_2\bullet + \text{I}\bullet$ (initiation)
3. $\text{ICF}_2\text{CF}_2\bullet + \text{CF}_2=\text{CF}_2 \rightarrow \text{ICF}_2\text{CF}_2\text{CF}_2\text{CF}_2\bullet$ (propagation)
4. $\text{I}(\text{C}_2\text{F}_4)_{n-1}\text{CF}_2\text{CF}_2\bullet + \text{CF}_2=\text{CF}_2 \rightarrow \text{I}(\text{C}_2\text{F}_4)_n\text{CF}_2\text{CF}_2\bullet$
(propagation)
5. $\text{I}(\text{C}_2\text{F}_4)_n\bullet + \text{ICF}_2\text{CF}_2\text{I} \rightarrow \text{I}(\text{C}_2\text{F}_4)_n\text{I} + \text{ICF}_2\text{CF}_2\bullet$
(transfer)
6. $\text{I}(\text{C}_2\text{F}_4)_n\bullet + \text{I}(\text{C}_2\text{F}_4)_n\bullet \rightarrow \text{I}(\text{C}_2\text{F}_4)_{2n}\text{I}$ (termination)
7. $\text{I}\bullet + \text{I}\bullet \rightarrow \text{I}_2$ (termination)

For several years the sulfur pentafluoride radical, $\text{SF}_5\bullet$, was thought to be an intermediate in various chemical reactions using SF_5Cl , S_2F_{10} , and SF_5Br , however, it had not been directly observed. The existence of SF_5 radicals has now been confirmed using both ESR and IR spectroscopy^{34,35,36}. The sulfur pentafluoride radical $\text{SF}_5\bullet$

is generated from SF_5X by heat or light and adds to a variety of multiple carbon-carbon bonds¹²; interestingly, S_2F_{10} was found not to add effectively to olefins³⁷.

In his communication regarding the preparation of telomers of "pentafluorosulphur iodide"¹¹, Hutchinson suggested the most important reactions in the formation of the telomers to be:

Although no classification is given to these reactions, reaction 1 would appear to be an initiation reaction, reaction 2 could be classified as a propagation reaction, reaction 3 seems to be transfer reactions, reaction 4 appears to be a fragmentation reaction, reaction 5 is a recombination of two radicals, and reaction 6 is an inhibition reaction.

CHAPTER TWO

EXPERIMENTAL METHODS

APPARATUS

Vacuum Line

All volatile compounds were transferred using a glass vacuum line. The vacuum line consists of a glass manifold made of 22 mm inside diameter (i.d.) Pyrex glass tubing and has a total volume of 0.44 liters (L). The manifold is equipped with four Kontes high vacuum stopcocks with Pyrex glass 10/30 female joints. The vacuum line was evacuated using a Welch Duo-Seal rotary vacuum pump which was connected to the line through a liquid nitrogen cooled trap. A Frederick Company Televac thermocouple gauge was used to monitor pressures from 1 - 100 μ m. To measure pressures from 1 - 1000 Torr, a Heise-Bourdon gauge was normally used. In a few instances a mercury manometer was used to measure pressures from 1 - 760 mm Hg. The permanent joints of the vacuum line were sealed with Glyptol Enamel. The joints and stopcocks were lubricated using Fluorolube GR-290 purchased from Fisher Scientific or a mixture of Fluorolube GR-290 and halocarbon wax. Halocarbon wax was used where a wax seal was required.

Reaction Vessels

Two types of reaction vessels were used. Reactions at pressures of less than 2 atmospheres (atm) were carried out in either Pyrex glass vessels or Carius tubes. Reactions which required higher pressures were carried out in stainless steel vessels.

The Pyrex glass vessels which were used were 1, 2 or 3 L in volume. They were equipped with Kontes Teflon stopcocks and standard male 10/30 tapered joints to allow connection with the vacuum line.

Figure 2³⁸ shows a typical Carius tube. Carius tubes consisting of heavy wall Pyrex glass and equipped with Kontes Teflon stopcocks and male 10/30 tapered joints were used. The volumes of Carius tubes which were used were 50, 100, 130, and 300 milliliters (mL).

Hoke stainless-steel metal vessels of 75 or 150 mL, equipped with Whitney stainless-steel valves and tapered brass 10/30 joints were used for the reactions carried out at pressures above 2 atm.

Figure 2
Carius Reaction Tube³⁸

which are downfield from the internal standard are reported as positive chemical shifts, while those which are upfield from the internal standard are reported as negative. The constants for coupled systems are reported in Hertz (Hz).

Mass Spectrometry (MS)

The mass spectra were measured on a VG 7070 HS mass spectrometer operated at 70 KeV. These analyses were performed at the Portland Veterans Hospital.

Elemental Analysis (EA)

All elemental analyses were determined by Beller Microanalytical Laboratory in Gottingen, Germany.

Melting Points (MP)

Melting points of solid compounds were determined using open capillary tubes in a Mel-Temp® apparatus.

Boiling Points (BP)

Boiling points were determined by distillation either at atmospheric or reduced pressure. A Kontes Pyrex glass distillation apparatus with 14/20 ground glass joints was generally used.

Irradiation

The source used for irradiation was either a Sylvania Capsylite Halogen Par 38 lamp or a GE Halogen

INSTRUMENTATION AND PHYSICAL METHODS

Infrared Spectrometry (IR)

The infrared spectra were obtained using a Perkin-Elmer System 2000 FTIR operating at 1.0 cm^{-1} resolution using KBr or NaCl plates for liquids and solids. The spectra for gas samples were taken using a 10 cm path length Pyrex glass gas cell fitted with KBr windows. The gas cell was equipped with a Kontes Teflon stopcock and a male 10/30 taper joint for easy access to the vacuum line. Scans for all samples were taken in the region $4000 - 400\text{ cm}^{-1}$.

NMR Spectrometry

The NMR spectra were obtained on a Varian EM-390 spectrometer operating at 90.00 MHz for ^1H and 84.67 MHz for ^{19}F or a Bruker AMX-400 spectrometer operating at 400.1 MHz for ^1H , 100.6 MHz for ^{13}C , and 376.5 MHz for ^{19}F . The Bruker AMX-400 spectra were obtained by Dr. David Peyton's group at Portland State University. Tetramethylsilane (TMS) was used as the internal standard for ^1H and ^{13}C spectra. Freon-11 (CFCl_3) was used as the internal standard for ^{19}F . The resonance of the standards was set to zero and chemical shifts are reported as ppm from the standard. Chemical shifts

90 watt lamp. The irradiation distance was 12 - 18 inches and the temperature in the warmest part of the irradiation zone was approximately 54°C. The irradiation period lasted for several days to weeks.

REAGENTS

Acetone, CH_3COCH_3 , was used as obtained from EM Science. Carbon tetrachloride, CCl_4 , was purchased from Aldrich and used as received.

Chloroform, CHCl_3 , was used as obtained from Mallinckrodt.

Diethyl ether, anhydrous, $(\text{CH}_3\text{CH}_2)_2\text{O}$, was obtained from J. T. Baker Co. and used without further purification. Disulfur decafluoride, S_2F_{10} , was used as obtained from PCR.

Ethylene, $\text{CH}_2=\text{CH}_2$, was purchased from Airco and was used as received.

Iodine, I_2 , Baker Analyzed Reagent, was used as received.

Mercury, Hg , was used as obtained from Nurnberg Scientific.

Oleum, fuming sulfuric acid, H_2SO_4 (27% SO_3), was obtained from DuPont.

Potassium carbonate, K_2CO_3 , was used as received from Mallinckrodt.

2-Pyrrolidinone, C_4H_7NO , was purchased from Aldrich and was used as received.

Sodium bisulfite, $NaHSO_3$, was used as obtained from Aldrich.

Tetrafluoroethylene (TFE), inhibited, $CF_2=CF_2$, was used as obtained from PCR.

Tributyltin hydride, $[CH_3(CH_2)_3]_3SnH$, was used as obtained from Aldrich.

1,1,2-Trifluoro-1,4-pentadiene, $CH_2=CH_2CH_2CF=CF_2$, was obtained from Dr. Donald J. Burton, University of Iowa, and was used without further purification.

REACTIONS

The following is a list of the reactions which will be detailed in this thesis.

* These compounds were originally synthesized by Dr. Robin J. Terjeson and were prepared using her methods.

GENERAL PROCEDURE FOR CARIUS TUBE REACTIONS

The Carius tube technique had been perfected by Dr. Robin J. Terjeson in Dr. Gard's laboratory. It had been used as a method of preparing SF_5 -containing alkyl dibromides³⁹ and iodides²⁰. The reactants were pipetted or condensed at -196°C into Carius tubes of the

appropriate size. In most cases, the Carius tubes contained approximately 0.5 - 1.0 grams (g) of mercury. Gases were condensed into the tube cooled to -196°C . The vessel was then placed under a halogen irradiation source at a distance of 12 -18 inches. The reaction time varied from several days to weeks. During the irradiation period, the reaction mixture was shaken approximately 5 times per day. The pressure of the volatile components was checked periodically to determine the extent of reaction. The reaction was considered to be complete when no additional pressure change was observed. At this point, the volatile components were transferred from the reaction vessel and distillation of the product was performed at either atmospheric or reduced pressure as appropriate. In the Carius tubes containing mercury, a red solid, HgI_2 , was formed as the reaction progressed.

REACTION OF IODINE WITH TETRAFLUOROETHYLENE

Subsequent synthesis of the SF_5 -containing iodides depended upon a continuing supply of the $\text{ICF}_2\text{CF}_2\text{I}$ starting material. Therefore, a simplified synthesis of this compound was investigated. Before this simplified

synthesis was accomplished, $\text{ICF}_2\text{CF}_2\text{I}$ was prepared based on the method of Dr. Rolf Winter, who had made modifications to the published methods²³. His method involved using a stainless-steel vessel and heating the reaction mixture to 120°C . The calculated pressure of this method was approximately 18 atm. When working with TFE, it is desired to keep the pressure as low as possible because TFE can spontaneously polymerize at pressures above 3 atm. The yield of the reaction using Dr. Winter's method was about 77%. The goal for the new synthesis was to come up with a methodology which employed lower pressures and had a yield equivalent to or better than the current synthesis. The Carius tube method and two modifications were then investigated. All three methods employed pressures of less than 2 atm and gave adequate yield; IR data showed all of the products to be equivalent to each other and to literature values reported for $\text{ICF}_2\text{F}_2\text{I}$. The experimental method for each of the modifications follows.

Preparation of $\text{ICF}_2\text{CF}_2\text{I}$ in Carius Tube

This reaction was carried out in a 130 mL Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock at pressures under 2 atm. The iodine, 2.8 grams (0.011 mol), was crushed using a mortar and pestle and added to the Carius tube. The reaction vessel was evacuated on the vacuum line and 1.1 g (0.011 mol) of $\text{CF}_2=\text{CF}_2$ was condensed into the vessel at -196°C . The reaction vessel was placed under the irradiation source for 7 days. An additional 0.5 g (0.005 mol) of $\text{CF}_2=\text{CF}_2$ was added after 5 days to insure an excess of this reactant. At the end of the reaction period, no solid I_2 was observed in the reaction tube. The sample was then distilled at atmospheric pressure: boiling point 116°C , 63% yield. The lower yield may have been due to incomplete distillation of the product. The distillation was stopped when the temperature began to decrease from 116°C . Subsequent IR spectra of the material remaining in the pot and the product were very similar. The pot was redistilled with another batch of the compound.

Preparation of $\text{ICF}_2\text{CF}_2\text{I}$ in Carius tube as a continuous reaction

This reaction was carried out in the same Carius tube used in the previous reaction. In this case, however, approximately 10 grams of I_2 was used, and the $\text{CF}_2=\text{CF}_2$ was added in increments during the reaction period so that the pressure in the Carius tube did not exceed 2 atm. This allowed a larger batch of the product to be synthesized. The iodine, 9.96 g (0.039 mol), was crushed using a mortar and pestle and added to the Carius tube. The reaction vessel was evacuated on the vacuum line and 1.1 g (0.011 mol) of $\text{CF}_2=\text{CF}_2$ was condensed into the vessel at -196°C . The reaction vessel was placed under the irradiation source for 20 days. Pressure checks of the $\text{CF}_2=\text{CF}_2$ were done periodically and when the pressure fell below approximately 0.5 atm, additional $\text{CF}_2=\text{CF}_2$ was added. $\text{CF}_2=\text{CF}_2$ was added four times using an additional 3.9 g (0.039 mol). At the end of the reaction period, no solid I_2 was observed in the reaction tube. The sample was then distilled at atmospheric pressure: boiling point $114 - 116^\circ\text{C}$, 90% yield.

Preparation of $\text{ICF}_2\text{CF}_2\text{I}$ in 2 L vessel

This reaction was carried out in a 2 L Pyrex-glass vessel equipped with a Kontes Teflon stopcock at pressures under 1.05 atm. The iodine, 22.42 g (0.088 mol), was crushed using a mortar and pestle and added to the vessel. The reaction vessel was evacuated on the vacuum line and 8.5 g (0.085 mol) of $\text{CF}_2=\text{CF}_2$ was condensed into the vessel at -196°C . The reaction vessel was placed under the irradiation source for 5 days. An additional 1.0 g (0.010 mol) of $\text{CF}_2=\text{CF}_2$ was added after 4 days to insure an excess of TFE. At the end of the reaction period, no solid I_2 was observed in the reaction vessel. The sample was then distilled at atmospheric pressure: boiling point $115 - 117^\circ\text{C}$, 94% yield.

Although the two modifications of the method were both similar in difficulty and resulted in nearly equivalent yields, the last one was preferred because more product was produced in a shorter time period.

SYNTHESIS OF $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Subsequent reaction of previously prepared $\text{ICF}_2\text{CF}_2\text{I}$ with ethylene gave a white crystalline product. The

solid was characterized and has been identified as $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ based on spectroscopic data (see Chapter 3). The reaction was carried out in a 100 mL Pyrex-glass Carius tube equipped with a Kontes Teflon stopcock at pressures under 2 atm. In this reaction, 3.04 g (0.0086 mol) of previously prepared $\text{ICF}_2\text{CF}_2\text{I}$ was added to the Carius tube along with 2 - 3 drops of Hg. The reaction vessel was evacuated on the vacuum line and 0.22 g (0.0079 mol) of $\text{CH}_2=\text{CH}_2$ was condensed into the vessel at -196°C . The reaction vessel was placed under the irradiation source for 7 weeks. A white crystalline product was formed along with the red HgI_2 . The product was purified by recrystallization in carbon tetrachloride: melting point $113 - 115^\circ\text{C}$, 46% yield.

Approximately 0.5 g (31% of the total weight of product formed) of a colorless liquid was also obtained. Due to the limited amount of product, further purification by distillation was not possible. The NMR spectrum suggested that it may be $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{I}$, but MS data showed a mixture of compounds. Positive identification of this compound was not possible due to the limited amount of material obtained.

SYNTHESIS OF PRECURSORS

Two other compounds were needed as starting materials for subsequent studies. They were $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ and its first ethylene addition product, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$. The preparation of both of these compounds had been accomplished by Dr. Robin J. Terjeson and the methodologies are included in a paper which has been accepted for publication²⁰. Each of these precursors were made several times. Examples of the preparations follow.

Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$

This reaction was carried out in a 150 mL stainless-steel vessel equipped with a Whitney stainless-steel valve at pressures of less than 10 atm. In this reaction, 11.36 g (0.032 mol) previously prepared $\text{ICF}_2\text{CF}_2\text{I}$ was pipetted into the reaction vessel. The reaction vessel was then evacuated and 9.64 g (0.038 mol) S_2F_{10} was condensed into the vessel at -196°C . After allowing the reaction vessel to stand for 2 - 3 days, 3.4 g (0.034 mol) $\text{CF}_2=\text{CF}_2$ was condensed into the vessel at -196°C . The reaction mixture was allowed to warm to room temperature and then the lower 1/2 of the vessel was heated in a heating tube or oil bath at $155 \pm$

5°C for 4.5 to 5 hours. The vessel was shaken every 20 to 30 minutes. After the heating period was over, the reaction was quenched by cooling the vessel with cold tap water and stored overnight at 0°C. The product was purified by two consecutive distillations. A simple distillation was used to collect five different fractions. Fraction 1 distilled over at temperatures below 75°C and contained S_2F_{10} which was stored for future use. The second fraction was collected from 75 - 86°C. Fraction 3 contained fairly pure product and was collected from 86 - 90°C. Fraction 4 was collected from 90 - 100°C. The final fraction was collected at temperatures above 100° C and contained mostly ICF_2CF_2I . The second distillation used a 2.5 mm x 100 mm column packed with 0.05" x 0.05" x 0.1" Monel helices to give better separation of fractions 2 and 4. A purple liquid was collected: boiling point 85 - 88°C, 53% yield. The product was treated with Hg to remove I_2 .

Preparation of $SF_5CF_2CF_2CH_2CH_2I$

5.53 g (0.015 mol) previously prepared $SF_5CF_2CF_2I$ was pipetted into a 300 mL Carius tube containing 3 - 4 drops Hg. The reaction vessel was evacuated at -196°C

and 0.46 g (0.017 mol) $\text{CH}_2=\text{CH}_2$ was condensed into the vessel. The vessel was placed under the irradiation source for 10 days. An additional 0.11 g (0.0038 mol) of ethylene was added after 7 days to insure that it was in excess. After the irradiation period, the product was distilled at reduced pressure: boiling point 59 - 61°C @ 20 Torr, 82.3 % yield.

SYNTHESIS OF ADDUCTS OF $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ USING THE CARIUS TUBE

METHODOLOGY

Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$

The first TFE addition to $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ was carried out in a 100 mL Carius tube; 3.04 g (0.0086 mol) of previously prepared $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ was added to the vessel which contained 2 - 3 drops Hg. The reaction vessel was evacuated at -196°C and 0.83 g (0.0083 mol) $\text{CF}_2=\text{CF}_2$ was added. The vessel was placed under the irradiation source for 14 days. After 5 days an additional 0.12 g (0.0012 mol) TFE was added to insure an excess. One week later, the volatile materials were condensed into a trap at -20°C and the sample was distilled at reduced pressure. Two fractions were collected from the distillation. Fraction 1 was collected from 45 - 72°C

and the boiling point of fraction 2 was 72 - 79°C. The pressure was 92 Torr. The lower boiling fraction was returned to the reaction vessel and allowed to react for an additional 13 days. The resulting product was then distilled at reduced pressure: boiling point 71°C at 104 Torr, 34.3% yield. (Note: The synthesis of this compound was included in a paper which has been accepted for publication²⁰.)

Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

$\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ 5.13 g (0.015 mol) was pipetted into a 130 mL Carius tube containing 2 - 3 drops Hg. The Carius tube was evacuated and 1.76 g (0.015 mol) $\text{CH}_2=\text{CHCH}_2\text{CF}=\text{CF}_2$ was condensed into the vessel. The vessel was placed under the irradiation source for 7 days. An additional 0.088 g (0.0007 mol) of the diolefin was added after 4 days to ensure an excess. After the 7 day irradiation period, the volatiles were transferred to a round-bottom flask for storage until distillation was performed. There appeared to be a viscous liquid remaining in the Carius tube, so the remaining material in the Carius tube was extracted with 4 - 5 mL portions of carbon tetrachloride. A simple distillation was then performed to remove the solvent.

The remaining material was added to the round-bottom flask containing the volatiles and distillation was carried out at reduced pressure: boiling point 86.5 - 88°C at 14 Torr, 74% yield.

SYNTHESIS OF DERIVATIVES

Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

By reacting tributyltin hydride with $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, the iodine atom was eliminated from the reactant, leaving an olefin. This synthesis was based on suggestions from Dr. Rolf Winter⁴⁰.

$\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ 4.55 g (0.0096 mol) was pipetted into a 25 mL three neck flask equipped with a Teflon stir bar, an inlet for a N_2 stream, a dropping funnel, and a condenser which was attached to a -78°C acetone/dry ice trap and a drying tube. The reaction flask was flooded with N_2 and placed in a -20°C ethanol/water/liquid N_2 slush bath; 3.33 g (0.115 mol) $[\text{CH}_3(\text{CH}_2)_3]_3\text{SnH}$ previously allowed to warm to room temperature was added slowly over a period of 1 hour via the dropping funnel. The reaction mixture was stirred constantly during the addition. After the addition of the tributyltin hydride was complete, the dropping

funnel was removed, the reaction flask was again flooded with nitrogen and capped. The reaction flask was allowed to warm to room temperature overnight. An orange liquid with two layers resulted. The material was transferred to a distillation apparatus and distilled at reduced pressure. A colorless liquid was recovered: boiling point 55.5 - 58°C at 14 Torr, 61% yield.

Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ using oleum

Two separate methodologies were used to synthesize the alcohol from $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$. The first method involved reacting the iodide with oleum and water and was based on previously published methods^{41,42}. Oleum, 33.85 g (27% SO_3 , 0.056 mol SO_3), was added to a 100 mL three neck flask equipped with a Teflon stir bar, a thermometer, a dropping funnel, and a condenser attached to a drying tube and a trap. A -60°C ethanol/water/liquid N_2 slush bath was used to cool the trap. The reactant, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, 6.17 g (0.016 mol) was added over a period of ten minutes via the dropping funnel. Care was taken to keep the temperature below 50°C. Once the reaction mixture was well mixed and attained a stable temperature it was heated at $45 \pm 5^\circ\text{C}$

for a period of one hour. The solution was cooled to room temperature and 60 mL of saturated NaHSO_3 was slowly added via the dropping funnel. The reaction temperature was kept at $95 \pm 5^\circ\text{C}$ by controlling the addition of NaHSO_3 and cooling with an ice bath. Two phases resulted: the top phase was a yellow aqueous liquid, the bottom phase was a oily nonaqueous liquid. The two phases were separated, placed in separatory funnels, and allowed to set overnight. The aqueous layer separated into more layers; the top layer was a yellow aqueous layer and the bottom layer was a yellow-brown gel. These two layers were separated. The top aqueous layer was extracted with 2 - 10 mL portions of ether. These extracts were added to the gel layer. The separatory funnel containing the aqueous layer was then drained and rinsed with ether. The ether rinse was again added to the gel layer. The gel layer and the oily liquid which had previously been separated were combined and dried over MgSO_4 . The liquid was poured off of the MgSO_4 and the mixture was treated with Hg to remove excess iodine. The ether was removed via a vacuum apparatus. The remaining material was a mixture of solid mercury iodides and a liquid thought to be the

desired alcohol. The liquid was transferred to another flask at -196°C . The solid remained behind. There was insufficient sample to distill, but analysis by MS showed a pure sample. The IR confirmed the presence of the O-H stretch at 3357.0 cm^{-1} . The yield was 35% based on $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$.

Preparation of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ by reaction with a lactam

The synthesis of the alcohol using the SO_3 method was not nearly as straightforward as desired. The synthesis required several steps and required the use of oleum which requires special handling procedures. Due to these shortcomings, a different method was sought for synthesis of the alcohol. In 1995, Brace reported a method for synthesizing 2-(perfluoroalkyl)ethanols using lactams⁴³. This method was modified slightly for use in our laboratory. The reactant, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, 7.27 g (0.019 mol) was pipetted into a 50 mL Carius tube equipped with a Teflon stir bar and then 17.0 g (0.20 mol) 2-pyrrolidinone was added. The reaction vessel was evacuated at -196°C and allowed to warm to room temperature. The vessel was then heated in a 130°C oil bath for 19 hours. The sample was then distilled at reduced pressure, 5.13g of a colorless liquid was

collected from 56 - 115°C at 6 Torr. The remaining nonvolatile salt residue in the pot was treated with a slurry of potassium carbonate 4.01 g (0.029 mol) in 15 mL acetone and 15 mL chloroform. The mixture was refluxed at $66 \pm 9^\circ\text{C}$ for 17 hours. A simple distillation was used to remove the solvents. A distillation at reduced pressure was then carried out on the remaining mixture; 2.10 g of a colorless liquid was collected between 47 - 115°C at 6 Torr. This 2.10 g sample was combined with the 5.13 g sample previously recovered. Another distillation followed at reduced pressure, but this gave insufficient separation. After a few more attempts at distillation, the sample was finally distilled using a fractionation column. The boiling point was 64 - 64.5°C at 13 Torr and the yield was 31% based on $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$. This synthesis of the alcohol was superior to the oleum method because of the fewer number of steps involved and the less difficulty encountered in using the reagents. Although the yield was slightly lower, this could be remedied by performing only one vacuum distillation using a fractionation column instead of several distillations with a short path column.

CHAPTER THREE

RESULTS

In this chapter, the characterization for each of the following six compounds will be discussed:

1. $\text{ICF}_2\text{CF}_2\text{I}$
2. $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$
3. $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}^*$
4. $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$
5. $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$
6. $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Four different analytical procedures were used: IR spectroscopy, NMR spectroscopy, mass spectroscopy, and elemental analysis. IR spectra were collected for all six compounds. ^1H , ^{13}C , and ^{19}F NMR spectra, where appropriate, were also gathered for the compounds. Mass spectra was performed on all compounds except for $\text{ICF}_2\text{CF}_2\text{I}$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$, and elemental analysis was performed on all compounds except for $\text{ICF}_2\text{CF}_2\text{I}$.

* Initial analysis of the NMR spectra for this compound was performed by Dr. Robin J. Terjeson.

IR SPECTROSCOPY

The IR spectra for the six compounds are summarized in tables 3.01 through 3.06. Copies of the original spectra are included in Appendix A. In the tables, terms used to refer to peak intensity are: very weak (vw), weak (w), medium (m), strong (s), and very strong (vs). Broad (b) peaks are also identified.

Cross and coworkers⁴⁴ studied the IR spectra of several compounds containing the SF₅ group. They found that the SF₅ group leads to very intense bands in the region 850 - 920 cm⁻¹ due to the S-F stretching modes and strong bands in the region of 600 cm⁻¹ due to S-F deformation modes. Four compounds containing the SF₅ group which were synthesized and characterized: SF₅CF₂CF₂CF₂CF₂I, SF₅CF₂CF₂CH₂CH₂OH, SF₅CF₂CF₂CH₂CHICH₂CF=CF₂, and SF₅CF₂CF₂CH₂CH₂CH₂CF=CF₂. The IR spectra of each of these compounds showed an intense peak in the region 875 - 885 cm⁻¹ which can be attributed to the S-F stretching mode. A peak with medium to strong intensity in the region 605 - 610 cm⁻¹ was also present for each of these compounds. This peak can be attributed to one of the S-F deformation modes. These values are very similar to

previously synthesized SF_5 -containing fluoroalkyl iodides synthesized by the Gard group²⁰.

Monomeric compounds with C-F and $-\text{CF}_2-$ groupings exhibit strong C-F stretching vibrations usually located in the $1000 - 1250 \text{ cm}^{-1}$ region⁴⁵. The diolefin, $\text{CF}_2=\text{CFCH}_2\text{CH}=\text{CH}_2$, which was used in the synthesis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, showed strong C-F absorptions in the $1100 - 1300 \text{ cm}^{-1}$ region⁴⁶. Strong C-F stretching bands were seen in the region $1103 - 1302 \text{ cm}^{-1}$ for the CF_2 group and a weak band at 1027 cm^{-1} was assigned to the CF stretch for the $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ olefin⁴⁷. The six compounds studied in this work: $\text{ICF}_2\text{CF}_2\text{I}$, $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ showed strong absorption bands in the region $1085 - 1307 \text{ cm}^{-1}$ which can be attributed to CF_2 stretching vibrations. $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ had less intense bands at 997 and 1009 cm^{-1} which can be attributed to the CF stretching.

Four of the compounds had absorptions due to the C-H stretching: $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. These peaks were of weak intensity and were located in

the 3001 - 2856 cm^{-1} region. These values correlate well when compared to previous work^{20,47}.

The C=C stretching frequency of unconjugated alkenes usually shows medium to weak absorption at 1667 - 1640 cm^{-1} when no fluorine atoms are attached to the carbons making up the double bond⁴⁸. The addition of highly electronegative fluorine to the olefinic bond leads to a much higher frequency for the C=C stretching absorption. The C=C stretching frequency for $-\text{CF}=\text{CF}_2$ is generally seen around 1800 cm^{-1} ⁴⁹. The C=C stretching for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ were seen with medium intensity at 1802 cm^{-1} and 1801 cm^{-1} respectively.

The hydroxyl group of alcohols and phenols is usually seen in the region 3550 - 3200 cm^{-1} when intermolecular hydrogen bonding occurs in solution⁴⁸. The broad absorption of medium intensity and centered at 3369 cm^{-1} in the spectra of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ can be attributed to the O-H stretching vibration.

Haszeldine⁵⁰ reported the C-I stretching frequency for perfluorinated iodides in the region 690 - 740 cm^{-1} . The four compounds containing iodine, $\text{ICF}_2\text{CF}_2\text{I}$, $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$, and

$\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, showed absorbances in the region 698 - 751 cm^{-1} which can be attributed to the C-I stretching.

Table 3.01
IR Spectrum of $\text{ICF}_2\text{CF}_2\text{I}$
(on KBr plates)

1207 (m)
1157 (vs)
1104 (vs)
974 (s)
835 (s)
698 (vs)
635 (vw)
575 (w)

Table 3.02
IR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$
(cast film on KBr plates)

3001 (w)
3032 (vw)
2978 (vw)
2962 (vw)
1438 (s)
1429 (w)
1352 (w)
1306 (m)
1191 (s)
1186 (s)
1158 (vs)
1059 (m)
1048 (vs)
922 (m)
915 (s)
754 (w)
735 (w)
560 (w)
506 (m)

Table 3.03
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$
(on KBr plates)

1309 (vw)
1227-1217 (s,b)
1154 (vs)
1114 (m)
1067 (w)
1044 (vw)
918 (s)
885 (vs)
838 (m)
815 (vw)
794 (vw)
786 (vw)
769 (m)
732 (w)
720 (vw)
687 (w)
669 (m)
653 (m)
610 (m)
588 (m)
570 (m)

Table 3.04
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$
(on KBr plates)

3649 (vw)
3369 (m, b)
2965 (w)
2909 (w)
1767 (vw)
1482 (vw)
1445 (wv)
1431 (w)
1399 (w)
1371 (w)
1335 (vw)
1307 (w)
1260 (w)
1196 (s)
1119 (s)
1051 (m)
1009 (m)
962 (w)
875 (vs)
833 (s)
804 (s)
760 (vw)
739 (m)
716 (w)
682 (m)
645 (vw)
605 (s)
574 (m)
550 (w)
529 (w)
486 (vw)
455 (w)
428 (w)

Table 3.05
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$
(on KBr plates)

2967 (vw)
2930 (vw)
2894 (vw)
1802 (m)
1427 (w)
1377 (vw)
1359 (w)
1307 (m, b)
1249 (m)
1201 (s)
1166 (m)
1124 (s)
1085 (m)
997 (w)
963 (vw)
926 (w)
881 (vs)
837 (s)
821 (m)
783 (vw)
751 (m)
684 (w)
605 (m)
576 (w)
540 (vw)
522 (w)
512 (vw)

Table 3.06
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$
(on KBr plates)

2968 (w)
2929 (w)
2894 (vw)
2856 (vw)
1801 (m)
1772 (w)
1559 (vw)
1492 (vw)
1467 (w)
1440 (w)
1390 (w)
1364 (vw)
1303 (m)
1254 (m)
1202 (s)
1139 (m)
1118 (m)
1009 (m)
974 (w)
924 (m)
881 (vs)
833 (s)
791 (m)
744 (m)
705 (vw)
682 (m)
640 (vw)
605 (m)
574 (w)
547 (w)
535 (w)
483 (vw)
449 (vw)
417 (vw)

NMR SPECTROSCOPY

The NMR spectra for the six compounds are summarized in tables 3.07 - 3.22. Copies of the original spectra are included in Appendix B. The spectra support the assigned structures and compare well with spectra for similar compounds previously reported in the literature. The tables include the chemical shift (δ) in ppm from the standard for each peak, and the coupling constants (J) are reported in Hz. A structure of each compound is also shown to specify peak assignments. The multiplicity of the peaks are designated as: singlet(s), doublet(d), triplet(t), pentet(p), or multiplet(m). In several cases more than one multiplicity is noted due to the coupling of the species to more than one nucleus. In general, proton-fluorine coupling constants are larger than proton-proton coupling constants and long-range effects (coupling through more than three bonds) are frequently found⁵¹.

The ^1H assignments for $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ vary from δ 1.93 to 4.48 ppm. The protons adjacent to iodine experience a greater

downfield shift (δ 3.22 and 4.48 ppm) than the protons adjacent to a CF_2 group (δ 2.19 to 2.92 ppm). This is consistent with earlier work²⁰.

The hydroxyl proton of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ is a singlet at δ 3.83 ppm. The protons on the carbon adjacent to the hydroxyl functional group are observed as a triplet at δ 3.94 ppm, showing a greater downfield shift than those protons adjacent to a CF_2 group.

The coupling constants between protons on adjacent carbons are in the range of 6.4 to 7.8 Hz. This compares to a coupling constant of 5.64 Hz found for the two protons on adjacent carbons in $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ ²⁰. The coupling constant between the proton adjacent to the CF_2 group and the fluorine was found to be 18.0 Hz for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. This is in the same range as the value of 22.55 Hz observed for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ ²⁰.

Four of the compounds characterized by ^{19}F NMR contained the SF_5 group: $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$, $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$, and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. The SF_5 group appears as an AB_4 pattern in ^{19}F NMR spectra^{20, 39, 47, 52-55}. The axial fluorine (A) appears as a distorted pentet at δ 63.5 - 65.2 ppm

and the equatorial fluorines (B) appear as a doublet of pentets at δ 43.5 - 44.7 ppm. These values compare favorably to those reported previously for SF₅-containing iodides^{8,11,20}. As a comparison, SF₅CF₂CF₂I and SF₅CF₂CF₂CH₂CH₂I exhibit the AB₄ splitting pattern at δ 65.4 and 65.3 ppm (distorted pentet), and δ 47.25 and 45.5 ppm (doublet), respectively²⁰. The coupling constants for the AB₄ fluorines were consistent in all compounds with J_{a,b} values ranging from 145.1 to 146.8 Hz. These values are again consistent with previous work^{14,15,20}.

The chemical shifts of the CF₂ fluorines adjacent to the SF₅ group range from δ -94.6 to -96.5 ppm. In all cases except for SF₅CF₂CF₂CF₂CF₂I, the peak appears as a broad pentet suggesting that the resolution of the instrument was not adequate to see the fine splitting of the peak. In SF₅CF₂CF₂CH₂CH₂I, this chemical shift is seen at δ -95.89 ppm²⁰. The coupling constants between the equatorial fluorines and those on the adjacent CF₂ group were in the range of 14.2 to 15.1 Hz. This compares to J_{b,c} of 15.0 Hz for SF₅CF₂CF₂CH₂CH₂I²⁰.

Internal CF_2 groups contain multiplets ranging from δ -112.7 to -122.1 ppm. The chemical shift for the internal CF_2 group in $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ also fell within this range (δ -115.7 ppm). The CF_2 fluorines adjacent to CH or CH_2 groups in other iodides range from δ -115.2 to -120.7 ppm⁴¹.

The CF_2I fluorines in $\text{ICF}_2\text{CF}_2\text{I}$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$, have chemical shifts of δ -52.6 and -59.9 ppm, respectively. These values compare well to the literature value of δ -60 ppm for $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ ¹¹.

In the two compounds containing the $-\text{CF}=\text{CF}_2$ group, the three fluorines were found to be non-equivalent. These fluorines are designated as h, i, and j (see structures). The h fluorine has a chemical shift of δ -176.1 ppm for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ and δ -176.9 for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. As a comparison, the equivalent fluorine in $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ has a chemical shift of δ -174.6 ppm⁴⁷. The chemical shift for i is δ -120.9 and -125.7 ppm, respectively. In $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$, this value has been reported as δ -121.2 ppm⁴⁷. The fluorine trans to the R group (j) has a chemical shift of δ

-102.9 and -106.4 ppm for the two compounds. The chemical shift of the equivalent fluorine in $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ was reported as δ -102.4. All three of the fluorines in the $-\text{CF}=\text{CF}_2$ group were coupled to the others. These peaks were seen as doublets of doublets with some additional coupling to protons in the R group. The coupling constants for the fluorines trans to one another ($J_{h,i}$) were 113 and 113.9 Hz. These values are within the range 105.8 - 148 Hz given in the literature⁵⁶. The cis fluorine-fluorine coupling constants ($J_{h,j}$) were found to be 33.4 and 33.9 Hz both within the literature range of 0 - 58 Hz⁵⁶. The coupling between the fluorines on the same carbon ($J_{i,j}$) were calculated to be 79.0 Hz for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ and 88.5 Hz for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. These values again fall within the range of 0 - 112 Hz given in the literature⁵⁶.

The ^{13}C NMR spectra are all proton decoupled, fluorine coupled. The chemical shifts for the alpha carbon adjacent to the SF_5 group, range from δ 121.2 to 122.5 ppm and for the beta carbon from δ 109.4 to 118.3 ppm. This range is consistent with the literature values reported for SF_5 -containing iodides, sulfonic

acids, bromides and dibromides^{20,39,55}. By comparison, the chemical shifts reported for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ are δ 121.65 and 117.4 ppm for the alpha and beta carbons, respectively²⁰. The coupling constants for the alpha carbon to the attached fluorines ranges from 305.9 to 377.8 Hz. These values are consistent with those reported previously²⁰.

The chemical shift for the carbon alpha to iodine in $\text{ICF}_2\text{CF}_2\text{I}$ is δ 93.6 ppm. This is consistent to the value reported for the equivalent carbon in $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ (δ 91.1 ppm)²⁰. The coupling constant, $J_{\alpha,a}$ was calculated as 318.9 Hz.

The alpha carbon to iodine in $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ is a singlet at δ -9.92 ppm and the beta carbon has a chemical shift of δ 35.4 ppm. As a comparison, the equivalent carbons in $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ have a chemical shift of δ -11.61 ppm and 37.50 ppm, respectively²⁰.

The chemical shifts for the internal carbons (γ, δ, ϵ) ranged from δ 11.5 to 55.4 ppm for CH_2 or CHI groups. The value was much greater, δ 93.4 to 118.0 ppm, for CF_2 groups.

The ^{13}C spectra for the two compounds containing the $-\text{CF}=\text{CF}_2$ olefinic group were very similar for those two carbons (ϕ, φ). The carbon attached to the SF_5 -containing fluoroalkyl chain is a doublet, doublet, doublet appearing at δ 127.5 and 127.8 ppm for these two compounds. The equivalent carbon in $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$ has a reported chemical shift of δ 126.0 ppm⁴⁷. The φ carbon is again a doublet, doublet, doublet with a chemical shift of δ 154.3 ppm for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ and δ 153.8 ppm for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$. A chemical shift of δ 154.5 ppm was reported for the equivalent carbon of $\text{SF}_5\text{CH}_2\text{CHBrCH}_2\text{CF}=\text{CF}_2$. Coupling constants between carbon and an attached fluorine ranged from 231.4 to 291.7 Hz.

Table 3.07
 ^{19}F NMR Spectrum of $\text{ICF}_2\text{CF}_2\text{I}$

Peak	Chemical Shift (ppm from CFCl_3)	Coupling Constants (in Hz)
a & b	-52.6(s)	

Table 3.08
 ^{13}C NMR Spectrum (^1H decoupled) of $\text{ICF}_2\text{CF}_2\text{I}$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
α	93.6(t, t)	$J_{\alpha, \text{a}} = 318.9$ $J_{\alpha, \text{b}} = 40.24$

Table 3.09
 ^1H NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
a	3.22 (d, d $\rightarrow$ overlapping)	$J_{a,b} = \sim 7.0$
b	2.65 (m)	

Table 3.10
 ^{19}F NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Peak	Chemical Shift (ppm from CFCl_3)	Coupling Constants (in Hz)
c	-115.7 (m)	

Table 3.11
 ^{13}C NMR Spectrum (^1H decoupled) of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
α	-9.92 (s)	
β	35.4 (m)	
γ	118.0 (t)	$J_{\gamma,c} = 251.5$ $J_{\gamma,d} = 40.2$

Table 3.12
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}^{20}$

Peak	Chemical Shift (ppm from CFCl_3)	Coupling Constants (in Hz)
a	63.5 (p, m)	$J_{a,b} = 146.6$
b	44.64 (d, p)	$J_{b,c} = 14.5$
c	-94.6 (p, m)	$J_{c,d} = 16$ $J_{c,e} = 4$
d	-122.1 (m)	$J_{d,e} = 16.9$ $J_{d,f} = \sim 3$
e	-112.8 (t, t)	$J_{e,f} = 15.5$
f	-59.9 (t, t)	

Table 3.13
 ^{13}C NMR Spectrum (^1H decoupled) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}^{20}$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
α	121.2 (t, p, t)	$J_{\alpha,b} = 36.8$ $J_{\alpha,c} = 311.8$ $J_{\alpha,d} = 27$
β	109.4 (t, t)	$J_{\beta,c} = 32.6$ $J_{\beta,d} = 275.1$
γ	108.8 (t, t)	$J_{\gamma,d} = 31.8$ $J_{\gamma,e} = 269.7$
δ	93.4 (t, t)	$J_{\delta,e} = 42$ $J_{\delta,f} = 321.4$

Table 3.14
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
e	2.39(t, t)	$J_{\text{e}, \text{f}} = 6.4$
f	3.94(t)	
g	3.83(s)	

Table 3.15
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Peak	Chemical Shift (ppm from CFCl_3)	Coupling Constants (in Hz)
a	65.0(p, t)	$J_{\text{a}, \text{b}} = 146.0$ $J_{\text{a}, \text{c}} = 4.31$
b	43.9(d, p)	$J_{\text{b}, \text{c}} = 14.2$ $J_{\text{b}, \text{d}} = 13.6$
c	-96.5(broad p)	
d	-115.0(m)	$J_{\text{d}, \text{e}} = 18.8$

Table 3.16
 ^{13}C NMR Spectrum (^1H decoupled) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
α	122.5 (t, m)	$J_{\alpha, c} = 305.2$
β	118.3 (t, t)	$J_{\beta, c} = 30.9$ $J_{\beta, d} = 256.6$
γ	35.1 (t)	$J_{\gamma, d} = 21.6$
δ	55.4 (s)

Table 3.17
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
e & g (overlapping)	2.92 (m)	
f	4.48 (t, t)	

Table 3.18
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Peak	Chemical Shift (ppm from CFCl_3)	Coupling Constants (in Hz)
a	65.2 (p, t)	$J_{a,b} = 146.8$ $J_{a,c} = 3.77$
b	44.7 (d, p)	$J_{b,c} = 15.1$ $J_{b,d} = 11.3$
c	-96.3 (broad p)	
d	-112.7 (d, m)	$J_{d,d'} = 269.2$
d'	-115.1 (d, m)	
h	-176.1 (d, d, d, d)	$J_{h,i} = 113$ $J_{h,j} = 33.4$ $J_{g,h} = 19.4$ $J_{g',h} = 10.8$
i	-120.9 (d, d, t)	$J_{i,j} = 79.0$
j	-102.9 (d, d, d)	

Table 3.19
 ^{13}C NMR Spectrum (^1H decoupled) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
α	121.7 (t, m)	$J_{\alpha, c} = 301.8$
β	117.5 (t, t)	$J_{\beta, c} = 30.2$ $J_{\beta, d} = 261.6$
γ	42.2 (t)	$J_{\gamma, d} = 21.1$
δ	11.5 (s)	
ϵ	37.4 (d)	$J_{\epsilon, h} = 21.1$
ϕ	127.5 (d, d, d)	$J_{\phi, h} = 231.4$ $J_{\phi, i} = 50.3$ $J_{\phi, j} = 20.1$
φ	154.3 (d, d, d)	$J_{\varphi, h} = 40.2$ $J_{\varphi, i} = 291.7$ $J_{\varphi, j} = 259.0$

Table 3.20
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
e	2.19(d, d $\rightarrow$ 7 line)	$J_{d,e} = 18.0$ $J_{e,f} = 7.8$
f	1.93(p)	$J_{f,g} = 7.6$
g	2.42(d, m)	$J_{g,h} = 22.2$ $J_{g,i} = \sim 7.5$ $J_{g,j} = \sim 3.8$

Table 3.21
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Peak	Chemical Shift (ppm from CFCl_3)	Coupling Constants (in Hz)
a	64.6(p, t)	$J_{a,b} = 145.1$ $J_{a,c} = 4.68$
b	43.5(d, p)	$J_{b,c} = \sim 15.0$ $J_{b,d} = \sim 13.9$
c	-96.3(broad p)	
d	-116.2(m)	
h	-176.9(d, d, t)	$J_{h,i} = 113.9$ $J_{h,j} = 33.9$
i	-125.7(d, d, t)	$J_{i,j} = 88.5$
j	-106.4(d, d, t)	

Table 3.22
 ^{13}C NMR Spectrum (^1H decoupled) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Peak	Chemical Shift (ppm from TMS)	Coupling Constants (in Hz)
α	122.4 (t, m)	$J_{\alpha, c} = 305.9$
β	118.0 (t, t)	$J_{\beta, c} = 30.8$ $J_{\beta, d} = 256.5$
γ	30.8 (t)	$J_{\gamma, d} = 22.6$
δ	16.9 (s)	
ϵ	24.9 (d)	$J_{\epsilon, h} = 21.1$
ϕ	127.8 (d, d, d)	$J_{\phi, h} = 241.4$ $J_{\phi, i} = 55.3$ $J_{\phi, j} = 20.1$
φ	153.8 (d, d, d)	$J_{\varphi, h} = 40.2$ $J_{\varphi, i} = 286.7$ $J_{\varphi, j} = 256.5$

MASS SPECTROSCOPY

A mass spectrometer, using the electron-impact (EI) mode, bombards molecules in the vapor phase with a high-energy electron beam and records the result of the impact as a spectrum of positive ions separated on the basis of mass/charge (m/z)⁵⁷. The major mass/charge spectral peaks for the four compounds analyzed by EI-MS are shown in tables 3.23 through 3.26. The spectra for the compounds were supportive of their assigned structure. Information contained in the tables includes the molecular weight (mol. wt.) of the compound, the retention time (ret. time) of the compound on the gas chromatography column, the major peaks recorded in the spectra, the relative intensity of the peak, and identification of the peak. The base peak, which refers to the most intense peak in the spectrum is also identified.

Molecular ion peaks (M^+), which represent the intact molecule (M) less one electron are seen for $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$. The highest peak seen for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ and $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ corresponds to the loss of one hydrogen atom and one

electron ($M-H^+$). Ions which were commonly observed included those due to the loss of an iodine atom or the SF_5 group ($M-I^+$; $M-SF_5^+$), $m/z = 127$ (I^+ ; SF_5^+), $m/z = 89$ (SF_3^+), and $m/z = 69$ (CF_3^+). These fragments correspond well to results obtained for SF_5 -containing fluoroalkyl iodides²⁰.

The spectrum of $SF_5CF_2CF_2CH_2CH_2OH$ had a base peak of $m/z = 31$ corresponding to CF^+ and CH_2OH^+ . The CH_2OH^+ ion is consistent with the cleavage of the C-C bond next to the oxygen atom which is generally seen in alcohols⁵⁷. A peak at $M-18$ corresponding to the loss of water is commonly seen for alcohols⁵⁷. Although $m/z = 254$ ($M-18$) was not seen in this spectrum, $m/z = 127$ consistent with a loss of water in addition to SF_5 was observed. The SF_5 fragment itself also has $m/z = 127$.

Since the compounds contain sulfur, oxygen, carbon, and hydrogen, isotopic peaks can occur. Isotopic peaks occur due to the existence of more than one isotope for each atom. Table 3.27 shows the naturally occurring isotopes for the elements making up the synthesized compounds. Due to their low abundance, 2H , ^{17}O , ^{18}O , and ^{33}S isotopic peaks were expected to be negligible. Isotopic peaks due to ^{34}S would be expected. A peak with

$m/z = N$ should have a companion peak at $m/z = N+2$ with 4.4% of its intensity. The ions which contained a sulfur atom were relatively small compared to the base peak, however. The resulting isotopic peaks due to ^{34}S , therefore, were not major peaks. In most cases, isotopic peaks from ^{13}C would also be negligible; due to the length of the carbon chain in $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ this was not the case. The peak at m/z 283 ($\text{M}-\text{I}^+$) was the base peak for this spectra. The relative intensity is 100%. Due to the 6 carbon atoms in the molecule, a peak at m/z 284 and a relative intensity of 6.6% would be expected. This peak was seen with a relative intensity of 6.51% observed.

Table 3.23
Mass Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

mol. wt. 410 g/mol ret. time 12.2 min			
Mass/ Charge	Relative Intensity	Identification	Notes
410	43.4	$\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}^+$	M^+
284	6.51	$^{13}\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}^+$	$\text{M}-\text{I}^+$
283	100	$\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}^+$	$\text{M}-\text{I}^+$; base peak
155	12.4	$\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}^+$	$\text{C}_6\text{F}_4\text{H}_7^+$
141	19.2	$\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}^+$	$\text{C}_5\text{F}_4\text{H}_5^+$
135	6.79	$\text{C}_6\text{F}_3\text{H}_6^+$	
127	15.2	I^+	
115	8.24	$\text{CF}_2\text{CF}_2\text{CH}_3^+$	$\text{C}_3\text{F}_4\text{H}_3^+$
97	5.55	$\text{CH}_2\text{CH}_2\text{CF}_3^+$	$\text{C}_3\text{F}_3\text{H}_4^+$
78	5.74	$\text{CH}_2\text{CH}_2\text{CF}_2^+$	$\text{C}_3\text{F}_2\text{H}_4^+$
77	64.5	$\text{CHCH}_2\text{CF}_2^+$	$\text{C}_3\text{F}_2\text{H}_3^+$
59	10.4	$\text{CH}_2\text{CH}_2\text{CF}^+$	C_3FH_4^+
51	13.1	HCF_2^+	CF_2H^+
47	6.11	$\text{FCH}_2\text{CH}_2^+$	C_2FH_4^+
27	15.0	CH_2CH^+	C_2H_3^+

Table 3.24
Mass Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$

mol. wt. 454 g/mol ret. time 4.2 min			
Mass/ Charge	Relative Intensity	Identification	Notes
454	23.2	$\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}^+$	M^+
327	18.8	$\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}^+$; $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2^+$	M-I^+ ; M-SF_5^+
239	17.8	$\text{C}_3\text{F}_4\text{I}^+$; $\text{SF}_5\text{C}_3\text{F}_4^+$	
219	100	$\text{FCF}_2\text{CF}_2\text{CF}_2\text{CF}_2$	C_4F_9^+ ; base peak
208	10.9	SC_2F_8^+	
181	43.1	$\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}^+$	C_4F_7^+
177	30.5	SF_5CF_2^+ ; CF_2I^+	
131	58.9	$\text{CF}_2\text{CF}_2\text{CF}^+$	C_3F_5^+
127	63.7	SF_5^+ ; I^+	
119	23.2	$\text{FCF}_2\text{CF}_2^+$	C_2F_5^+
100	40.5	CF_2CF_2^+	C_2F_4^+
89	34.6	SF_3^+	
69	90.2	CF_3^+	

Table 3.25
Mass Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

mol. wt. 272 g/mol ret. time 5.4 min			
Mass/ Charge	Relative Intensity	Identification	Notes
271	0.1	$\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{O}^+$	M-H^+
127	6.08	SF_5^+ ; $\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}^+$	SF_5^+ ; $\text{M-SF}_5\text{-H}_2\text{O}^+$
119	6.05	$\text{FCF}_2\text{CF}_2^+$	C_2F_5^+
114	6.89	$\text{CF}_2\text{CF}_2\text{CH}_2^+$	$\text{C}_3\text{F}_4\text{H}_2^+$
113	13.8	$\text{CF}_2\text{CF}_2\text{CH}^+$	$\text{C}_3\text{F}_4\text{H}^+$
105	18.3	C_4F_3^+	
95	21.5	$\text{CF}_2\text{CF}_2\text{CH}_2^+$; $\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}^+$	$\text{C}_3\text{F}_3\text{H}_2^+$; $\text{C}_3\text{F}_2\text{H}_5\text{O}^+$
89	28.2	SF_3^+	
77	25.8	$\text{CF}_2\text{CH}_2\text{CH}^+$	$\text{C}_3\text{F}_2\text{H}_3^+$
69	11.4	CF_3^+	
67	8.55	$\text{C}_4\text{H}_3\text{O}^+$	
65	9.08	CF_2CH_3^+	$\text{C}_2\text{F}_2\text{H}_3^+$
64	12.2	CF_2CH_2^+	$\text{C}_2\text{F}_2\text{H}_2^+$
51	10.9	SF^+ ; CF_2H^+	
31	100	CF^+ ; CH_2OH^+	base peak
29	15.6	CH_2CH_3^+	C_2H_5^+
27	6.58	CH_2CH^+	C_2H_3^+

Table 3.26
Mass Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

mol. wt. 476 g/mol ret. time 9.1 min			
Mass/ Charge	Relative Intensity	Identification	Notes
475	5.77	$\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CICH}_2\text{CFCF}_2^+$	$\text{M}-\text{H}^+$; $\text{SC}_7\text{F}_{12}\text{H}_4\text{I}$
349	23.1	$\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHCH}_2\text{CFCF}_2^+$ $\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CFCF}_2^+$	$\text{M}-\text{I}^+$; $\text{M}-\text{SF}_5^+$
221	32.7	$\text{CF}_2\text{CF}_2\text{CH}_2\text{CCH}_2\text{CFCF}_2^+$	$\text{C}_7\text{F}_7\text{H}_4^+$
201	26.9	$\text{C}_7\text{F}_6\text{H}_3^-$	
177	73.1	SF_5CF_2^-	
151	28.8	$\text{C}_6\text{F}_4\text{H}_3^-$	
127	84.6	SF_5^+ ; I^+	
121	60.8	$\text{C}_5\text{F}_3\text{H}_4^-$	$\text{C}_5\text{F}_3\text{H}_4^+$
113	34.6	$\text{CF}_2\text{CF}_2\text{CH}^+$	$\text{C}_3\text{F}_4\text{H}^+$
109	31.9	$\text{C}_4\text{F}_3\text{H}_2^-$	
100	63.5	CF_2CF_2^-	C_2F_4^+
95	100	$\text{CF}_2\text{CF}_2\text{CH}_2^+$	$\text{C}_3\text{F}_3\text{H}_2^+$; base peak
89	42.3	SF_3^+	
77	61.5	$\text{CF}_2\text{CH}_2\text{CH}^+$	$\text{C}_3\text{F}_2\text{H}_3^+$
69	67.7	CF_3^+	
51	38.5	SF^+	

Table 3.27
Relative Abundance of Isotopes⁵⁸

Element	Most Common Isotope	Other Isotopes (Abundance Relative to the Most Common Isotope)	
carbon	^{12}C	^{13}C (1.08)	
fluorine	^{19}F		
hydrogen	^1H	^2H (0.016)	
iodine	^{127}I		
oxygen	^{16}O	^{17}O (0.04)	^{18}O (0.20)
sulfur	^{32}S	^{33}S (0.78)	^{34}S (4.40)

ELEMENTAL ANALYSIS

An elemental analysis of the compound gives the percentage of each element contained in the sample. Tables 3.28 through 3.32 show the results of the analysis performed on five of the compounds. The tables contain the expected results as well as the experimental results. In all but one case, the experimental results and expected results agree to within 1%. The one exception is the analysis of fluorine for $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$. In this case the difference between the expected and experimental results is 2.56% with the analysis showing more fluorine than expected. One possible explanation for this discrepancy could be that the sample is contaminated with either $\text{ICF}_2\text{CF}_2\text{I}$ or $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{I}$. Both cases would result in a higher percentage of fluorine in the sample, but a lower value for the hydrogen and carbon percentages. The hydrogen number is lower than expected, but the carbon number is higher. If a contaminant of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ was present, a higher percentage of fluorine and carbon would be expected for the sample, and a lower percentage of hydrogen. This is what the experimental results

showed, but it is not consistent with the methodology used. There was no source of extra $\text{-CF}_2\text{-}$ units.

Table 3.28
Elemental Analysis of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$
mol. wt. 410 g/mol

Element	Calculated Analysis	Reported Analysis
C	17.58	17.87
H	1.97	1.88
F	18.54	21.1

Table 3.29
Elemental Analysis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$
mol. wt. 454 g/mol

Element	Calculated Analysis	Reported Analysis
C	10.58	10.63
H	0.0	<0.1
F	54.4	54.2

Table 3.30
Elemental Analysis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$
mol. wt. 272 g/mol

Element	Calculated Analysis	Reported Analysis
C	17.65	17.73
H	1.86	1.86
F	62.8	63.2

Table 3.31
Elemental Analysis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$
mol. wt. 476 g/mol

Element	Calculated Analysis	Reported Analysis
C	17.66	17.91
H	1.06	1.11
F	47.9	48.1

Table 3.32
Elemental Analysis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$
mol. wt. 476 g/mol

Element	Calculated Analysis	Reported Analysis
C	24.00	24.35
H	1.73	1.80
F	65.1	64.8
S	9.16	8.97

SUMMARY

The results of the analytical procedures used to characterized the newly synthesized compounds were in agreement with the proposed structures:

- (i) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$
- (ii) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$
- (iii) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$
- (iv) $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

The structures for $\text{ICF}_2\text{CF}_2\text{I}$ and its derivative, $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, were also confirmed.

The IR spectra for the compounds show the peaks characteristic to SF_5 -containing fluoroalkyl iodides. The four compounds containing the SF_5 group had intense bands in the region of $875 - 885 \text{ cm}^{-1}$ due to S-F stretching modes. A medium band in the $605 - 610 \text{ cm}^{-1}$ region attributed to a S-F deformation mode was also observed for each of these compounds. A peak consistent with the C-I stretching frequency for perfluorinated iodides was also present in the infrared spectra of the four compounds containing iodine.

In the ^1H , ^{19}F , and ^{13}C NMR spectra the chemical shifts were in the regions expected for SF_5 -containing fluoroalkyl iodides. The number of peaks observed in

each spectrum and the chemical shift of those peaks were supportive of the assigned structures. The coupling constants also compare favorably with those reported previously in the literature.

The mass spectral data were consistent with the assigned structures for the four compounds analyzed. The molecular ion peak (M^+) or the molecular ion peak less one hydrogen ($M-H^+$) were recorded for the compounds. Commonly observed ions included those due to the loss of an iodine atom or the SF_5 group, the ion due to SF_5 and iodine ($m/z = 127$), and fragments of $m/z = 89$ and 69 which correspond to SF_3^+ and CF_3^+ respectively. These results are again consistent with those recorded in the literature for SF_5 -containing fluoroalkyl iodides.

In general, the results reported for the elemental analyses of the compounds agreed very well with the calculated percentages for each structure. The one exception is the fluorine value for $ICH_2CH_2CF_2CF_2CH_2CH_2I$, however the results for the NMR, IR and MS for this compound were consistent with the assigned structure.

Work with these newly synthesized compounds will continue. Methods will be sought for increasing yields while reducing reaction time. Attempts will also be made to increase the length of the fluoroalkyl chain. Ultimately, these compounds will be used in preparing other fluoro-organic and fluoro-organometallic derivatives for use as SF₅ systems for new dielectrics and polymers. There are several possible commercial applications for these SF₅ polymers including dielectrics, surfactants, optical coatings, perfluorinated blood substitutes, and fumigants.

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APPENDIX A
INFRARED SPECTRA

Figure 3
IR Spectrum of $\text{ICF}_2\text{CF}_2\text{I}$

Figure 4
IR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Figure 5
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$

Figure 6
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Figure 7
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Figure 8
IR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

APPENDIX B
NMR SPECTRA

Figure 9
NMR Peak Assignments for $\text{ICF}_2\text{CF}_2\text{I}$

Figure 10
 ^{19}F NMR Spectrum of $\text{ICF}_2\text{CF}_2\text{I}$

Figure 11
 ^{13}C NMR Spectrum of $\text{ICF}_2\text{CF}_2\text{I}$

Figure 12
NMR Peak Assignments for $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Figure 13
 ^1H NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Figure 14
 ^1H NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ - Peak b
(Refer to Figure 12)

Figure 15
 ^{19}F NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Figure 16
 ^{13}C NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$

Figure 17
 ^{13}C NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ - Peak β
(Refer to Figure 12)

Figure 18
 ^{13}C NMR Spectrum of $\text{ICH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ - Peak γ
(Refer to Figure 12)

Figure 19
NMR Peak Assignments for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$

Figure 20
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$

Figure 21
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak a
(Refer to Figure 19)

Figure 22
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak b
(Refer to Figure 19)

Figure 23
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak c
(Refer to Figure 19)

Figure 24
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak d
(Refer to Figure 19)

Figure 25
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak e
(Refer to Figure 19)

Figure 26
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak f
(Refer to Figure 19)

Figure 27
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$

Figure 28
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peaks α, β, γ
(Refer to Figure 19)

Figure 29
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{I}$ - Peak δ
(Refer to Figure 19)

Figure 30
NMR Peak Assignments for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Figure 31
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

Figure 32
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - Peak a
(Refer to Figure 30)

Figure 33
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - Peak b
(Refer to Figure 30)

Figure 34
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - Peak c
(Refer to Figure 30)

Figure 35
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - Peak d
(Refer to Figure 30)

Figure 37
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - Peak α
(Refer to Figure 30)

Figure 38
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$ - Peak β
(Refer to Figure 30)

Figure 39
NMR Peak Assignments for $SF_5CF_2CF_2CHICH_2CF=CF_2$

Figure 40
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Figure 41
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peaks e, g
(Refer to Figure 39)

Figure 42
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak f
(Refer to Figure 39)

Figure 43
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Figure 44
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak a
(Refer to Figure 39)

Figure 45
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak b
(Refer to Figure 39)

Figure 46
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak c
(Refer to Figure 39)

Figure 47
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peaks d, d'
(Refer to Figure 39)

Figure 48
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak h
(Refer to Figure 39)

Figure 49
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak i
(Refer to Figure 39)

Figure 50
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak j
(Refer to Figure 39)

Figure 51
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$

Figure 52
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peaks α, β, ϕ
(Refer to Figure 39)

Figure 53
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peaks γ, ϵ
(Refer to Figure 39)

Figure 54
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CHICH}_2\text{CF}=\text{CF}_2$ - Peak ϕ
(Refer to Figure 39)

Figure 55
 NMR Peak Assignments for $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Figure 56
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak e
(Refer to Figure 55)

Figure 57
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak f
(Refer to Figure 55)

Figure 58
 ^1H NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak g
(Refer to Figure 55)

Figure 59
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak a
(Refer to Figure 55)

Figure 60
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak b
(Refer to Figure 55)

Figure 61
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak c
(Refer to Figure 55)

Figure 62
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak d
(Refer to Figure 55)

Figure 63
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak h
(Refer to Figure 55)

Figure 64
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak i
(Refer to Figure 55)

Figure 65
 ^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak j
(Refer to Figure 55)

Figure 66
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$

Figure 67
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peaks α, β, ϕ
(Refer to Figure 55)

Figure 68
 ^{13}C NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}=\text{CF}_2$ - Peak ϕ
(Refer to Figure 55)