

AD-A043 037

MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/G 7/2
SYNTHESIS OF NOVEL INORGANIC FLUORINE COMPOUNDS BY DIRECT FLUOR--ETC(U)
JUL 77 R J LAGOW N00014-75-C-0994

UNCLASSIFIED

[OF]

AD43037



NL



AD A 043037

12

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0994
Task No. NR 053-601

Final Report

SYNTHESIS OF NOVEL INORGANIC FLUORINE COMPOUNDS

BY DIRECT FLUORINATION

by

Richard J. Lagow

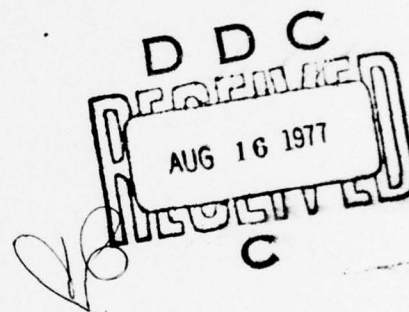
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

DISTRIBUTION STATEMENT A

Approved for public release,
Distribution Unlimited

Reproduction in whole or in part is permitted for
any prupose of the United States Government.

AD No. _____
DDC FILE COPY



unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SYNTHESIS OF NOVEL INORGANIC FLUORINE COMPOUNDS BY DIRECT FLUORINATION.		5. TYPE OF REPORT & PERIOD COVERED Final Report
7. AUTHOR(s) Richard J. Lagow		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0994
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-601
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE 7/28/77
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 28 Jul 77 12, 54 p.		13. NUMBER OF PAGES 54
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Perfluoro organometallic compounds; Trifluoromethyl compounds; Trifluoromethyl radicals; Fluorine		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) It has been found possible to preserve metal-carbon and metalloid-carbon bonds during direct fluorination. The reaction of dimethylmercury with fluorine gives bis(trifluoromethyl)mercury in 6.5% yield. Fluorination of tetramethylsilane has led to the isolation of the new polyfluorotetramethylsilanes of the following type, $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$, $x+y+z = 4$. Also		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

220 007

characterized were compounds containing Si-CF₃. It has been possible to synthesize tetrakis(trifluoromethyl)germanium in 63.5% yield from the reaction of fluorine with tetramethylgermanium. Also characterized were many polyfluorotetramethylgermanes of the following type,
 $\text{Ge}(\text{CF}_3)_x(\text{CF}_2\text{H})_y(\text{CFH}_2)_z, x + y + z = 4.$

unclassified

Contribution from the
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

Fluorination of Dimethylmercury, Tetramethylsilane and Tetramethylgermanium.
Synthesis and Characterization of Polyfluorotetramethylsilanes,
Polyfluorotetramethylgermanes, Bis(trifluoromethyl)mercury
and Tetrakis(trifluoromethyl)germanium.

by

Edmund K. S. Liu and Richard J. Lagow*

APPROVED FOR	
YES	White Section <input checked="" type="checkbox"/>
NO	Blue Section <input type="checkbox"/>
UNANNOUNCED <input type="checkbox"/>	
DISSEMINATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
SPECIAL	
A	

ABSTRACT

It has been found possible to preserve metal-carbon and metalloid-carbon bonds during direct fluorination. The reaction of dimethylmercury with fluorine gives bis(trifluoromethyl)mercury in 6.5% yield. Fluorination of tetramethylsilane has led to the isolation of the new polyfluoro-tetramethylsilanes of the following type, $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$, $x+y+z = 4$. Also characterized were compounds containing $\text{Si}-\text{CF}_3$. It has been possible to synthesize tetrakis(trifluoromethyl)germanium in 63.5% yield from the reaction of fluorine with tetramethylgermanium. Also characterized were many polyfluorotetramethylgermanes of the following type, $\text{Ge}(\text{CF}_3)_x(\text{CF}_2\text{H})_y(\text{CFH}_2)_z$, $x+y+z = 4$.

INTRODUCTION

We wish to report an unusual and unexpected method for the synthesis of trifluoromethyl organometallic compounds. Recently, by controlled direct fluorination we were able to convert dimethylmercury to bis(trifluoromethyl)mercury.¹ This work was extended to the fluorination of group IVA compounds in an effort to produce perfluoro organometallic compounds. We report here our work with dimethylmercury, tetramethylsilane and tetramethylgermane, including the conversion of tetramethylgermane to tetrakis(trifluoromethyl)germane, $\text{Ge}(\text{CF}_3)_4$, in 63.5% yield.

Controlled direct fluorination has proven extremely successful in replacing hydrogens with fluorine on a wide range of compounds and materials to produce perfluoro analogs. This method has been developed as a synthesis for many perfluoro and polyfluoro-organic and inorganic compounds in good yield. The versatility of the method has been extended from the synthesis of perfluoro analogs of neopentane³, hexamethylethane and cyclooctane⁴ to perfluoroethers such as glyme and diglyme⁵, to fluorinate inorganic systems such as sulfur tetranitride⁶ and lower carboranes.⁷ The extent to which direct fluorination can be used as a synthetic method is not fully established. In an effort to expand the range of fluorination as a synthetic tool, several organometallic systems such as $\text{Pb}(\text{CH}_3)_4$, $\text{Sn}(\text{CH}_3)_4$ and $\text{Ge}(\text{CH}_3)_4$ were examined.

EXPERIMENTAL SECTION

Materials

Dimethylmercury and tetramethylgermanium from Alfa Products and tetramethylsilane from Stohler Isotope Chemicals were used without further purification. Fluorine (98+%) used was obtained from Allied Chemical Company.

Physical Measurements:

Infrared spectra were obtained in gas phase cells with KBr windows using a Beckman IR20A spectrophotometer. Mass spectra were obtained in the gas phase with either a Hitachi-Perkin-Elmer RMU-6 mass spectrometer or a Bell and Howell CEC 21-491 mass spectrometer operating at 70 eV. The temperature of the mass spectrometer was at its normal operating temperature, inlet at 150°C, unless otherwise indicated. Proton and fluorine nmr were obtained using either a Hitachi-Perkin-Elmer R20B nmr spectrometer, a Varian A56/60 instrument, or a Varian A60-B nmr spectrometer operating at 60.0 MHz and 56.47 MHz, respectively. Chemical shifts and coupling constants were measured with a Takeda-Riken TR-3824X frequency counter in conjunction with the R20B instrument. Homonuclear fluorine-19 decoupling was done on the R20B instrument equipped with an external frequency synthesizer. Fluorine fourier transforms were done on the R20B instrument interfaced with a Digilab FTS/NMR Fourier Transform Data System.

Apparatus

Fluorinations were done in a cryogenic zone reactor previously described.² Temperature was controlled by a temperature controller made by Cryogenic Controls Company. The products from the reaction were transferred to a vacuum system to prevent exposure to air and moisture. The compounds were separated on a Bendix 2300 Gas Chromatograph, equipped with an automatic temperature controller and thermal conductivity detector. Gas chromatograph columns used were 10% SE-30 on chromosorb P and 10% fluorosilicone on chromosorb P. Both columns were 3/8" by 24'. All infrared spectra were obtained in the gas phase. Mass spectra were obtained as gaseous samples. All nmr's were obtained using neat liquids in sealed glass tubes and were referenced to external tetramethylsilane (TMS) for proton and external trifluoroacetic acid (TFA) for fluorine.

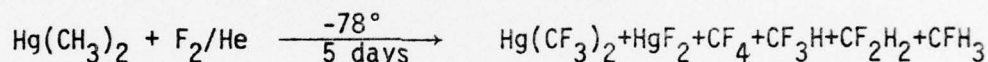
General Procedure

A typical reaction is described here. A low temperature reactor was assembled, passivated and dried with fluorine and helium. The reactor was cooled to approximately -120°C with a liquid nitrogen temperature control system. After the system had been cooled for an hour, the starting material was syringed into the reactor in conjunction with a high flow of helium, (about 150 cc/min.) through a swagelok-T assembly. The reactor was purged for an hour to insure that all the material was at the desired temperature. The helium flow was then reduced and the temperature set for the reaction to occur. Downstream from the reactor, after the sodium fluoride

scrubber, a liquid nitrogen trap was used to trap all volatiles. After the fluorination was terminated, the liquid nitrogen trap was transferred to a vacuum line and the products transferred into a vacuum system. The products were fractionated at -95° , -131° and -196° . The products were separated on a gas chromatograph using preparative scale columns. Precautions were taken to exclude moisture and air. Infrared, mass spectra and nmr's were taken of the pure samples.

Fluorination of Dimethylmercury

The reaction can be summarized as:

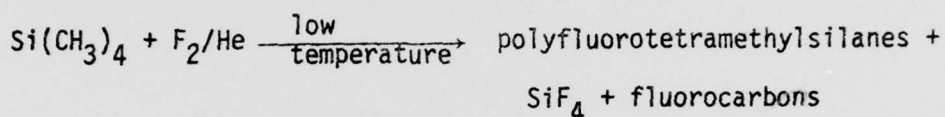


0.725 ml. of $\text{Hg}(\text{CH}_3)_2$ was syringed into the low temperature reactor with zone 4 cooled to -78° . After 1/2 hours of purging, zones 1, 2, and 3 were also cooled to -78° . Fluorination conditions used were 1.0 cc/minute of fluorine to 60.0 cc/minute of helium. After 120 hours, the fluorine was terminated. The reactor was allowed to warm and the volatile materials were collected at -196°C . The volatile material was fractionated through a -45° slush. The reactor was evacuated and any marginally volatile material was collected. All this material was placed in ether. The fluorine -19 nmr showed a singlet at -37.70 ppm downfield from TFA with $J_{199\text{Hg}-\text{F}} = 1251\text{hz}$. After purification by gas chromatography, a yield of 6.5%, $\text{Hg}(\text{CF}_3)_2$ was obtained. The material in the reactor was HgF_2 , identified by x-ray diffraction powder pattern. The volatile materials were mainly CF_4 , CF_3H , and CFH_3 . Fluorination

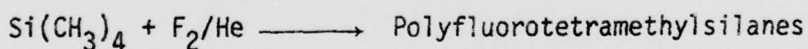
at other temperatures gave lower yields of $\text{Hg}(\text{CF}_3)_2$. Separation by gas chromatography helped to identify the compound as $\text{Hg}(\text{CF}_3)_2$, and preclude $\text{Hg}(\text{CF}_3)(\text{CH}_3)$. Using a SE-30, 3/8" x 24' column, operating at 80° isothermal, retention times are the following: $\text{Hg}(\text{CH}_3)_2$, 15'10", $\text{Hg}(\text{CF}_3)(\text{CH}_3)$, 50', and $\text{Hg}(\text{CF}_3)_2$, (comes off only upon raising the temperature to 165°).

Fluorination of Tetramethylsilane

The reaction is summarized as:



Reactions were run at temperatures between -100°C and -150°C. It was found that -100°C and -110°C were the best temperatures. The best fluorine and helium mixture was found to be 1.0 cc/minute fluorine to 60 cc/minute helium. The length of fluorination depended on the amount of material used, but generally it was found that five to seven days per ml of TMS was ideal. Therefore, a set of conditions would be described as:



F_2 1.0 cc/minute - temperature: -110°C

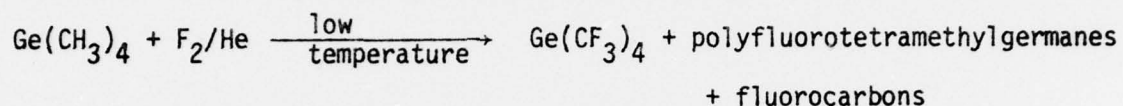
He 60 cc/minute - length of reaction: 7 days

Starting with 1 ml., tetramethylsilane we are able to recover in 70 - 80% overall yield, the polyfluorotetramethylsilanes. The volatile materials were fractionated at -131° and -196°. The volatile materials in the -196° fraction consisted of mainly CF_4 , CF_3H , CF_2H_2 and SiF_4 . The compounds in

the -131° fractions were separated on the gas chromatograph using a fluoro-silicon column.

Fluorination of Tetramethylgermanium

The reaction can be summarized as:



0.90 ml (6.55×10^{-3} mole) of $\text{Ge}(\text{CH}_3)_4$ was syringed into the reactor with zone 2 at -100°C. With zone 2 being cooled to the temperature indicated, the following reaction conditions were used.

<u>F₂(cc/minute)</u>	<u>He(cc/minute)</u>	<u>Temperature</u>	<u>Time</u>
1.0	60	-100	48 hours
1.0	60	- 90	12
1.0	60	- 80	14
1.0	60	- 70	8
1.0	60	- 60	14
1.0	60	- 50	10
1.0	60	- 40	12
1.0	60	- 30	10
1.0	60	- 20	14
0.0	60	- 20	8
0.0	60	RT	24

The volatile materials were separated into -95°, -131° and -196° fractions. Very little material was in the -196° fraction. Identified by infrared spectra were CF_4 , CF_3H and C_2F_6 . Both the -95° and -131° fractions contained $\text{Ge}(\text{CF}_3)_4$. The bulk of the material was in the -95° trap. The NMR of the -95° fraction showed the presence of only three compounds $\text{Ge}(\text{CF}_3)_4$ (-27.0 ppm), $\text{Ge}(\text{CF}_3)_3\text{F}$ (-21.9), and $\text{Ge}(\text{CF}_3)_3(\text{OH})$ (-21.4). After separation from impurities on the gas chromatograph, 1.45 grams of pure $\text{Ge}(\text{CF}_3)_4$ were isolated, giving a minimum yield of 63.5%. IR, NMR and mass spectra of $\text{Ge}(\text{CF}_3)_4$ agree well with the reported results.⁸

Other fluorination conditions led to low yields of $\text{Ge}(\text{CF}_3)_4$. However, one can separate and characterize many polyfluorotetramethylgermanium compounds from these reactions. The following conditions led to only 6% $\text{Ge}(\text{CF}_3)_4$. The rest of the material was partially fluorinated material.

$\text{F}_2(\text{cc/minute})$	$\text{He}(\text{cc/minute})$	Temperature	Time
1.0	60	-100	42 hours
1.0	60	- 90	24
1.0	60	- 80	24
1.0	60	- 70	24
1.0	60	- 60	15
0.0	60	- 60	9
0.0	60	RT	48

All the compounds were separated and purified by gas chromatography.

SEPARATION OF COMPOUNDS BY GAS CHROMATOGRAPHY

Separation of Partially Fluorinated Tetramethylsilanes

Material from several of the tetramethylsilane reactions were collected together. To this was added reaction products consisting of mainly partially fluorinated tetramethylsilanes. The material was fractionated through a -131° slush to remove any extremely volatile decomposition products.

The gas chromatograph program selected was the following:

Fluorosilicone column (10% on Chromosorb P) $3/8"$ x 24'
0° isothermal for 53.45'
1° per minute to 30° for 50'
1.5° per minute to 50° for 50'
70° for 3 minutes, isothermal until 240'
5° per minute to 100° for 30'
5° per minute to 185° bake

Approximately 100 μ l of sample was injected with an air-tight syringe each time. The compounds of interest were collected over a time span from 108'30" to 255'50". Compounds which were collected earlier were shown later to contain no silicon.

During the separation, the initial compounds (just after air) were identified as SiF_4 , $\text{C}_2\text{F}_2\text{H}_2$, CF_3H and other apparently decomposition products. Seventeen different peaks were collected. These compounds from the gas chromatograph separation were sealed off in glass tubes for ^1H and ^{19}F nmr. Mass spectra were then taken of each sample. Infrared spectra were recorded before and after each mass spectrum. Blanks of the infrared cell were taken at each point to insure no spurious absorptions from decomposition onto the KBr windows. The spectral data have been tabulated and is shown

in Tables I - IV. (Several samples were sent for elemental analysis. However, the samples upon combustion, destroyed several analyzers at Schwartzkopf Microanalytical Laboratory, Woodside, New York.)

Note of caution: Care should be taken when handling the polyfluoro-tetramethylsilanes. The compounds can spontaneously explode and ignite.

Separation of $\text{Ge}(\text{CF}_3)_4$ From Impurities

The following gas chromatograph conditions were used.

SE-30 column, 3/8" x 24'
0° isothermal for 10'
2°/minute to 60°
bake at 185°

Depending on the amount of material injected into the gas chromatograph, the retention times varied. Generally approximately 100 μ l was injected. If 75 μ l was used, $\text{Ge}(\text{CF}_3)_4$ had a retention time of 3'17", $\text{Ge}(\text{CF}_3)_3(\text{C}_2\text{F}_5)$, 6'10", $\text{Ge}(\text{CF}_3)_3(\text{OH})$, 20'43" and $\text{Ge}(\text{CH}_3)_4$, 29'16". The two major impurities comprised about 4% of the material.

Separation of Polyfluorotetramethylgermanium

The following gas chromatograph condition was used with an average of 100 μ l of liquid injected into the gas chromatograph.

SE-30 column, 3/8" x 24"
30° isothermal for 30 minutes
2°/minute to 60° for 15 minutes
2.5°/minute to 100° for 50'
bake at 185°

Excellent baseline separation was obtained for the compounds. Usually by 84', the last compound of interest was off the column. Using the retention time as a general rule for the volatility of the samples, it was found, as was to be expected, that with increasing number of fluorine atoms on the molecule, the volatility of the molecule increased and the retention time decreased for the particular column used.

After the materials were separately collected and transferred into containers, infrared spectra were taken of each, checking the background of the cell each time to be careful of decomposition. Subsequently, nmr and mass spectra were recorded for each of the samples.

Table I. Proton NMR Spectra

<u>Compound</u>	CH_3	CH_2F^*	J_{HF}	CHF_2^{**}	J_{HF}
$\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})^1$	0.06	4.30	46.9		
$\text{Si}(\text{CH}_3)_2(\text{CH}_2\text{F})_2$	-0.18	4.16	47.5		
$\text{Si}(\text{CH}_3)_3(\text{CHF}_2)$	0.07			6.43	52
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_3$	-0.23	4.17	47.0		
$\text{Si}(\text{CH}_3)_2(\text{CH}_2\text{F})(\text{CHF}_2)$	-0.11	4.22	47.4	5.62	46.2
$\text{Si}(\text{CH}_3)_2(\text{CHF}_2)_2$	0.31			5.91	45.6
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CHF}_2)$	-0.06	4.32	47.3	5.68	45.9
$\text{Si}(\text{CH}_2\text{F})_4$		4.24	47.0		
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)_2$	0.04	4.39	46.8	5.74	45.4
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CF}_3)$	0.12	4.42	47.1		
$\text{Si}(\text{CH}_2\text{F})_3(\text{CHF}_2)$		4.54	46.6	5.87	45.4
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)(\text{CF}_3)$	0.08	4.36	46.3	5.69	45.4
$\text{Si}(\text{CH}_2\text{F})_2(\text{CHF}_2)_2$		4.66	46.6	5.91	45.4
$\text{Si}(\text{CH}_2\text{F})(\text{CHF}_2)_3$		4.68	46.2	5.82	45.0

* doublet

** triplet

Shifts in ppm from external TMS, + downfield from TMS.
Coupling constants in hertz.

¹ Literature: ⁹CH₃ (0.31) CH₂F (4.53) J_{HF} (46.8)

Table II. Fluorine NMR Spectra

Compound	CF ₃	CHF ₂ *	J _{HF}	CH ₂ F**	J _{HF}
Si(CH ₃) ₃ (CH ₂ F) ¹				196	46.8
Si(CH ₃) ₂ (CH ₂ F) ₂				195.14	47.1
Si(CH ₃)(CH ₂ F) ₃				197.73	46.8
Si(CH ₃) ₂ (CH ₂ F)(CHF ₂)		61.17	45.6	196.61	46.4
Si(CH ₃) ₂ (CHF ₂) ₂		59.22	46.0		
Si(CH ₃)(CH ₂ F) ₂ (CHF ₂)		61.08	45.8 ^a	199.60	47.0 ^b
Si(CH ₂ F) ₄				200.13	46.9
Si(CH ₃)(CH ₂ F)(CHF ₂) ₂		60.85	45.7 ^c	201.00	46.7 ^d
Si(CH ₃)(CH ₂ F) ₂ (CF ₃)	-15.48 ^e			199.92	46.3
Si(CH ₂ F) ₃ (CHF ₂)		60.03	45.4 ^f	201.41	46.6 ^g
Si(CH ₃)(CH ₂ F)(CHF ₂)(CF ₃)	-16.53 ^h	61.15	45.0	201.19	+
Si(CH ₂ F) ₂ (CHF ₂) ₂		58.88	45.4 ⁱ	202.87	46.4 ^j
Si(CH ₂ F)(CHF ₂) ₃		59.57	45.0 ^k	204.39	46.6 ^l

* doublet

** triplet

+ not recorded

Shifts in ppm from external TFA, + upfield from TFA.
Coupling constants in hertz.

¹ Literature : Reference 19

^a J_{FF} = 1.4 (triplet)

^b J_{FF} = 1.5 (multiplet)
J_{HHF} ≈ 1.0

^c J_{FF} = 1.8 (doublet)

^d J_{FF} = 1.4 (multiplet)
J_{HHF} ≈ 0.5

^e J_{FF} = 3.2 (quartet of triplets)
J_{HHF} ≈ 1.0

^f J_{FF} = 1.8 (quartet)

^g J_{FF} = 1.6 (triplet)

^h J_{FF} = 3.0 (quartet or doublet
of triplets)

ⁱ J_{FF} = 2.0 (triplet)

^j J_{FF} = 1.9 (pentet)

^k J_{FF} = 2.1

^l J_{FF} = 2.0

J_{HHF} ≈ 0.4

Table III. Mass Spectra of Polyfluorotetramethylsilanes*

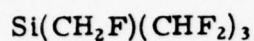
$\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$ mw = 106.22	77 (14) 73 (100) 63 (52) 59 (5) 49 (9) 47 (20) 45 (43) 43 (22) 33 (9) 31 (5) 29 (7) 27 (8) 15 (9) 14 (5)
$\text{Si}(\text{CH}_3)_3(\text{CHF}_2)$ mw = 124.21	100 (15) 99 (6) 81 (100) 51 (31) 50 (8) 47 (36) 45 (11) 33 (15) 31 (21) 29 (7) 27 (19) 26 (5) 15 (9) 14 (3)
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_3$ mw = 142.2	99 (5) 85 (8) 81 (100) 67 (15) 63 (51) 62 (11) 47 (56) 41 (18) 33 (16) 29 (16) 27 (38) 15 (11) 14 (3)
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CHF}_2)$ mw = 160.19	99 (19) 85 (49) 81 (100) 67 (17) 51 (38) 47 (68) 45 (30) 33 (42) 29 (20) 27 (54) 26 (7) 15 (11) 14 (6)
$\text{Si}(\text{CH}_2\text{F})_4$ mw = 160.19	99 (44) 91 (9) 85 (35) 81 (8) 80 (26) 67 (9) 47 (57) 33 (100) 27 (52) 26 (9) 15 (6) 14 (2)
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)_2$ mw = 178.18	117 (4) 99 (14) 85 (24) 81 (100) 67 (16) 51 (38) 47 (68) 33 (31) 29 (16) 27 (68) 26 (7) 15 (13)
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CF}_3)$ mw = 178.13	163 (0.4) 149 (5) 145 (2) 117 (4) 99 (14) 95 (19) 85 (30) 81 (100) 80 (8) 69 (10) 67 (51) 64 (15) 51 (21) 47 (69) 45 (44) 33 (17) 31 (24) 29 (39) 27 (51) 26 (6) 15 (10) 14 (7)
$\text{Si}(\text{CH}_2\text{F})_3(\text{CHF}_2)$ mw = 178.18	117 (4) 99 (47) 85 (77) 80 (14) 51 (33) 47 (42) 33 (100) 27 (50) 26 (12) 14 (18)
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)(\text{CF}_3)$ mw = 196.18	111 (4) 100 (11) 99 (8) 85 (34) 81 (100) 76 (7) 69 (5) 67 (31) 51 (37) 47 (48) 33 (17) 31 (24) 29 (39) 27 (51) 26 (6) 15 (7) 14 (4)
$\text{Si}(\text{CH}_2\text{F})_2(\text{CHF}_2)_2$ mw = 196.18	117 (10) 99 (62) 85 (100) 81 (11) 51 (97) 47 (55) 33 (94) 31 (17) 29 (26) 27 (72) 26 (14) 15 (8) 14 (22)
$\text{Si}(\text{CH}_2\text{F})(\text{CHF}_2)_3$ mw = 214.16	117 (8) 99 (22) 85 (58) 81 (100) 67 (17) 64 (16) 51 (39) 47 (62) 45 (38) 33 (42) 31 (11) 29 (17) 27 (52) 26 (17) 15 (12) 14 (11)
Lit: ⁹ $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$ mw = 106.22	77 (12) 73 (100) 63 (54) 59 (4) 49 (8) 47 (15) 45 (30) 43 (14) 29 (7)

(* Number in parenthesis is the intensity corresponding to the m/e given.)

Table IV. Infrared Spectra of Polyfluorotetramethylsilanes

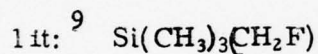
$\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$	2980 (sh) 2960 (s) 1870 (m) 1425 (m) 1255 (vs) 1200-1100 (br) 1060 (s) 1000 (vs) 850 (vvs) 755 (s) 700 (s) cm^{-1}
$\text{Si}(\text{CH}_3)_3(\text{CHF}_2)$	2960 (m) 1408 (m) 1320 (s) 1291 (s) 1260 (s) 1239 (s) 1100 (vs) 1030 (vs) 910 (s) 800 (s) 700 (w) cm^{-1}
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_3$	2990 (m) 2960 (s) 2930 (s) 2855 (m) 1440 (m) 1390 (w) 1375 (vw) 1270 (s) 1230 (s) 1220 (sh) 1119 (m) 1069 (m) 1005 (vs) 905 (m) 850 (vs) 810 (s) cm^{-1}
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CHF}_2)$	2990 (sh) 2955 (sh) 2940 (s) 1440 (m) 1325 (s) 1299 (m) 1270 (s) 1220 (s) 1095 (vs) 1050 (sh) 1025 (vvs) 1000 (vvs) 910 (br) 845 (vs) 815 (vs) cm^{-1}
$\text{Si}(\text{CH}_2\text{F})_4$	2960 (m) 2930 (m) 1430 (m) 1385 (w) 1300 (vw) 1225 (m) 1215 (sh) 1025 (sh) 1005 (sh) 1000 (vs) 905 (w) 845 (m) 805 (m) cm^{-1}
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)_2$	3000 (sh) 2930 (s) 1440 (m) 1330 (s) 1325 (s) 1300 (w) 1270 (s) 1225 (m) 1091 (vs) 1025 (vvs) 900 (w) 880 (sh) 808 (s) cm^{-1}
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CF}_3)$	2990 (sh) 2950 (m) 2930 (m) 1415 (m) 1385 (w) 1295 (s) 1275 (s) 1219 (vs) 1130 (m) 1092 (vvs) 1052 (s) 1020 (s) 920 (m) 900 (m) 840 (s) 801 (s) 830-810 (br) cm^{-1}
$\text{Si}(\text{CH}_2\text{F})_3(\text{CHF}_2)$	2965 (sh) 2945 (m) 1431 (m) 1389 (w) 1330 (m) 1273 (w) 1231 (m) 1111 (s) 1071 (sh) 1032 (vs) 950 (vs) 906 (vs) 803 (s) cm^{-1}
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)(\text{CF}_3)$	3000 (sh) 2965 (sh) 2960 (m) 1420 (m) 1390 (w) 1330 (m) 1300 (m) 1275 (m) 1220 (s) 1100 (vs) 1035 (s) 900 (m) 830 (sh) 805 (s) cm^{-1}
$\text{Si}(\text{CH}_2\text{F})_2(\text{CHF}_2)_2$	2945 (m) 1431 (m) 1390 (w) 1371 (vw) 1325 (m) 1300 (w) 1225 (m) 1090 (s) 1039 (vs) 980 (m) 906 (s) 791 (m) 700 (m) cm^{-1}

Table IV. Infrared Spectra of Polyfluorotetramethylsilanes (cont'd)



2980 (sh) 2960 (s) 2920 (sh) 2850 (w) 1439 (m)
1320 (s) 1265 (m) 1221 (m) 1091 (vs) 1039 (vs)
1001 (s) 910 (w) 850 (s) 809 (s) cm^{-1}

vw = very weak
w = weak
m = medium
s = strong
vs = very strong
vvs = very, very strong
br = broad
sh = shoulder



3.45 (m), 5.03 (w), 6.78 (w), 7.02 (s), 7.72 (m),
7.88 (vs), 7.98 (vs), 8.23 (m), 8.50 (w), 9.46 (m)
9.57 (m), 10.01 (vs), 11.57 (vs), 12.30-12.60 (m-br)
13.05 (s), 14.23 (vs) μm

Table V. Melting Points of Polyfluorotetramethylsilanes

<u>Compound</u>	<u>Melting Point (°C)</u>
$\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$	-86.5 to -85.0
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_3$	-89.5 to -84.5
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CHF}_2)$	-63.5 to -62.0
$\text{Si}(\text{CH}_2\text{F})_4$	-18.0 to -16.6
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)_2$	-58.7 to -56.8
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CF}_3)$	-144 to -142.7
$\text{Si}(\text{CH}_2\text{F})_3(\text{CHF}_2)$	-54.0 to -53.2
$\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)(\text{CF}_3)$	-144 to -138
$\text{Si}(\text{CH}_2\text{F})_2(\text{CHF}_2)_2$	-68.2 to -66.8
$\text{Si}(\text{CH}_2\text{F})(\text{CHF}_2)_3$	-72.6 to -71.0
$\text{Si}(\text{CH}_3)_4$	-91.1

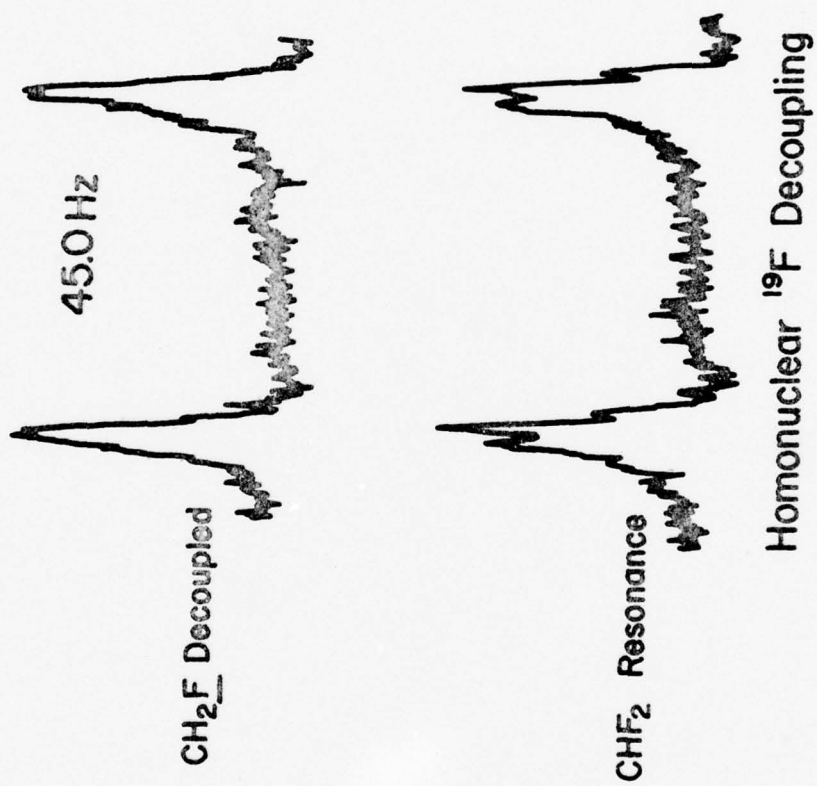
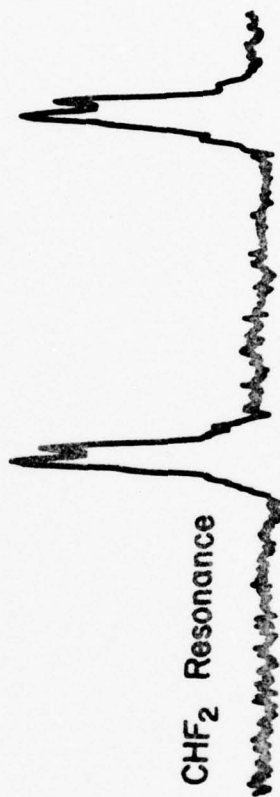
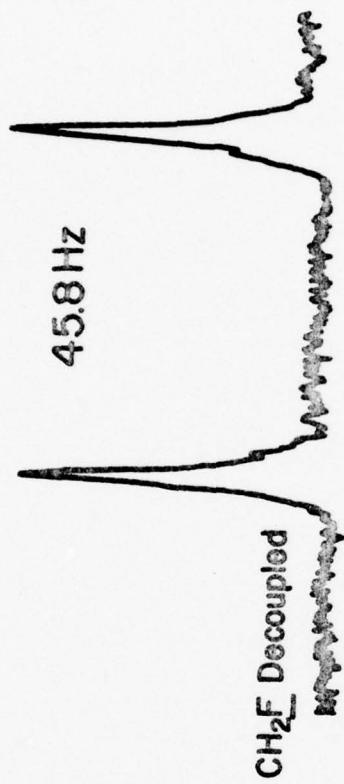


FIGURE 1.



Homonuclear ^{19}F Decoupling

FIGURE 2.

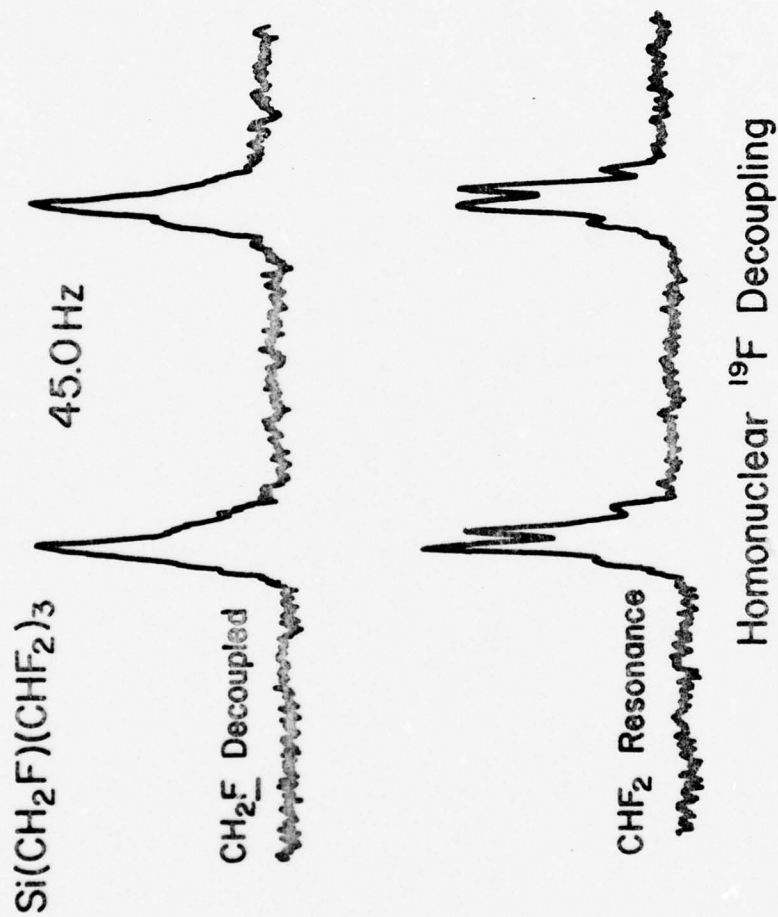


FIGURE 3.

Table VI.

Proton NMR Spectra of Polyfluorotetramethylgermanium

Compound	CH_3^*	CH_2F^{**}	J_{HF}	CHF_2^{***}	J_{HF}^b
$\text{Ge}(\text{CF}_3)_3(\text{CF}_2\text{H})$				6.10 ^a	45.0 ^b
$\text{Ge}(\text{CF}_3)_3(\text{CFH}_2)$					
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})_2$				6.23	45.5
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})(\text{CFH}_2)$		4.98	46.5	6.24	45.7
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_3$				6.25	45.5
$\text{Ge}(\text{CF}_3)_2(\text{CFH}_2)_2$					
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CFH}_2)$		4.89	46.0	6.15	45.5
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CH}_3)$	0.51			6.10	45.6
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)_2$		4.90	46.0	6.25	45.6
$\text{Ge}(\text{CF}_2\text{H})_3(\text{CFH}_2)$		5.02	45.7	6.28	45.6
$\text{Ge}(\text{CF}_2\text{H})_2(\text{CFH}_2)_2$		4.97	46.0	6.26	45.2
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)(\text{CH}_3)$	0.47	4.79	46.0	6.08	46.0
$\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_3$		4.97	46.5	6.29	46.0
$\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_2(\text{CH}_3)$	0.34	4.78	46.0	6.10	46.0
$\text{Ge}(\text{CFH}_2)_4$		4.87	47.0		
$\text{Ge}(\text{CF}_3)_3(\text{OH})^c$					

* Singlet

** Doublet

*** Triplet

a Shifts in ppm downfield from external TMS

b Coupling constants in hertz

c OH(2.43), singlet

Table VII.

Fluorine NMR Spectra of Polyfluorotetramethylgermanium

Compound	CF_3^*	J_{FF}	CHF_2^{**}	J_{HF}	J_{FF}	$\text{CH}_2\text{F}^{***}$	J_{HF}	J_{FF}
$\text{Ge}(\text{CF}_3)_4$	-27.0							
$\text{Ge}(\text{CF}_3)_3(\text{C}_2\text{F}_5)$	-27.7	2.7 ^a						
$\text{Ge}(\text{CF}_3)_3(\text{CF}_2\text{H})$	-27.2	3.0 ^b	49.0	45.5	3.1 ^c			
$\text{Ge}(\text{CF}_3)_3(\text{CFH}_2)$	-25.8							
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})_2$	-27.6	3.2 ^d	49.4	46.0	3.1 ^e			
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})(\text{CFH}_2)$	-26.3	3.3 ^f	50.6	45.5	3.0 ^g	193.2	46.5	3.3 ^h
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_3$	-27.9	3.2 ⁱ	49.7	46.0	3.1 ^j			
$\text{Ge}(\text{CF}_3)_2(\text{CFH}_2)_2$	-24.8	3.4 ^k				193.0	47.0	3.5 ^l
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CFH}_2)$	-26.8	3.2 ^m	50.5	45.6	3.0 ⁿ	193.0	46.0	2.9 ^o
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CH}_3)$	-23.5	3.4 ^p	53.0	46.5	3.2 ^q			
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)_2$	-25.2	3.2 ^r	51.8	45.5	3.0 ^s	192.0	46.0	2.7 ^t
$\text{Ge}(\text{CF}_2\text{H})_3(\text{CFH}_2)$			50.5	46.2	2.2 ^u	192.9	46.0	2.4 ^v
$\text{Ge}(\text{CF}_2\text{H})_2(\text{CFH}_2)_2$			51.4	46.0	2.5 ^w	192.5	46.6	2.5 ^x
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)(\text{CH}_3)$	-22.3	3.4 ^y	53.7	46.0	3.0 ^z	192.5	46.0	3.0
$\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_3$			52.0	46.0	2.1 ^{aa}	191.9	46.6	1.8 ^{bb}
$\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_2(\text{CH}_3)$			53.9	46.2	2.1 ^{cc}	192.5	46.5	2.0 ^{dd}
$\text{Ge}(\text{CFH}_2)_4$						191.4	46.7	
$\text{Ge}(\text{CF}_3)_3(\text{OH})$	-21.6							

Table VII. continued

*	Singlet	1	5 of 7 lines
**	Doublet	m	sextet
***	Triplet	n	pentet
	Shifts in ppm from external TFA + upfield from TFA	o	6 of 8 lines
	Coupling constants in hertz	p	pentet
a	Basic quartet	q	quartet
	C ₂ F ₅ group: CF ₃ , 6.76, multiplet;	r	pentet
	CF ₂ , 38.4, J _{FF} = 3.3, septet	s	sextet
b	triplet	t	sextet
c	4 of 10 lines	u	doublet
d	pentet	v	5 of 7 lines
e	septet	w	pentet
f	quartet	x	pentet
g	6 of 8 lines	y	quartet
h	7 of 9 lines	z	pentet
i	septet	aa	quartet
j	quartet	bb	triplet
k	triplet	cc	triplet
		dd	triplet

Table VIII.

Mass Spectra^a of Polyfluorotetramethylgermanium

$\text{Ge}(\text{CF}_3)_4^*$ mw = 350 ^b	331 ^c (9.3), 281(54.2), 231(30.6), 182(38.1), 143(10.6), 119(83.6), 100(0.01), 93(59.2), 81(3.5), 69(100), 50(2.6), 31(8.3)
$\text{Ge}(\text{CF}_3)_3(\text{C}_2\text{F}_5)^{**}$ mw = 400	381(13.8), 331(48.7), 281(36.8), 231(30.3), 212(0.53), 193(2.8), 181(68.4), 143(14.5), 131(13.8), 119(100), 100(88.5), 93(82.9), 69(91.4), 51(11.2), 50(3.3), 31(11.8)
$\text{Ge}(\text{CF}_3)_3(\text{CF}_2\text{H})$ mw = 332	281(20.0)(10.4), 269(10.0)(), 259(2.1)(0.01), 247(9.0) (), 231(99.0)(67.2), 219(13.4)(), 197(5.9)(), 181(48.6)(48.8), 159(1.7)(1.0), 143(4.8)(5.2), 119(100) (100), 93(40.0)(46.4), 81(1.7)(6.8), 69(77.6)(76.0), 67(5.1)(8.8), 51(1.4)(2.4), 50(2.0)(6.0), 31(3.1)(4.8)
$\text{Ge}(\text{CF}_3)_3(\text{CFH}_2)^*$ mw = 314	313(0.92), 295(8.2), 281(5.8), 263(4.8), 245(62.3), 231(10.9), 213(4.34), 195(100), 181(15.0), 145(76.7), 125(25.1), 113(7.2), 93(74.8), 82(10.6), 81(7.2), 69(49.2), 64(15.9), 51(21.7), 33(14.0), 31(8.2)
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})_2$ mw = 314	314(0.04)(), 295(5.9)(2.0), 263(43.0)(24.0), 245(20.4) (18.0), 231(0.07)(), 227(1.5)(), 213(22.2)(20.5), 195(13.7)(11.4), 181(10.7)(8.5), 163(1.1)(1.1), 143(32.2) (30.0), 125(22.2)(23.0), 101(1.5)(2.1), 93(76.7)(81.5), 82(14.4)(12.0), 69(28.1)(33.0), 64(5.5)(5.0), 51(100)(100), 33(1.5)(1.7), 32(2.0)(1.8), 31(3.0)(2.9)
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})(\text{CFH}_2)$ mw = 296	293(2.3)(1.7), 277(4.6)(2.9), 262(0.76)(), 245(53.5) (40.0), 227(27.9)(29.2), 213(7.0)(9.2), 195(44.2)(49.2), 177(25.6)(27.7), 145(51.1)(66.2), 143(51.1)(64.6), 107(9.3)(12.3), 93(100)(100), 69(27.9)(29.2), 51(53.5)(60.0), 33(23.3)(20.0), 27(72.0)(58.4)

Table VIII.

continued

$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_3^{\text{d}}$ mw = 296	296(0.74)(≤ 0.01), 277(1.3)(0.15), 259(0.18)(), 245(67.4)(10.6), 227(0.82)(0.15), 209(5.6)(3.0), 195(12.6)(4.7), 181(1.3)(), 159(2.6)(3.9), 142(33.0) (13.6), 125(36.9)(24.2), 107(1.7)(2.5), 93(85.6)(72.2), 82(8.7)(3.0), 69(25.6)(18.2), 64(26.5)(15.1), 51(100)(100), 45(36.5)(21.2), 33(3.9)(6.0), 27()(4.5).
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CFH}_2)^{\text{e}}$ mw = 278	278(0.79)(0.12), 259()(1.0), 245(1.5)(0.72), 227(100) (68.7), 209(3.5)(1.8), 195(1.4)(7.2), 177(29.2)(24.1), 145(25.7)(25.3), 143(30.2)(27.7), 125(22.7)(21.7), 107(23.2) (24.1), 93(93.1)(100), 82(8.4)(6.0), 69(19.8)(21.7), 65(21.8)(25.3), 64(24.2)(21.7), 51(65.3)(72.2), 45(15.8) (16.9), 33(24.7)(22.9), 27(19.3)(66.2).
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)_2$ mw = 260	278(1.5)(0.29), 260(0.41)(0.48), 227(14.9)(5.6), 209(60.2) (29.1), 195(5.6)(3.3), 191(7.2)(3.2), 177(11.2)(5.8), 159(26.9)(16.5), 145(13.6)(8.7), 125(45.0)(39.8), 113(3.6) (3.9), 107(13.2)(9.7), 93(100)(84.5), 69(6.4)(4.9), 65(8.4)(5.8), 64(44.2)(27.1), 51(21.3)(100), 45(24.0)(17.5) 33(20.1)(11.7), 27(39.0)(24.2).
$\text{Ge}(\text{CF}_2\text{H})_3(\text{CFH}_2)$ mw = 260	260(1.97)(0.43), 227()(5.7), 209(20.6)(11.3), 195(1.0) (1.4), 173(12.1)(7.4), 159(7.0)(4.3), 145(22.1)(19.1), 129(2.7)(), 125(28.5)(26.0), 113(3.9)(3.5), 107(14.5) (15.6), 93(94.2)(99.1), 65(10.0)(11.3), 64(32.7)(43.5), 51(100)(100), 46(14.7)(), 45(14.7)(), 33(41.5)(40.0), 27(42.7)(42.6).
$\text{Ge}(\text{CF}_2\text{H})_2(\text{CFH}_2)_2^{*\text{f}}$ mw = 242	242(1.9), 227(0.1), 209(1.4), 191(29.5), 155(6.7), 145(25.3), 125(14.0), 107(22.2), 93(100), 65(9.3), 64(40.9), 56(0.52), 51(46.6), 46(22.2), 43(9.3), 33(18.6), 27(23.8).

Table VIII. continued

Ge(CF ₂ H)(CFH ₂) ₃ mw = 224	229(18.5)(4.8), 191(2.8)(), 173(100)(68.1), 155(18.5)(8.1), 145(9.2)(6.5), 141(9.2)(6.5), 107(20.0)(21.0), 93(96.9)(100), 81(26.9)(3.2), 57(31.9)(), 56(27.3)(), 51(19.7)(12.9), 33(95)(75), 27(60)(44.4).
Ge(CF ₃) ₃ (OH) mw = 298	281(34.3)(22.7), 263(30.3)(31.8), 231(14.0)(13.6), 213(40.3)(47.7), 193(2.3)(2.5), 181(19.7)(22.7), 163(2.0)(2.5), 152(5.0)(4.5), 143(45.7)(54.5), 131(10.3)(11.3), 119(33.7)(36.3), 101(3.0)(3.1), 100(2.7)(2.0), 93(92.7)(100), 82(13.7)(11.4), 81(10.7)(6.8), 69(63.3)(59.0), 51(20.0)(86.4), 31(3.0)(6.3).
Ge(CFH ₂) ₄ mw = 206	206(6.0)(2.0), 173(92.8)(74.1), 141(19.8)(12.4), 107(16.2)(17.2), 93(100)(100), 69(12.6)(2.0), 16(15.0)(4.7).

- a Intensities of m/e are reported for instrument at (room temperature)(150°).
- b Molecular weight calculated for Ge = 74.
- c m/e containing germanium isotope pattern reported with Ge = 74.
- d Sample contained 2.5% Ge(CF₃)₂(CFH₂)₂
- e Sample contained 9% Ge(CF₃)(CF₂H)(CFH₂)(CH₃)
- f Sample contained 12% Ge(CF₂H)(CFH₂)₃(CH₃)
- * Did not record spectrum at 150°.
- ** Did not record spectrum at room temperature.

Table IX.

Infrared Spectra^a of Polyfluorotetramethylgermanium

$\text{Ge}(\text{CF}_3)_3(\text{C}_2\text{F}_5)$	1345(wsh) 1335(w) 1240(m) 1202(m) 1175(vs) 1122(vw) 972(w) 745(vw)
$\text{Ge}(\text{CF}_3)_3(\text{CF}_2\text{H})$	2959(vw) 1329(w) 1209(m) 1175(vs) 1155(s) 1135(m) 1095 (w) 1079(w) 645(vw)
$\text{Ge}(\text{CF}_3)_3(\text{CFH}_2)$	2950(vvw) 1299(w) 1259(m) 1165(vs) 1152(s) 1129(m) 1039(w) 779(vvw) 739(vvw)
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})_2$	2970(w) 1305(m) 1197(vs) 1173(vs) 1145(vs) 1125(sh) 1090(m) 740(w)
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})(\text{CFH}_2)$	2960(vw) 1315(w) 1300(w) 1200(s) 1180(vs) 1140(s) 1115(m) 1070(m) 1040(w) 799(vw) 765(vvw) 735(vvw)
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_3^b$	2980(m) 1339(w) 1310(s) 1180(s) 1139(vs) 1100(vs) 1070(s) 1040(sh) 740(vw) 660(w)
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CFH}_2)^c$	2980(w) 1305(m) 1190(vs) 1130(vs) 1100(s) 1060(s) 1030(m) 800(vw) 740(w)
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)_2$	2960(m) 1440(w) 1305(s) 1185(vs) 1119(vs) 1090(sh) 1050(s) 1021(s) 900(w) 820(m) 770(w) 660(vw)
$\text{Ge}(\text{CF}_2\text{H})_3(\text{CFH}_2)$	2970(m) 1435(w) 1300(s) 1220(w) 1185(m) 1105(sh) 1085(vs) 1045(vs) 1015(s) 815(w) 793(vw) 620(vw)
$\text{Ge}(\text{CF}_2\text{H})_2(\text{CFH}_2)_2^d$	2950(w) 1305(m) 1180(m) 1160(w) 1090(s) 1040(s) 1015(s) 820(w)

Table IX. continued

$\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_3$	2980(w) 2940(w) 1440(vw) 1310(w) 1290(w) 1265(w) 1225(vw) 1180(m) 1130(w) 1089(m) 1040(m) 1015(s) 955(m) 915(w) 830(w) 820(w)
$\text{Ge}(\text{CF}_3)_3(\text{OH})$	1200(w) 1181(vs) 1163(s) 950(w) 740(vw) (OH stretch at 3680 (vww))

- a Numbers in cm^{-1}
- b Contains 2.5% $\text{Ge}(\text{CF}_3)_2(\text{CFH}_2)_2$
- c Contains 9% $\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)(\text{CH}_3)$
- d Contains 12% $\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_2(\text{CH}_3)$

Table X.

Weight Percentage Yields^a of Polyfluorotetramethylgermanium

$\text{Ge}(\text{CF}_3)_4$	63.5 ^b
$\text{Ge}(\text{CF}_3)_3(\text{C}_2\text{F}_5)$	0.25
$\text{Ge}(\text{CF}_3)_3(\text{CF}_2\text{H})$	0.38
$\text{Ge}(\text{CF}_3)_3(\text{CFH}_2)$	0.06
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})_2$	6.20
$\text{Ge}(\text{CF}_3)_2(\text{CF}_2\text{H})(\text{CFH}_2)$	4.16
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_3/\text{Ge}(\text{CF}_3)_2(\text{CFH}_2)_2/\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CH}_3)$	13.35 ^c
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CFH}_2)/\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)(\text{CH}_3)$	13.94 ^d
$\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)_2$	28.51
$\text{Ge}(\text{CF}_2\text{H})_3(\text{CFH}_2)$	15.47
$\text{Ge}(\text{CF}_2\text{H})_2(\text{CFH}_2)_2/\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_2(\text{CH}_3)$	11.87 ^e
$\text{Ge}(\text{CF}_2\text{H})(\text{CFH}_2)_3$	4.18
$\text{Ge}(\text{CF}_3)_3(\text{OH})$	1.40
$\text{Ge}(\text{CFH}_2)_4$	0.22

a Yield for $\text{Ge}(\text{CF}_3)_4$ calculated independent of the compounds. When yield of $\text{Ge}(\text{CF}_3)_4$ is high, only trace amounts of two other compounds appear, $\text{Ge}(\text{CF}_3)_3(\text{C}_2\text{F}_5)$ and $\text{Ge}(\text{CF}_3)_3(\text{OH})$.

b Based on 0.87 gm $\text{Ge}(\text{CH}_3)_4$ as starting material.

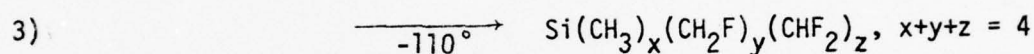
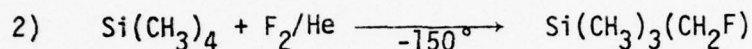
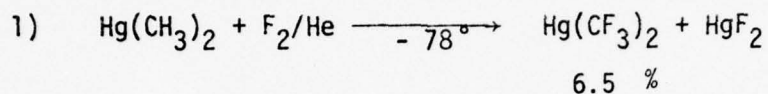
c Ratio of three compounds: 6.1/1.4/1

d Ratio of two compounds: 10/1

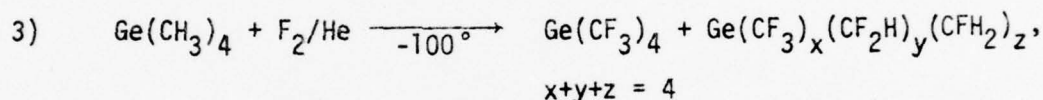
e Ratio of two compounds: 14.3/1

RESULTS AND DISCUSSION

The reaction of fluorine with dimethylmercury, tetramethylsilane and tetramethylgermanium can be summarized as follows:



i) only small yields of Si-CF₃ compounds



i) increase in temperature from -100° to -60° leads to

low yields of Ge(CF₃)₄, 1-6%

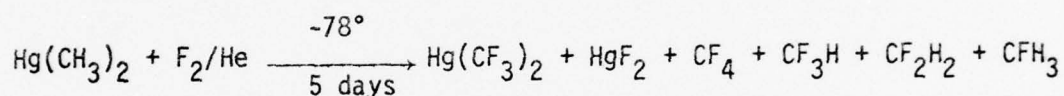
ii) increase in temperature from -100° to -20° leads to

high yields of Ge(CF₃)₄, 63.5% but no Ge(CF₃)_x(CF₂H)_y(CFH₂)_z

The spectral and physical data for the polyfluorotetramethylsilanes have been tabulated above. The ¹⁹F and ¹H NMR, infrared and mass spectra are given in the tables above for the polyfluorotetramethylgermanes.

Dimethylmercury

Dimethylmercury can be fluorinated to its perfluoro analog, bis-(trifluoromethyl)mercury, $\text{Hg}(\text{CF}_3)_2$, by low temperature fluorination. Yields of 6.5% (based on 1.53 grams of $\text{Hg}(\text{CH}_3)_2$) can be obtained by fluorination at -78° to -90° . A fluorine concentration of 1.67% obtained by using a mixture of 1 cc/minute fluorine to 60 cc/minute helium, was used for 5 days in the cryogenic zone reactor. The bis(trifluoromethyl)-mercury was separated from the fluorocarbons and unreacted dimethylmercury on a vacuum line and by gas chromatography. The reaction can be represented as follows:



The physical properties and ^{19}F nmr agree with authentic samples prepared by alternative methods.^{8,10,11}

The formation of $\text{Hg}(\text{CF}_3)_2$ from $\text{Hg}(\text{CH}_3)_2$ and fluorine is remarkable in that one could write several mechanisms for cleavage of the metal-carbon bonds such that failure would have been predicted. Although one does get a considerable amount of HgF_2 from the cleavage of the Hg - C bond, it is possible to form $\text{Hg}(\text{CF}_3)_2$, nevertheless. Evidently efficient relaxation processes occur on the cold surfaces to allow energy dissipation so that the mercury carbon bond is maintained as the methyl group undergoes successive fluorination.

It is believed that once $\text{Hg}(\text{CF}_3)_2$ forms, the compound is stable under the conditions of the experiment. It has been found that $\text{Hg}(\text{CF}_3)_2$ does

not react with 3% fluorine at -78° . It has also been found that $\text{Hg}(\text{CF}_3)_2$ reacts slowly with 3% fluorine at 0° and appreciably at room temperature, forming HgF_2 and CF_4 . Therefore with a low fluorine concentration of 1.67% and low temperature, -78° , $\text{Hg}(\text{CF}_3)_2$ can form. However HgF_2 is the major product. This is to be expected in light of thermodynamic factors of bond strengths, that of C-HgR (CH_3HgCH_3) being 50 kcal/mole¹² while F-Hg is 100 kcal/mole¹² and HF is 153 kcal/mole.¹³

It is strange that there appears to be no evidence that any partially fluorinated $\text{Hg}(\text{CH}_3)_2$ was present. One can conclude that either $\text{Hg}(\text{CF}_3)_2$ or HgF_2 is formed as the only mercury products or that any partially fluorinated dimethylmercury species are unstable at temperatures higher than the reaction temperature. The latter has some credibility in that one of the experiments, a large quantity of decomposition product, high in fluorine content remained. The compound could be a polymer with C, H, and F present in unknown amounts.

Even though $\text{Hg}(\text{CF}_3)_2$ is not a new compound, the fluorination of $\text{Hg}(\text{CH}_3)_2$ has demonstrated that the fluorination process can be controlled and manipulated to produce highly fluorinated species. Experimental conditions are indeed crucial. It is important that the $\text{Hg}(\text{CH}_3)_2$ be at the temperature stated or only HgF_2 is formed. In our reactors, a tremendous temperature gradient exists. The temperature outside the zone of interest is normally about $20-30^{\circ}$ warmer downstream and much higher upstream of the helium flow. A single zone fluorination of $\text{Hg}(\text{CH}_3)_2$ demonstrates this very well. The $\text{Hg}(\text{CH}_3)_2$ freezes at the entrance of the reactor which is probably at $\sim -20^{\circ}$ and not at the

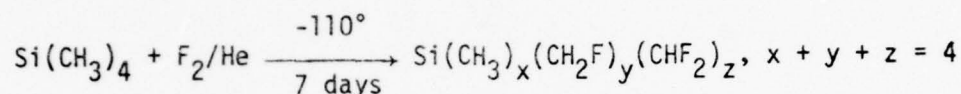
desired -78° temperature. Consequently the fluorination process is too exothermic and energy dissipation not sufficient to allow $\text{Hg}(\text{CF}_3)_2$ to form. The described reaction solves this problem well and one gets 6.5% yield of $\text{Hg}(\text{CF}_3)_2$.

Tetramethylsilane

From all the experiments studied, of which a representative one has been described in the experimental section, there appears to be no evidence for the synthesis of $\text{Si}(\text{CF}_3)_4$. However, it is clear that the silicon-carbon bond was preserved during direct fluorination. It is possible to isolate in excellent quantities, the partially fluorinated tetramethylsilanes of the general formula: $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$, $x + y + z = 4$. The fact that $\text{Si}(\text{CF}_3)_4$ was not isolated by this method is intriguing in light of the isolation of the partially fluorinated tetramethylsilanes, which are at least thermally stable, and other compounds containing $\text{Si}-\text{CF}_3$ bonds.

In an effort to prepare $\text{Si}(\text{CF}_3)_4$, many variables in reaction conditions were tried. Some were fixed temperature and varying fluorine concentration, fixed temperature and varying fluorine flow and length of reaction, varying temperature with fixed fluorine flow and time, varying temperature with fixed fluorine flow and/or length of reaction, and fixed temperature with fluorine flow with varying length of reaction. All experiments which were attempted were unsuccessful in producing isolable $\text{Si}(\text{CF}_3)_4$. However, some

conditions were better than others in preparing the partially fluorinated tetramethylsilanes. Several conditions produced more highly fluorinated species than others but the best condition for the preparation of $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$, $x + y + z = 4$ was the following:



with F_2/He flow ratio of 1.0 cc/minute to 60 cc/minute. Starting with 1.0 ml of tetramethylsilane, one can recover approximately 0.8 ml of volatile liquid which stops in a -131° trap. The material which passed a -131° trap consisted mainly of SiF_4 , CF_3H and CF_4 . It was noted during the separation of the partially fluorinated tetramethylsilanes that many of the compounds were quite low in volatility. It was felt that maybe one could capitalize on the low volatility and presumed lower reactivity of the species by using more drastic conditions, eg. higher fluorine concentrations and higher temperatures, in an effort to produce $\text{Si}(\text{CF}_3)_4$. However, this was unsuccessful. Aside from the two compounds reported here with $\text{Si}-\text{CF}_3$ bonds one was unable to produce large quantities of $\text{Si}-\text{CF}_3$ type compounds.

Several of the $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$, $x + y + z = 4$, compounds were isolated and characterized. Many others were not characterized due to the inability to separate several compounds.

Nuclear Magnetic Resonance

The proton and fluorine nmr's of the polyfluorotetramethylsilane compounds are summarized in Table I and II. Ready identification of the groups on silicon is obtained in the nmr spectra through chemical shifts, integration and coupling constants, both H-F and F-F. In the proton spectra, the methyl resonance falls in the range of +0.31 to -0.23 ppm with respect to TMS=0 ppm. No long range couplings with the other protons or fluorines are observed as the CH_3 resonance remains a singlet. The CH_2F group appears as a doublet in the proton spectrum while the CHF_2 group appears as a triplet, both resulting from H-F coupling. The chemical shift of the CH_2F group falls in the range 4.16 - 4.68 ppm downfield from TMS while the chemical shift of the CHF_2 group falls in the range 5.62 - 5.91 ppm. The H-F coupling constants for the CH_2F group range from 46.2 - 47.5 hz while that for the CHF_2 group 45.0 - 46.2 hz. (The exception to the above is the CHF_2 resonance for $\text{Si}(\text{CH}_3)_3(\text{CHF}_2)$ which is 6.43 ppm and the corresponding $J(\text{H-F})$ is 52 hz.) These coupling constants were in good agreement with those obtained in the fluorine nmr.

Characteristic resonances also appear in the fluorine nmr spectra. The CH_2F group appears as a triplet from H-F coupling. Coupling constants range from 46.3 - 47.1 hz., in good agreement with that obtained in the proton spectra. Chemical shifts for the CH_2F group fall between 195.14 - 204.39 ppm upfield from TFA. The CHF_2 group appears as a doublet due to H-F coupling with coupling constants between 45.0 - 46.0 hz. Chemical shifts fall between 59.22 - 61.17 ppm. The CF_3 group resonance is downfield from TFA. The two compounds reported here have resonance at -15.48 and -16.53 ppm. The fluorine - fluorine coupling constants were 3.0 and

3.2 hz. Based on the ^{19}F nmr shifts for $\text{M}(\text{CF}_3)_4$, $\text{M} = \text{C}, \text{Ge}, \text{Sn}$, one can predict that the ^{19}F resonance for $\text{Si}(\text{CF}_3)_4$ will be ~ -21 ppm downfield from trifluoroacetic acid. For $\text{Si}(\text{CF}_3)\text{F}_3$,¹⁴ the CF_3 resonance is about -10 ppm downfield from TFA. On several of the compounds reported, it was possible to resolve long range F-F coupling. In these cases, the corresponding groups, CF_3 , CHF_2 and CH_2F gave the normal splitting which one would expect from fluorine-fluorine couplings among the groups. Homonuclear fluorine-fluorine decoupling experiments confirmed this. (See figure 1, 2, and 3.) Coupling constants from these long range F-F coupling were 1.4 - 2.1 hz. In several cases, there appeared to be long range H-F coupling, between groups on silicon. These were not well resolved even through fourier transform nmr. Coupling constants in these cases were normally less than 1.0 hz., generally about 0.4 - 0.5 hz. (Long range proton-fluorine coupling for $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$ was reported to be 0.7 hz.⁹)

It should be noted that for the partially fluorinated tetramethylsilanes, J_{HF} for $\text{CH}_2\text{F} > \text{CHF}_2$. This is the reverse of that observed for the partially fluorinated neopentanes. Also J_{FF} for the two compounds with Si- CF_3 groups are 3.0 and 3.2 hz compared to the J_{FF} for the other compounds, 1.4 - 2.1 hz.

Mass Spectra

The mass spectra of the compounds are tabulated in Table III. All spectra were run at 70 eV. There was no change in spectra pattern or peak intensities if the sample was introduced in the instrument which was cooled to room temperature or if the instrument was heated to its normal operating temperature. One can see from the table that a considerable amount of

rearrangement occurs. No parent peaks were observed in any of the spectra. The largest peaks were normally $85(\text{SiF}_3^+)$, $81(\text{SiCH}_3\text{F}_2^+)$, $73(\text{SiC}_3\text{H}_9^+)$, $51(\text{CHF}_2^+)$, and $33(\text{CH}_2\text{F}^+)$. The mass spectra show the correct isotope pattern for a single silicon in the compounds.

It is interesting to note that for the two compounds with CF_3 groups, $\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CF}_3)$ and $\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})(\text{CHF}_2)(\text{CF}_3)$, there is only a small peak due to CF_3^+ in the mass spectra. Similar results are seen in the $\text{SiF}_3(\text{CF}_3)$ mass spectrum.¹⁴

Infrared

The infrared spectra of the polyfluorotetramethylsilane compounds have been tabulated in Table IV. All the spectra look very similar, as expected. All spectra were recorded in the gas phase with a 10 cm gas cell.

Melting Points

Melting points for several of the compounds are listed in Table V. One should note that both compounds containing CF_3 groups have melting points lower than that of tetramethylsilane. A plot of melting points versus total number of fluorine atoms shows a maximum melting point at 4 or 5 fluorines. Therefore, as more fluorines replace hydrogens on tetramethylsilane, the melting point increases until one places 4-5 fluorines on the molecules. Then the melting points of the compounds decrease. More compounds with CF_3 groups will help one to extrapolate the trend due to the CF_3 group. It would be interesting to see if the melting point would fall between those of $\text{C}(\text{CF}_3)_4$, $72.5^\circ - 73^\circ$; and $\text{Ge}(\text{CF}_3)_4$, -19.7° .

One would not have expected the silicon-carbon bond to survive reactions with elemental fluorine based on a reported electrochemical fluorination of $\text{Si}(\text{CH}_3)_4$.¹⁵ Seavers obtained only decomposition products from silicon-carbon bond cleavage. He obtained the expected methylfluorosilanes. One could conceivably write several mechanisms for the cleavage of the silicon-methyl bond and the formation of silicon-fluorine bonds. However, it is also conceivable that one could control the energetics of direct fluorination so that one could preserve silicon-carbon bonds during the formation of hydrogen fluoride and carbon-fluorine bonds from the reaction of fluorine with a silicon-methyl moiety.

As can be seen from the results, we are able to preserve the silicon-carbon bond during direct fluorination. Rapid metal-carbon bond vibrational and translational relaxation process occurring at cryogenic surfaces may account for the isolation of these compounds. The dilute fluorine concentrations also allow sufficient time between collisions for all relaxation processes to occur.

As expected, the fluorine concentration and temperature are crucial for the success of the reaction. Many combinations of fluorine concentration, temperature and length of reaction were tried. The conditions given above proved to be ideal for 1 ml of tetramethylsilane. If the reaction were run at higher temperatures, more SiF_4 , CF_4 and CF_3H were produced. Higher fluorine concentrations also give cleavage of the silicon-carbon bonds. Silicon-carbon bond cleavage also occurred if one increased temperature and/or fluorine concentration after the tetramethylsilane has been partially

fluorinated. This delicate balance of concentration and temperature demonstrated the difficulty and subtleties involved in the fluorination of tetramethylsilane.

It is only at temperatures of -130° to -150°C that one can isolate the monofluoro compound, $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$. At such low temperatures, the activation energy for a reaction is barely available so most of the material remains tetramethylsilane.

We are able to recover from 60 - 80% of the polyfluorotetramethylsilanes after the reaction. Of the recovered partially fluorinated tetramethylsilanes, about 2% are the two $\text{Si}-\text{CF}_3$ compounds, $\text{Si}(\text{CF}_3)(\text{CH}_2\text{F})(\text{CHF}_2)(\text{CH}_3)$ and $\text{Si}(\text{CF}_3)(\text{CH}_2\text{F})_2(\text{CH}_3)$. Several other compounds containing CF_3 groups have been separated but remain unidentified due to insufficient quantity of material. 80% of the fluorinated material consists of the following compounds: $\text{Si}(\text{CH}_2\text{F})_4$, $\text{Si}(\text{CH}_2\text{F})_3(\text{CHF}_2)$, $\text{Si}(\text{CH}_3)(\text{CH}_2\text{F})_2(\text{CHF}_2)$, $\text{Si}(\text{CH}_2\text{F})_2(\text{CHF}_2)_2$ and $\text{Si}(\text{CH}_2\text{F})(\text{CHF}_2)_3$ of which $\text{Si}(\text{CH}_2\text{F})_2(\text{CHF}_2)_2$ comprises 20% of the total products.

One would have expected the isolation of $\text{Si}(\text{CH}_3)_3\text{F}$, $\text{Si}(\text{CH}_3)_2\text{F}_2$ and $\text{Si}(\text{CH}_3)\text{F}_3$ as major products from the reaction of elemental fluorine with tetramethylsilane. One could probably attribute the absence of the three methylfluorosilanes to the low reaction temperatures employed in which there is insufficient energy to cleave a silicon-carbon bond initially.

However, the absence of methylfluorosilanes can be understood but the lack of large quantities of polyfluoromethylfluorosilanes is puzzling. There are several apparent polyfluoromethylfluorosilanes, but whether they are formed as a result of decomposition during handling or from the actual

experiment is difficult to determine. The amount is extremely low, well under 1% of the total material recovered.

(Si(CH₃)(CH₂F)(CHF₂)F; ¹H: CH₃ (-0.06, doublet, J_{HF} = 6.9 hz.), CH₂F (4.12, doublet of doublets, J_{HF} = 47.4 hz., J_{HFF} = 5.5 hz.), CHF₂ (5.48, doublet of triplets, J_{HF} = 45.4); ¹⁹F: CHF₂ (63.3, doublet), CH₂F (203.89, triplet), F (101.1, singlet); Si(CH₃)(CH₂F)₂F; ¹H: CH₃ (-0.16, doublet, J_{HF} = 5.8 hz.), CH₂F (4.04, doublet of doublets, J_{HF} = 47.4 hz., J_{HFF} = 4.8 hz.); ¹⁹F: CH₂F (201.5, triplet), F (97.5, singlet)). One would expect to produce large quantities of Si-F materials. But this did not occur.

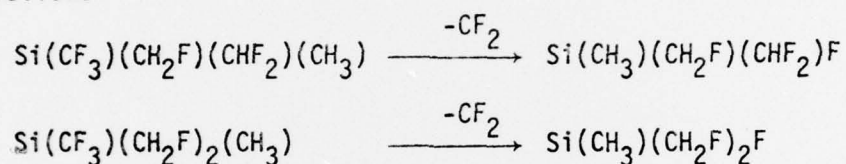
What apparently happens during the fluorination process is that once one silicon-carbon bond is cleaved, the other three also cleave leaving SiF₄ and the corresponding fluoromethanes, depending on the degree of fluorination, CF₄, CF₃H or CF₂H₂. The amount of CF₂H₂ is always much less than that of CF₄ and CF₃H. However, we were still unable to isolate the desired Si(CF₃)₄ compound despite altering conditions. We also did not isolate any Si(CF₃)F₃ or any compounds with combinations of CF₃, CF₂H, CFH₂ on silicon with Si-F bonds. This agrees well with our hypothesis of silicon-carbon bond cleavage mentioned.

Another unusual feature is the fact that the degree of fluorination appears to stop at 7 or 8 fluorines. From all our experience in fluorination of compounds, we realize that it becomes progressively more difficult to add fluorine as the total number of fluorines increases on a compound. We have often overcome this problem by increasing fluorine concentrations or increasing the temperature as the reaction is proceeding.

However, this is not the case with tetramethylsilane and fluorine.

Varying the conditions given above increases the amount of SiF_4 , CF_3H and CF_4 and decreases the amount of polyfluorotetramethylsilanes.

This anomalous feature suggests that the two compounds containing Si-F bonds result from the decomposition of other compounds, not from reaction conditions. The generation of the two compounds can be represented as follows:



If this is indeed the mechanism of decomposition of the Si- CF_3 compounds, the Si- CF_3 compounds and in all likelihood, $\text{Si}(\text{CF}_3)_4$, would be excellent difluorocarbene generators. Evidence in support of the above observation is supplied by work on $\text{Si}(\text{CF}_3)\text{F}_3$ ¹⁴ and by Haszeldine on his polyfluoroalkylsilanes.¹⁶ $\text{Si}(\text{CF}_3)\text{F}_3$ decomposes by difluorocarbene elimination to give mainly C_2F_4 and some C_3F_6 . Polyfluorotetramethylsilanes appear to have similar routes of decomposition. Decomposition of the polyfluorotetramethylsilanes even on standing at room temperatures in sealed glass tubes, generally lead to $\text{C}_2\text{F}_2\text{H}_2$ both as $\text{CF}_2 = \text{CH}_2$ and $\text{CFH} = \text{CFH}$ and a very viscous liquid assumed to be a fluoro-silicon polymer material. There appears also to be another pathway for decomposition by means of possibly HF elimination or fluoride elimination since often KBr is attacked, leaving KF formation. The mode of decomposition can be construed as consistent with the warning issued in the experimental section. Decom-

position can be indeed rapid, upon heating or moisture contact (and possibly thermal shock), leading to a clean combustion, depositing carbon ash. Therefore, it is possible that $\text{Si}(\text{CF}_3)_4$ is indeed formed but is unstable at room temperature, eliminating difluorocarbene.

Tetramethylgermanium

As can be seen from the experiments described, the synthesis of $\text{Ge}(\text{CF}_3)_4$ is very much dependent on the experimental conditions. It was felt that if one went to possibly higher temperatures, one could yet obtain higher yields. This was indeed the case. In fact when the yield was extremely high, 63.5% (based on starting material), there was only a small amount of other fluorinated materials. One was $\text{Ge}(\text{CF}_3)_3\text{F}$, identified by its hydrolysis product of $\text{Ge}(\text{CF}_3)_3(\text{OH})$. There were no partially fluorinated tetramethylgermanium present. If one tried other conditions to shorten the reaction time, one can obtain excellent yields of $\text{Ge}(\text{CF}_3)_4$ on the order of 50%, but a lot of cleavage products were present.

The crucial factor in the successful high yield was the observation that the partially fluorinated tetramethylgermanes were very much less volatile than $\text{Ge}(\text{CH}_3)_4$. This decrease in volatility causes a decrease in reactivity at low temperature. The crucial temperature range in the synthesis of $\text{Ge}(\text{CF}_3)_4$ from $\text{Ge}(\text{CH}_3)_4$ was in the -20° to -60°C range. The 40 degree increase caused an excess of 10-fold increase in yield. A further point of interest, which will be discussed in more detail later, is the presence of $\text{Ge}(\text{CF}_3)_3\text{F}$. The presence of this material is most evident when the yield of $\text{Ge}(\text{CF}_3)_4$ is high. When the yield is marginal,

on the order of a few percent, there is almost no $\text{Ge}(\text{CF}_3)_3\text{F}$. Thus bond cleavage occurs most predominately after CF_3 groups are produced on germanium.

The spectral data has been tabulated in Table VI through IX.

Nuclear Magnetic Resonance

Together, the ^1H and ^{19}F nmr lead to ready identification of the groups on germanium. With integration, the relative number of groups on germanium were identified. Coupling patterns, both proton-fluorine and fluorine-fluorine were in agreement with the compounds identified.

The following observations were made:

- ^1H : (1) The CH_3 resonance shifted to larger δ values as the total number of fluorine atoms on the molecule increased. The shifts were 0.34 (4 fluorines) to 0.47 (6 fluorines) to 0.51 (7 fluorines). The total deshielding effect of the fluorines produced the corresponding deshielding effect on the CH_3 resonance.
- (2) The variation in chemical shifts for the CH_2F and CHF_2 groups relative to the total number of fluorines was almost negligible. The CH_2F resonance appears as a characteristic doublet at approximately 4.9 ppm from TMS. The CHF_2 resonance appears as a characteristic triplet at approximately 6.15 ppm from TMS.
- (3) The proton-fluorine coupling constants were for all practical purposes, identical for both the CH_2F and CF_2H groups.
- (4) The OH chemical shift for $\text{Ge}(\text{CF}_3)_3(\text{OH})$ was at 2.43 and was a broad singlet.

- ¹⁹F: (1) The chemical shift for the CF₃ group on germanium varies between -21.6 to -27.9, with Ge(CF₃)₃(OH) and Ge(CF₃)(CF₂H)₃ at opposite ends of the shifts, respectively. Ge(CF₃)₄ occurs at -27.0. There appears to be no direct correlation between the CF₃ resonance and the total number of fluorine atoms on the molecule. The fluorine-fluorine interactions among the various types of groups make meaningful interpretations here difficult.
- (2) The CF₂H chemical shift occurs between 49.0 and 53.9. There is a slight trend toward increasing chemical shift with less number of total fluorines on the molecule.
- (3) The chemical shift of the CFH₂ group has a slight trend toward increase chemical shifts with increasing total number of fluorine atoms. Shifts vary between 191.4 and 193.2
- (4) Fluorine-fluorine coupling constants were a few hertz in size. When the compound contained CF₃ groups, the coupling constants were generally 3.0 - 3.5 hz. When there were no CF₃ groups on the molecule, the J_{FF} was approximately 2 hz. It is curious that with CF₃ groups, the coupling constant changes by 1 hz.
- (5) The fluorine-fluorine long-range coupling led to splitting patterns which confirmed structures consistent with the integration.

Infrared

The infrared stretching frequencies have been listed. The bands get quite broad when there are several types of groups present. Absorptions are very sharp when there are a few CF₃ groups on germanium.

Mass Spectra

The mass spectra of several of the compounds were recorded at two temperatures, room temperature and at 150°, regular operating temperature of the mass spectrometer. Subtle differences can be seen by close examination of the m/e intensities. However, detailed analysis will not be given. The general feature is normally weak peaks, if any for the parent or P^+ - total number of protons. Much more intense peaks result from P^+ -F or P^+ - one group. Several of the compounds with CF_2H and CHF_2 groups show large m/e for these groups.

The largest m/e peak intensities is normally either GeF or one of the groups. Some of the compounds show a considerable amount of rearrangement to give say CFH_2 , m/e 33 when no CFH_2 was present in the compound.

All the compounds gave the characteristic isotope envelop for a single germanium being present in the compound.

Some of the characteristic m/e were 33 (CFH_2), 51 (CF_2H), 69 (CF_3), 93 (GeF), 143 ($GeCF_3$), 212 ($Ge(CF_3)_2$) and 281 ($Ge(CF_3)_3$).

All the compounds tend to decompose slowly, leaving behind a clear viscous oil with no apparent vapor pressure at 1μ vacuum. Some of the compounds leave behind a white involatile film on the glass. Some of the decomposition undoubtedly resulted from some moisture in the system. The $Ge(CF_3)_3F$ alluded to earlier, is a good example. The compound is readily identified in the nmr mixtures from its characteristic doublet. No matter how careful we were to handle the compound, eventually only the hydroxide was found and characterized, as $Ge(CF_3)_3OH$. Often moisture attack the partially fluorinated tetramethylgermanium compounds leaving hydroxides as identified by NMR.

The relative amounts of each of the compounds is given in Table X. Of the partially fluorinated material, five compounds $\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_3$, $\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})_2(\text{CFH}_2)$, $\text{Ge}(\text{CF}_3)(\text{CF}_2\text{H})(\text{CFH}_2)_2$, $\text{Ge}(\text{CF}_2\text{H})_3(\text{CFH}_2)$ and $\text{Ge}(\text{CF}_2\text{H})_2(\text{CFH}_2)_2$ comprise over 70% of the material. In fact, fluorination has occurred to a high degree on germanium since there is very little material which contain CH_3 groups. The large number of compounds with CF_3 groups indicates the ease with which methyl groups on germanium can be converted to trifluoromethyl groups. But the interesting point to note is that all the compounds contain four germanium-carbon bonds, which remain intact during fluorination. A small amount of Ge-C bonds are cleaved as the isolation of $\text{Ge}(\text{CF}_3)_3(\text{OH})$ shows, however, this is only 1.4% of the material. It is also noted that there is apparently almost no bond cleavage when the yield of $\text{Ge}(\text{CF}_3)_4$ is very low. So it is possible that bond cleavage in the fluorination of $\text{Ge}(\text{CH}_3)_4$ to $\text{Ge}(\text{CF}_3)_4$ occurs predominately at the Ge- CF_3 stage and to some extent at the Ge- CF_2H stage. But these are not catastrophic in that one can indeed isolate $\text{Ge}(\text{CF}_3)_4$ if the conditions are correct. If the fluorination conditions are too vigorous, cleavage occurs more readily, thus the yield of the $\text{Ge}(\text{CF}_3)_4$ decreases.

One apparent advantage it appears in this reaction is the surprising thermal stability of $\text{Ge}(\text{CF}_3)_4$. It is stable at 165°C for several days. Also the compounds appear chemically quite unreactive.

CONCLUSION

The fluorination of the Group IVA tetramethyl compounds lead to some interesting results. The preservation of silicon-carbon bonds during direct fluorination had not been studied as a method for the synthesis of new, highly fluorinated silanes. The question has now been settled, for we are able to preserve the silicon-carbon bond during fluorination. Direct fluorination has led to the identification of many partially fluorinated tetramethylsilanes of the following composition, $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_z$, $x+y+z = 4$. Also produced were several compounds containing a $\text{Si}-\text{CF}_3$ moiety. Previous to this report, the only well-characterized $\text{Si}-\text{CF}_3$ bond has been reported by Sharpe and Coyle¹⁴ for $\text{Si}(\text{CF}_3)_3\text{F}$. There have been several reports¹⁷ of $\text{Si}-\text{CF}_3$ compounds, but no physical characterizations were given. There has only been one partially fluorinated tetramethylsilane previously characterized, $\text{Si}(\text{CH}_3)_3(\text{CH}_2\text{F})$.⁹

Of further significance is the extent to which we are able to preserve silicon-carbon bonds during the fluorination process. This leads to the possible synthesis of new poly- and perfluoro-organometallic compounds unobtainable by conventional methods. This may eventually lead to a much sought - after organometallic CF_3 transfer reagent. Our goal has been partially obtained through the synthesis of tetrakis(trifluoromethyl)germanium in 63.5% on a 1.45 gram scale from the controlled reaction of fluorine with tetramethylgermanium. Many interesting polyfluorotetramethylgermane compounds of the following composition were also obtained: $\text{Ge}(\text{CF}_3)_x(\text{CF}_2\text{H})_y(\text{CFH}_2)_z$, $x + y + z = 4$.

Presently we are working on other metal-alkyl systems. Our goal is the synthesis of new CF_3 organometallic transfer reagent.

ACKNOWLEDGEMENT

This work was supported by the Air Force Office of Scientific Research and the Office of Naval Research.

REFERENCES

1. E. Liu and R. J. Lagow, J. Amer. Chem. Soc., 98, 8270 (1976).
2. N. J. Maraschin, Ph.D. Thesis, Massachusetts Institute of Technology, (1975).
3. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 12, 1459 (1973).
4. N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen and R. J. Lagow, J. Amer. Chem. Soc., 97, 513 (1975).
5. J. L. Adcock and R. J. Lagow, J. Org. Chem., 38, 3617 (1973).
6. N. J. Maraschin and R. J. Lagow, J. Amer. Chem. Soc., 94, 8601 (1972).
7. N. J. Maraschin and R. J. Lagow, Inorg. Chem., 14, 1855 (1975).
8. R. J. Lagow, L. L. Gerchman, R. A. Jacob and J. A. Morrison, J. Amer. Chem. Soc., 97, 518 (1972).
9. E. S. Alexander, R. N. Haszeldine, M. J. Newlands and A. E. Tipping, J. Chem. Soc. (A), 1970, 2285.
10. R. Eujen and R. J. Lagow, Inorg. Chem., 14, 3128 (1975).
11. I. L. Knunyants, Y. F. Komissarov, B. L. Dyatkin and L. T. Lantseva, Izv. Akad. Nauk. SSSR., Ser. Khim., 4, 943 (1973).
12. T. L. Cottrell, "The Strengths of Chemical Bonds", Butterworth Scientific Publications, London, (1958).
13. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd ed. London, 1953.

14. K. G. Sharp and T. D. Coyle, *J. Fluorine Chem.*, 1, 249 (1971).
K. G. Sharp and T. D. Coule, *Inorg. Chem.*, 11, 1259 (1972).
15. R. E. Seavers, N.A.S.A. Technical Note, D-1089, 7pp (1961).
16. R. N. Haszeldine, "New Pathways in Inorg. Chem.", ed. Ebsworth, Maddock and Sharpe; Cambridge University, Press, London, 1968, ch 6, p. 115.
17. H. J. Emeléus, *J. Chem. Soc.*, 1954, 2979.
H. J. Emeléus, *Chem. and Ind.*, 1952, 1235.
R. N. Haszeldine, *Angew. Chem.*, 66, 693 (1954).
R. N. Haszeldine, *Nature*, 168, 1028 (1951).
J. H. Simons and R. D. Dunlop, U. S. Patent #2,651,651 (1953).
H. J. Passino and L. C. Rubin, U. S. Patent #2,686,194 (1954).

Progress - Synthesis of New Inorganic Fluorine Compounds by
Direct Fluorination

Professor R. J. Lagow

1. Synthesis of Bistrifluoromethylmercury by Controlled Low Temperature
Fluorination of Dimethylmercury

Recently, in our laboratory, an experiment was conducted which has far reaching implications in synthetic organometallic chemistry. Bistrifluoromethylmercury, CF_3HgCF_3 , has been synthesized by direct fluorination of dimethylmercury. CH_3HgCH_3 0.5 ml (1.534 gm, 6.65×10^{-3} mole) of CH_3HgCH_3 was syringed into a low temperature zone reactor with 165 cc/min of He. The low temperature reactor was held at -85°C . Fluorination began with zone 3 at -85° and zone 2 at -78°C . After 2 days zone 2 was allowed to warm up to -38°C . Fluorination condition was 1.0 cc/min to 60 cc/min helium for 5 days. After the fluorine was terminated, the reactor was flushed for 9 hours with 100 cc/min helium. The temperature controller was then turned off and the reactor flushed with 175 cc/min helium for 2 1/2 days. The volatiles were collected in a liq. N_2 trap and the products separated on a vacuum line.

Based on starting material a 2-3% yield of CF_3HgCF_3 was recovered in the liquid nitrogen trap. The actual yield is probably much higher in that CF_3HgCF_3 is not really too volatile at room temperature. (CF_3HgCF_3 sublimes very slowly in vacuum). However, the reactor was not checked for any further CF_3HgCF_3 . Physical properties and ^{19}F nmr agreed with authentic

sample. The success of the synthetic procedure was a great surprise even in our laboratory. One might expect that such a synthetic procedure would have extensive synthetic application.

2. Tetramethylsilane

Many partially substituted TMS compounds have been prepared, separated on a gas chromatograph and identified by ^1H and ^{19}F nmr. Almost every combination of $\text{Si}(\text{CH}_3)_x(\text{CH}_2\text{F})_y(\text{CHF}_2)_2$ has been identified. No methylfluoro-silanes, $\text{Si}(\text{CH}_3)_x\text{F}_{y-x}$ have been identified, so it appears that if a Si-C band is broken, SiF_4 is formed along with C fluorocarbons.

It has been found that the fluorination is highly dependent on temperature, which must be less than -100°C , and fluorine concentration must be 1.5% initially.

SiF_4 and CF_3H have been identified, as well as CF_2CH_2 .

- i) $\text{Si} - \text{CF}_3 + \text{H}_2\text{O} \rightarrow \text{Si-O} + \text{CF}_3\text{H}$
- ii) $\text{Si} - \text{CHF}_2 + \text{F}_2 \rightarrow \text{Si-F} + \text{CF}_3\text{H}$
- iii) $\text{Si} - \text{CF}_3 + \text{HF} \rightarrow \text{Si-F} + \text{CF}_3\text{H}$

The silicon compounds mentioned above are all much less volatile than TMS itself. They are liquids at room temperature with several freezing around -78°C .

General nmr characteristics are:

$$J_{\text{F-H}} = \sim 46-48 \text{ hz}$$

$$^1\text{H}^* \quad \text{CH}_2\text{F} = 4.2 - 4.7 \text{ ppm}$$

$$^{19}\text{F}^{**}\text{CH}_2\text{F} = 196 - 206 \text{ ppm}$$

$$^1\text{H} \quad \text{CHF}_2 = 5.70 - 6.10 \text{ ppm}$$

$$^{19}\text{F} \quad \text{CHF}_2 = 62.64 \text{ ppm}$$

$$^1\text{H} \quad \text{CH}_3 = \sim 0.0 \text{ ppm}$$

$$^1\text{H} \text{ ref to TMS } 1\% \text{ integration. } ^{19}\text{F} \text{ ref to } 1\% \text{ TFA.}$$

*downfield from TMS

**upfield from TFA

Tetraalkylammonium salts:

3. Tetramethylammonium chloride

Fluorination of $\text{N}(\text{CH}_3)_4^+\text{Cl}^-$ at -78° , 0° and RT has been attempted. There is no positive indication of any CF infrared stretch or any CF, ^{19}F nmr peak. However, there have been occasions where one can observe a broad band at 1240 m^{-1} in the infrared, which could be attributed to a CF stretch. But ^{19}F m this sample ins H_2O has proven negative. When the sample (after fluorine has been passed over) is dissolved in water, no apparent gases are given off. One can get $\text{N}(\text{CH}_3)_4^+\text{Cl}^-$ to char by passing pure fluorine over the sample for a few weeks.

What has been isolated, has been identified as $\text{N}(\text{CH}_3)_4^+\text{F}^-\cdot\text{nHF}$. If the sample is heated to $140-170$, a cloudy liquid comes off and a white powder is left behind at 170° , which does not decompose to 270°C . $\text{N}(\text{CH}_3)_4^+\text{F}^-\cdot\text{nHF}$ is extremely hygroscopic.

4. Tetraethylammonium bromide

Upon passing fluorine over $\text{N}(\text{C}_2\text{H}_5)_4^+\text{Br}^-$ at RT, the sample turns to an "oily" liquid. If one uses a liquid nitrogen trap to monitor any volatiles given off, one can see bromine being given off $1/2 - 1$ hr after F_2 flow is started. Most products in the liquid nitrogen trap are fluorinated and appear to be $\text{NR}_1\text{R}_2\text{R}_3$. This material (in liq. N_2 trap) fumes in contrast with air, leaving behind a white, hygroscopic powder. ^{19}F nmr of the

material in the boat (oil) shows a broad peak at 42.41 and a sharp singlet at 54.06 ppm (TFA ref., all peaks upfield). The white powder gave a peak at 74.03 ppm upfield from TFA. Both samples are still unidentified.

The hypothesis is that the bromide gets converted to fluoride and then fluorination occurs on the ethyl group which may partially decompose to amines.

The white material is stable to 300°C and appears to be hygroscopic.

5. Tetramethylammonium Hexafluorophosphate

$(\text{CH}_3)_4\text{N}^+\text{PF}_6^-$ shows no reaction at all towards fluorine and methods employing ultraviolet initiation procedures are now being attempted.

Decarborane

BF_3 was the main product upon fluorination of decarborane at room temperature. There appears to be some material, which stops in both a -45 and -95 traps, which decomposes to BF_3 upon warming. No fluorodecarboranes were identified. Unreacted material was identified as decarborane by melting point.