*Journal of Organometallic Chemistry*, 145 (1978) 167—182

# FLUORINATION OF DIMETHYLMERCURY, TETRAMETHYLSILANE AND TETRAMETHYLGERMANIUM. SYNTHESIS AND CHARACTERIZATION OF POLYFLUOROTETRAMETHYLSILANES, POLYFLUOROTETRAMETHYLGERMANES, BIS(TRIFLUOROMETHYL)MERCURY AND TETRAKIS(TRIFLUOROMETHYL)GERMANIUM

EDMUND K.S. LIU and RICHARD J. LAGOW*
*Department of Chemistry, University of Texas at Austin, Austin, Texas 78712 (U.S.A.)*

(Received July 1st, 1977)

## Summary

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, $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$. Also characterized were compounds containing Si—$CF_3$. 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, $Ge(CF_3)_x(CF_2H)_y(CFH_2)_z$ ($x + y + z = 4$).

## 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, $Ge(CF_3)_4$, 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 neopentane [3], hexamethylethane and cyclooctane [4] to perfluoroethers such as glyme and diglyme [5], to fluorinate inorganic systems such as sulfur tetranitride [6] 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 were examined.

## Experimental

### *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 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 of gaseous samples. All NMR spectra 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.

### *Fluorination of dimethylmercury*

The reaction can be summarized as:

$$\mathrm{Hg(CH_3)_2 + F_2/He \xrightarrow[5\,days]{-78^\circ C} Hg(CF_3)_2 + HgF_2 + CF_4 + CF_3H + CF_2H_2 + CFH_3}$$

A 0.725 ml sample of $Hg(CH_3)_2$ was syringed into the low temperature reactor with zone 4 cooled to —78°C. After 30 minutes of purging zones 1, 2 and 3 also were cooled to —78°C. Fluorination conditions used were 1.0 $cm^3$/min of helium. After 120 h, the fluorine flow 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°C slush. The reactor was evacuated and any marginally volatile material was collected. All this material was placed in ether. The fluorine-19 NMR spectrum showed a singlet at —37.70 ppm downfield from TFA with $J(^{199}Hg—F)$ 1251 Hz. After purification by gas chromatography, a yield of 6.5%, $Hg(CF_3)_2$ 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 $Hg(CF_3)_2$. Separation by gas chromatography helped to identify the compound as $Hg(CF_3)_2$, and preclude $Hg(CF_3)(CH_3)$. Using a SE-30, 3/8" × 24′ column, operating at 80°C isothermal, retention times are the following $Hg(CH_3)_2$, 15.2 minute and $Hg(CF_3)(CH_3)$, 50 minutes; $Hg(CF_3)_2$, comes off only upon raising the temperature to 165°C.

*Fluorination of tetramethylsilane*

The reaction is summarized as:

$$Si(CH_3)_4 + F_2He \xrightarrow[\text{low temperature}]{} \text{polyfluorotetramethylsilanes} + SiF_4 + \text{fluorocarbons}$$

Reactions were run at temperatures between —100 and —150°C. Optimum results were obtained at —100 and —110°C. The best fluorine and helium mixture was found to be 1.0 $cm^3$/min fluorine to 60 $cm^3$/min 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 $cm^3$/min; He 60 $cm^3$/min; temperature: —110°C; reaction time: 7 days. Starting with 1 ml of tetramethylsilane we are able to recover polyfluorotetramethylsilanes (in 70—80% overall yield). The volatile materials were fractionated at 131 and —196°C. The volatile materials in the —196°C fraction consisted mainly of $CF_4$, $CF_3H$, $CF_2H_2$ and $SiF_4$. The compounds in the —131°C fractions were separated on the gas chromatograph using a fluorosilicone column.

*Fluorination of tetramethylgermanium*

The reaction can be summarized as:

$$Ge(CH_3)_4 + F_2/He \xrightarrow[\text{low temperature}]{} Ge(CF_3)_4 + \text{polyfluorotetramethylgermanes} + \text{fluorocarbons}$$

A 0.90 ml ($6.55 \times 10^{-3}$ mol) sample of $Ge(CH_3)_4$ 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:

| $F_2$(cm$^3$/min) | He(cm$^3$/min) | Temperature (°C) | Time (h) |
|---|---|---|---|
| 1.0 | 60 | −100 | 48 |
| 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 | room temperature | 24 |

The volatile materials were separated into −95, −131 and −196°C fractions. Very little material was in the −196°C fraction. Identified by their infrared spectra were $CF_4$, $CF_3H$ and $C_2F_6$. Both the −95 and −131°C fractions contained $Ge(CF_3)_4$. The bulk of the material was in the −95°C trap. The NMR spectrum of the −95°C fraction showed the presence of only three compounds, $Ge(CF_3)_4$ (−27.0 ppm), $Ge(CF_3)_3F$ (−21.9), and $Ge(CF_3)_3(OH)$ (−21.4). After separation from impurities on the gas chromatograph, 1.45 g of pure $Ge(CF_3)_4$ was isolated, giving a minimum yield of 63.5%. The IR, NMR and mass spectra of $Ge(CF_3)_4$ agreed well with the reported results [8].

Other fluorination conditions led to low yields of $Ge(CF_3)_4$. However, one can separate and characterize many polyfluorotetramethylgermanium compounds from these reactions. The rest of the material was partially fluorinated material. The following conditions led to only a 6% yield of $Ge(CF_3)_4$:

| $F_2$(cm$^3$/min) | He(cm$^3$/min) | Temperature (°C) | Time (h) |
|---|---|---|---|
| 1.0 | 60 | −100 | 42 |
| 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 | room temperature | 48 |

All the compounds were separated by gas chromatography.

### *Separation of compounds by gas chromatography*

*Separation of partially fluorinated tetramethylsilanes.* The gas chromatograph program selected was the following: fluorosilicone column, QF-1-0065, (10% Chromosorb P), 3/8" × 24'; 0°C isothermal for 53.45 minutes; 1° per minute on 30°C for 50 minutes; 1.5° per minute 50°C for 50 minutes; 70°C for 3 minutes, isothermal until 240 minutes; 5°C per minute to 100°C for 30 minutes; 5° per minute to 185°C.

Approximately 100 μl of sample was injected with an air-tight syringe each time. The compounds of interest were collected over a time span from 105 to

260 minutes. Compounds which had shorter retention times were shown later to contain no silicon.

During the separation, the initial compounds (just after air) were identified as $SiF_4$, $C_2F_2H_2$, $CF_3H$ and other apparent 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 then were 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 are shown in Tables 1 and 2. Several samples were sent for elemental analysis. However, the samples exploded during combustion and destroyed several analyzers at Schwarzkopf Microanalytical Laboratory, Woodside, New York.

*Note of caution:* Care should be taken when handling the polyfluorotetramethylsilanes. The compounds can spontaneously explode and ignite.

*Separation of $Ge(CH_3)_4$ from impurities.* The following gas chromatograph conditions were used: SE-30 column, 3/8" × 24'; 0°C isothermal for 10 minutes; 2° per minute to 60°C; bake at 185°C. If 75 μl was used, $Ge(CF_3)_4$ had a retention time of 3.3 minutes; $Ge(CF_3)_3(C_2F_5)$, 6.2 minutes; $Ge(CF_3)_3(OH)$, 20.7 minutes; and $Ge(CH_3)_4$, 29.3 minutes. The two major impurities comprised about 4% of the material.

*Separation of polyfluorotetramethylgermanium compounds.* The following gas chromatographic conditions were used with an average of 100 μl of liquid injected into the gas chromatograph. SE-30 column, 3/8" × 24'; 30°C isothermal for 30 minutes; 2° per minute to 60°C for 15 minutes; 2.5° per minute to 100°C for 50 minutes; bake at 185°C.

Usually by 84 minutes, the last compound of interest was off the column.

TABLE 1

PROTON NMR SPECTRA OF POLYFLUOROTETRAMETHYLSILANE

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

| Compound | $CH_3$ | $CH_2F$ [a] | J(HF) | $CHF_2$ [b] | J(HF) |
|---|---|---|---|---|---|
| $Si(CH_3)_3(CH_2F)$ [c] | 0.06 | 4.30 | 46.9 | | |
| $Si(CH_3)_2(CH_2F)_2$ | −0.18 | 4.16 | 47.5 | | |
| $Si(CH_3)_3(CHF_2)$ | 0.07 | | | 6.43 | 52 |
| $Si(CH_3)(CH_2F)_3$ | −0.23 | 4.17 | 47.0 | | |
| $Si(CH_3)_2(CH_2F)(CHF_2)$ | −0.11 | 4.22 | 47.4 | 5.62 | 46.2 |
| $Si(CH_3)_2(CHF_2)_2$ | 0.31 | | | 5.91 | 45.6 |
| $Si(CH_3)(CH_2F)_2(CHF_2)$ | −0.06 | 4.32 | 47.3 | 5.68 | 45.9 |
| $Si(CH_2F)_4$ | | 4.24 | 47.0 | | |
| $Si(CH_3)(CH_2F)(CHF_2)_2$ | 0.04 | 4.39 | 46.8 | 5.74 | 45.4 |
| $Si(CH_3)(CH_2F)_2(CF_3)$ | 0.12 | 4.42 | 47.1 | | |
| $Si(CH_2F)_3(CHF_2)$ | | 4.54 | 46.6 | 5.87 | 45.4 |
| $Si(CH_3)(CH_2F)(CHF_2)(CF_3)$ | 0.08 | 4.36 | 46.3 | 4.69 | 45.4 |
| $Si(CH_2F)_2(CHF_2)_2$ | | 4.66 | 46.6 | 5.91 | 45.4 |
| $Si(CH_2F)(CHF_2)_3$ | | 4.68 | 46.2 | 5.82 | 45.0 |
| $Si(CH_3)(CH_2F)(CHF_2)F$ | −0.06 [d] | 4.12 | 47.2 [e] | 5.48 | 45.4 |
| $Si(CH_3)(CH_2F)_2F$ | −0.16 [f] | 4.04 | 47.4 [g] | | |

[a] Doublet. [b] Triplet. [c] Lit. [9] $CH_3$ (0.31) $CH_2F$ (4.53) J(HF) (46.8). [d] J(HF) 6.9 Hz. [e] J(HFF) 5.5 Hz. [f] J(HF) 5.8 Hz. [g] J(HFF) 4.8 Hz.

TABLE 2

FLUORINE NMR SPECTRA OF POLYFLUOROTETRAMETHYLSILANE

| Compound | $CF_3$ | $CHF_2$ [a] | $J(HF)$ | $CH_2F$ [b] | $J(HF)$ |
|---|---|---|---|---|---|
| $Si(CH_3)_3(CH_2F)$ [c] | | | | 196 | 46.8 |
| $Si(CH_3)_2(CH_2F)_2$ | | | | 195.14 | 47.1 |
| $Si(CH_3)(CH_2F)_3$ | | | | 197.73 | 46.8 |
| $Si(CH_3)_2(CH_2F)(CHF_2)$ | | 61.17 | 45.6 | 196.61 | 46.4 |
| $Si(CH_3)_2(CHF_2)_2$ | | 59.22 | 46.0 | | |
| $Si(CH_3)(CH_2F)_2(CHF_2)$ | | 61.08 | 45.8 [d] | 199.60 | 47.0 [e] |
| $Si(CH_2F)_4$ | | | | 201.13 | 46.9 |
| $Si(CH_3)(CH_2F)(CHF_2)_2$ | | 60.85 | 45.7 [f] | 201.00 | 46.7 [g] |
| $Si(CH_3)(CH_2F)_2(CF_3)$ | —15.48 [h] | | | 199.92 | 46.3 |
| $Si(CH_2F)_3(CHF_2)$ | | 60.03 | 45.4 [i] | 201.41 | 46.6 [j] |
| $Si(CH_3)(CH_2F)(CHF_2)(CF_3)$ | —16.53 [k] | 61.15 | 45.0 | 201.19 | [l] |
| $Si(CH_2F)_2(CHF_2)_2$ | | 58.88 | 45.4 [n] | 202.87 | 46.4 [n] |
| $Si(CH_2F)(CHF_2)_3$ | | 59.57 | 45.0 [o] | 204.39 | 46.6 [p] |
| $Si(CH_3)(CH_2F)(CHF_2)F$ [q] | | 63.3 | | 203.89 | |
| $Si(CH_3)(CH_2F)_2F$ [r] | | | | 201.5 | |

[a] Doublet. [b] Triplet. [c] Lit. [9]. [d] $J(FF)$ 1.4(tr). [e] $J(FF)$ 1.5 (m), $J(HF)$ 1.0. [f] $J(FF)$ 1.8 (d). [g] $J(FF)$ 1.4 (m), $J(H'F)$ 0.5. [h] $J(FF)$ 3.2 (q of tr), $J(H'F)$ 1.0. [i] $J(FF)$ 1.8 (q). [j] $J(FF)$ 1.6 (tr). [k] $J(FF)$ 3.0 (q or d of tr). [l] Not resolved. [m] $J(FF)$ 2.0 (tr). [n] $J(FF)$ 1.9 (p). [o] $J(FF)$ 2.1. [p] $J(FF)$ 2.0, $J(H'F)$ 0.4. [q] F 101.1. [r] F 97.5.

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.

## Results and discussion

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

$$Hg(CH_3)_2 + F_2/He \xrightarrow{-78^\circ C} \underset{6.5\%}{Hg(CF_3)_2} + HgF_2 \qquad (1)$$

$$\begin{aligned} Si(CH_3)_4 + F_2/He &\xrightarrow{-150^\circ C} Si(CH_3)_3(CH_2F) \\ &\xrightarrow{-110^\circ C} Si(CH_3)_x(CH_2F)_y(CHF_2)_z \ (x + y + z = 4) \qquad (2) \end{aligned}$$

(only small yields of $SiCF_3$ compounds)

$$Ge(CH_3)_4 + F_2/He \xrightarrow{-100^\circ C} Ge(CF_3)_4 + Ge(CF_3)_x(CF_2H)_y(CF_2H)_y(CFH_2)_z \qquad (3)$$

$(x + y + z = 4)$

(increase in temperature from —100 to —60°C leads to low yields of $Ge(CF_3)_4$, 1—6% and increase in temperature from —100 to —20°C leads to high yields of $Ge(CF_3)_4$, 63.5% but no $Ge(CF_3)_x(CF_2H)_y(CFH_2)_z$)

The spectral and physical data for the polyfluorotetramethylsilanes have been tabulated above. The $^{19}F$ and $^1H$ NMR are given in Tables 4 and 5 for the polyfluorotetramethylgermanes. The infrared and mass spectral data have been deposited with NAPS *.

### *Dimethylmercury*

Dimethylmercury can be fluorinated to its perfluoro analog, bis(trifluoromethyl)mercury, $Hg(CF_3)_2$, by low temperature fluorination. Yields of 6.5% (based on 1.53 g of $Hg(CH_3)_2$) can be obtained by fluorination at —78 to —90°C. A fluorine concentration of 1.67% obtained by using a mixture of 1 $cm^3$/min of fluorine to 60 $cm^3$/min of 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 physical properties and $^{19}F$ NMR agree with authentic samples prepared by alternative methods [8,10,11].

The formation of $Hg(CF_3)_2$ from $Hg(CH_3)_2$ 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 $Hg(CF_3)_2$. 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 $Hg(CF_3)_2$ forms, the compound is stable under the conditions of the experiment. It has been found that $Hg(CF_3)_2$ does not react with 3% fluorine at —78°C. It has also been found that $Hg(CF_3)_2$ reacts slowly with 3% fluorine at 0°C and appreciably at room temperature, forming $HgF_2$ and $CF_4$. Therefore with a low fluorine concentration of 1.67% and low temperature, —78°C, $Hg(CF_3)_2$ 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/mol [12] while F—Hg is 100 kcal/mol [12] and HF is 153 kcal/mol [13].

It is strange that there appears to be no evidence that any partially fluorinated $Hg(CH_3)_2$ was present. One can conclude that either $Hg(CF_3)_2$ 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 fluorination of $Hg(CH_3)_2$ has demonstrated that the fluorination process can be controlled and manipulated to produce highly fluorinated species. Experimental conditions are crucial. It is important that the $Hg(CH_3)_2$ 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° warmer downstream and much higher upstream of the helium flow. A single zone fluorination of $Hg(CH_3)_2$ demonstrates this very well. The $Hg(CH_3)_2$ freezes at the entrance of the reactor which is probably at ~—20°C and not at the desired —78°C temperature. Consequently, the fluorination process is too exothermic and energy dissipation is not sufficient to allow $Hg(CF_3)_2$

---

* The table of infrared and mass spectral data have been deposited as NAPS Document No. 03165 (11 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

to form. The described reaction solves this problem to some extent and one obtain 6.5% yield of $Hg(CF_3)_2$.

### Tetramethylsilane

In 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 $Si(CF_3)_4$. However, silicon—carbon bond was preserved during direct fluorination. It is possible to isolate in excellent quantities partially fluorinated tetramethylsilanes of the general formula: $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$ $(x + y + z = 4)$. The fact that $Si(CF_3)_4$ 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 $Si—CF_3$ bonds.

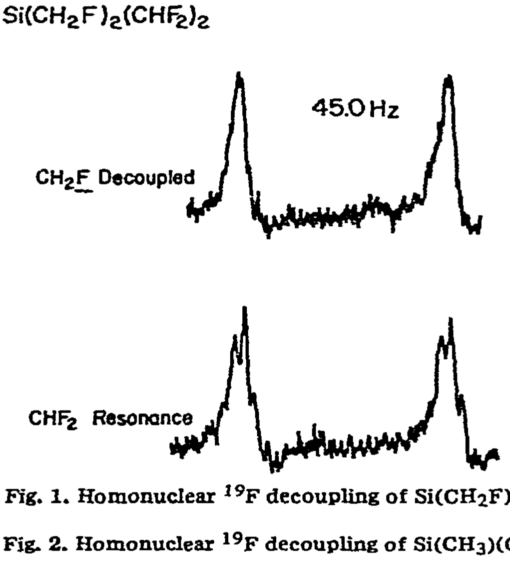
In an effort to prepare $Si(CF_3)_4$, many variables in reaction conditions were investigated. Some were fixed temperature and varying fluorine concentration, fixed temperature and varying fluorine flow and length of reaction, varying temperature with fixed fluorine flow and time, varying temperature 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 $Si(CF_3)_4$. However, some conditions were better than others in preparing the partially fluorinated tetramethylsilanes. Several conditions produced more highly fluorinated species than others but the optimum condition for the preparation of $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$ $(x + y + z = 4)$ was the following: temperature, —110°C; reaction time, 7 days; and $F_2$/He flow ratio of 1.0 $cm^3$/min to 60 $cm^3$/min. Starting with 1.0 ml of tetramethylsilane, one can recover approximately 0.8 ml of volatile liquid which stops in a —131°C trap. The material which passed a —131°C 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, e.g. higher fluorine concentrations and higher temperatures, in an effort to produce $Si(CF_3)_4$. However, this was unsuccessful. Aside from the two compounds reported here with $Si—CF_3$ bonds, we were unable to produce large quantities of $Si—CF_3$ type compounds.

Several of the $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$ $(x + y + z = 4)$, compounds were isolated and characterized. Many others were not characterized due to our inability to separate several compounds.

*Nuclear magnetic resonance.* The proton and fluorine NMR spectra of the polyfluorotetramethylsilane compounds are summarized in Tables 1 and 2. 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 shifts 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 $Si(CH_3)_3(CHF_2)$ which is 6.43 ppm and the corresponding *J*(H—F) is 52 Hz.) These coupling constants were in good agreement with those obtained in the $^{19}F$ NMR.

Characteristic resonances also appear in the $^{19}F$ 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 $M(CH_3)_4$ ($M = C$, Ge, Sn) one can predict that the $^{19}F$ resonance for $Si(CF_3)_4$ will be ~—21 ppm downfield from trifluoroacetic acid. For $Si(CF_3)F_3$ [14] the $CF_3$ resonance is about —10 ppm downfield from TFA. In the spectra of 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 Fig. 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 $Si(CH_3)_3(CH_2F)$ was reported to be 0.7 Hz [9].)

It should be noted that for the partially fluorinated tetramethylsilanes, *J*(HF)



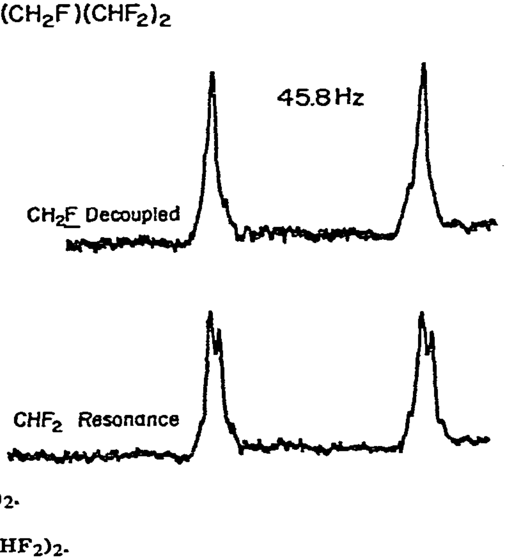


Fig. 1. Homonuclear $^{19}F$ decoupling of $Si(CH_2F)_2(CHF_2)_2$.

Fig. 2. Homonuclear $^{19}F$ decoupling of $Si(CH_3)(CH_2F)(CHF_2)_2$.

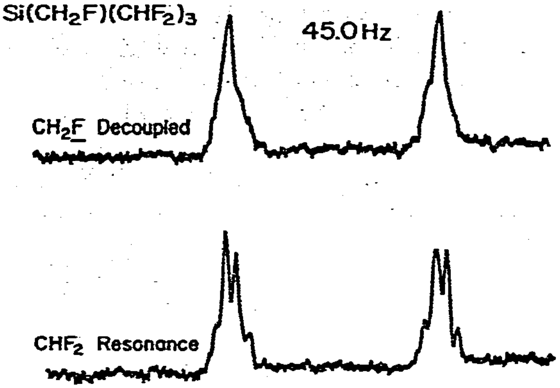


Fig. 3. Homonuclear $^{19}F$ decoupling of $Si(CH_3F)(CHF_2)_3$.

for $CH_2F > CHF_2$. 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.* 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. No parent peaks were observed in any of the spectra. The largest peaks were normally 85 ($SiF_3^+$), 81 ($SiCH_3F_2^+$), 73 ($SiC_3H_9^+$), 51 ($CHF_2^+$), and 33 ($CH_2F^+$). 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. $Si(CH_3)(CH_2F)_2(CF_3)$ and $Si(CH_3)(CH_2F)(CHF_2)(CF_3)$, there is only a small peak due to $CF_3^+$ in the mass spectra. Similar results are seen in the $SiF_3(CF_3)$ mass spectrum [14].

*Melting points.* Melting points for several of the compounds are listed in Table 3. 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 one the molecules. Then the melting

TABLE 3

MELTING POINTS OF POLYFLUOROTETRAMETHYLSILANE

| Compound | Melting point (°C) |
|---|---|
| $Si(CH_3)_3(CH_2F)$ | —86.5 to —85.0 |
| $Si(CH_3)(CH_2F)_3$ | —89.5 to —84.5 |
| $Si(CH_3)(CH_2F)_2(CHF_2)$ | —63.5 to —62.0 |
| $Si(CH_2F)_4$ | —18.0 to —16.6 |
| $Si(CH_3)(CH_2F)(CHF_2)_2$ | —58.7 to —56.8 |
| $Si(CH_3)(CH_2F)_2(CF_3)$ | —144 to —142.7 |
| $Si(CH_2F)_3(CHF_2)$ | —54.0 to —53.2 |
| $Si(CH_3)(CH_2F)(CHF_2)(CF_3)$ | —144 to —138 |
| $Si(CH_2F)_2(CHF_2)_2$ | —68.2 to —66.8 |
| $Si(CH_2F)(CHF_2)_3$ | —72.6 to —71.0 |
| $Si(CH_3)_4$ | —91.1 |

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 $C(CF_3)_4$, 72.5—73°C; and $Ge(CF_3)_4$, —19.7°C.

One would not have expected the silicon—carbon bond to survive reactions with elemental fluorine based on a reported electrochemical fluorination of $Si(CH_3)_4$ [15]. Seavers [15] 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 methylsilicon 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 processes 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.

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 subtilties involved in the fluorination of 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 Si—$CF_3$ compounds, $Si(CF_3)(CH_2F)(CHF_2)(CH_3)$ and $Si(CF_3)(CH_2F)_2(CH_3)$. 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: $Si(CH_2F)_4$, $Si(CH_2F)_3(CHF_2)$, $Si(CH_3)(CH_2F)_2(CHF_2)$, $Si(CH_2F)_2(CHF_2)_2$ and $Si(CH_2F)(CHF_2)_3$ of which $Si(CH_2F)_2(CHF_2)_2$ comprises 20% of the total products. It is only at temperatures of —130 to —150°C that one can isolate the monofluoro compound $Si(CH_3)_3(CH_2F)$.

One would have expected the isolation of $Si(CH_3)_3F$, $Si(CH_3)_2F_2$ and $Si(CH_3)F_3$ as major products from the reaction of elemental fluorine with tetramethylsilane. One probably can 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.

What apparently happens during the fluorination process is that once the silicon—carbon bond is cleaved, the other three also cleave, leaving $SiF_4$ and the corresponding fluoromethanes, depending on the degree of fluorination, $CF_4$, $CF_3H$ or $CF_2H_2$. The amount of $CF_2H_2$ is always much less than that of $CF_4$ and $CF_3H$.

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 organic compounds, we realize that it becomes progressively more difficult to add fluorine as the total number of fluorines in a compound increases. We have often overcome this problem by increasing fluorine concentrations or by increasing the temperature as the reaction is proceeding. However this is not successful in the case of the reaction of 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, which comprise under 1% of the total products, can be represented as follows:

$$Si(CF_3)(CH_2F)(CHF_2)(CH_3) \xrightarrow{-CF_2} Si(CH_3)(CH_2F)(CHF_2)F$$

$$Si(CF_3)(CH_2F)_2(CH_3) \xrightarrow{-CF_2} Si(CH_3)(CH_2F)_2F$$

If this is indeed the mechanism of decomposition of the Si—$CF_3$ compounds, the Si—$CF_3$ compounds and in all likelihood $Si(CF_3)_4$ would be excellent difluorocarbene generators. Evidence in support of this is provided by work on $Si(CF_3)F_3$ [14] and by Haszeldine on his polyfluoroalkylsilane [16]. $Si(CF_3)F_3$ decomposes by difluorocarbene elimination to give mainly $C_2F_4$ and some cyclo-$C_3F_6$. Polyfluorotetramethylsilanes appear to have similar routes of decomposition. Decomposition of the polyfluorotetramethylsilanes, even on standing at room temperature in sealed glass tubes, generally leads to $C_2F_2H_2$ ($CF_2$=$CH_2$ and CFH=CFH) and a very viscous liquid which is assumed to be a fluorosilicon polymer. There appears also to be another possible pathway for decomposition by means of fluoride elimination since KBr often is attacked, leading to KF formation.

### *Tetramethylgermanium*

As can be seen from the experiments described, the synthesis of $Ge(CF_3)_4$ is very much dependent on the experimental conditions. When the yield was 63.5% (based on starting material), there was only a small amount of other fluorinated materials. One was $Ge(CF_3)_3F$, identified by its hydrolysis product, $Ge(CF_3)_3(OH)$. There were no partially fluorinated tetramethylgermanium compounds present. On shortening the reaction time, we obtained excellent yields of $Ge(CF_3)_4$ in the order of 50%, but much cleavage occurred.

The crucial factor in obtaining a high yield was the observation that the partially fluorinated tetramethylgermanes were very much less volatile than $Ge(CH_3)_4$. This decrease in volatility causes a decrease in reactivity at low temperature. The crucial temperature range in the synthesis of $Ge(CF_3)_4$ from $Ge(CH_3)_4$ was in the —20 to —60°C range. The 40° increase caused a greater than ten-fold increase in yield. A further point of interest, which will be discussed in more detail later, is the presence of $Ge(CF_3)_3F$. The presence of this material is most evident when the yield of $Ge(CF_3)_4$ is high. When the yield is marginal, on the order of a few percent, there is almost no $Ge(CF_3)_3F$. Thus bond cleavage occurs most predominately after $CF_3$ groups are produced on germanium.

*Nuclear magnetic resonance (Tables 4 and 5).* Together, the $^1H$ and $^{19}F$ NMR

TABLE 4

PROTON NMR SPECTRA OF POLYFLUOROTETRAMETHYLGERMANIUM

Chemical shifts in ppm. + downfield from TMS (ext). Coupling constants in hertz.

| Compound | $CH_3$ [a] | $CH_2F$ [b] | $J$(HF) | $CHF_2$ [c] | $J$(HF) |
|---|---|---|---|---|---|
| $Ge(CF_3)_3(CF_2H)$ | | | | 6.10 | 45.0 |
| $Ge(CF_3)_3(CFH_2)$ | | | | | |
| $Ge(CF_3)_2(CF_2H)_2$ | | | | 6.23 | 45.5 |
| $Ge(CF_3)_2(CF_2H)(CFH_2)$ | | 4.98 | 46.5 | 6.24 | 45.7 |
| $Ge(CF_3)(CF_2H)_3$ | | | | 6.25 | 45.5 |
| $Ge(CF_3)_2(CFH_2)_2$ | | | | | |
| $Ge(CF_3)(CF_2H)_2(CFH_2)$ | | 4.89 | 46.0 | 6.15 | 45.5 |
| $Ge(CF_3)(CF_2H)_2(CH_3)$ | 0.51 | | | 6.10 | 45.6 |
| $Ge(CF_3)(CF_2H)(CFH_2)_2$ | | 4.90 | 46.0 | 6.25 | 45.6 |
| $Ge(CF_2H)_3(CFH_2)$ | | 5.20 | 45.7 | 6.28 | 45.6 |
| $Ge(CF_2H)_2(CFH_2)_2$ | | 4.97 | 46.0 | 6.26 | 45.2 |
| $Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$ | 0.47 | 4.79 | 46.0 | 6.08 | 46.0 |
| $Ge(CF_2H)(CFH_2)_3$ | | 4.97 | 46.5 | 6.29 | 46.0 |
| $Ge(CF_2H)(CFH_2)_2(CH_3)$ | 0.34 | 4.78 | 46.0 | 6.10 | 46.0 |
| $Ge(CFH_2)_4$ | | 4.87 | 47.0 | | |
| $Ge(CF_3)_3(OH)$ [d] | | | | | |

[a] Singlet. [b] Doublet. [c] Triplet. [d] OH (2.43) singlet.

spectra 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 $\delta$ values as the total number of fluorine atoms on the molecule increased.

(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.

$^{19}F$: (1) The chemical shift for the $CF_3$ group on germanium varies between —21.6 to —27.9, with $Ge(CF_3)_3(OH)$ and $Ge(CF_3)(CF_2H)_3$ at opposite ends of the shifts, respectively. $Ge(CF_3)_4$ occurs at —27.0. There appears to be no direct correlation between the $CF_3$ resonance and the total number of fluorine atoms on the molecule.

(2) The $CF_2H$ chemical shift occurs between 49.0 and 53.9. There is a slight trend toward increasing chemical shift with lower number of total fluorines on the molecule.

(3) The chemical shift of the $CFH_2$ 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 Hz in size. When the compound contained $CF_3$ groups, the coupling constants were generally 3.0—3.5 Hz. When there were no $CF_3$ groups on the molecule, the $J$(FF) was approx-

TABLE 5

FLUORINE NMR SPECTRA OF POLYFLUOROTETRAMETHYLGERMANIUM

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

| Compound | $CF_3$ [a] | $J$(FF) | $CHF_2$ [b] | $J$(HF) | $J$(FF) | $CH_2F$ [c] | $J$(HF) | $J$(FF) |
|---|---|---|---|---|---|---|---|---|
| $Ge(CF_3)_4$ | −27.0 | | | | | | | |
| $Ge(CF_3)_3(C_2F_5)$ | −27.7 | 2.7 [d] | | | | | | |
| $Ge(CF_3)_3(CF_2H)$ | −27.2 | 3.0(tr) | 49.0 | 45.5 | 3.1(4 of 10 lines) | | | |
| $Ge(CF_3)_3(CFH_2)$ | −25.8 | | | | | | | |
| $Ge(CF_3)_2(CF_2H)_2$ | −27.6 | 3.2(p) | 49.4 | 46.0 | 3.1(sp) | | | |
| $Ge(CF_3)_2(CF_2H)(CFH_2)$ | −26.3 | 3.3(q) | 50.6 | 45.5 | 3.0(6 of 8 lines) | 193.2 | 46.5 | 3.3(7 of 9 lines) |
| $Ge(CF_3)(CF_2H)_3$ | −27.9 | 3.2(sp) | 49.7 | 46.0 | 3.1(q) | | | |
| $Ge(CF_3)_2(CFH_2)_2$ | −24.8 | 3.4(tr) | | | | 193.0 | 47.0 | 3.5(5 of 7 lines) |
| $Ge(CF_3)(CF_2H)_2(CFH_2)$ | −26.8 | 3.2(sx) | 50.5 | 45.6 | 3.0(p) | 193.0 | 46.0 | 2.9(6 of 8 lines) |
| $Ge(CF_3)(CF_2H)_2(CH_3)$ | −23.5 | 3.4(p) | 53.0 | 46.5 | 3.2(q) | | | |
| $Ge(CF_3)(CF_2H)(CFH_2)_2$ | −25.2 | 3.2(p) | 51.8 | 45.5 | 3.0(sx) | 192.0 | 46.0 | 2.7(sx) |
| $Ge(CF_2H)_3(CFH_2)$ | | | 50.5 | 46.2 | 2.2(d) | 192.9 | 46.0 | 2.4(5 of 7 lines) |
| $Ge(CF_2H)_2(CHF_2)_2$ | | | 51.4 | 46.0 | 2.5(p) | 192.5 | 46.6 | 2.5(p) |
| $Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$ | −22.3 | 3.4(q) | 53.7 | 46.0 | 3.0(p) | 192.5 | 46.0 | 3.0 |
| $Ge(CF_2H)(CFH_2)_3$ | | | 52.0 | 46.0 | 2.1(q) | 191.9 | 46.6 | 1.8(tr) |
| $Ge(CF_2H)(CFH_2)_2(CH_3)$ | | | 53.9 | 46.2 | 2.1(tr) | 192.5 | 46.5 | 2.0(tr) |
| $Ge(CFH_2)_4$ | | | | | | 191.4 | 46.7 | |
| $Ge(CF_3)_3(OH)$ | −21.6 | | | | | | | |

[a] Singlet. [b] Doublet. [c] Triplet. [d] Basic quartet. $C_2F_5$ group: $CF_3$, 6.76, multiplet. $CF_2$, 38.4, $J$(FF) 3.3, septet.

imately 2 Hz. It is curious that with $CF_3$ 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.

*Mass spectra* *. The mass spectra of several of the compounds were recorded at two temperatures, room temperature and at 150°C, the 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 of $P^+$ — 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 ($Ge(CF_3)_3$).

The compounds tend to decompose slowly, leaving behind a clear viscous oil with no apparent vapor pressure at 1 μ 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 by its characteristic doublet. No matter how carefully we handled the com-

TABLE 6

WEIGHT PERCENTAGE YIELDS OF POLYFLUOROTETRAMETHYLGERMANIUM[a]
Total weight of fluorinated sample for three reactions upon which all yields except $Ge(CF_3)_4$ was calculated was 4.13 g.

| | |
|---|---|
| $Ge(CF_3)_4$ | 63.5[b] |
| $Ge(CF_3)_3(C_2F_5)$ | 0.25 |
| $Ge(CF_3)_3(CF_2H)$ | 0.38 |
| $Ge(CF_3)_3(CFH_2)$ | 0.06 |
| $Ge(CF_3)_2(CF_2H)_2$ | 6.20 |
| $Ge(CF_3)_2(CF_2H)(CFH_2)$ | 4.16 |
| $Ge(CF_3)(CF_2H)_3/Ge(CF_3)_2(CFH_2)_2/Ge(CF_3)(CF_2H)_2(CH_3)$ | 13.35[c] |
| $Ge(CF_3)(CF_2H)_2(CFH_2)/Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$ | 13.94[d] |
| $Ge(CF_3)(CF_2H)(CFH_2)$ | 28.51 |
| $Ge(CF_2H)_3(CFH_2)$ | 15.47 |
| $Ge(CF_2H)_2(CFH_2)_2/Ge(CF_2H)(CFH_2)_2(CH_3)$ | 11.87[e] |
| $Ge(CF_2H)(CFH_2)_3$ | 4.18 |
| $Ge(CF_3)_3(OH)$ | 1.40 |
| $Ge(CFH_2)_4$ | 0.22 |

[a] Yield for $Ge(CF_3)_4$ calculated independent of the compounds. When the yield of $Ge(CF_3)_4$ is high, only trace amounts of two other compounds appear, $Ge(CF_3)_3(C_2F_5)$ and $Ge(CF_3)_3(OH)$. [b] Based on 0.87 g $Ge(CH_3)_4$ 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.

---

* See footnote page 173.

pound, eventually only the hydroxide was found and characterized, as $Ge(CF_3)_3OH$. Often moisture attacked the partially fluorinated tetramethylgermanium compounds leaving hydroxides which were identified by NMR.

The relative amount of each of the compounds is given in Table 6. Of the partially fluorinated material, five compounds $Ge(CF_3)(CF_2H)_3$, $Ge(CF_3)(CF_2H)_2$-$Ge(CF_3)(CF_2H)_2(CFH_2)$, $Ge(CF_3)(CF_2H)(CFH_2)_2$, $Ge(CF_2H)_3(CFH_2)$ and $Ge(CF_2H)_2(CFH_2)_2$ comprise over 70% of the material. 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. A small percentage of Ge—C bonds are cleaved as the isolation of $Ge(CF_3)_3(OH)$ 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 $Ge(CF_3)_4$ is very low. So it is possible that bond cleavage in the fluorination of $Ge(CH_3)_4$ to $Ge(CF_3)_4$ occurs predominately at the $Ge—CF_3$ stage and to some extent at the $Ge—CF_2H$ stage. If the fluorination conditions are too vigorous, cleavage occurs more readily, thus the yield of the $Ge(CF_3)_4$ decreases. The thermal stability of $Ge(CF_3)_4$ is surprising. It is stable at 165°C for several days and also appears to be chemically quite unreactive.

## Acknowledgment

This work was supported by the Air Force Office of Scientific Research (AFOSR 76-3031) and the Office of Naval Research (N00014-75-C-0994).

## References

1 E. Liu and R.J. Lagow, J. Amer. Chem. Soc., 98 (1976) 8270.
2 N.J. Maraschin, Ph.D. Thesis, Massachusetts Institute of Technology, 1975.
3 N.J. Maraschin and R.J. Lagow, Inorg. Chem., 12 (1973) 1459.
4 N.J. Maraschin, B.D. Catsikis, L.H. Davis, G. Jarvinen and R.J. Lagow, J. Amer. Chem. Soc., 97 (1975) 513.
5 J.L. Adcock and R.J. Lagow, J. Org. Chem., 38 (1973) 3617.
6 N.J. Maraschin and R.J. Lagow, J. Amer. Chem. Soc., 94 (1972) 8601.
7 N.J. Maraschin and R.J. Lagow, Inorg. Chem., 14 (1975) 1855.
8 R.J. Lagow, L.L. Gerchman, R.A. Jacob and J.A. Morrison, J. Amer. Chem. Soc., 97 (1972) 518.
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 (1975) 3128.
11 L.L. Knunyants, Y.F. Komissarov, B.L. Dyatkin and L.T. Lantseva, Izv. Akad. Nauk SSSR., Ser. Khim., 4 (1973) 943.
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 (1971) 249; Inorg. Chem., 11 (1972) 1259.
15 R.E. Seavers, NASA Technical Note, D-1089, 7 pages, 1961.
16 Haszeldine in E.A.V. Ebswarth, A.G. Marddock and A.G. Sharpe (Eds.), New Pathways in Inorganic Chemistry, Cambridge Univ. Press, London, 1968.