Portland State University

PDXScholar

Dissertations and Theses

Dissertations and Theses

6-9-1976

The Addition of SF5Br to Unsaturated Systems

Qui-Chee Wendy Wang
Portland State University

Follow this and additional works at: https://pdxscholar.library.pdx.edu/open_access_etds

Part of the [Chemistry Commons](#)

Let us know how access to this document benefits you.

Recommended Citation

Wang, Qui-Chee Wendy, "The Addition of SF5Br to Unsaturated Systems" (1976). *Dissertations and Theses*. Paper 2552.

<https://doi.org/10.15760/etd.2549>

This Thesis is brought to you for free and open access. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

AN ABSTRACT OF THE THESIS OF Qui-Chee Wendy Wang for the Master of Science in Chemistry presented June 9, 1976.

Title: The Addition of SF_5Br to Unsaturated Systems

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

Gary L. Gard, Chairman

Alfred S. Levinson

Horace F. White

Addition reactions of pentafluorosulfur bromide with unsaturated substrates were studied and four new compounds containing the pentafluorosulfur group have been prepared.

The mechanism for these reactions seems to involve a radical addition pathway. In reaction with $\text{CH}_2=\text{CFCl}$, $\text{CF}_3\text{C}\equiv\text{CH}$ and $\text{CH}_3\text{C}\equiv\text{CH}$ the $\text{SF}_5\cdot$ radical attacks the carbon atoms carrying the most hydrogens. The reaction with $\text{CF}_2=\text{CHCl}$ is interesting, as by analogy with other fluoroolefins, the SF_5 primary attack should occur at the CHCl group, however, $\text{SF}_5\text{CF}_2\text{CHClBr}$ was found as the only product for this reaction. The reaction of SF_5Br with $\text{CF}_3\text{C}\equiv\text{CH}$ produced two isomers but with $\text{CH}_3\text{C}\equiv\text{CH}$ only one isomer was formed.

Analytical data, infrared, nmr and mass spectra are presented supporting the proposed structures for these new compounds.

THE ADDITION OF SF_5Br TO UNSATURATED SYSTEMS

by

QUI-CHEE WENDY WANG

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

MASTER OF SCIENCE
in
CHEMISTRY

Portland State University
1976

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of
Qui-Chee Wendy Wang presented June 9, 1976.

[REDACTED]

Gary L. Gard, Chairman

[REDACTED]

Alfred S. Levinson

[REDACTED]

Horace F. White

APPROVED:

[REDACTED]

Gary L. Gard, Head, Chemistry Department

[REDACTED]

Richard B. Halley, Acting Dean of Graduate Studies and Research

ACKNOWLEDGMENTS

The author wishes to thank Dr. Gary L. Gard for his patience, guidance and help in this work; to Dr. Alfred S. Levinson for his interest and helpful discussions; to Dr. Horace F. White for his help in interpreting the nmr spectra; to Mr. W. Anderson of the Oregon Graduate Center for obtaining the mass spectra.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vii
CHAPTER	
I INTRODUCTION	1
II EXPERIMENTAL METHODS	15
III SYNTHESIS OF NEW ADDUCTS OF SF ₅ Br REACTION WITH	20
FLUOROOLEFINS AND ACETYLENES	20
BIBLIOGRAPHY	59

LIST OF TABLES

TABLE		PAGE
I	SF ₅ Br and Fluoroolefin Adducts	2
II	Infrared Spectra Data for SF ₅ Br and Fluoroolefin Adducts	3
III	Gas Chromatography Data for SF ₅ Br and Fluoroolefin Adducts	3
IV	NMR Spectra Data for SF ₅ Br and Fluoroolefin Adducts .	4
V	SF ₅ Cl Adducts with Olefins	6
VI	SF ₅ Olefins	7
VII	Derivatives of SF ₅ Compounds	7
VIII	Reactions of Arylsulfur Pentafluorides	11
IX	Reaction of S ₂ F ₁₀ with Olefins	12
X	Gas Chromatography Data for SF ₅ Br Adducts	24
XI	Elemental Analysis for SF ₅ Br Adducts	24
XII	Physical Properties of the Adducts	25
XIII	Infrared Absorption Bands for Saturated Adducts . . .	27
XIV	Infrared Absorption Bands for Unsaturated Adducts . .	28
XV	Mass Spectra for SF ₅ CH ₂ CFClBr	30
XVI	Mass Spectra for SF ₅ CF ₂ CHClBr	31
XVII	Mass Spectra for SF ₅ CH=C(CH ₃)Br	33
XVIII	Mass Spectra for SF ₅ CH=C(CF ₃)Br	34
XIX	Mass Spectra for SF ₅ CH=C(CF ₃)Br, First G.C. Isomer . .	36
XX	Mass Spectra for SF ₅ CH=(CF ₃)Br, Second G.C. Isomer . .	38

TABLE

PAGE

XXI	Mass Spectra for $\text{SF}_5\text{CH}=\text{CH}_2$	40
XXII	NMR Data for New SF_5Br Adducts	42

LIST OF FIGURES

FIGURE		PAGE
I	Glass Vacuum Manifold	16
II	Infrared Spectrum for $\text{SF}_5\text{CF}_2\text{CHClBr}$	49
III	Infrared Spectrum for $\text{SF}_5\text{CH}_2\text{CFC1Br}$	50
IV	Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$	51
V	Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ Mixture . . .	52
VI	Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ - First G.C. Fraction	53
VII	Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ - Second G.C. Fraction	54
VIII	NMR Proton Spectrum for $\text{SF}_5\text{CF}_2\text{CHClBr}$	55
IX	NMR Proton Spectrum for $\text{SF}_5\text{CH}_2\text{CFBrCl}$	56
X	NMR Proton Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$	57
XI	NMR Proton Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ Mixture . .	58

CHAPTER I

INTRODUCTION

The Addition of SF₅Br to Unsaturated Systems

Pentafluorosulfur bromide (SF₅Br) was first prepared by C. Merrill (1962) by reacting SF₄ with Br₂ and BrF₅ at 100°C under pressure (1). Later (1965), B. Cohen and A. MacDiarmid prepared SF₅Br by reacting S₂F₁₀ with Br₂ at 138° (2). SF₅Br boils at 3.1° at one atmosphere and melts at -78.8° to -78.4°. Its density is 2.098 g/cc at -20.1° (1).

Strong S-F infrared absorption bands are found for SF₅Br at 11.22, 11.80 and 14.49 μ (3). In the liquid state SF₅Br has a faintly yellow color. It decomposes above 150° and is easily hydrolyzed at room temperature (1) according to the following equations:

Pentafluorosulfur bromide is a particularly valuable intermediate for the incorporation of SF₅ groups into molecules (4). A. Berry and W. Fox unsuccessfully tried to generate the corresponding SF₅-silicon derivatives via reactions of pentafluorosulfur bromide with appropriately substituted silanes (5). However, it is known that SF₅Br adds to fluoroolefins to form SF₅-carbon derivatives readily (4). Results of this work are summarized in Tables I, II, III, and IV. The authors concluded that SF₅Br should be a useful reagent for introducing SF₅

groups into carbon compounds. It added more readily and directly than either SF_5Cl or S_2F_{10} and like SF_5Cl the SF_5 group bonds to the carbon of the fluoroolefins carrying the most hydrogens.

Dehydrobromination of the adducts in Table I yield the corresponding SF_5 containing olefins (4).

More recent work by W. Fox and A. Berry (5) showed that SF_5Br will add to the olefinic double bonds of several vinyl silanes as follows:

Also, W. Fox and A. Berry (6) reported that the addition of SF_5Br to pentafluorosulfur ethane ($\text{SF}_5\text{CH}=\text{CH}_2$) produced a bis(pentafluorosulfur) ethane bromide:

Surprisingly, more highly halogenated pentafluorosulfur ethylenes ($\text{SF}_5\text{CH}=\text{CHF}$, $\text{SF}_5\text{CH}=\text{CF}_2$, $\text{SF}_5\text{CF}=\text{CFH}$, $\text{SF}_5\text{CF}=\text{CF}_2$) did not undergo SF_5Br addition to a measurable extent even under more stringent conditions(6).

TABLE I

SF_5Br and Fluoroolefin Adducts			
Reactants	Reaction Conds.	B.P. ($^\circ\text{C}$)	Adducts
$\text{SF}_5\text{Br} + \text{CH}_2 = \text{CHF}$	24 hours R.T.	99.5-100.5	$\text{SF}_5\text{CH}_2\text{CHFBr}$ ✓
$\text{SF}_5\text{Br} + \text{CH}_2 = \text{CF}_2$	24 hours R.T.	86-87	$\text{SF}_5\text{CH}_2\text{CF}_2\text{Br}$ ✓
$\text{SF}_5\text{Br} + \text{CHF} = \text{CF}_2$	24 hours R.T.	74-75	$\text{SF}_5\text{CHFCF}_2\text{Br}$ ✓
$\text{SF}_5\text{Br} + \text{CFCl} = \text{CF}_2$	24 hours R.T.	94-95	$\text{SF}_5\text{C}_2\text{F}_3\text{ClBr}$

TABLE II
INFRARED SPECTRA DATA* FOR SF₅Br AND FLUOROOLEFIN ADDUCTS
Cm⁻¹*

SF ₅ CH ₂ CHBr	1416 (w),* 1364 (w), 1307 (w), 1196 (w), 1086 (s), 1042 (s), 900 (vs), 874 (vs), 847 (vs), 751 (w), 681 (w)
SF ₅ CH ₂ CF ₂ Br	1416 (w), 1323 (w), 1274 (w), 1224 (m), 1189 (w), 1124 (s), 1047 (m), 955 (vs), 914 (m), 891 (vs), 873 (vs), 855 (vs), 797 (m), 741 (w), 694 (w)
SF ₅ CHFCF ₂ Br	1324 (w), 1295 (w), 1232 (s), 1161 (vs), 1060 (m), 983 (vs), 968 (s), 883 (vs), 808 (m), 775 (m), 758 (w), 706 (s)
SF ₅ C ₂ F ₃ ClBr	1214 (s), 1175 (w), 1117 (s), 1055 (w), 1020 (w), 936 (vs), 894 (vs), 854 (m), 816 (m), 760 (m), 724 (s), 685 (m)

*w = weak; m = medium; s = strong; vs = very strong

TABLE III
GAS CHROMATOGRAPHY DATA* FOR SF₅Br AND FLUOROOLEFIN ADDUCTS

<u>Compound</u>	<u>Retention Time (min.)</u>	
SF ₅ CH ₂ CHBr	35	
SF ₅ CH ₂ CF ₂ Br	15	*The column temperature was 59±1°. Helium flow rate was 2.5 ml/sec.
SF ₅ CHFCF ₂ Br	5.6	
SF ₅ C ₂ F ₃ ClBr	3.8	
CCl ₄	7.5	

TABLE IV

NMR SPECTRA DATA FOR SF₅Br AND FLUOROOLEFIN ADDUCTS

			Chemical Shifts, Band Centers*					
			S-F	SF ₄	CF	CF ₂	CH ₂	CH
Proposed Structure			-79.9	-66.4	139.2		4.27	6.95
Skeletal Atom Number			-77.3	-70.5		51.5	4.46	
			-70.0	-53.7	163.5	63.1		5.58
			-65.4	-48.5	76.8	88.5		
1	2	3						
SF ₅	CH ₂	CHFBr						
SF ₅	CH ₂	CF ₂ Br						
SF ₅	CHF	CF ₂ Br						
SF ₅ C ₂ F ₃ ClBr ⁺								
			J ^{H,F} _{1,2}	J ^{H,F} _{2,3}	J ^{H,H} _{2,2}	J ^{H,H} _{2,3}	J ^{H,H} _{2,3}	J ^{H,F} _{3,3}
			8	24	***	***	***	50
			7	14				
			5		J ^{H,F} _{2,3} = 3	J ^{H,F} _{2,3} = 13		44

*Chemical shifts in parts per million upfield from CFC1₃ internal standard or downfield from Si(CH₃)₄ internal standard.

**Measured in cycles per second.

***Data unavailable as a detailed analysis of this compound is incomplete; J^{H,H}_{2,3} + J^{H,H}_{2,3} = 11 cps.

+Structure unknown.

In addition to SF_5Br , two other compounds, SF_5Cl and S_2F_{10} , have been studied.

SF_5Cl is a less active potential reagent for introducing SF_5 groups into simple molecular structures than the bromo-analog as indicated by the reaction conditions (4). Nevertheless, its reactions have been intensely studied. SF_5Cl is a colorless gas (b.p. -21°) that reacts with aqueous alkali solutions very rapidly (7). Table V lists the reactions of SF_5Cl with unsaturated systems (8-11).

Dehydrohalogenation of the adducts in Table V produced the corresponding unsaturated SF_5 compounds (8,9) as shown in Table VI.

The extent to which these and other SF_5 compounds are used in preparing new and interesting derivatives is illustrated in Table VII (8-15).

It is reported that arylsulfur pentafluorides cannot be prepared using SF_5Cl (16).

The first synthesis of aryl sulfur pentafluorides was accomplished by the reaction of aryl disulfides or arylsulfur trifluorides with silver difluoride at 120°C in a teflon reactor.

Later a modified procedure involved the addition of bis-(phenyl)disulfide to five molar equivalents of silver difluoride, suspended in "Freon 113," in a copper reactor. This was found particularly useful for the reaction of bis-(m- and p-nitrophenyl) disulfides with silver difluoride. The above procedure has also been employed for the preparation of an aromatic compound substituted with two sulfur pentafluoride

groups (17) as shown below:

TABLE V

SF₅Cl ADDUCTS WITH OLEFINS

Reactants	Reaction Conds.	B.P. (°C)	Products (Adducts)
SF ₅ Cl + CH ₂ =CH ₂	10 hrs. 90°	92 171-172	SF ₅ CH ₂ CH ₂ Cl + SF ₅ (CH ₂ CH ₂) ₂ Cl
SF ₅ Cl + CFC1=CF ₂	10 hrs. 100°	79.5-82	SF ₅ CFC1CF ₂ Cl
SF ₅ Cl + CF ₂ =CF ₂	10 hrs. 90°	47 99 142	SF ₅ CF ₂ CF ₂ Cl + SF ₅ (CF ₂ CF ₂) ₂ Cl + SF ₅ (CF ₂ CF ₂) ₃ Cl
SF ₅ Cl + CH ₃ CH=CH ₂	3 hrs. 100°	109	SF ₅ CH ₂ CHClCH ₃
SF ₅ Cl + CF ₂ =CFH	6 hrs. 150°	59-61	SF ₅ CHF-CF ₂ Cl
SF ₅ Cl + CF ₂ =CFC1	10 hrs. 100°	80-83	SF ₅ CF ₂ CFC1 ₂
SF ₅ Cl + CH ₂ =CHCl	6 hrs. 150°	108 72/9 mm	SF ₅ CH ₂ CHCl ₂ (35%) + SF ₅ CH ₂ CHClCH ₂ CHCl ₂ (25%)
SF ₅ Cl + CF ₃ CF=CF ₂	U.V.	71-73	SF ₅ CF ₂ CFC1CF ₃ + CF ₃ SF ₅ CFC1CF ₂
SF ₅ Cl + CH≡CH	U.V.		SF ₅ CH=CHCl
SF ₅ Cl + CH ₃ C≡CH	4 hrs. 90° (or U.V.)		SF ₅ CH=CC1CH ₃
SF ₅ Cl +	R.T.	188-190
SF ₅ Cl + CH ₃ - -O-C(CH ₃)=CH ₂	1 hr. 100°	126	SF ₅ CH ₂ - -CH ₃
SF ₅ Cl + CH ₂ =C=O	20 hrs. R.T.	102	SF ₅ CH ₂ - -Cl
SF ₅ Cl + CH ₃ - -O-CH=CH ₂	1 hr. 50°	36/2.7 mm	SF ₅ CH ₂ CHClO- -CH ₃
SF ₅ Cl + CH ₃ O-CF=CF ₂	6 hrs. 100° (Bz ₂ O ₂ cat.)		SF ₅ CF ₂ CF ₁ ClOCH ₃
SF ₅ Cl + C ₂ H ₅ O-CF=CF ₂	6 hrs. 100° or (Bz ₂ O ₂)		SF ₅ CF ₂ CFC1OC ₂ H ₅

TABLE VI
SF₅ OLEFINS

<u>Reactants</u>	<u>Reaction Conds.</u>	<u>B.P. (°C)</u>	<u>Products</u>
SF ₅ CH ₂ CH ₂ Cl + KOH	1 hr. (ethanol as solvent)	41	SF ₅ CH=CH ₂
SF ₅ CH ₂ CHClCH ₃ + KOH	2.5 hr. (methanol)	80-82	SF ₅ CH=CHCH ₃ major SF ₅ CH ₂ CH=CH ₂
+ KOH	15 min. (ethanol)	161
SF ₅ CHClCH ₃ + KOH	20 min. (pet ether) 75°C	66	SF ₅ CH=CH ₂

TABLE VII
DERIVATIVES OF SF₅ COMPOUNDS

<u>Reactants</u>	<u>Reaction Conds.</u>	<u>B.P. (°C)</u>	<u>Products</u>
SF ₅ CH=CH ₂ + Cl ₂	U.V.	111	SF ₅ CHClCH ₂ Cl
SF ₅ CF=CF ₂ + Cl ₂	U.V.	79.5-82	SF ₅ CFC1CF ₂ Cl
SF ₅ CF=CF ₂ + CF=CF ₂	10-60 atm. 50-100°C		(CF ₂ -CF ₂ -CF ₂ -C ^F -) SF ₅
SF ₅ C≡CH + CH ₃ OH	OH ⁻ as cat.	144
SF ₅ CH=CHCl + CH ₃ OH	OH ⁻ as cat.	115

TABLE VII (cont.)

Reactants	Reaction Conds.	B.P. (°C)	Products
$\text{SF}_5\text{C}\equiv\text{CH} + \text{CH}_2\text{N}_2$			$ \begin{array}{c} \text{H}-\text{C}-\text{C}-\text{SF}_5 \\ \parallel \parallel \\ \text{H}-\text{C} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{N} \\ \\ \text{H} \end{array} + \begin{array}{c} \text{F}_5\text{S}-\text{C}-\text{CH} \\ \parallel \parallel \\ \text{C} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{H} \\ \\ \text{N} \\ \\ \text{H} \end{array} $ 60% 40%
$\text{SF}_5\text{C}\equiv\text{CH} + \text{CH}_2=\text{CHCH}=\text{CH}_2$	120°		$ \begin{array}{c} \text{SF}_5-\text{C}=\text{C}-\text{H} \\ \quad \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \quad \\ \text{HC}=\text{CH} \end{array} $
$ \begin{array}{c} \text{SF}_5-\text{C}=\text{C}-\text{CH} \\ \quad \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \quad \\ \text{C}=\text{C} \\ \quad \quad \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array} $	Chloranil
$\text{SF}_5\text{CH}=\text{CHCl} + \text{Br}_2$	U.V.	70 (13 mm)	$\text{SF}_5\text{CHBrCHBrCl}$
$\text{SF}_5\text{CHBrCHBrCl} + \text{K}_2\text{CO}_3$	12 hrs. 35°	50 (52 mm)	$\text{SF}_5\text{CBr}=\text{CHCl}$
$\text{SF}_5\text{CBr}=\text{CHCl} + \text{Zn}$	1-1/2 hrs. 140°	6	$\text{SF}_5\text{C}\equiv\text{CH}$
$\text{SF}_5\text{CH}=\text{CHCl} + \text{KOH}$		6	$\text{SF}_5\text{C}\equiv\text{CH}$
$\text{SF}_5\text{CF}_2\text{CFCIOCH}_3 + \text{EtOH}$	80-85° $\xrightarrow{\text{H}_2\text{SO}_4}$		$\text{SF}_5\text{CF}_2\text{COOEt}$
$ \begin{array}{c} \text{SF}_5-\text{C}=\text{C}-\text{H} \\ \quad \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \quad \\ \text{HC}=\text{CH} \quad \text{CH}_3 \quad \text{CH}_3 \end{array} $	Pt. gauze, 575°	147
$\text{SF}_5\text{C}\equiv\text{CH} + \text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$	120-140°		$ \begin{array}{c} \text{SF}_5-\text{C}=\text{C}-\text{H} \\ \quad \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \quad \\ \text{C}=\text{C} \\ \quad \quad \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array} $

TABLE VII (cont.)

<u>Reactants</u>	<u>Reaction Conds.</u>	<u>B.P. (°C)</u>	<u>Products</u>
$\text{SF}_5\text{CH}=\text{CH}_2 + \text{Br}_2$	U.V. (37 min.)	50-52/22 mm	$\text{SF}_5\text{CHBrCH}_2\text{Br}$
$\text{SF}_5\text{CHBrCH}_2\text{Br} + \text{K}_2\text{CO}_3$	33° (75 min.)	86	$\text{SF}_5\text{CBr}=\text{CH}_2$
$\text{SF}_5\text{CBr}=\text{CH}_2 + \text{Br}_2$	2 hrs. U.V.	42/0.5 mm	$\text{SF}_5\text{CBr}_2\text{CH}_2\text{Br}$
$\text{SF}_5\text{CH}_2\text{CHO} + (\text{CH}_3\text{CO})_2\text{O}$		49/0.15 mm	$\text{SF}_5\text{CH}_2\text{CH}(\text{O}_2\text{CCH}_3)_2$
$\text{SF}_5\text{CH}_2\text{COCl} + \text{H}_2\text{O}$	20 min. 47°	m.p. 62-64	$\text{SF}_5\text{CH}_2\text{COOH}$
$\text{SF}_5\text{CH}_2\text{COCl} + \text{C}_2\text{H}_5\text{OH}$		60/41mm	$\text{SF}_5\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$
$\text{SF}_5\text{CH}_2\text{COCl} + \text{C}_6\text{H}_5\text{NH}_2$		m.p. 114-116	$\text{SF}_5\text{CH}_2\text{CONHC}_6\text{H}_5$
$\text{SF}_5\text{CH}_2\text{CHClO}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_3 +$ $\text{KOH} + \text{P}_2\text{O}_5$			$\text{SF}_5\text{CH}_2\text{CHO}$
$\text{SF}_5\text{CH}_2\text{COCl} + \text{NH}_3$		m.p. 143-144	$\text{SF}_5\text{CH}_2\text{CONH}_2$
$\text{SF}_5\text{C}\equiv\text{CH} + \text{AgNO}_3$	0°	Decomp. at R.T.	$\text{SF}_5\text{C}\equiv\text{CAg}$
$\text{SF}_5\text{CF}=\text{CF}_2 + \text{IF}$	3 hrs. 140-150°	80-82	$\text{SF}_5\text{CFICF}_3$
$\text{SF}_5\text{CFICF}_3 + \text{CH}_2=\text{CH}_2$	U.V.	98	$\text{SF}_5\text{CFCF}_3\text{CH}_2\text{CH}_2\text{I}$
$\text{SF}_5\text{CF}=\text{CF}_2 + \text{O}_3$	FC-43 (solvent) -80°		$\text{SF}_5\text{O}-\text{CF}_2-\text{COF}$
$\text{SF}_5\text{CF}=\text{CF}_2 + \text{O}_2$	No Solvent (45°)		$\text{SF}_5\text{OCF}_2\text{COF}$
$\text{SF}_5\text{OCF}_2\text{COF} + \text{H}_2\text{O}$			$\text{SF}_5\text{OCF}_2\text{COOH}$
$\text{SF}_5\text{OCF}_2\text{COOH} + \text{NH}_3$			$\text{SF}_5\text{OCF}_2\text{CONH}_2$
$\text{SF}_5\text{OCF}_2\text{COF} + \text{CH}_3\text{OH}$			$\text{SF}_5\text{OCF}_2\text{COOCH}_3$
$\text{SF}_5\text{CF}_2\text{COOET} + \text{NH}_3$	ET ₂ O as solvent		$\text{SF}_5\text{CF}_2\text{CONH}_2$
$\text{SF}_5\text{CF}_2\text{CONH}_2$	(alc. NaOH) $\xrightarrow[\Delta]{\text{H}_2\text{SO}_4}$		$\text{SF}_5\text{CF}_2\text{COOH}$
$\text{SF}_4\text{CF}_2\text{CO}_2\text{Ag} + \text{I}_2$	Heat		$\text{SF}_5\text{CF}_2\text{I}$

The sulfur pentafluoride group, like the trifluoromethyl group, is electron withdrawing and meta directing towards electrophilic aromatic substitution. Representative reactions of phenyl sulfur pentafluoride and some arylsulfur pentafluorides are shown in Table VIII (17).

Disulfur decafluoride (S_2F_{10}) is a colorless liquid boiling at 29° (18). In practice, it has been found that despite the fact that the S-S bond in disulfur decafluoride breaks readily at 150°C (16), the reaction of S_2F_{10} with olefins proceeds at best in very poor yield and in other cases not at all. It appears that S_2F_{10} gives as its principal reaction, destructive oxidations due to the reactions:

and that as a reagent for introducing the SF_5 group into organic molecules it is much less efficient than SF_5Cl , not to mention SF_5Br (4,20). Table IX gives the reactions of S_2F_{10} with some olefins (20-22).

The mechanism for these reactions seems to undergo a radical addition pathway. In the case of SF_5Cl and SF_5Br the $\text{SF}_5^\cdot$ radical attacks the carbon of the fluoroolefins carrying the most hydrogens (8,9,13). The proposed elementary steps are as follows (8-9):

TABLE VIII
REACTIONS OF ARYLSULFUR PENTAFLUORIDES

<u>Reactants</u>	<u>Reaction Conds.</u>	<u>Products</u>
$C_6H_5SF_5 + HNO_3$	H_2SO_4 as cat.	m-($F_5SC_6H_4NO_2$)
$C_6H_5SF_5 + H_2SO_4$	100°	$C_6H_5SO_2F$
$F_5SC_6H_4NO_2 + H_2$	Pt as cat.	$SF_5C_6H_4NH_2$
$F_5SC_6H_4NH_2 + HONO/HX$		$F_5SC_6H_4OH \xleftarrow{H_2O/H^+} F_5SC_6H_4N_2^{+}X^{-}$ <div style="display: flex; justify-content: center; align-items: center;"> <div style="text-align: center;"> $\swarrow$ CuBr HBr $F_5SC_6H_4Br$ </div> <div style="text-align: center;"> $\searrow$ H_3PO_2 $C_6H_5SF_5$ </div> </div>
$F_5SC_6H_4Br + Mg + CH_3I + CO_2$	ether as solvent	$F_5SC_6H_4CO_2H$
$F_5SC_6H_4Br + Mg + CH_3I + CH_3\overset{O}{\parallel}CH$	ether as solvent	$F_5SC_6H_4CHOHCH_3$
$F_5SC_6H_4CHOHCH_3 + P_2O_5$		$F_5SC_6H_4CH=CH_2$

TABLE IX

REACTIONS OF S_2F_{10} WITH OLEFINS

<u>Reactants</u>	<u>Reaction Conds.</u>	<u>B.P. (°C)</u>	<u>Products</u>
$S_2F_{10} + CH_3CH=CH_2$	10 hrs. 90°	high b.p. residue	not identified
$S_2F_{10} + CH_2=CHCl$	10 hrs. 150°	110-120°	$SF_5CH_2-CHClSF_5$
$S_2F_{10} + CF_3CF=CF_2$	15 hrs. 200°	96°C	$SF_5CF_2-CFSF_5CF_3$
$S_2F_{10} + CF_2=CF_2$	10 hrs. 200°	soften at 260°	white solid
$S_2F_{10} + $	10 hrs. 180° (CCl_3F) solvent	147°
$S_2F_{10} + CH_2=CHCl$	125-140°		$CH_2FCHClSF_5$
$S_2F_{10} + CH_2=CHBr$	125-140°		$CH_2FCHBrSF_5$
			$CH_2FCHBrCH_2CHBrSF_5$
$S_2F_{10} + CH_2=CHF$	140-150°		$CH_2FCHFCH_2CHFSF_5$
			$CH_2=CHCHFCH_2SF_5$
$S_2F_{10} + IC_2F_4I$	4 hrs. 150°		$SF_5(C_2F_4)I$
			$SF_5(C_2F_4)_n I,$ $n = 4 \sim 9$
$S_2F_{10} + CH_2=C=CH_2$	125°		$SF_5CH_2CF_2CH_2F$
$S_2F_{10} + C_2H_5C\equiv CH$	125°		$SF_5CHFCF_2C_2H_5$

With ultraviolet excitation homolysis of the SF_5X molecule produces both $\text{SF}_5\cdot$ and $\text{X}\cdot$ radicals which then compete with each other for the substrates as illustrated below (23-24):

SF_5 compounds exhibit a wide range of useful and interesting properties. For example, SF_5 (25), CF_3SF_5 (25), $\text{SF}_5\text{CF}=\text{CF}_2$ (26), and SF_5 -oxetanes (27) possess unusual dielectric strength while S_2F_{10} (25), and $\text{SF}_5\text{CF}=\text{CF}_2$ (28) are biologically active. In addition, SF_6 (25), RFSF_5 (29), SF_5 -oxetanes (27) and S_2F_{10} (25) have high chemical stability towards concentrated acids and bases. It is expected that new SF_5 compounds will provide the basis for further study regarding the above properties and new SF_5 -olefins should be useful in preparing surface active polymers.

The purposes of this work were to further study the reaction of SF_5Br with fluoroolefins and to extend the SF_5Br addition reaction to compounds containing a triple bond. Four new compounds were prepared:

All these new compounds are clear, water-white readily distillable liquids. They have been characterized via their infrared spectra, mass spectra, and nuclear magnetic spectra. Particularly interesting was the fact that reaction (19) produced two isomers while all other reactions yielded essentially only one product.

CHAPTER II

EXPERIMENTAL METHODS

Vacuum System

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

Reaction Vessels

Pyrex-Glass Reaction Vessels. For those reactions occurring at room temperature 1, 2, or 3-liter Pyrex glass vessels were used.

These vessels were equipped with a cold finger at the bottom for condensing the materials and were closed with 2 mm high vacuum Teflon stopcocks. These vessels were tipped with 10/30 joints for attaching to the vacuum line.

Metal High Pressure Vessel

Sulfur bromide pentafluoride was prepared in a 75 ml Monel vessel equipped with a Whitey-Stainless steel valve tipped with a brass 10/30

Figure 1. Glass Vacuum Manifold

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

inner joint. Reactions of SF_5Br requiring heat were carried out in a 200 cm^3 stainless steel vessel equipped with a brass valve tipped with a brass 10/30 inner joint. The pressure vessel was placed in an oven heated to approximately 100° .

Physical Methods

Fractional Distillation. The products of the reactions were purified by fractional distillation. A Bantam-ware (Kontes) distillation apparatus was used. The distillation column was connected to atmosphere through a -78° trap.

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

Molecular Weights. Molecular weights were determined on the vacuum line by the vapor density method. A 209.6 cm^3 Pyrex bulb, equipped with a Teflon stopcock was used.

Infrared Spectra

Infrared spectra were obtained over the range $4000\text{--}250\text{ cm}^{-1}$ on a Perkin-Elmer 467 spectrometer. Gaseous samples were contained in a 8.25 cm Monel cell fitted with AgCl windows and a Whitey-Brass valve which was connected to a brass 10/30 inner joint for attachment to a vacuum line.

Nuclear Magnetic Resonance Spectra.

The proton spectra were recorded on a Varian Model A-60 or a Varian model EM 300X NMR spectrometers.

Mass Spectra

Mass spectra were taken on a CEC 21-110 B double focus Mass Spectrometer equipped with a 6 KV ion accelator and operated at 70 volts. Perfluorokerosine (PFK) was used on an internal standard.

Chemical Analysis

Chemical analyses were performed by Beller Microanalytical Laboratory in Gottingen, West Germany.

Reagents

Pentafluorosulfur Bromide. SF_5Br was prepared by the method of Berry and Fox (6) in which S_2F_{10} and Br_2 are heated at 150° in a Monel reactor for 16 hours. No attempts were made to purify the SF_5Br (possible contaminants are SF_6 , SF_4 , S_2F_{10} and Br_2) other than transferring it from the Monel reactor at -60 to -50° .

1-Chloro-1-fluoroethylene

The 1-Chloro-1-fluoroethylene was purchased from Peninsular ChemResearch and used without further purification. The purity was checked by infrared analysis.

2-Chloro-1, 1-difluoroethylene

2-Chloro-1, 1-difluoroethylene was purchased from Peninsular ChemResearch and was used without further purification. The purity was checked by infrared analysis.

Methyl Acetylene

Methyl Acetylene was purchased from Air Products and Chemicals and was used without further purification. The purity was checked by

infrared analysis.

Disulfurdecafluoride

S_2F_{10} was obtained as a gift from Dr. Meude Tremblay, Centre Canadien de Recherches et Perfectionnement des Armes (CARDE) Quebec, Canada. The molecular weight was found to be 254.8 g/mole (theor. = 254.1 g/mole).

Bromine

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

CHAPTER III

SYNTHESIS OF NEW ADDUCTS OF SF₅Br REACTION WITH FLUOROOLEFINS AND ACETYLENES

Introduction

Pentafluorosulfur bromide reacts with

according to the following equations:

All of the new products were clear, colorless hydrolytically stable liquids. The product reported in equation (23) is in reality a mixture of two isomers (see below)

Entgegen Isomer

and

Zusammen Isomer

that have been separated by gas chromatography and identified via their

mass spectra, infrared spectra, and nmr spectra. For the other adducts, essentially one compound was found.

EXPERIMENTAL

Reaction of SF₅Br with CH₂=CFCl

In a 3-liter pyrex vessel, 6.25×10^{-2} moles of CH₂=CFCl and 7.3×10^{-2} moles of SF₅Br were condensed at -196°. The vessel was warmed slowly from -196° to room temperature and the disappearance of yellow SF₅Br and appearance of a colorless clear liquid were then observed. The reaction was allowed to stand overnight and was essentially complete after 24 hours. The clear liquid was distilled through a Kontes all-glass distillation apparatus and fraction boiling at 119° was collected. The infrared spectrum of this product showed contamination by the starting olefin. The adduct was purified by washing with water, drying with MgSO₄ and redistillation. The yield for this reaction was 28%.

Reaction of SF₅Br with CF₂=CHCl

The reaction of SF₅Br with CF₂=CHCl was first tried in a 1-liter Pyrex glass reaction vessel, in which 2.1×10^{-2} moles of CF₂CHCl and 2.4×10^{-2} moles of SF₅Br were condensed at -196°. When warmed to room temperature, no reaction was evident until after 7 days. For 24 days the yield of this reaction was 14%. An improved method was found in which 3.4×10^{-2} moles of CF₂=CHCl and 8.2×10^{-2} moles of SF₅Br were condensed in a 200 ml Hoke stainless steel vessel at -196° and the mixture was heated, in an oven, at 100° for 14 days.

The product was distilled and the fraction boiling at 111 - 111.5° was collected. The yield for this modified procedure was 73%. The infrared spectrum of this fraction showed the product to be contaminated with the olefin. The procedure used to purify SF₅CH₂CFC1Br did not work in this case. A pure sample was obtained via gas chromatography.

Reaction of SF₅Br with CH₃C ≡ CH

In a 3-liter Pyrex glass vessel, 6.25×10^{-2} moles of CH₃C≡CH and 5.6×10^{-3} moles of SF₅Br were condensed at -196°. Upon warming to room temperature a clear colorless liquid as well as some dark residue were observed. The reaction was complete after standing overnight. The clear liquid was distilled through a Kontes all glass distillation apparatus and the fraction boiling at 111 -111.5° was collected. The dark residue dissolved in acetone but not water and could not be analyzed. The yield for this reaction was 30%.

Reaction of SF₅Br with CF₃C ≡ CH

This reaction was first tried in a 1-liter Pyrex glass vessel in which 2.14×10^{-3} moles of CF₃C≡CH and 2.07×10^{-3} moles of SF₅Br were condensed at -196°. The yield after 20 days at room temperature was 43%. A modified method in which 5.3×10^{-2} moles of CF₃C=CH and 6.1×10^{-2} moles of SF₅Br were condensed in a 200 ml Hoke stainless steel vessel at -196°. The reactants were heated in an oven at 100° for four days. The mixture was then distilled. The product, a colorless liquid, boiled at 93±1°. The yield for this method was 58%.

Gas Chromatography

The products were analyzed with an Auto-prep gas chromatograph as

described under physical methods. For the olefins, the column temperature was $59 \pm 1^\circ$ and the helium flow rate was 3 ml/sec. Table X lists the times of appearance of the various compounds. CCl_4 , $\text{SF}_5\text{CH}=\text{CH}_2$ are also shown for comparison. The presence of two peaks in $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ indicated the existence of entgegen and zusammen isomers. For all other products only one substance was present. For the saturated adducts, the column temperature was 118° and the helium flow rate was 3 ml/sec.

Chemical Analysis

The compounds were analyzed by Beller Microanalytical Laboratory (See physical methods) for C, H, S, Cl, Br and F. The results are shown in Table XI. There was good agreement with calculated compositions except for the $\text{CF}_2=\text{CHCl}$ adduct. The authors are at a loss to explain the discrepancies for the fluorine and bromine analyses in light of the good agreement found for C, H, S, and Cl.

Physical Properties

The physical properties of the adducts are summarized in Table XII. The molecular weights were found using a calibrated bulb and compared very well with the expected values. From Table XII it can be seen that boiling point is lower for the 1, 1-difluoro olefin adduct than the monofluoro adduct. Trifluoromethylacetylene has a lower boiling point than the methyl-analogy. This can be explained by the importance of intermolecular hydrogen-bonding in partially fluorinated compounds.

TABLE X

GAS CHROMATOGRAPHY DATA FOR SF₅Br ADDUCTS

<u>Compound</u>	<u>Time (Min.)</u>
CCl_4	7.3
$\text{SF}_5\text{CH}=\text{CH}_2$	2.8
$\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$	12
$\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$	1st G.C. isomer 3.7
	2nd G.C. isomer 6.5
<hr/>	
CCl_4	2.17
$\text{SF}_5\text{CH}_2\text{CFClBr}$	4.33
$\text{SF}_5\text{CF}_2\text{CHClBr}$	3.17

TABLE XI

ELEMENTAL ANALYSES FOR SF₅Br ADDUCTS

<u>ADDUCTS</u>	<u>C</u> wt.% <u>Expt'l/Calc.</u>	<u>H</u> wt.% <u>Expt'l/Calc.</u>	<u>S</u> wt.% <u>Expt'l/Calc.</u>
SF ₅ CH ₂ CFC1Br	8.51/8.35	0.72/0.70	11.03/11.15
SF ₅ CF ₂ CHClBr	8.10/7.86	0.32/0.33	9.35/10.50
SF ₅ CH=C(CH ₃)Br	15.37/14.58	1.70/1.62	12.40/12.98
SF ₅ CH=C(CF ₃)Br	11.79/11.96	0.40/0.33	10.74/10.65

TABLE XI (cont'd)

ADDUCTS	F	Cl	Br
	wt. %	wt. %	wt. %
	<u>Expt'l/Calc.</u>	<u>Expt'l/Calc.</u>	<u>Expt'l/Calc.</u>
$\text{SF}_5\text{CH}_2\text{CFClBr}$	38.8/39.66	12.48/12.33	28.10/27.80
$\text{SF}_5\text{CF}_2\text{CHClBr}$	39.5/43.55	10.68/11.61	32.16/26.15
$\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$	36.5/38.47	0	34.18/32.35
$\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$	50.2/50.51	0	26.71/26.55

TABLE XII

PHYSICAL PROPERTIES OF THE ADDUCTS

<u>Compound</u>	<u>B.P. (°C)</u>	<u>Mol. Wt. (Expt'l/Calc.)</u>
$\text{SF}_5\text{CH}_2\text{CFClBr}$	119	285.6/287
$\text{SF}_5\text{CF}_2\text{CHClBr}$	111-111.5	296.5/305
$\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$	111-111.5	245.3/247
$\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$	93-94°C	301.8/301

Infrared Spectra

The infrared spectra for the saturated adducts are listed in Table XIII. The common feature of all the compounds studied is the presence of the SF_5 group and its observed infrared absorption bands centered on or about 870 cm^{-1} which can be directly related to vibrational modes within this group. Cross and co-workers (30) reported that in compounds containing the SF_5 group the most intense bands should occur in the region $850\text{--}920\text{ cm}^{-1}$ due to S-F stretching modes and in the region of 600 cm^{-1} due to S-F deformation modes. Therefore, the absorption bands at 912 , 870 , and 845 cm^{-1} in $\text{SF}_5\text{CH}_2\text{CFClBr}$, and for $\text{SF}_5\text{CF}_2\text{CHClBr}$, at 960 , 885 and 863 cm^{-1} are assigned to S-F stretching modes. The S-F deformation modes are located at 600 cm^{-1} and 596 cm^{-1} for $\text{SF}_5\text{CF}_2\text{CHClBr}$ and $\text{SF}_5\text{CH}_2\text{CFClBr}$ respectively. For compounds containing a C-F group, the C-F stretching absorption band is usually located in $1000\text{--}1110\text{ cm}^{-1}$ region while for CF_2 groups the region is $1050\text{--}1250\text{ cm}^{-1}$ (31). Therefore, with $\text{SF}_5\text{CH}_2\text{CFClBr}$, the absorption band at 1020 cm^{-1} is probably the C-F absorption band while for $\text{SF}_5\text{CF}_2\text{CHClBr}$ the C-F absorption bands for the CF_2 group are found in the $1145\text{--}1288$ region (31). The absorption bands at 3020 cm^{-1} and 3040 cm^{-1} for $\text{SF}_5\text{CF}_2\text{CHClBr}$ and $\text{SF}_5\text{CH}_2\text{CFClBr}$ are assigned to C-H stretching vibrations.

The infrared spectra for the olefin adducts are listed in Table XIV. The presence of the highly electronegative SF_5 group on one end of an olefinic bond leads to a high intensity for C=C stretching frequency. This occurs with medium intensity at 1615 and 1653 cm^{-1} , respectively, for $\text{SF}_5\text{CH=CHCl}$ and $\text{SF}_5\text{CH=CClCH}_3$, but only quite feebly

TABLE XIII

INFRARED ABSORPTION BANDS FOR SATURATED ADDUCTS

SF₅CF₂CHClBr (gas)cm⁻¹

1288 (m)
1225 (s)
1189 (m)
1163 (s)
1145 (s)
1032 (w)
960 (m)
885 (vs)
863 (vs)
815 (m)
792 (w)
778 (w)
731 (s)
702 (w)
660 (s)
600 (s)
588 (m-with sh. at 588 and 573)

SF₅CF₂CHClBr (liquid)cm⁻¹

3020 (w)	735 (s)
2920 (vw)	702 (w)
2850 (vs)	672 (w)
1287 (m)	660 (s)
1261 (w)	600 (s)
1225 (s)	588 (m)
1189 (m)	576 (m)
1160 (s)	
1142 (m-s)	
1062 (w)	
1032 (w-m)	
998 (w)	
960 (w-m)	
870 (vs, b)	
810 (m)	
790 (m-w)	
778 (w)	
749 (w)	

SF₅CH₂CFClBr (gas)cm⁻¹

1410 (w)
1149 (m-s)
1020 (s)
974 (w)
912 (vs)
870 (vs)
845 (vs)
790 (w)
720 (w)
664 (w)
618 (vw)
596 (s)
568 (m)

SF₅CH₂CFClBr (liquid)cm⁻¹

3040 (w)	845 (vs)
2924 (s)	790 (m)
2849 (m)	720 (w)
1470 (w)	664 (w)
1410 (s)	618 (w)
1320 (w)	596 (s)
1256 (w)	568 (m)
1200 (w)	
1149 (m-s, b)	
1020 (s)	
974 (m)	
912 (vs)	
870 (vs, b)	

TABLE XIV

INFRARED ABSORPTION BANDS FOR UNSATURATED ADDUCTS

SF₅CH=C(CH₃)Br (gas)cm⁻¹

3100 (vw)
1643 (m)
1435 (w-m)
1383 (m)
1296 (w)
1084 (m)
980 (s)
863 (s)
883 (s)
735 (m)
619 (m)
598 (s, with sh. at 575)

SF₅CH=C(CH₃)Br (liquid)cm⁻¹

3100 (m)
1643 (m)
1435 (w)
1383 (w)
1296 (w)
1084 (m)
980 (m)
836 (s, b, with sh. at 865 and 882)
735 (m)
616 (m)
598 (m)
575 (w)
569 (w)

SF₅CH=C(CF₃)Br (gas)Mixture - cm⁻¹

3100 (m)
1630 (m, with sh. at 1637)
1336 (m)
1285 (w)
1262 (vs)
1226 (m)
1191 (vs, b)
1120 (w)
960 (vs)
944 (vs)
882 (vs, b)
832 (w)
768 (m)
724 (m-w)
654 (m)
635 (m)
604 (m-s)
572 (w)
534 (w)

SF₅CH=C(CF₃)Br (gas)First - G.C. Isomer -
cm⁻¹

3100 (m)
1637 (m)
1285 (w-m)
1262 (vs, b)
1191 (vs, b)
1120 (w)
960 (vs with sh. at 982)
882 (vs, b-with sh. at 832)
765 (m-s)
635 (m-s)
604 (m-s)
572 (w)
534 (w)

SF₅CH=C(CF₃)Br (gas)Sec. G. C. Isomers -
cm⁻¹

3100 (w)
1630 (m)
1336 (s)
1285 (w)
1262 (m)
1226 (s)
1191 (vs, b)
1120 (w)
944 (vs)
882 (vs, b)
832 (w)
770 (m-w)
724 (m)
654 (m)
604 (m-s)
572 (w)
534 (w)

for the olefins $\text{SF}_5\text{CH}=\text{CHCH}_3$ (1663 cm^{-1}), $\text{SF}_5\text{CH}=\text{CH}_2$, and $\text{SF}_5\text{CH}_2\text{CH}=\text{CH}_2$ (30). $\text{SF}_5\text{CF}=\text{CF}_2$ exhibits an absorption band at 1782 cm^{-1} which is typical of the values obtained for other fluoroolefins (32). For $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ the $\text{C}=\text{C}$ stretching frequency occurs at 1643 cm^{-1} . The $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ compound is a mixture of two isomers (zusammen and entgegen forms). The $\text{C}=\text{C}$ stretching frequency for one isomer (first gas chromatographic isomer) is located at 1637 cm^{-1} and for the other isomer (second gas chromatographic isomer) is located at 1630 cm^{-1} . The absorption bands at 980 and 870 cm^{-1} for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ and 960 and 882 cm^{-1} for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ (first g. c. isomer) and 944 and 882 cm^{-1} for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ (second g.c. isomer) represent the $\text{S}-\text{F}$ stretching frequency for these compounds. The $\text{S}-\text{F}$ deformation modes are located 598 cm^{-1} and 604 cm^{-1} for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ and $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ respectively.

The absorption band at 3100 cm^{-1} for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ and $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ is assigned to the $\text{C}-\text{H}$ stretching. In $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ the symmetric and asymmetric bending vibration for the CH_3 group are tentatively assigned to the 1383 and 1435 cm^{-1} absorption bands.

Mass Spectra

The major mass spectra peaks for these adducts are listed in Tables XV to XXI and for the purpose of comparison the spectra for $\text{SF}_5\text{CH}=\text{CH}_2$ is also shown (Table XXI). A comparison of the major peaks shows that all of the spectra have strong peaks at $m/e = 89$, the SF_3^+ peak, and $m/e = 51$, the SF^+ peak. In $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$, the CF_3^+ peak ($m/e = 69$) is the most intense one. The compounds, $\text{SF}_5\text{CF}_2\text{CHClBr}$, $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$, $\text{SF}_5\text{CH}=\text{CH}_2$ had good parent peaks, while $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$

TABLE XV

MASS SPECTRA FOR $\text{SF}_5\text{CH}_2\text{CFClBr}$

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
26	6.7	C_2H_2^+	99	83.3	$\text{CH}_2\text{FCFC1}^+$
28	3.3	$\text{N}_2^+, \text{CO}^+$	100	13.3	BrF^+
31	3.3	CF^+	101	43.3	$\text{SF}_3\text{C}^+, \text{CH}_2\text{FCFC1}^+$
44	13.3	$\text{CO}_2^+, \text{CS}^+$	117	6.7	BrF_2^+
45	24.4	$\text{C}_2\text{H}_2\text{F}^+$	119	6.7	BrF_2^+
49	10	CCl^+	123	13.3	SCBr^+
51	8.3	$\text{SF}^+ \text{CCl}^+$	124	10.0	SCHBr^+
60	3.3	C_2HCl^+	125	13.3	SCBr^+
61	6.7	$\text{C}_2\text{H}_2\text{Cl}^+$	126	10.0	SCHBr^+
62	1.1	C_2HCl^+	127	50	SF_5^+
63	3.3	$\text{SFC}^+, \text{C}_2\text{H}_2\text{Cl}^+$	129	3.3	$\text{SF}_2\text{C}_2\text{Cl}^+$
64	13.3	SFCH^+	138	16.7	SC_2HBr^+
67	3.3	$\text{CF}_3^+, \text{SCl}^+$	140	23.3	$\text{SF}_5\text{CH}^+, \text{SC}_2\text{HBr}^+$
69	3.3	$\text{CF}_3^+ \text{SCl}^+$	141	3.3	$\text{SC}_2\text{H}_2\text{Br}^+$
70	13.3	SF_2^+	142	30.0	SFCBr^+
79	30	CHCFC1^+	143	3.3	$\text{SC}_2\text{H}_2\text{Br}^+$
80	56.7	$\text{C}_2\text{H}_2\text{ClF}^+$	144	30.0	SFCBr^+
81	10.3	CHCFC1^+	146	6.7	SClBr^+
82	18.9	$\text{C}_2\text{H}_2\text{ClF}^+$	148	2.2	SClBr^+
89	100	SF_3^+	158	40	SF_5CF^+
91	6.7	SF_3H_2^+	160	55	$\text{SF}_5\text{CH}_2\text{F}^+$
98	13.3	BrF^+	162	13.3	SCHClBr^+

TABLE XV (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
175	3.3	SF ₂ CH ₂ CBr ⁺	207	35	SF ₅ CH ₂ CFCl ⁺
177	3.3	SF ₂ CH ₂ CBr ⁺	209	11.7	SF ₅ CH ₂ CFCl ⁺

TABLE XVI

MASS SPECTRA FOR SF₅CF₂CHClBr

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
25	1.1	C ₂ H ⁺	67	43.5	SCl ⁺
28	1.1	N ₂ ⁺ , CO ⁺	69	17.3	CF ₃ ⁺ , SCl ⁺
29	4.1	COH ⁺	70	8.6	SF ₂ ⁺
32	17.4	S ⁺ , O ₂ ⁺	78	4.3	C ₂ FCI ⁺
36	17.4	HCl ⁺	79	21.7	CHCFCl ⁺ , Br ⁺
38	5.8	HCl ⁺	80	3.8	HBr ⁺
44	15.2	CO ₂ ⁺ , CS ⁺	81	7.4	CHCFCl ⁺ , Br ⁺
47	15.2	CCl ⁺	82	3.8	HBr ⁺
48	34.8	CHCl ⁺	85	21.7	CF ₂ Cl ⁺
49	6.5	CCl ⁺	86	19.6	HCF ₂ Cl ⁺
50	15.2	CHCl ⁺	89	39.1	SF ₃ ⁺
51	6.5	SF ⁺	98	100	CF ₂ CHCl ⁺ , BrF ⁺ , SFCCl ⁺
62	4.3	C ₂ HCl ⁺	99	15.2	SFCHCl ⁺
63	37	SCF ⁺	100	82.5	CF ₂ CHCl ⁺ , SFCCl ⁺ , BrF ⁺
64	4.3	SFCH ⁺	101	4.9	SFCHCl ⁺
66	1.3	CFCl ⁺	105	4.9	SClF ₂ ⁺

TABLE XVI (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
111	4.5	SBr ⁺	196	39.1	SFHC1 ³⁵ CF ₂ Br ⁷⁹⁺
113	4.5	SBr ⁺	198	56.1	CFHC1 ³⁵ CF ₂ Br ⁸¹⁺
117	93.7	SF ₂ CHCl ⁺			CFHC1 ³⁷ CF ₂ Br ⁷⁹⁺
118	17.4	SF ₂ CHCl ⁺	200	11.8	CFHC1 ³⁷ CF ₂ Br ⁸¹⁺
119	31.1	SF ₂ CCl ⁺	304	3.2	SF ₅ CHCl ³⁵ CF ₂ Br ⁷⁹⁺
120	5.7	SF ₂ CHCl ⁺	306	6.5	SF ₅ CHCl ³⁵ CF ₂ Br ⁸¹⁺
127	82.6	SF ₅ ⁺			SF ₅ CHCl ³⁷ CF ₂ Br ⁷⁹⁺
129	39.1	SF ₂ C ₂ Cl ⁺	308	1.0	SF ₅ CHCl ³⁷ CF ₂ Br ⁸¹⁺
131	13.1	SF ₂ C ₂ Cl ⁺			
142	4.3	SFCBr ⁺			
144	4.3	SFCBr ⁺			
177	39.1	CHCF ₂ Cl ³⁵ Br ⁷⁹⁺			
179	55.6	CHCF ₂ Cl ³⁵ Br ⁸¹⁺			
		CHCF ₂ Cl ³⁷ Br ⁷⁹⁺			
181	14.5	CHCF ₂ Cl ³⁷ Br ⁸¹⁺			

TABLE XVII

MASS SPECTRA FOR $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
28	18.8	C_2H_4^+
31	3.1	CF^+
32	3.1	CHF^+
33	12.5	CH_2F^+
37	12.5	C_3H^+
38	18.8	C_3H_2^+
39	100	C_3H_3^+
51	3.1	SF^+
40	12.5	C_3H_4^+
57	6.3	C_2HS^+
59	18.8	$\text{C}_3\text{H}_4\text{F}^+$
69	12.5	CF_3^+
71	6.3	SF_2H^+
89	50	SF_3^+
93	6.3	$\text{C}_2\text{H}_3\text{Br}^+$
95	6.3	$\text{C}_2\text{H}_3\text{Br}^+$
119	18.8	$\text{C}_3\text{H}_4\text{Br}^+$
121	18.8	$\text{C}_3\text{H}_4\text{Br}^+$
127	18.8	SF_5^+
137	18.8	$\text{C}_3\text{H}_3\text{BrF}^+$
139	18.8	$\text{C}_3\text{H}_3\text{BrF}^+$
167	25	$\text{SF}_5\text{C}_3\text{H}_4^+$

There are also minor peaks for masses 18(H_2O^+), 44(CO_2^+), 65($\text{CH}_2\text{CHF}_2^+$).

TABLE XVIII

MASS SPECTRA FOR $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
25	3.0	C_2H_1^+	106	4.6	$\text{C}_2\text{HBr}^+, \text{SF}_2\text{C}_3^+$
28	15.2	$\text{N}_2^+, \text{CO}^+$	108	1.5	SF_4^+
31	12.1	CF^+	113	27.3	SF_3C_2^+
32	3.0	S^+, O_2^+	123	3.0	SCBr^+
44	3.0	CO_2^+	125	3.0	SCBr^+
50	3.0	CF_2^+	127	30.3	SF_5^+
51	25	SF^+	129	6.1	?
55	3.0	C_3F^+	131	4.6	$\text{C}_2\text{F}_2\text{CF}_3^+$
56	4.6	C_3HF^+	142	4.6	$\text{C}_2\text{F}_2\text{HBr}^+$
57	3.0	C_2HS^+	144	4.6	$\text{C}_2\text{F}_2\text{HBr}^+$
69	100	CF_3^+	153	3.0	$\text{C}_3\text{F}_2\text{Br}^+$
70	13.6	SF_2^+	155	3.0	$\text{C}_3\text{F}_2\text{Br}^+$
74	3.0	C_2CF_2^+	173	48.5	$\text{CHCCF}_3\text{Br}^+$
75	30.3	CHCCF_2^+	175	48.5	CHCF_3Br^+
79	3.0	Br^+	191	3.0	$\text{CFCCF}_3\text{Br}^+$
81	3.0	$\text{Br}^+, \text{CCF}_3^+$	192	28.8	$\text{CHFCCF}_3\text{Br}^+$
85	6.1	?	193	3.0	$\text{CFCCF}_3\text{Br}^+$
89	51.5	SF_3^+	194	28.8	$\text{CHFCCF}_3\text{Br}^+$
93	9.1	C_2CF_3^+	221	3.0	$\text{SF}_5\text{CHCCF}_3^+$
94	9.1	C_2HCF_3^+	281	7.6	$\text{SF}_5\text{C}_2\text{HBrCF}_2^+$
104	4.6	C_2HBr^+	283	7.6	$\text{SF}_5\text{C}_2\text{HBrCF}_2^+$

TABLE XVIII (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
300	30.3	$\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^+$
302	30.3	$\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^+$

TABLE XIX

 MASS SPECTRA FOR $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$
 FIRST G.C. ISOMER

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
25	1.6	C_2H^+	104	9.4	C_2HBr^+
28	3.1	$\text{N}_2^+, \text{CO}^+$	106	9.4	C_2HBr^+
31	7.8	CF^+	108	1.6	SF_4^+
32	1.6	S^+, O_2^+	113	37.5	SF_3C_2^+
44	3.1	CO_2^+	123	6.3	SCBr^+
50	3.1	CF_2^+	125	6.3	SCBr^+
51	6.3	SF^+	127	42.2	SF_5^+
55	1.6	C_3F^+	129	6.3	?
56	6.3	C_3HF^+	131	6.3	$\text{C}_2\text{F}_2\text{CF}_3^+$
57	1.6	C_2HS^+	142	7.8	$\text{C}_2\text{F}_2\text{HBr}^+$
			144	7.8	$\text{C}_2\text{F}_2\text{HBr}^+$
69	100	CF_3^+	153	3.1	$\text{C}_3\text{F}_2\text{Br}^+$
70	15.6	SF_2^+	155	3.1	$\text{C}_3\text{F}_2\text{Br}^+$
74	3.1	C_2CF_2^+	173	53.1	$\text{C}_2\text{HCF}_3\text{Br}^+$
75	34.4	CHCCF_2^+	175	53.1	$\text{C}_2\text{HCF}_3\text{Br}^+$
79	6.3	Br^+	191	3.1	$\text{CFCCF}_3\text{Br}^+$
81	6.3	$\text{Br}^+, \text{CCF}_3^+$	192	50.0	$\text{CHFCCF}_3\text{Br}^+$
89	46.9	SF_3^+	193	3.1	$\text{CFCCF}_3\text{Br}^+$
91	3.1	?	194	50.0	$\text{CHFCCF}_3\text{Br}^+$
93	10.9	C_3F_3^+	221	3.1	$\text{SF}_5\text{CHCCF}_3^+$
94	10.9	CHCCF_3^+	281	28.1	$\text{SF}_5\text{C}_2\text{HBrCF}_2^+$
99	6.3	?			

TABLE XIX (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
283	28.1	$\text{SF}_5\text{C}_2\text{HBrCF}_2^+$
300	68.8	$\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^+$
302	68.8	$\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^+$

TABLE XX

MASS SPECTRA FOR $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$
SECOND G. C. ISOMER

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>	<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
25	2.2	C_2H^+	104	11.1	C_2HBr^+
28	4.1	$\text{N}_2^+, \text{CO}^+$	106	11.1	C_2HBr^+
31	7.8	CF^+	108	2.2	SF_4^+
32	1.1	S^+, O_2^+	113	24.4	SF_3C_2^+
44	4.4	CO_2^+	123	4.1	SCBr^+
50	4.4	CF_2^+	125	4.1	SCBr^+
51	4.4	SF^+	127	33.3	SF_5^+
55	2.2	C_3F^+	129	6.7	?
56	4.1	C_3HF^+	131	6.7	$\text{C}_2\text{F}_2\text{CF}_3^+$
57	2.2	C_2HS^+	142	5.6	$\text{C}_2\text{F}_2\text{HBr}^+$
69	100	CF_3^+	144	5.6	$\text{C}_2\text{F}_2\text{HBr}^+$
70	14.4	SF_2^+	153	4.4	$\text{C}_3\text{F}_2\text{Br}^+$
74	4.4	C_2CF_2^+	155	4.4	$\text{C}_3\text{F}_2\text{Br}^+$
75	22.2	CHCCF_2^+	173	56.6	$\text{C}_2\text{HCF}_3\text{Br}^+$
79	4.4	Br^+	175	56.6	$\text{C}_2\text{HCF}_3\text{Br}^+$
81	4.4	$\text{Br}^+, \text{CCF}_3^+$	191	2.2	$\text{CFCCF}_3\text{Br}^+$
89	55.6	SF_3^+	192	56.6	$\text{CHFCCF}_3\text{Br}^+$
91	4.1	?	193	2.2	$\text{CFCCF}_3\text{Br}^+$
93	11.1	C_3F_3^+	194	56.6	$\text{CHFCCF}_3\text{Br}^+$
94	10.8	C_3HF_3^+	221	4.4	$\text{SF}_5\text{CHCCF}_3^+$
99	2.0	?	281	6.7	$\text{SF}_5\text{C}_2\text{HBrCF}_2^+$

TABLE XX (con't)

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
283	6.7	$\text{SF}_5\text{C}_2\text{HBrCF}_2^+$
300	53.3	$\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^+$
302	53.3	$\text{SF}_5\text{C}_2\text{HCF}_3\text{Br}^+$

TABLE XXI

MASS SPECTRA PEAKS FOR $\text{SF}_5\text{CH} = \text{CH}_2$

<u>M/e</u>	<u>Rel. Int.</u>	<u>Type</u>
26	14.5	C_2H_2^+
27	100	C_2H_3^+
28	5.3	$\text{N}_2^+, \text{CO}^+$
44	2.6	CO_2^+
46	17.1	$\text{C}_2\text{H}_3\text{F}^+$
51	3.9	SF^+
56	1.3	C_2S^+
57	1.3	C_2HS^+
58	1.3	$\text{C}_2\text{H}_2\text{S}^+$
69	1.3	CF_3^+ (impurity ?)
70	9.2	SF_2^+
89	100	SF_3^+
91	2.6	SF_3H_2^+
108	2.6	SF_4^+
109	1.3	SF_4H^+
127	7.9	SF_5^+
135	9.2	$\text{SF}_4\text{C}_2\text{H}_3^+$
154	2.6	$\text{SF}_5\text{C}_2\text{H}_3^+$

There are also minor peaks for masses 18(H_2O^+), 20(HF^+), 97($\text{SF}_2\text{C}_2\text{H}_3^+$), 113(SF_3C_2^+).

and $\text{SFCH}_2\text{CFC1Br}$ had no parent peaks. The major peaks for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)-\text{Br}$ (mixture) and its two isomers are essentially the same. The difference between the peaks of two isomers is the relatively higher tendency for the first g.c. isomer to lose a fluorine atom as indicated by the relative intensity of peaks at $m/e = 281$ and $m/e = 283$ (the $\text{SF}_5\text{C}_2\text{BrCF}_2^+$ peaks).

It is thought that this loss of fluorine is from the SF_5 group rather than from the CF_3 group because the S-F bond strength is about 76 kcal/mole while the C-F bond strength is ~ 116 kcal/mole and because the CF_3^+ molecular ion is much more abundant than the SF_5^+ ion. The mass spectrum of $\text{SF}_5\text{C}\equiv\text{CH}$ (12) had peaks at $m/e = 152$ (parent), 133 ($\text{SF}_4\text{C}_2\text{H}^+$), 127 (SF_5^+), 89 (SF_3^+) and 44 (C_2HF^+). The presence of the $m/e = 133$ demonstrates that fluorine loss from the SF_5 group of the parent compound is possible. It is interesting to note however, that the mass spectrum of $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ does not show either a parent peak or a peak due to the loss of a fluorine atom.

Nuclear Magnetic Resonance

The nuclear magnetic resonance data for the adducts are listed in Table XXII. The proton nmr spectrum for $\text{SF}_5\text{CH}_2\text{CClFBr}$ is a multiplet of 13 lines with a band center of 4.5 ppm. The spectrum was not resolved but its complexity and the band center establishes that the SF_5 group is attached to the CH_2 group. In $\text{SF}_5\text{CH}_2\text{CHFBr}$ and $\text{SF}_5\text{CH}_2\text{CF}_2\text{Br}$ the band centers are 4.27 and 4.46 respectively (4). For $\text{SF}_5\text{CF}_2\text{CHClBr}$, the proton nmr spectrum consists of four bands with a band center of 5.9 ppm. The four line pattern unambiguously demonstrates that the SF_5 group is attached to the CF_2 group and the CF_2 group is attached

TABLE XXII

			NMR DATA					
Proposed Structure Skeletal Atom Number			Chemical Shifts Band Centers *			Coupling Constants		
1	2	3	CH	CH ₂	CH ₃	J _{1,1} ^{H,F}	J _{3,2} ^{H,F}	J _{3,2} ^{M,F'}
SF ₅	CH ₂	CFClBr		4.5@				
SF ₅	CF ₂	CHClBr	5.9				12.6	6.0
SF ₅	CH	C(CF ₃)Br***	7.60			6.5		
SF ₅	CH	C(CF ₃)Br****	7.13			8.6		
SF ₅	CH	C(CH ₃)Br	6.76		2.57	7.8		

*Chemical shifts in parts per million downfield from Si(CH₃)₄ internal standard.

**Measured in cycles per second

***First gas Chromatographic isomer.

****Second gas Chromatographic isomer.

@Band center of multiplet of 13 major lines.

to the CH group. The fluorine atoms of the CF_2 group are non-equivalent and split the hydrogen into the four line pattern. The coupling constants, $J_{3,2}^{\text{H},\text{F}}$ and $J_{3,2}^{\text{H},\text{F}^1}$ and 12.6 and 6.0 cps respectively. For $\text{SF}_5\text{CHFCF}_2\text{Br}$ the corresponding coupling constants were 13 and 3.0 cps (4). The band center for $\text{SF}_5\text{CHFCF}_2\text{Br}$ was 5.58 ppm (4).

The first g.c. isomer of $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ had a band center of 7.60 ppm while the second g.c. isomer had a band center of 7.13 ppm. The proton spectra for both isomers gave a five line pattern due to splitting of the SF_5 group attached to the carbon with the hydrogen. It is interesting to note that the $J_{1,1}^{\text{H},\text{F}}$ coupling constant for the two isomers are different. The values for these two coupling constants are in line with the values reported for other SF_5 olefins (12).

Integration of the areas for the CH peaks in the starting mixture indicates that the concentration of the two isomers are approximately equal.

In order to differentiate between the entgegen and zusammen isomers present in the starting mixture the relative values for the long range coupling between the CF_3 and H groups were determined. The A-60 nmr instrument was unable to determine the coupling constant expected for the four line pattern and therefore the relative width at half-peak height was used. For the first g.c. isomer. The width at half-peak height was 3.6 cps and for the second g.c. isomer the width was 2.4 cps. This analysis definitely proves that the CF_3 -H coupling is much stronger in the first g.c. isomer. W. G. Finnegan and W. P. Norris (33) found that for

and

the trans-1, 2-dichloro-3,3,3-trifluoropropene a chemical shift of 7.11 ppm and $J^{H,F} = 1.1$ while for the cis isomer a 6.64 ppm and $J^{H,F} < 0.2$. Since Cl and SF_5 groups have a similar electronegativity the only difference between the 1,2 dichloro isomers and the SF_5 isomers is that bromine is present in the latter. It is felt that this difference is unimportant in comparing the relative coupling constants between the CF_3 and H groups in the 1,2 dichloro isomers and the SF_5 isomers.

Since the CF_3 -H long range coupling in the first g.c. isomer is much larger than the second g.c. isomer it is assigned by analogy to the trans-1, 2-dichloro-3,3,3-trifluoropropene the entgegen form:

Entgegen isomer

trans-

It is also important to note that the CH chemical shift is further downfield from TMS for both the entgegen isomer and the trans 1,2-dichloro-isomer relative to the zusammen and cis 1,2-dichloro-isomer.

The second g.c. isomer is assigned as the zusammen isomer:

Zusammen isomer

cis-

The proton nmr spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ gives for the CH proton a five line pattern with a band center of 6.76 ppm and a coupling constant $J_{1,1}^{\text{H},\text{F}} = 7.8$ cps. The basic CH five line pattern also shows additional long-range splitting by the CH_3 protons. The coupling constant for this long range effect splits the CH_3 protons into a five line spectra with a coupling constant of 1.5-2.0 cps. Integration of the areas for the CH peaks and for the CH_3 peaks for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$ gives a ratio of 1:3. The band center for the CH_3 protons is 2.57 ppm downfield from TMS. The overall nmr data for this compound is more similar to the nmr data for the second g.c. isomer of $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$. The proposed tentative structure for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$, by analogy to the structure assignment for the zusammen isomer for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ is:

Discussion

Previous work in our group has shown that when SF_5Br adds to fluoroolefins the SF_5 group is always attached to the carbon with the most hydrogens:

The work reported in this thesis for the addition of SF_5Br to $\text{CH}_2=\text{CFCl}$ and $\text{CF}_2=\text{CClH}$ is interesting in that the first exception to the above rule is found with $\text{CF}_2 = \text{CClH}$ but not for $\text{CH}_2 = \text{CFCl}$:

It is tempting to rationalize these results using steric effects (larger chlorine versus fluorine for $\text{CF}_2 = \text{CFH}$ and $\text{CF}_2 = \text{CClH}$) or using the stability of secondary radicals ($\text{SF}_5\text{CF}_2\text{CClH}$ vs. $\text{SF}_5\text{CClHCF}_2$.) but the author feels that additional model compounds (i.e. $\text{CHCl} = \text{CHF}$) must be examined before reaching any definite conclusions. The infrared spectra, mass spectra, and nmr spectra have adequately characterized the structure of these compounds.

In addition to the work dealing with fluoroolefins, the addition of SF_5Br to alkynes ($\text{CF}_3\text{C}\equiv\text{CH}$ and $\text{CH}_3\text{C}\equiv\text{CH}$) was studied. In both cases the SF_5 group attached itself to the carbon with most hydrogens:

With $\text{CH}_3\text{C}\equiv\text{CH}$ only one isomer was found and by analogy to the $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ isomers is thought to have the following structure:

It was extremely interesting to find that reaction product, $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$, was a mixture of two isomers with following structures:

Entgegen (E) isomer

Zusammen (Z) isomer

The infrared and mass spectra of the E and Z isomers are particularly interesting. The infrared, C=C stretching frequency for the E isomer is 1637cm^{-1} and for the Z isomer is 1630cm^{-1} . The shift to lower frequency for the Z isomer is probably best explained by a mass effect. Having the two heaviest groups (SF_5 and Br) cis to each other creates more of a strain on the carbon-carbon double bond which can only be relieved by some distortion of that bond. This shift to lower frequency is a result of that distortion. This effect is also noted for other cis-trans olefins [(i.e. $\text{CHBr} = \text{CHF}$)]. As already mentioned the E isomer (first g.c. isomer) loses fluorine more readily than the Z isomer (second g.c. isomer). In attempting to explain this result the following sequence of events is visualized:

First the E isomer loses an electron, probably from bromine to create a primary positive radical:

The lone electron on bromine and an electron from the double bond join to form a C = Br bond:

The next step involves a sulfur fluorine bond in which one of the electrons in a sulfur-fluorine bond joins with the lone electron on the secondary radical to form a C = S bond and eliminate a fluorine free radical:

Since the CF_3 group is larger than a bromine group* the repulsion between the SF_5 - CF_3 groups in the cis position is reduced by the elimination of the fluorine atom. When the SF_5 group is cis to bromine the repulsion is less and fluorine elimination is not as pronounced.

The infrared and proton nmr spectra for the new compounds are shown in Figures II - XI.

*The covalent diameter as calculated from the observed inter-atomic distance in suitable covalent compounds is 3.3 Å for a CF_3 group, 2.8 Å for a CH_3 group and 2.3 Å for a Br atom (34).

Figure 2. Infrared Spectrum for $\text{SF}_5\text{CF}_2\text{CHClBr}$

Figure 3. Infrared Spectrum for $\text{SF}_5\text{CH}_2\text{CFBrCl}$

Figure 4. Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$

Figure 5. Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ Mixture

Figure 6. Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ - First G.C. Fraction

Figure 7. Infrared Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ - Second G.C. Fraction

Figure 8. NMR Proton Spectrum for $\text{SF}_5\text{CF}_2\text{CHClBr}$

Figure 9. NMR Proton Spectrum for $\text{SF}_5\text{CH}_2\text{CFBrCl}$

Figure 10. NMR Proton Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CH}_3)\text{Br}$

Figure 11. NMR Proton Spectrum for $\text{SF}_5\text{CH}=\text{C}(\text{CF}_3)\text{Br}$ Mixture.

BIBLIOGRAPHY

1. C. Merrill, Ph.D. Thesis, University of Washington, Seattle, Wash. (1962).
2. B. Cohen and A. G. MacDiamid, Inorg. Chem., 4, 1782 (1965).
3. R. Kriohnanachari and N. Mohan, Acta. Phys., 36, 915 (1969).
4. J. Stewart, L. Kegly, H. F. White and G. L. Gard, J. Org. Chem., 34, 760 (1969).
5. A. D. Berry and W. B. Fox, J. Fluorine Chem., 6, 175 (1975).
6. A. D. Berry and W. B. Fox, J. Fluorine Chem., to be published.
7. H. L. Roberts and N. H. Ray, J. Chem. Soc., 136, 665 (1960).
8. H. L. Roberts, et al., J. Chem. Soc., 2066 (1961).
9. H. L. Roberts, et al., J. Chem. Soc., 2070 (1961).
10. Canadian Patent, No. 728186 (1966).
11. R. A. Bekhen, B. L. Gyatkin, and I. L. Knunyants, I. Z. V. Akad. Nauk. SSSR, 2738 (1970).
12. F. W. Hoover and D. D. Coffman, J. Org. Chem., 29, 3567 (1964).
13. G. L. Gard and C. Woolf, J. Fluorine Chem., 1, 487 (1971/72).
14. S. Sherratt, British Patent, No. 929990 (1963).
15. A. Marcellis and R. E. Eibeck, J. Fluorine Chem., 5, 71 (1975).
16. H. L. Roberts, Quart. Rev., 15, 30 (1961).
17. W. A. Sheppard, J. Amer. Chem. Soc., 84, 3072 (1962).
18. K. C. Denbigh and R. Whytlaw-Gray, J. Chem. Soc., 1346, (1964).
19. W. R. Trost and R. L. McIntosh, Can. J. Chem., 29, 508 (1951).
20. H. L. Roberts, J. Chem. Soc., 3183 (1962).
21. M. Tremblay, Can. J. Chem., 43, 219 (1965).

22. J. Hutchinson, J. Fluorine Chem., 3, 429 (1973).
23. J. C. Walton, et al., Trans. Faraday Soc., 65, 2103 (1969).
24. J. C. Walton, et al., Trans. Faraday Soc., 66, 2039 (1970).
25. G. H. Cady, "Fluorine Containing Compounds of Sulfur," Advances in Inorganic Chemistry and Radiochemistry, Vol. 2 (1960).
26. G. L. Gard, C. Woolf and R. Shaw, British Patent, No. 1, 167, 228 (1969).
27. C. Woolf and G. L. Gard, United States Patent, No. 3,448,121 (1969).
28. E. E. Gilbert and G. L. Gard, United States Patent No. 3,475,453 (1969).
29. R. D. Dresdner, T. J. Kao and J. A. Young, J. Am. Chem. Soc., 80, 3007 (1958).
30. L. H. Cross, G. Cushing and H. L. Roberts, Spectrochim. Acta., 17, 364 (1961).
31. J. K. Brown and K. J. Morgan, "The Vibrational Spectra of Organic Fluorine Compounds," Advances in Fluorine Chemistry, Vol. 4 (1965).
32. L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London (1958).
33. W. G. Finnegan and W. P. Norris, J. Org. Chem., 28, 1139 (1963).
34. H. P. Braendlin and E. T. McBee, "Effects of Adjacent Perfluoroalkyl Groups on Carbonyl Reactivity Advances in Fluorine Chemistry, Vol. 3 (1963).