DIRECT FLUORINATION: A NEW METHOD FOR THE SYNTHESIS OF TRIFLUOROMETHYL COMPOUNDS

by

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B.S., The University of Chicago
(1973)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF

DOCTOR OF PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June, 1977

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Submitted to the Department of Chemistry on June, 1977, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The utility of direct fluorination for the synthesis of trifluoromethyl compounds has been studied. The reactions of fluorine with $Cd(CH_3)_2$, $Hg(CH_3)_2$, $C(CH_3)_4$, $Si(CH_3)_4$, $Ge(CH_3)_4$, $Sn(CH_3)_4$, and $Pb(CH_3)_4$ have been studied and are reported here.

We have demonstrated that it is possible to preserve both metal-carbon and metalloid-carbon bonds during direct fluorination to produce interesting fluorine compounds. It has been possible to convert dimethylmercury to bis(trifluoromethyl)mercury with elemental fluorine in 6.5% yield. We have been able to produce many new and interesting partially fluorinated tetramethylsilanes. The synthesis of tetrakis-(trifluoromethyl)germanium from the reaction of fluorine with tetramethylgermanium has been accomplished in extremely high yield, 63.5%. Also produced were many interesting polyfluorotetramethylgermanium compounds. Several fluorine containing methyltinfluorides have been identified by methyl exchange reactions. The success of this research has been dependent on careful control of fluorine concentration and low temperature.

Spectral properties of the polyfluorotetramethyl silicon, germanium, and tin compounds are given. Trends in spectral properties are discussed for the fluorinated Group IVA tetramethyl compounds.

The new fluorine compounds demonstrate the utility of carefully controlled fluorination techniques. A discussion is given on the nature of the fluorination process for the compounds mentioned above. Several interesting conclusions can be drawn from the complete study given in this dissertation. The compounds produced are generally unattainable by classical synthetic methods.

The last chapter describes a few of the unsuccessful and incomplete fluorination experiments. These experiments, nevertheless, shed considerable light on the fluorination process.

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ACKNOWLEDGEMENTS

The author is indebted to Professor R. J. Lagow for his financial support for the last three years. Financial support from the Department of Chemistry for the first year as a teaching assistant is gratefully acknowledged.

I would like to especially thank two members of Prof. Lagow's research group, Timothy Juhlke and Dr. Reint Eujen, for their professional aid and friendship during my research years. Countless many others made my four years bearable both in and out of the laboratories, both scientific and social. Special thanks go to S.Y., Y.T., G.I., L.W., F.H., M.H., L.H., C.L., L.T., S.K., M.L., G.L., R.H., S.L., B.H., L.C., J.M., L.G., R.F., K.T., B.S., D.T., J.S., and R.B. I would not be where I am today if it had not been for Dr. Norma Maraschin, who taught me everything she knew about fluorination and who had confidence in me.

Finally, I would like to thank my brothers and sister as well as my parents for unending moral support during these four years away from Hawaii.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

CHAPTER I

INTRODUCTION

The synthesis of highly substituted trifluoromethyl, CF_3, compounds is of considerable interest.[1] Trifluoromethyl containing compounds and particularly the fully substituted compounds are of interest due to the probability of unusual properties. A good example has been the compound bis(trifluoromethyl)mercury, $Hg(CF_3)_2$, first prepared by Emeleus and Haszeldine.[2] The compound is a white crystalline solid and water soluble. In contrast, dimethylmercury is insoluble in water and is a liquid which is hydrolytically stable under conditions which decompose bis(trifluoromethyl)mercury. The study of perfluoroalkyl derivatives of the metals has been hindered by the lack of suitable synthetic methods. Due to the possibility of novel properties and reactions in comparison to their hydrocarbon analogs, these perfluoroalkyl compounds have been sought.

The figure on the following page shows the well characterized trifluoromethyl compounds in their normal oxidation states. There have been many claims to other trifluoromethyl containing compounds, but only fragmentary evidence was presented. Some of the examples include CF_3Li[3], $Si(CF_3)Cl_3$[4], and CF_3MgI[5]. The failure in the attempted isolation of the compounds has been attributed to the facile α-elimination of the CF_3 to leave a fluorine bond and a difluorocarbene. However, it has been possible to isolate some unusual compounds containing fluorines on the α-carbon, such as CF_3BF_2[6] and CFH_2BF_2[7]. This leads to the possibility of unusual new fully substituted CF_3 containing compounds if proper synthetic methods were available.

Some of the general methods for synthesis of trifluoromethyl compounds have been the following:[1]

						HCF_3	
			$C(CF_3)_4$	$N(CF_3)_3$	$O(CF_3)_2$	FCF_3	
				$P(CF_3)_3$	$S(CF_3)_2$	$ClCF_3$	
			$Ge(CF_3)_4$	$As(CF_3)_3$	$Se(CF_3)_2$	$BrCF_3$	
	$Cd(CF_3)_2$		$Sn(CF_3)_4$	$Sb(CF_3)_3$	$Te(CF_3)_2$	ICF_3	
	$Hg(CF_3)_2$			$Bi(CF_3)_3$			

Figure 1. Trifluoromethyl compounds.

1. From the elements:

$$CF_3I + P \longrightarrow P(CF_3)_3$$

$$CF_3I + Cd/Hg \longrightarrow Hg(CF_3)_2$$

2. From coupling reactions

$$CF_3I + KGeH_3 \longrightarrow CF_3GeH_3$$

$$CF_3C(O)Cl + LiMn(CO)_5 \longrightarrow CF_3Mn(CO)_5 + CO$$

3. From the cleavage of metal-metal bonds

$$CF_3I + Me_3Sn\text{-}SnMe_3 \longrightarrow CF_3SnMe_3 + ISnMe_3$$

$$CF_3I + [(C_5H_5)Ni(CO)] \longrightarrow (C_5H_5)Ni(CO)CF_3$$

4. From oxidative addition reactions

$$CF_3I + GeI_2 \longrightarrow CF_3GeI_3 + (CF_3)_2GeI_2$$

$$CF_3I + (\phi_3P)_2Ir(CO)Cl \longrightarrow CF_3(\phi_3P)_2Ir(CO)ClI.$$

To this can be added methods such as CF_3 transfer reactions with $Hg(CF_3)_2$ and plasma synthesis with CF_3 radicals from C_2F_6.[8] A synthetic route for one compound may not be the method of choice for another. One example is the following:[9]

$$CF_3I + GeI_2 \xrightarrow[\text{autoclave}]{130^o} CF_3GeI_3 + (CF_3)_2GeI_2 \ .$$

CF_3SnI_3 cannot be obtained by the method used for CF_3GeI_3. Both the perfluorocompounds, $Ge(CF_3)_4$[8] and $Sn(CF_3)_4$[10] have only recently been synthesized by a nonconventional method. However, the Group IVA elements still lack $Si(CF_3)_4$ and $Pb(CF_3)_4$ as well characterized compounds. Several CF_3 silicon[11] and lead[12] compounds have been reported or alluded to but none have been well characterized.[13]

During the past several years, several new techniques have been developed which led to the successful synthesis of several new CF_3 compounds.[8] However, the exploratory nature of these new methods have not been fully examined yet. There may be limitations and thus far $Si(CF_3)_4$ has not been prepared. $Si(CF_3)_4$[11] has elluded many researchers in the past, although there have been many claims to its synthesis. Therefore new methods of synthesis must be sought in an effort to synthesize new CF_3 containing compounds.

During the past five years, we have been examining a new method of synthesis, direct fluorination.[14,15] The method has proven extremely successful in replacing hydrogens with fluorine on a material to produce perfluoro analogs. It has been possible to synthesize many perfluoro- or polyfluoro- organic and inorganic compounds in fairly good yields. The versatility of the method has been extended from the synthesis of perfluoro analogs of neopentane,[16] hexamethylethane and cyclooctane[17] to perfluoroethers[18] such as glyme and diglyme, to fluorinated inorganic systems such as sulfur tetranitride[19] and the lower carboranes[20], just to mention a few.

The extent to which direct fluorination can be used as a synthetic tool has only been explored to a limited extent. In an effort to see the possible limits of fluorination as a synthetic tool, several organometallic systems such as $Pb(CH_3)_4$, $Sn(CH_3)_4$, $Ge(CH_3)_4$, $Hg(CH_3)_2$ and $Cd(CH_3)_2$ were examined. The question was posed: Could a metal-carbon bond or a metalloid-carbon bond survive fluorination as methyl groups are converted to trifluoromethyl groups?

The fluorination of organometallic compounds is more difficult than that of hydrocarbons or organic compounds based simply on bond strength considerations. Metal-carbon bonds are much weaker than carbon-carbon bonds.[21,22] Therefore one would not be at all surprised to have a substantial amount of metal-carbon bond cleavage, leading to the formation of metal fluorides and fluorinated methanes. Nevertheless, it is also true that many fluorinated organometallic compounds, such as $Hg(CF_3)_2$, are quite stable. In fact, many reviews[1,23] attribute the apparent inherent stability of CF_3 containing compounds, especially to transition metals and elements, to possible "p-d" orbital participation. Therefore, in light of the apparent bond strength considerations, one can possibly produce perfluoromethyl compounds by direct fluorination. As mentioned earlier, a general synthetic method for the synthesis of totally substituted trifluoromethyl compounds is not established. It was for this reason that this research was undertaken. It was hoped that one could show the possible synthetic utility of the fluorination technique as an alternative synthetic route. It will be seen that this is indeed possible.

GENERAL EXPERIMENTAL

APPARATUS

Fluorinations were done in reactors described in detail previously.[15] Liquid nitrogen cooling was used for subambient cooling, unless otherwise indicated. Temperature was controlled by a temperature controller made by Cryogenic Controls Company.

Much care was taken to insure that the reactors were oxygen and moisture free. The reactors were normally purged with fluorine/helium mixtures to remove the water and routinely purged with 60-100 cc/minute helium for a day to insure that all oxygen was flushed from the reactor.

Starting materials were admitted into the reactors by methods which allowed minimum water and oxygen contamination. Air sensitive starting materials were syringed into the reactor by an air-tight syringe. A swagelok T-assembly was placed before the reactor. The cap was replaced by a no-air stopper, through which the material was syringed. After purging for an appropriate time, the no-air septum was replaced with the swagelock cap. If this method was not satisfactory, normally for compounds with low boiling points, then the material was admitted into the reactor through a stopcock assembly, into which the material had been condensed. All liquids were degassed.

Volatile materials were collected in glass traps placed after the NaF scrubber in the fluorination system. The volatiles were transferred onto a vacuum line and separated by trap to trap methods[24] to remove extremely volatile materials of little interest, generally material which passes a -131° slush trap.

Separation of the various compounds was accomplished on a Bendix 2300 Gas Chromatograph, equipped with an automatic temperature controller and a thermal conductivity detector. Gas chromatograph columns used were 10% SE-30 on Chromosorb P and 10% fluorosilicone on Chromosorb P. Preparative scale columns were used. Helium flow rates were 120 cc/minute.

All infrared spectra were obtained in the gas phase. Mass spectra were obtained as gaseous samples. All NMR's, when possible, were obtained using neat liquids and were referenced to external tetramethylsilane (TMS) for protons, external trifluoroacetic acid (TFA) for fluorine and external TMS for carbon. No corrections were made for bulk susceptibility differences from the glass tube used. Normally spectra were obtained in sealed 4mm glass tubes, obtained from the same batch of glass tubing.

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 & 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 experiments were done on the R20B instrument equippped with an external frequency synthesizer. Fluorine fourier transform spectra were taken on the R20B instrument interfaced with a Digilab FTS/NMR Fourier Transform Data System. Carbon-13 NMR's were obtained on a Bruker WH-90 instrument equipped with fourier transform capabilities. X-ray diffractions were done on a Norelco X-ray Diffraction Unit manufactured by Phillips Electronic Corporation. Melting points were taken in sealed tubes against a Leeds & Northrup 8690-2 Millivolt Potentiometer.

MATERIALS

Fluorine (98+%) used was obtained from Allied Chemical Company. The fluorine was used without further purification. NaF pellets were obtained from the Harshaw Chemical Company as $NaHF_2$ pellets. NaF was generated by heating the $NaHF_2$ pellets under a stream of nitrogen. The purity of the NaF pellets generated in this manner was checked by its x-ray powder pattern against that of $NaHF_2$.

Neopentane (99%) from Chemical Samples Company, tetramethylsilane (NMR grade) from Stohler Isotope Chemicals, tetramethylgermanium (99.9%), tetramethyltin(99.5%), $Sn(CH_3)_2F_2$, and dimethylmercury (98%) all from Alfa Products, were used without further purification after the samples were degassed. Dimethylcadmium[25] and tetramethyllead[26] were prepared by literature methods. 1-adamantamine, $Si(CH_3)_3Cl$, $Si(CH_3)_2Cl_2$ and several tetramethylammonium salts were obtained from Aldrich Chemical Company.

TYPICAL REACTION

A typical reaction for tetramethylsilane is described here. (Other low temperature reactions were handled in essentially the same manner. Details are given in the experimental section for each compound.) A low temperature reactor was assembled and passivated and dried with fluorine and helium. The reactor was cooled to say -120^{o} with a liquid nitrogen temperature control system. After the system has been cooled for almost an hour, the tetramethylsilane was syringed into the reactor with a high flow of helium, generally about 150 cc/minute through a swagelok T-assembly. The reactor was flushed for an hour to insure that all the tetramethylsilane was at the desired temperature. Then the helium flow was reduced and the temperature set for the reaction to occur. Downstream from the reactor was placed a liquid nitrogen trap to freeze volatile materials. After the fluorination was terminated, the liquid nitrogen trap was transferred to a vacuum line and the products transferred into a vacuum system. As an added measure to insure that no moisture was present, the volatile materials were pumped through molecular sieves. The products were fractionated at -131^{o}. The only silicon-containing material that passed -131^{o} was found to be SiF_4. Therefore, all material that passed a -131^{o} slush bath was discarded. The products were then separated on a gas chromatograph using preparative scale columns. At all times the material was handled to exclude moisture and air. After separation, infrared, mass spectra and NMR's were taken of the pure samples.

ORGANIZATION

The experiments discussed in the following pages have been organized into two major sections, Group IIB, cadmium and mercury, and Group IVA, carbon, silicon, germanium, tin and lead. Each of the major sections will discuss the results for each of the elements.

The order in which the elements will be discussed does not reflect the success or failure of the experiments but rather the comparative nature of the elements. For each of the elements, representative reactions will be described to summarize the wide variety of conditions attempted. Results, when necessary, will be summarized in tabular form rather than by individual compounds. A discussion will be given for each of the elements following the results. Comments concerning possible trends in the reaction of each group will be discussed where appropriate.

A final chapter on several of the many miscellaneous experiments attempted will be discussed. Only those of relevance to the general fluorination mechanism observed for the Group IIB or IVA fluorination experiments will be discussed. Other reactions of general curiosity are not discussed.

GENERAL CONSIDERATIONS

The advantages and disadvantages of fluorination have been discussed by Dr. Norma Maraschin in her doctoral thesis.[15] A discussion was presented comparing the LaMar technique to other fluorination techniques. Besides the clearcut advantage as a new technique, one can use direct fluorination as an exploratory tool. Discussed below are some general laboratory observations which play an important role in the fluorination process as discovered by this author.

Advantages. Any sample, whether solid, liquid, or gas, may be subjected to the fluorination technique. It would be misleading to claim that one could successfully study every material. However, one may use the technique to investigate new synthetic routes where others have been shown to fail. From our understanding of the fluorination technique, it has been clear that certain compounds fluorinate better than others. Hydrocarbons can be fluorinated extremely well by the direct fluorination technique, due mainly to the inherent strength of the C-C bond and the ability to use generally harsher conditions on the partially fluorinated compounds. Organic compounds work well although very little has been done with functional groups.

One has many variables in the fluorination process. The obvious variables are temperature, fluorine concentration, and length of reactions. All the variables are very much interrelated but can be employed to yield the synthesis of materials where other methods can fail.

Disadvantages. There may be disadvantages to any synthetic route. The starting material must be stable in fluorine and hydrofluoric acid, at least to the extent that one can control a fluorination process rather than start a combustion. Bond instabilities play an important role, but experimental conditions can often be used to overcome this problem. The advantages of temperature, fluorine concentration, and length of reaction can turn out to be very difficult disadvantages if one has to vary all three variables over several reactions to insure the successful synthesis of a compound or to prove that the experiment did not succeed. Time is a crucial factor. One normally has to run at least a mole equivalent of fluorine to starting material to insure perfluorination, if each collision leads to bond breaking and bond formation. Since every collision does not lead to a C-F bond or a fluorine bond formation, excess fluorine is usually employed. But the question is how much excess fluorine, and in what manner, increase fluorine flow or length of reaction. Since it is known that fluorination becomes statistically more difficult as the molecule gets more highly fluorinated, one necessarily has to use more fluorine. Since one can only estimate the amount of fluorine required, many reactions of varying lengths are required. Then how does one get activation energy to get a perfluorinated material, increase the temperature of the reaction with possible decomposition, or increase fluorine flow, and possibly increase bond cleavage? The question also arises as to whether the perfluorinated compound of interest is stable in an atmosphere of fluorine. Will excess fluorine destroy the compound as it vaporizes out of the reactor? Fluorocarbons probably will be unaffected, but certainly many organometallic compounds will react further. Then what about reaction with free hydrofluoric acid that might form in the reaction? What about reaction with the sodium fluoride pellets? It appears that one can increase fluorine flow rate and temperature quite rapidly when fluorinating hydrocarbons. After the hydrocarbons are initially lightly fluorinated, one can, without worrying about combustion, go to harsher conditions to get perfluorination. In fact, if one does not do so, the bulk of the material isolated will have one to two hydrogens remaining, with the yield of perfluoromaterial generally low. Once partial fluorination has been achieved without fragmentation, polymerization or combustion, successful perfluorination can result.

Clearly several of the above items can make it difficult to isolate compounds. But again certain factors are not as important as others in the successful synthesis of perfluorinated materials.

However, there are still experimental difficulties to be overcome in direct fluorination. Hydrofluoric acid formation is often a difficult problem to deal with. The danger of HF formation in a manner whereby their reaction with the NaF pellets causes the pellets to fuse can result in a blockage in the system. At this stage, the danger is HF, anhydrous, under pressure and its danger when released to the unexpecting researcher. Another problem is air and moisture in the system. The successful synthesis of many fluorinated compounds only results from the exclusion of air and moisture. Other compounds are not affected to the same extent. Whenever one runs subambient temperatures, moisture and oxygen can enter the system if a small leak in the system is not detected. A more fundamental problem is the temperature gradient. Without devising an elaborate system, which certainly would involve a considerable monetary investment, one has to worry about the temperature of the reaction. Does one really know that the reaction is occuring at the temperature one says it is occuring at or is it occuring at a higher or lower temperature? The higher temperature problem is more of a "problem". This is generally the problem in injecting starting materials of low volatility which freeze upon contact with a cold surface, and thus are not at the desired temperature surface. For many compounds, temperature is an important factor for successful results. Certain compounds are not as sensitive to temperature variations for fluorination to occur. The temperature factor can be overcomed with some ingenious injection methods. When one warms a particular zone and subsequently cools another zone, materials of low volatility, generally material with only a few fluorines on the molecule, may not move and thus fluorinate at a much higher temperature than the researcher desires. This can cause much polymerization to occur. Some times the researcher is fortunate and this works to his advantage.

What then can be done? I feel certain compounds obviously are easier to do than others. From purely thermodynamic considerations, the stronger the bond the better. The more stable the fluorinated material the better, although this information is often not available when unknown compounds are sought. The limits of cryogenic cooling is -150^{0}C, although probably not many reactions occur at that temperature. Solid fluorinations are usually successful but the technique is best suited for liquids. The best liquid physical properties for fluorination are those which freeze between -80^{0} to -50^{0}C and which boil around 40-70^{0}C. It is best to start the fluorination process below the freezing point. Volatile products are desired since they are easily separated by gas chromatography. Solids pose a different problem, especially if they are involatile and insoluble. Very few compounds lend themselves ideally to ready fluorination, therefore the fluorination technique becomes a scientific art. Rather than work with alkanes which fluorinated more easily, a researcher might select challenging starting materials. This approach is all the more satisfying if someone has predicted that the product sought would be unstable or non-existent. Many of the new compounds reported in this thesis fall into this category.

CHAPTER II

DIRECT FLUORINATION OF GROUP IIB METAL ALKYLS

Fluorination of dimethylcadmium and dimethylmercury.

FLUORINATION OF DIMETHYLCADMIUM, $Cd(CH_3)_2$

EXPERIMENTAL

Reaction 1.

With zone 3 cooled to -78^0, 0.40 ml of $Cd(CH_3)_2$ was syringed into the 4-zone reactor with a helium flow of 100 cc/minute. The following fluorination conditions were used.

F_2 (cc/minute)	He (cc/minute)	Zone	Time
0.0	100	3 (-78)	1 hour
0.0	100	1,2,3 (-78)	2
1.0	60	1,2,3 (-78)	75
0.0	60	1,2,3 (-78)	8
0.0	100	1,2,3,4 (RT)	32

The contents of the liquid nitrogen trap were then fractionated into -95^{o}and -196^o. The volatiles in the -196^{o}trap were mainly CF_3H, COF_2 and SiF_4. There was no evidence for CF_4. The portion that stopped in a -95^{o}slush was predominantly starting material, $Cd(CH_3)_2$.

There was some decomposition in the glass trap. A white polymer was deposited on the walls of the glass system. CdF_2 was also believed to be present. A quantity of methane was present in the infrared spectrum portion of that which stopped in the -95^{o}bath, indicating some decomposition of the material.

Reaction 2.

0.32 ml of $Cd(CH_3)_2$ was syringed into the reactor with a helium flow of 100 cc/minute and with zone 4 at -78^{0}C. The following fluorination conditions were then used.

F_2 (cc/minute)	He (cc/minute)	Zone	Time
0.0	100	4 (-78)	1 hour
0.0	100	1,2,3,4 (-78)	¼
1.0	60	1,2,3,4 (-78)	41
3.0	60	1,2,3,4 (-78)	22
3.0	30	1,2,3,4 (-78)	10
0.0	30	1,2,3,4 (-78)	21
0.0	60	1,2,3,4 (RT)	24

The contents of the liquid nitrogen trap were fractionated at -95° and -196°. Approximately 0.27 ml of starting material was recovered. Present in the trap upon transferring was a white precipitate and CdF_2. Also present, but unidentified, was a waxy, white substance.

Reaction 3.

0.275 ml of $Cd(CH_3)_2$ was syringed into the reactor with zone 2 at -100° and a helium flow of 100 cc/minute. The following reaction conditions were then used with zone 2 always cooled as indicated.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
0.0	100	-100	1 hour
1.0	60	-80	10
1.0	60	-75	12
1.0	60	-70	4
1.0	60	-65	10
1.0	60	-60	10
1.0	60	-55	4
1.0	60	-50	3
1.0	60	-45	7
0.0	60	-45	10
0.0	60	RT	24

The contents of the liquid nitrogen trap were then fractionated into -95° and -196°. The -196° fraction contained mainly CF_4 and CF_3H. There was very little material in the -95° trap. What stopped in a -95° trap was condensed onto pyridine. A white precipitate formed but there was no color change in pyridine. The ^{19}F NMR was negative for fluorine containing material.

Reaction 4.

0.275 ml of $Cd(CH_3)_2$ was syringed into the reactor with zone 3 held at -90° with a helium flow of 100 cc/minute. The following reaction conditions were tried with zone 3 always cooled.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
0.0	100	-90	2 hours
0.0	100	-70	2
1.0	60	-70	7
1.0	60	-65	10
1.0	60	-60	6
1.0	60	-55	8
1.0	60	-50	9
1.0	60	-45	8
0.0	60	-45	7
0.0	60	RT	22

The material in the liquid nitrogen trap was fractionated into -95° and -196°. The material in the -95° trap was placed in pyridine. No ^{19}F NMR signal was observed. There was no indication of starting material present at all. The -196° fraction contained mainly CF_4 and CF_3H.

DISCUSSION

There was no evidence for the synthesis of $Cd(CF_3)_2$ by the fluorination of $Cd(CH_3)_2$. What happens is apparently one of two possibilities: (1) the preferential cleavage of the metal-carbon bond by fluorine during the fluorination or (2) the fluorinated materials were unstable and decompose readily.

The presence of mainly CF_3H and CF_4 as volatile materials support the first suggested explanation for the absence of $Cd(CF_3)_2$ among the volatile products. The possible presence of a CF_3 group on cadmium could lead to the polarization of the metal-carbon bond to result in easier cleavage by fluorine. Several facts also support the second possibility above. Upon transfer of the volatiles, a decomposition material always resulted. This could be due to the unstable nature of the compound or the compounds' reaction with glass. The instability of fluorinated $Cd(CH_3)_2$ species is a possible explanation. Dyatkin[27] and his co-workers report what appears to be $Cd(CF_3)_2$. Although the compound was never isolated and characterized, its inference from the ^{19}F NMR shows it to be fairly unstable. Upon repeating this work in our laboratories,[28] it has been found that the pyridine solution turns brown after remaining at room temperature for a few minutes, whereby the fluorine signals disappear.

Therefore it may not be possible to isolate the desired compound, $Cd(CF_3)_2$ pure by itself without a strong complexing agent. The stability of the compound might be only marginal at room temperature, just long enough for its ^{19}F NMR to be recorded.

However, in the experiments performed here, where the volatiles were condensed into pyridine, the pyridine did not turn brown on sitting but rather a white precipitate formed. So it is fair to say we did not have a compound similiar to that reported by the Russians.[27]

The four representative reactions show the general approach that would lead to the isolation of the compound if it were possible by this technique. The first reaction was analogous to that of $Hg(CH_3)_2$ which led to the successful fluorination to $Hg(CF_3)_2$. However, with the large amounts of starting material present, it was felt that possibly a higher fluorine concentration was necessary. Reaction two was designed to use more fluorine. Again the large amount of starting material indicated that the reaction was not occurring at -78^0 but that warmer conditions were required. Reaction three was done with varying temperatures to obtain more activation energy. This reaction showed that a definite reaction had occurred but none of the desired compound was isolated. Reaction four was the same as reaction three but for a shorter period of time. Again the results were negative.

Since dimethylcadmium is a better methyl transfer agent than dimethylmercury, it was felt that bis(trifluoromethyl)cadmium might be a more facile source of CF_3 group than bis(trifluoromethyl)mercury. $Hg(CF_3)_2$ does not transfer a CF_3 group as readily as one would desire. Temperatures higher than desired are often needed for reactions to occur and at these temperatures, the new CF_3 compounds can be unstable.

FLUORINATION OF DIMETHYLMERCURY, $Hg(CH_3)_2$

EXPERIMENTAL

Reaction 1.

The low temperature fluorine reactor was used. Zone 3 of the reactor was cooled to -85°. 0.5 ml of $Hg(CH_3)_2$ was syringed into the reactor through a swagelok T-assembly with a helium flow of 165 cc/minute. Zone 2 was then cooled to -78° with a dry ice/ethanol slush. After allowing the reactor to equilibrate for half an hour, fluorine flow was started. 1.0 cc/minute of fluorine to 60 cc/minute of helium was used. After 36 hours, zone 2 was allowed to warm up slowly. After 12 more hours, zone 2 was at -40°. The reaction was allowed to continue for three more days. The fluorine flow was then stopped and the helium flow increased to 150 cc/minute. After seven hours, the temperature controller was turned off. After flushing for 36 hours, the contents of the liquid nitrogen trap were pumped out on a vacuum line.

CF_4 made up a considerable part of the volatiles. There appeared to be material present which decomposed on sitting, leaving behind HgF_2 (identified by X-ray diffraction). Fractionation was done at -78° and -196°. The -196° fraction contained CF_4, SiF_4, CF_3H, CF_2H_2, CH_3F, C_2F_6 and COF_2. These were identified by both infrared spectra[29] and ^{19}F NMR[30]. The material which stopped in the -78° trap was condensed with ether for a ^{19}F NMR. A resonance occurred with a chemical shift of -37.24 from external TFA and the mercury satellites gave a J = 1288 hz. The material was separated on the gas chromatograph to yield 0.041 gm of $Hg(CF_3)_2$, which gives a 1.82% yield.

The gas chromatograph was calibrated with the following program.

SE-30, 3/8" x 24'
80^{0} isothermal

$Hg(CH_3)_2$	15'40"
$Hg(CH_3)(CF_3)$	50'
$Hg(CF_3)_2$	after warming to 185^{0} at 10^{0}/minute

The -78^{0} sample contained no $Hg(CF_3)(CH_3)$ and a little $Hg(CH_3)_2$ which eluted at 18'0" (infrared was used to positively identify $Hg(CH_3)_2$). The $Hg(CF_3)_2$ came out 20 minutes after the temperature was raised from 80^{0} to 185^{0}.

The material in the reactor was removed and identified as HgF_2 by X-ray diffraction. There was also some higher fluorocarbons present in the volatiles, but there was insufficient material for identification by NMR. The low volatility of the material made infrared spectral identification difficult.

Reaction 2.

0.5 ml of $Hg(CH_3)_2$ was syringed into the reactor with zone 3 at -85^{0} and a helium flow of 165 cc/minute. Zone 2 was then cooled to -78^{0} and the fluorine flow began after two hours. A helium to fluorine ratio of 60/1 cc/minute was used. After 30 hours, zone 2 was allowed to warm up. After 72 hours, the fluorine flow was terminated. After purging for 12 hours, the temperature controller was turned off.

Upon pumping the contents of the liquid nitrogen trap, a considerable amount of white material deposited on the glass trap. A powder pattern of the white material showed it was not HgF_2, HgO or SiO_2. The material was not soluble in benzene, chloroform, acetronitrile, carbon tetrachloride, ether, water and methanol. Elemental analysis showed no mercury present.

There was 45.9% F, 1.75% C and 1.44% H from the elemental analysis. The remaining elements were not identified. KBR pellet showed a broad band peaked at 3020 and another at 1020 cm^{-1}. There was 1.18 gm of the white solid. This material remained unidentified.

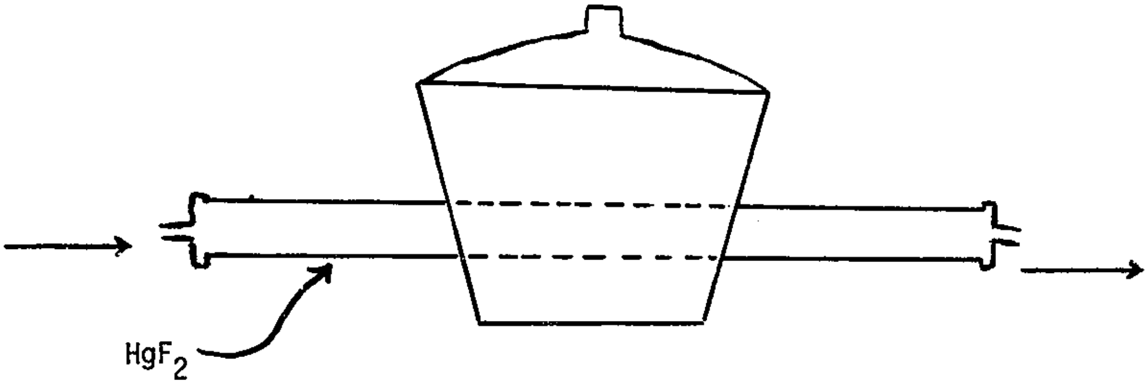
The volatile materials were fractionated at -45°and -196°. The -45°fraction was condensed in ether. No $Hg(CF_3)_2$ was present but rather a singlet at +80 ppm from external TFA. The compound leading to this chemical shift was not immediately identifiable. The material which passed the -45°trap contained mainly CF_4, CF_3H, CF_2H_2, COF_2 and SiF_4.

The material in the reactor was mainly HgF_2, as identified by X-ray diffraction.

Reaction 3.

A bucket reactor was cooled to -78° with a dry ice/ethanol slush. With a helium flow of 175 cc/minute, 0.525 ml of $Hg(CH_3)_2$ was syringed into the reactor packed with copper turnings. After ½ hour, fluorine flow was initiated with 1 cc/minute of fluorine to 60 cc/minute of helium. After 72 hours, the fluorine flow was stopped. The reactor was allowed to warm to room temperature after helium flushing for 8 hours.

The volatile materials in the liquid nitrogen trap were mainly CF_4, CF_3H, SiF_4 and COF_2. There was no evidence for $Hg(CF_3)_2$. When the reactor was opened, the turnings were coated with HgF_2. Most of the HgF_2 was in an area where the temperature of the reactor was higher than -78°.



Reaction 4.

0.725 ml of $Hg(CH_3)_2$ was syringed into the low temperature zone reactor with zone 4 cooled to -78° with a helium flow of 130 cc/minute. After ½ hour of flushing, zones 1, 2 and 3 were also cooled to -78°. Fluorine flow was started with a helium flow of 60 cc/minute to a fluorine flow of 1.0 cc/minute. After 120 hours, the fluorine was turned off. The reactor was allowed to warm up after purging with helium for 6 hours. The liquid nitrogen trap was pumped on and fractionated with the material stopping at -45°being added to ether. The reactor was also pumped on to remove any material with low volatility. The material from the reactor was placed with that which had stopped in a -45°trap. The fluorine NMR showed a singlet at -37.70 ppm downfield from external TFA and a ^{199}Hg-F coupling constant of 1251 hz. A yield of 6.5% was obtained for $Hg(CF_3)_2$ after purification by gas chromatography.

The material in the reactor was HgF_2 and the volatiles mainly CF_4, CF_3H, and CF_2H_2.

DISCUSSION

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 gm of $Hg(CH_3)_2$) can be obtained by fluorination at -78^o to -90^o. A fluorine concentration of 1.67% obtained by a mixture of 1 cc/minute of fluorine to 60 cc/minute 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 reaction can be represented as follows:

$$Hg(CH_3)_2 + F_2/He \xrightarrow[\text{5 days}]{-78^o} Hg(CF_3)_2 + HgF_2 + CF_4 + CF_3H + CF_2H_2 + CFH_3.$$

The physical properties and ^{19}F NMR agree with authentic samples prepared by alternative methods.[8,31,32]

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 $Hg(CF_3)_2$, nevertheless. Evidently efficient relaxation processes occur on the cold surfaces to allow energy dissipation so that CF_3 groups can form as HF is formed.

It is believed that once $Hg(CF_3)_2$ forms, the compound is stable under the conditions of the experiment. We have found that $Hg(CF_3)_2$ does not react with 3% fluorine at -78^o. We have also found that $Hg(CF_3)_2$ reacts slowly with 3% fluorine at 0^o and appreciably at room temperature, forming HgF_2 and CF_4. Therefore with a low fluorine concentration of 1.67% and low temperature, -78^o, $Hg(CF_3)_2$ can form. This result is not too surprising in that $Hg(CF_3)_2$ is quite unreactive toward the halogens. To get high conversion to the mercuric halides, the following conditions have to be used.[33]

$$Hg(CF_3)_2 + \begin{array}{l} Cl_2,\ 100\text{-}150^o \\ Br_2,\ 100\text{-}150^o \\ I_2,\ 100\text{-}150^o \end{array} \longrightarrow \begin{array}{l} CF_3Cl\ (95\%) + HgCl_2 \\ CF_3Br\ (92\%) + HgBr_2 \\ CF_3I\ \ (97\%) + HgI_2 \end{array}$$

One would indeed be surprised if the yield were much higher than reported for HgF_2 is indeed the preferred product. This is to be expected in light of thermodynamic factors of bond strengths, that of C-HgR (CH_3HgCH_3) being 50 kcal/mole[21] while F-HgF is 100 kcal/mole[21] and HF is 153 kcal/mole.[34]

A high degree of fluorination must occur as evidenced by the large quantities of CF_4 produced. Bond cleavage evidently occurs as the fluorination process occurs due to the compounds identified, CF_3H, CF_2H_2 and CFH_3.[35] The yield of $Hg(CF_3)_2$ might be increased if one could find a method of better relaxation of the energy processes occurring on the partially fluorinated species such as RHg-CH_2F and RHg-CHF_2.

The curious fact is that there appears to be no evidence that any partially fluorinated $Hg(CH_3)_2$ was present. One might 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 latter comment has some credibility in that in one of the experiments, a large quantity of decomposition product, high in fluorine content resulted. The compound could be a polymer with C, H, and F present in unspecified amounts.

Although not a new compound, the synthesis of $Hg(CF_3)_2$ has demonstrated that the fluorination process can be controlled and manipulated to produce highly fluorinated species. Experimental conditions are indeed crucial as representative reactions have demonstrated. It is important that the $Hg(CH_3)_2$ be at the temperature stated, otherwise HgF_2 is the only mercury product. In our reactors, a tremendous temperature gradient exists in that the temperature outside the zone of interest is normally about $20\text{-}30^{0}$ warmer downstream and much higher upstream of the helium flow. The bucket reactor fluorination of $Hg(CH_3)_2$ demonstrates this well. The $Hg(CH_3)_2$ is frozen at the entrance of the reactor which is probably at -20^{0} and not at the desired -78^{0} temperature. Consequently the fluorination process is too exothermic and energy dissipation not sufficient to allow $Hg(CF_3)_2$ to form. Reaction 4 solves this problem well and one gets a 6.5% yield of $Hg(CF_3)_2$.

REACTION OF FLUORINE WITH $Cd(CH_3)_2$ and $Hg(CH_3)_2$

The reaction of fluorine with dimethylmercury can be controlled by low temperature and dilute fluorine concentrations to produce bis(trifluoromethyl)mercury. The synthesis of bis(trifluoromethyl)cadmium has not been possible by the fluorine reaction conditions tried. It would be difficult to discuss all the possible factors that might account for this difference in reactivity.

The reaction of halogens with $Cd(CH_3)_2$ is quite rapid leading to CdX_2 and CH_3X, X = Br, Cl, I.[36] Therefore the reaction with fluorine towards dimethylcadmium would be expected to be even more rapid. With all the attempts described here, it is obvious that we have not found a way to surpress the cleavage of the cadmium-carbon bond. The same situation arises for dimethylmercury. However, in the mercury case, we are able to prevent complete attack of the mercury-carbon bond to allow formation of $Hg(CF_3)_2$. Although the first dissociation energy of $Hg(CH_3)_2$ is only 6 kcal/mole greater than that of $Cd(CH_3)_2$, 51 kcal/mole versus 45 kcal/mole,[37,38] this appears to be enough to allow CF_3 to form on mercury. Examining the bond lengths in the starting material leads to the same conclusion. Although the bond lengths of $Cd(CH_3)_2$ is only 0.018 A^o longer than that of $Hg(CH_3)_2$, 2.112 A^o versus 2.094 A^o,[39] one could say that this was enough to allow preferential bond cleavage.

A more likely reason for the success for the fluorination of $Hg(CH_3)_2$ and not $Cd(CH_3)_2$ is the stability of the product. As has been pointed out earlier, $Hg(CF_3)_2$ is quite stable in dilute fluorine and at room temperature. On the other hand, $Cd(CF_3)_2$[27], as has been reported by NMR evidence, appears to have marginal stability at room temperature. It was thought the $Cd(CF_3)_2$ might have been ustable in the medium in which it was produced. It was hoped that if $Cd(CF_3)_2$ were isolated pure it would have some increased stability since no solvent was present. However, our failure to isolate the compound by fluorination was disheartening.

Direct fluorination of group IIB dimethyl compounds can be summarized as:

$$\begin{aligned} Cd(CH_3)_2 + F_2/He &\longrightarrow Cd(CH_3)F + CdF_2 + R \\ Hg(CH_3)_2 + F_2/He &\longrightarrow \underset{6.5\%}{Hg(CF_3)_2} + HgF_2 + R \end{aligned}$$

R = fluorinated methanes and HF.

CHAPTER III

DIRECT FLUORINATION OF GROUP IVA ELEMENTS

Fluorination of neopentane, tetramethylsilane, tetramethylgermanium, tetramethyltin, and tetramethyllead.

FLUORINATION OF NEOPENTANE, $C(CH_3)_4$

EXPERIMENTAL

1.77 gm of neopentane was condensed into a container with a stopcock attachment. This container was attached to the flow system of the low temperature reactor through a Cajon fitting at the swagelok T-assembly. The neopentane was blown into the cryogenic reactor with a helium flow of 30 cc/minute. Zones 1 and 2 were cooled to -78°. Neopentane was too volatile to syringe through normal techniques. The following fluorination conditions were used.

F_2 (cc/minute)	He (cc/minute)	Zone	Time
1.5	20	1,2 (-78)	24 hours
1.5	20	2,3 (-78)	24
1.5	20	3,4 (-78)	24
1.5	20	4 (-78)	24
0.0	20	4 (-78)	18
0.0	60	1,2,3,4 (RT)	24

The volatile products were pumped out of the liquid nitrogen trap and separated on a vacuum line. All material which passed a -95° slush bath was discarded. The material which stopped in a -95° trap was transferred into tubes and diluted with CCl_4 for ^1H and ^{19}F NMR. Solubility in CCl_4 was quite low.

DISCUSSION

The synthesis of perfluoroneopentane, $C(CF_3)_4$, by the reaction of elemental fluorine and neopentane was accomplished in our laboratories previously.[16] At that point in the development of the fluorination technique, the perfluorinated material was of primary interest. For completeness in the Group IVA, C, Si, Ge, Sn, and Pb, some NMR data was desirable for comparison of coupling constants and chemical shifts. Also of interest was the comparison of product distribution for Group IVA fluorination.

Therefore the fluorination of neopentane was accomplished with the intent of looking at the partially substituted material and not perfluoroneopentane. We did not wish to separate the various products since some of the partially substituted neopentanes have been characterized.[40,41,42] General NMR trends were of interest. The reaction condition was chosen to get partial substitution only. These partially fluorinated neopentanes could have been made by other literature methods but these methods produce many fragmentation products.[42,43]

High degree of fluorination occurred on neopentane. From the ^1H and ^{19}F NMR, the following trends can be observed. (Comparison data agrees with proton-fluorine coupling for fluoroalkanes.[44,45])

^1H: (1) CH_3 resonance occurs between 0.70 and 0.90.

(2) CH_2F resonance occurs between 3.97 and 4.71, J_{HF}=46-48 hz.

(3) CHF_2 resonance occurs between 5.97 and 6.08, J_{HF}=50-54 hz.

(4) J_{HF} for CHF_2 is always greater than J_{HF} for CH_2F.

^{19}F: (1) CF_3 resonance occurs in three regions, -8.8 to -9.1, -10.8 to -11.2, and -12.8 to -13.5, J_{FF}=8-9.5 hz.

(2) CF_2H resonance occurs between 49.7 to 51.0, J_{HF}=52-55 hz.

(3) CFH_2 resonance occurs in two groups, 157.1 to 158.7 and 163.1 to 167.5, J_{HF}=46-48 hz.

The observed chemical shifts and coupling constants are what is to be expected from simple C, H, and F systems.[41,44] What is of importance here is that J_{HF} for CHF_2 is always greater than that for CH_2F. This is what is to be expected from deshielding effects on protons from fluorine, i.e. with increasing number of fluorines, the chemical shift moves toward more deshielding and coupling constants increase. It is the type of groups, CH_3, CH_2F, CHF_2 and CF_3 which make ready identification unambiguous from chemical shifts and coupling constants.

Collectively, the partially fluorinated neopentanes are semi-glassy to solid at room temperature. Slight decomposition occurs on sitting at room temperature to give a pinkish material which upon removal of volatile materials leaves behind a brown, viscous liquid. All the partially fluorinated neopentanes are very much less volatile than perfluoroneopentane. The fluorination conditions used were similiar to those described by Maraschin and Lagow,[16] except the pure fluorine stage was eliminated. By eliminating that step, one does not isolate any perfluoroneopentane. The fluorination becomes more difficult after the partially fluorinated compounds are produced. It appears necessary to go from about 8% fluorine to 100% fluorine to necessitate conversion to perfluoroneopentane at -78°. As can be seen from this experiment, one can stop the fluorination to yield only partially fluorinated materials. This experimental observation will be important in the discussion of the other Group IVA compounds, especially tetramethylsilane and tetramethylgermanium. In the original fluorination of neopentane,[16] only a 10.4% yield was obtained and therefore one would expect that partially fluorinated neopentanes were also present. We have demonstrated that all four possible groups, CF_3, CF_2H CFH_2 and CH_3, are present on the central carbon atom.

FLUORINATION OF TETRAMETHYLSILANE, $Si(CH_3)_4$

INTRODUCTION

Although there have been claims to the synthesis of $Si(CF_3)_4$,[46] there has not been any characterization of the compound. Many claims exist for CF_3 groups on silicon,[47] such as $Si(CF_3)Cl_3$[48] and $Si(CF_3)_2Cl_2$[11,48,49,50] but again no characterization of the compounds were given. It is interesting to note that the authors predicted interesting polymers resulting from the reactions, once one had $Si(CF_3)_4$.[50] Sequences of reactions were typically,

$$CF_3MgI + SiCl_4 \longrightarrow (CF_3)_2SiCl_2$$

$$CF_3Li + SiCl_4 \longrightarrow (CF_3)_2SiCl_2 + (CF_3)SiCl_3 \ .$$

However, the well-characterized perfluoroalkyl silicon compounds remain CF_3SiF_2X, X = Cl, Br, I, F,[51,52] $C_2F_5SiF_3$,[53] $C_3F_7SiF_3$[54] and $CF_3SiF_2SiF_3$.[54]

Perfluoroalkyl silicon compounds have been subject of much discussion in terms of both α- and β- elimination to form a carbene and Si-F.[55,56,57] Much of the work has been done by Haszeldine and his coworkers[55] on polyfluoroalkylsilanes. The difficulty in making trifluoromethylsilanes has limited study to Si-CF_3 as a facile source of difluorocarbene.

Several compounds were known with fluorine on a methyl group on silicon. Two are $Si(CH_3)_3(CH_2F)$[58] and $Si(C_2H_5)_3(CFClH)$[59]. Chlorinated methyl groups on tetramethylsilane are known.[60,61] Eaborn[62] made note that since one was able to chlorinate tetramethylsilane,[63] the Si-C bond was fairly stable towards homolytic cleavage. It was surprising that cleavage of a C-H bond occurred more rapidly than a Si-C bond. Therefore, knowing that the reactivity of fluorine to be greater than that of chlorine, we thought it might be possible to isolate some fluorinated tetramethylsilane species without too many bond cleavages. If the reaction conditions were chosen carefully enough, we felt there might be a reasonable chance to isolate $Si(CF_3)_4$. With this in mind, we proceeded to study the reaction of fluorine with tetramethylsilane.

EXPERIMENTAL

Reaction 1.

Zone 1 of the 4-zone low temperature reactor was cooled to -150°. With a helium flow of 30 cc/minute, 1.0 ml of $Si(CH_3)_4$ was syringed into the reactor through a swagelok T-assembly. After purging for about ½ hour, the following reaction conditions were used.

F_2 (cc/minute)	He (cc/minute)	Zone	Time
0.5	30	1 (-150)	28.5 hours
0.5	30	2 (-150)	18.5
1.0	25	3 (-150)	6
1.0	5	3 (-150)	6.5
1.0	5	4 (-150)	20.5
0.0	30	4 (-150)	3
0.0	100	1,2,3,4 (RT)	16

The volatile materials were separated into -131° and -196° traps. Residue pressure of 10-15 microns was present for several hours, indicating the presence of a large quantity of CF_4.

The material which stopped in the -196° fraction was mainly CF_4, CF_3H and SiF_4. The material in the -131° trap was sent through the gas chromatograph, with a gas chromatograph program of:

SE-30, 3/8" x 25'
0° isothermal for 43.45'
5° per minute to 160°.

The peaks which came out before tetramethylsilane were fluorocarbons as identified by infrared and mass spectra. There was one major peak after tetramethylsilane with an approximate retention time of 71'.

Mass spectrum, along with infrared and NMR spectra, confirmed the compound to be $Si(CH_3)_3(CH_2F)$. The physical data for the compound is listed in the tables to follow and was in good agreement to that previously reported.[58]

Reaction 2.

1.0 ml tetramethylsilane was syringed into the low temperature zone reactor with zone 1 at -130°. A helium flow of 30 cc/minute was used to flush the reactor. The following reaction conditions were then used.

F_2 (cc/minute)	He (cc/minute)	Zone	Time
0.5	30	1 (-130)	24 hours
0.5	30	2 (-130)	24
0.5	30	3 (-130)	24
0.5	30	4 (-130)	24
0.0	30	4 (-130)	9
0.0	100	1,2,3,4, (RT)	18

The volatile materials were separated into -131° and -196° fractions. The -196° fraction contained mainly fluorocarbons and SiF_4. A considerable quantity of CF_4 was present. A gas chromatograph of the -131° fraction showed 5 major peaks, each containing Si, C, H, and F from the mass spectra. The peaks of lowest retention time were identified as fluorocarbons.

Using the following program,

SE-30, 3/8" x 25'
50^{o} isothermal for 65'
5^{o}/minute to 70^{o} for 30" ,

two peaks of major interest came out at 48'45" and 56'45". Using ^{1}H and ^{19}F NMR, the compounds were identified as $Si(CH_2F)_2(CHF_2)_2$ and $Si(CH_2F)_4$, respectively. Their spectral properties are listed in tables following. The other major peaks remained unidentified.

Reaction 3.

1.0 ml (7.35×10^{-3} mole) of $Si(CH_3)_4$ was syringed into the low temperature reactor with a helium flow of 30 cc/minute and with zone 2 at -120^{o}. After purging with helium for 1 hour, the fluorine flow was started. For 7 days, a fluorine flow of 0.5 cc/minute to the helium flow of 30 cc/minute was used. After purging the fluorine out of the system for eight hours, the reactor was allowed to warm up.

The volatile materials were separated into -131^{o} and -196^{o} fractions. The -196^{o} fraction contained mainly CF_4, CF_3H and SiF_4. There was present some CF_2=CH_2. The material which stopped in the -131 trap was gas chromatographed for peak distribution. There were seven major peaks of interest. Using the following program,

SE-30, 3/8" x 25'
0^{o} isothermal for 53.45"
1^{o}/minute to 30^{o} for 50 minutes
2.5^{o}/minute to 50^{o} for 50 minutes
185^{o} bake,

the peaks of interest had retention times between 2 -3.5 hours after air.

The infrared and mass spectra of all the material which came out before 2 hours showed mainly fluorocarbons. There was possibly some Si containing material but they were in extremely small quantities only. Several gas chromatograph runs were made and material collected for identification of the compounds. The compounds identified were $Si(CH_3)_2(CH_2F)_2$, $Si(CH_3)(CH_2F)_2(CHF_2)$, $Si(CH_2F)_3(CHF_2)$, and $Si(CH_2F)_4$. The other peaks collected showed the presence of several compounds, which required further separation. Infrared and mass spectra were taken of all the compounds. Spectral data has been compiled and presented in tabular form later.

Reaction 4.

Zone 2 of the low temperature reactor was cooled to -110°. With a helium flow of 30 cc/minute, 0.98 ml of tetramethylsilane was syringed into the reactor. After 1 hour, the following reaction conditions were used with zone 2 always cooled to the temperature indicated.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
0.5	30	-110	145 hours
1.0	30	-110	11
1.0	30	-100	50
1.0	30	-95	75
0.0	100	-95	18
0.0	100	RT	18

The volatile materials were separated on a vacuum line into -131° and -196° fractions. A considerable amount of CF_4 was present as evident by the pressure in the system. There was present greater than 1 ml of liquid in the -196° fraction, comprised mainly of CF_4, CF_3H and SiF_4.

A small amount, approximately 100 µl, of material stopped in the -131° trap. A gas chromatograph showed the presence of a few peaks not in previous gas chromatograph runs. Mass spectra showed these samples contained no silicon. Therefore the material was discarded.

Reaction 5.

Zone 2 was cooled to -110°. With a helium flow of 30 cc/minute, 1 ml of tetramethylsilane was syringed into the reactor. A flow of 0.5 cc/minute of fluorine to 30 cc/minute of helium was used for 10 days during which time the reactor was always cooled to -110°.

After the volatile materials were separated into -131° and -196° fractions, the -196° fraction was discarded. A gas chromatograph of a sample of the -131 fraction showed several peaks of interest not present in previous reactions. NMR and mass spectra showed the material to be partially fluorinated tetramethylsilanes again. However, there were two samples which showed a possibility of the presence of $Si-CF_3$ moiety. Both had resonances in the CF_3 region of the fluorine spectrum, one at -14.7 and the other at -12.6. Unfortunately there was very little of each and the coupling was unresolved. From the rest of the ^{19}F and ^{1}H spectra, it was known that there were also present CF_2H and CHF_2 type groups. The mass spectra of the two compounds showed silicon present but no 69, CF_3^+ peak was evident. (However, this is not too surprising since the CF_3^+ m/e for $SiF_3(CF_3)$[52] is very weak compared to the other m/e values in the spectrum.)

(These reaction conditions were repeated several times, with longer and shorter reaction times. Each time the amount of the two compounds of interest did not increase substantially. Each of the reactions using these conditions gave the resonances in the CF_3 region of the spectrum. But no new resonances appeared. One interesting feature was the presence of $C_2F_2H_2$ either as CF_2=CH_2 or CFH=CFH in several of the reactions.)

Reaction 6.

1.0 ml of tetramethylsilane was syringed into the reactor with zone 2 at -110°. For five days the temperature was kept at -110° and a fluorine flow of 1.0 cc/minute to a helium flow of 60 cc/minute was used. The reaction was continued with the temperature lowered to -120° and a fluorine flow of 5 cc/minute to a helium flow of 60 cc/minute. This was used for 3 days after which time the fluorine flow was terminated and the reactor purged with helium.

The volatile materials were separated into -131° and -196° fractions. There was very little material in the -196° fraction. However, a gas chromatograph of the material which stopped in a -131° trap showed no new compounds from earlier reactions although peak distributions were different. This material was kept for future sample collection and separation.

Reaction 7.

1.0 ml of tetramethylsilane was syringed into the reactor with zone 2 at -110° with a helium flow of 120 cc/minute. A fluorine flow of 1.5 cc/minute to a helium flow of 20 cc/minute was used for 2 days. Then the helium flow was stopped and the fluorine flow continued for 3 days. After purging the system of fluorine, the volatile materials were separated into -131° and -196° fractions. There was a considerable amount of material in the -196° fraction, consisting of mainly CF_4, CF_3H and SiF_4.

A gas chromatograph of the material which stopped in the -131° trap showed far fewer compounds than before. It was noted also that more $C_2F_2H_2$ was present than in other reactions. Also present in larger than normal quantities were $Si(CH_2F)_2(CHF_2)_2$ and $Si(CH_2F)_3(CHF_2)$. However, there were no compounds present which had the possibility of a CF_3 group on silicon. The material was saved for future complete separation.

Reaction 8.

1.0 ml of tetramethylsilane was syringed into the reactor with a helium flow of 120 cc/minute. Zone 2 was cooled to -120°. The following reaction conditions were then used with zone 2 being cooled at all times.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
1.0	60	-110	48 hours
1.0	60	-108	1
1.0	60	-106	1
1.0	60	-104	1
1.0	60	-102	1
1.0	60	-100	23
1.0	60	-98	6
1.0	60	-96	13
1.0	60	-94	10
1.0	60	-92	3
0.0	60	-92	24
0.0	60	RT	24

Separation of the volatile materials gave about ½ ml of liquid in the -131°fraction. A gas chromatograph of a sample of the -131° fraction showed some possible CF_3 containing silicon compounds. However, the quantity of material was very small. The other polyfluorotetramethylsilane compounds were also present. This material was kept for future separation.

Reaction 9.

1.0 ml of tetramethylsilane was syringed into the reactor with zone 2 at -110°. A helium flow of 100 cc/minute was used. The following reaction conditions were used with zone 2 cooled at all times.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
1.0	60	-100	52 hours
1.0	60	-90	16
1.0	60	-80	8
1.0	60	-70	14
1.0	60	-60	10
1.0	60	-50	14
1.0	60	-40	10
1.0	60	-30	14
1.0	60	-20	10
0.0	60	-20	13
0.0	60	RT	24

Separation of the volatile materials into -131° and -196° fractions showed the presence of large quantities of CF_4, CF_3H and SiF_4, as almost exclusive products in the -196° fraction. Very little material was in the -131° trap. There was no evidence of $Si(CF_3)_4$. Only partially fluorinated material was present and in small quantities. Higher fluorocarbons were also present.

(Reactions involving raising the temperature from -110° to other higher temperatures were tried with various terminating temperatures, e.g. -80°, -60° and -40°. All showed considerable amounts of CF_4, CF_3H and SiF_4 and very little other silicon containing materials.)

Separation of Partially Fluorinated Tetramethylsilanes.

Material from several of the tetramethylsilane reactions were collected. 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 materials.

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 μl of sample was injected with an air-tight syringe each time. The compounds of interest came out over a time span from 108'30" to 255'50". Compounds which came out earlier 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 apparently decomposition products. Seventeen different peaks were collected. These compounds from the gas chromatograph separation were sealed off in glass tubes for ^{1}H 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 on the following pages. Several samples were sent for elemental analysis. However, the samples upon combustion destroyed several analyzers at Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Note of Caution: In handling the partially fluorinated tetramethylsilanes, one should be cognizant of possible unexplained explosions, leaving mainly carbon deposits.

DISCUSSION

From all the experiments done, of which a few representative ones have been described in the experimental section, there appears to be no evidence for the synthesis of $Si(CF_3)_4$, or at least none was isolated. The stability of $Si(CF_3)_4$ will be discussed later. However, of foremost importance is, 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, $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$. The question as to why $Si(CF_3)_4$ 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 a few compounds containing $Si\text{-}CF_3$ bonds.

In an effort to prepare $Si(CF_3)_4$, 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 and fluorine flow with varying length of reaction. All conditions which were tried were unsuccessful in producing $Si(CF_3)_4$. However, some conditions were better than others in preparing the partially fluorinated tetramethylsilanes. Several conditions produced more highly fluorinated species than others but the best condition for the preparation of $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$ was the following:

$$Si(CH_3)_4 + F_2/He \xrightarrow[7\text{ days}]{-110^0} Si(CH_3)_x(CH_2F)_y(CHF_2)_z,\ x + y + z = 4$$

with F_2/He flow ratio of 1.0/60 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, e.g. higher fluorine concentrations and higher temperatures, in an effort to produce $Si(CF_3)_4$. However, this was not successful. Aside from the two compounds reported here with $Si\text{-}CF_3$ bonds and several alluded to in the experimental section, one was unable to produce large quantities of $Si\text{-}CF_3$ 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 several compounds being present and the inability to separate the compounds. Tabulated on the next pages are the spectral and physical data for the partially fluorinated tetramethylsilanes.

Table I. Proton NMR Spectra of Polyfluorotetramethylsilane

Compound	CH_3	CH_2F^*	J_{HF}	CHF_2^{**}	J_{HF}
$Si(CH_3)_3(CH_2F)^1$	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	5.69	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

* doublet

** triplet

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

[1] Literature: Ref. 58
CH_3(0.31) CH_2F(4.53) J_{HF}=46.8 $J_{H'F}$=0.7.

Table II. Fluorine NMR Spectra of Polyfluorotetramethylsilane

Compound	CF_3	CHF_2*	J_{HF}	CH_2F**	J_{HF}
$Si(CH_3)_3(CH_2F)$[1]				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[a]	199.60	47.0[b]
$Si(CH_2F)_4$				201.13	46.9
$Si(CH_3)(CH_2F)(CHF_2)_2$		60.85	45.7[c]	201.00	46.7[d]
$Si(CH_3)(CH_2F)_2(CF_3)$	-15.48[e]			199.92	46.3
$Si(CH_2F)_3(CHF_2)$		60.03	45.4[f]	201.41	46.6[g]
$Si(CH_3)(CH_2F)(CHF_2)(CF_3)$	-16.53[h]	61.15	45.0	201.19	+
$Si(CH_2F)_2(CHF_2)_2$		58.88	45.4[i]	202.87	46.4[j]
$Si(CH_2F)(CHF_2)_3$		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: Ref. 58

a J_{FF}=1.4 (triplet)

b J_{FF}=1.5 (multiplet)
$J_{H'F}\approx1.0$

c J_{FF}=1.8 (doublet)

d J_{FF}=1.4 (multiplet)
$J_{H'F}\approx0.5$

e J_{FF}=3.2 (quartet of triplets)
$J_{H'F}\approx1.0$

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
$J_{H'F}\approx0.4$

Table III. Mass Spectra of Polyfluorotetramethylsilane*

$Si(CH_3)_3(CH_2F)$ 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)
$Si(CH_3)_3(CHF_2)$ 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)
$Si(CH_3)(CH_2F)_3$ 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)
$Si(CH_3)(CH_2F)_2(CHF_2)$ 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)
$Si(CH_2F)_4$ 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)
$Si(CH_3)(CH_2F)(CHF_2)_2$ 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)
$Si(CH_3)(CH_2F)_2(CF_3)$ MW=178.18	163 (0.4) 149(5) 145(2) 117(4) 99(14) 95(19) 85(30) 81(100) 80(8) 61(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)
$Si(CH_2F)_3(CHF_2)$ MW=178.18	117(4) 99(47) 85(77) 80(14) 51(33) 47(42) 33(100) 27(50) 26(12) 14(18)
$Si(CH_3)(CH_2F)(CHF_2)(CF_3)$ 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)

Table III. (continued)

$Si(CH_2F)_2(CHF_2)_2$	117(10)	99(62)	85(100)	81(11)	51(97)	47(55)	33(94)	31(17)	
MW=196.18	29(26)	27(72)	26(14)	15(8)	14(22)				
$Si(CH_2F)(CHF_2)_3$	117(8)	99(22)	85(58)	81(100)	67(17)	64(16)	51(39)	47(62)	
MW=214.16	45(38)	33(42)	31(11)	29(17)	27(52)	26(17)	15(12)	14(11)	
Literature: Ref. 58									
$Si(CH_3)_3(CH_2F)$	77(12)	73(100)	63(54)	59(4)	49(8)	47(15)	45(30)	43(14)	29(7)
MW=106.22									

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

Table IV. Infrared Spectra of Polyfluorotetramethylsilane

$Si(CH_3)_3(CH_2F)$	2980(sh) 2960(s) 1870(m) 1425(m) 1255(vs) 1200-1100(br) 1060(s) 1000(vs) 850(vvs) 755(s) 700(s)
$Si(CH_3)_3(CHF_2)$	2960(m) 1408(m) 1320(s) 1291(s) 1260(s) 1239(s) 1100(vs) 1030(vs) 910(s) 800(s) 700(w)
$Si(CH_3)(CH_2F)_3$	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)
$Si(CH_3)(CH_2F)_2(CHF_2)$	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)
$Si(CH_2F)_4$	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)
$Si(CH_3)(CH_2F)(CHF_2)_2$	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)
$Si(CH_3)(CH_2F)_2(CF_3)$	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)
$Si(CH_2F)_3(CHF_2)$	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)

Table IV. (continued)

$Si(CH_3)(CH_2F)(CHF_2)(CF_3)$	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)
$Si(CH_2F)_2(CHF_2)_2$	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)
$Si(CH_2F)(CHF_2)_3$	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)

All numbers in cm^{-1}.

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

Literature: Ref. 58

$Si(CH_3)_3(CH_2F)$	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

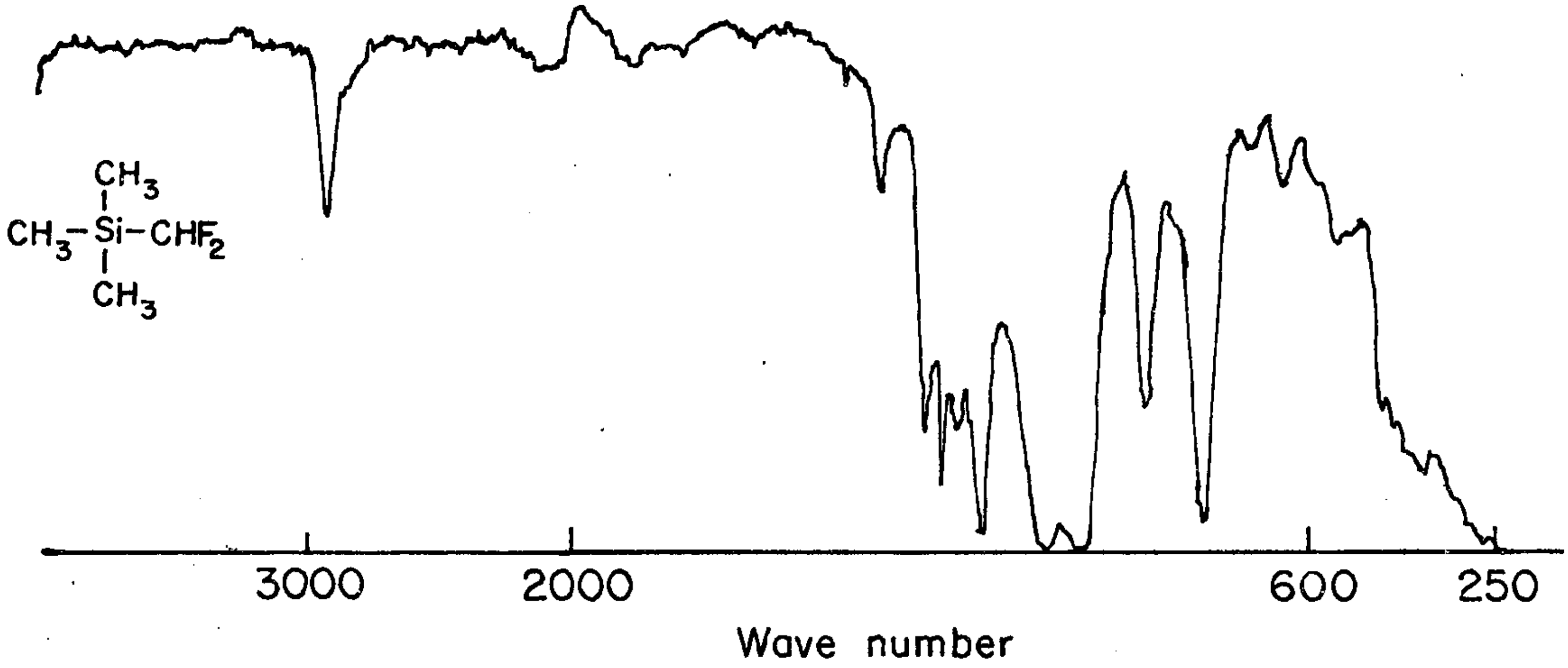


Figure 2. Infrared Spectrum of $Si(CH_3)_3(CHF_2)$

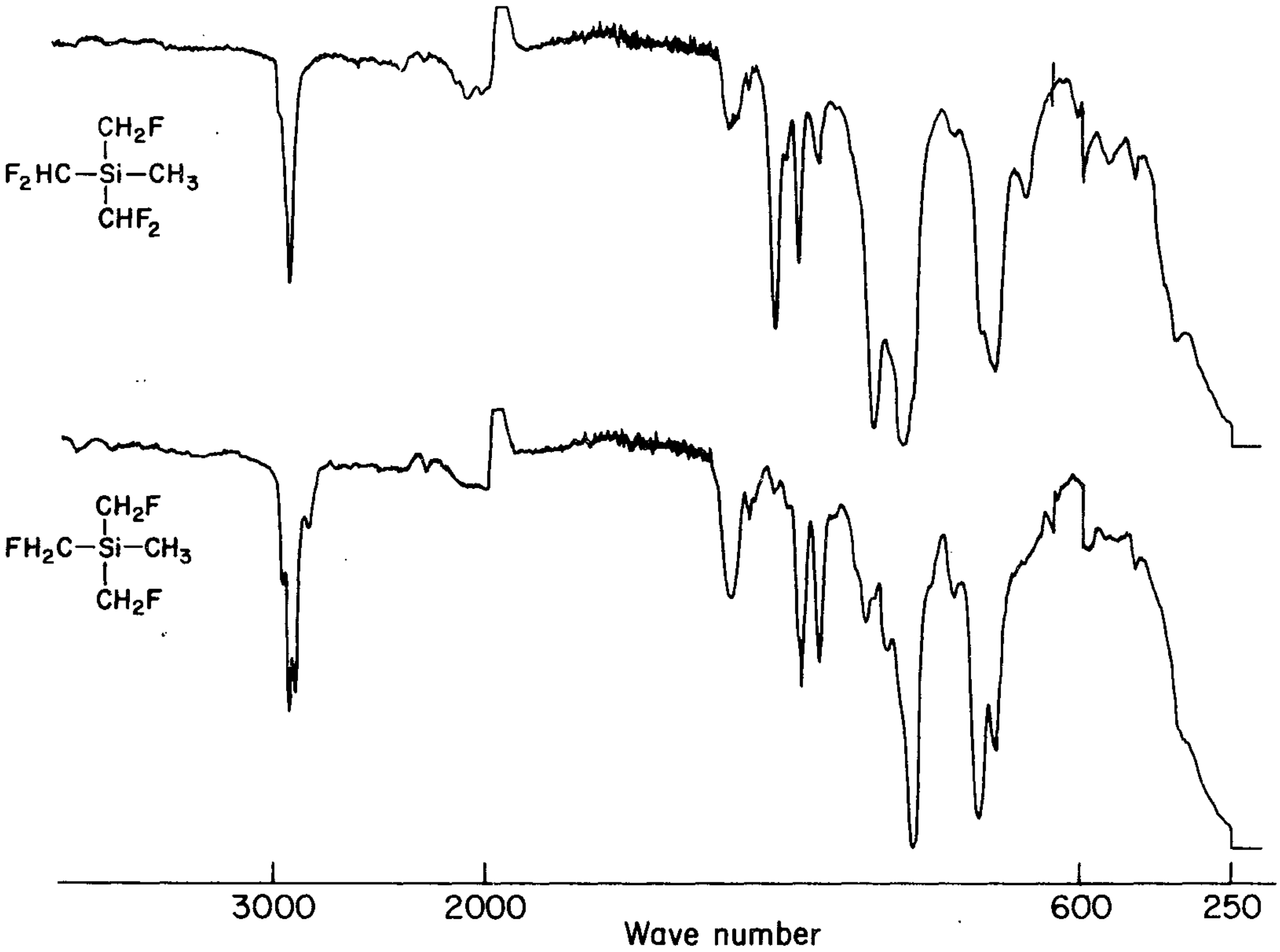


Figure 3. Infrared spectra of $Si(CH_3)(CH_2F)(CHF_2)_2$ and $Si(CH_3)(CH_2F)_3$

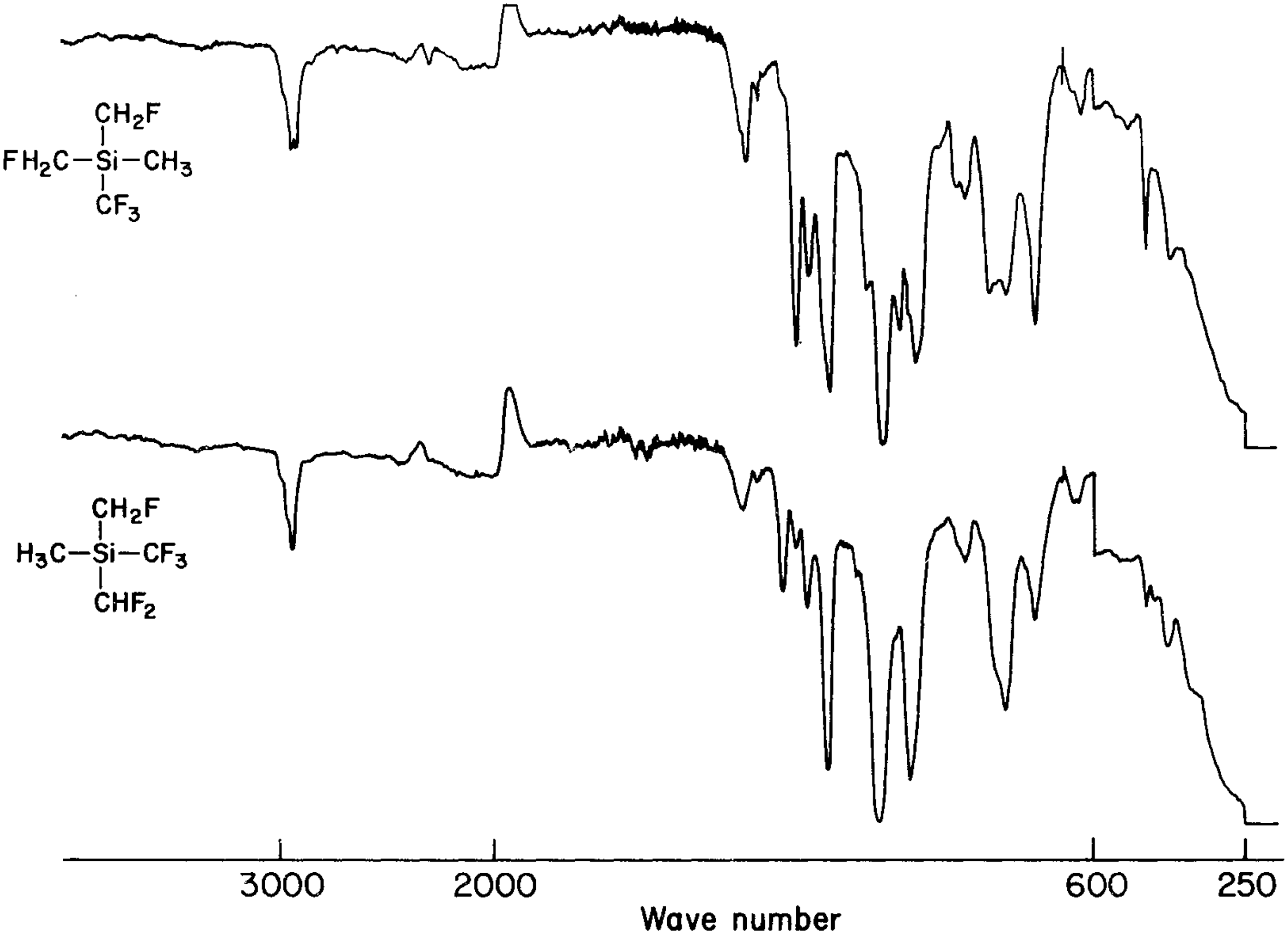


Figure 4. Infrared spectra of $Si(CH_3)(CH_2F)(CHF_2)(CF_3)$ and $Si(CH_3)(CH_2F)_2(CF_3)$

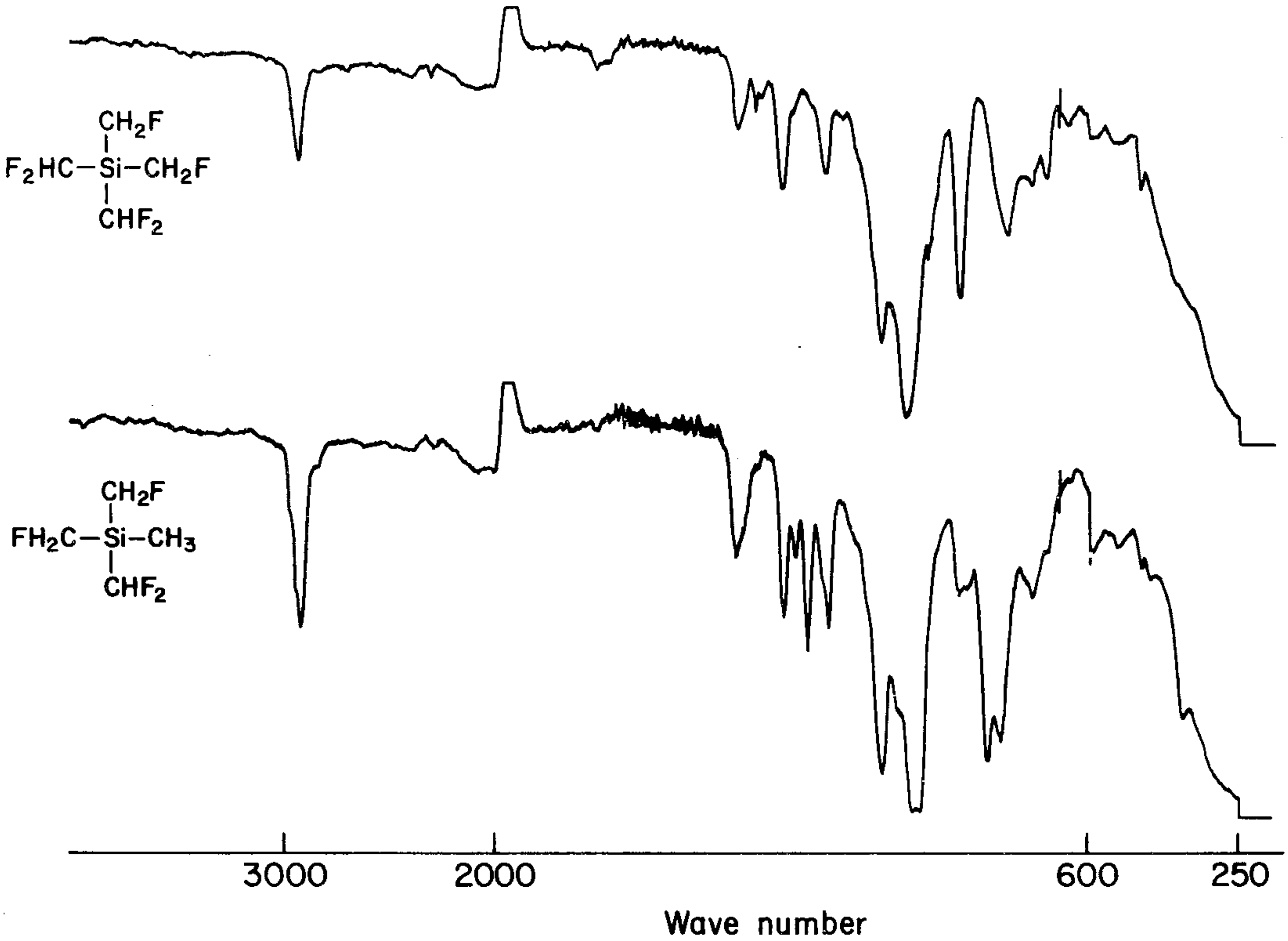


Figure 5. Infrared spectra of $Si(CH_3)(CH_2F)_2(CHF_2)$ and $Si(CH_2F)_2(CHF_2)_2$

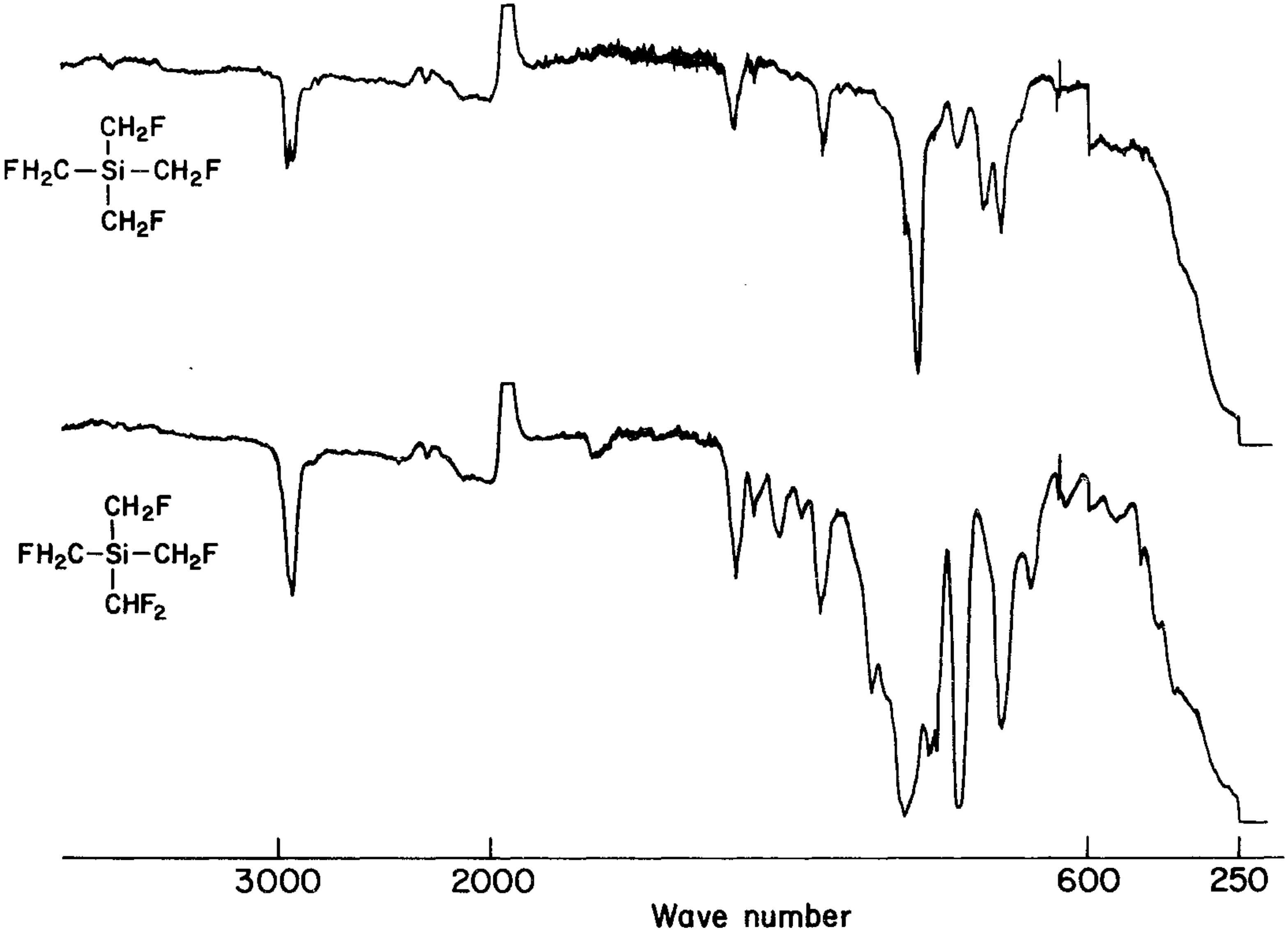


Figure 6. Infrared spectra of $Si(CH_2F)_3(CHF_2)$ and $Si(CH_2F)_4$

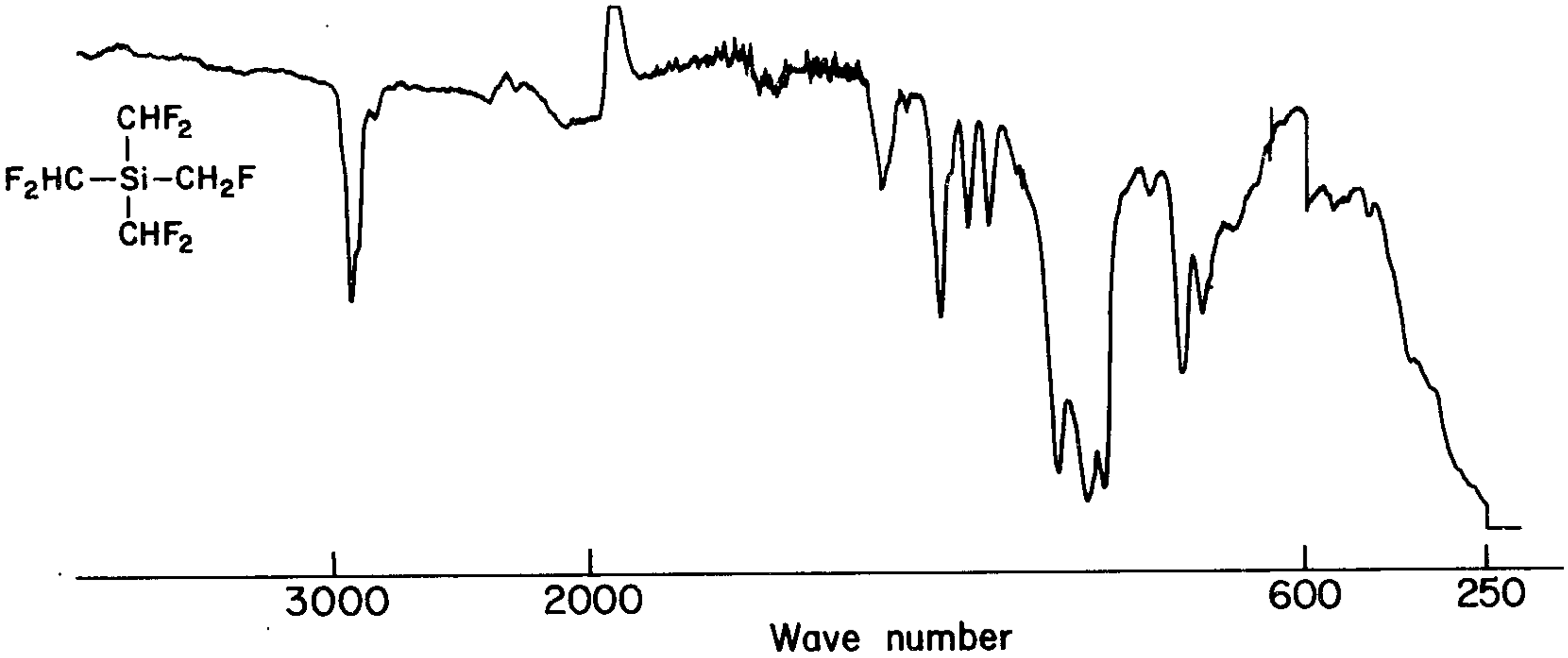


Figure 7. Infrared spectrum of $Si(CH_2F)(CHF_2)_3$

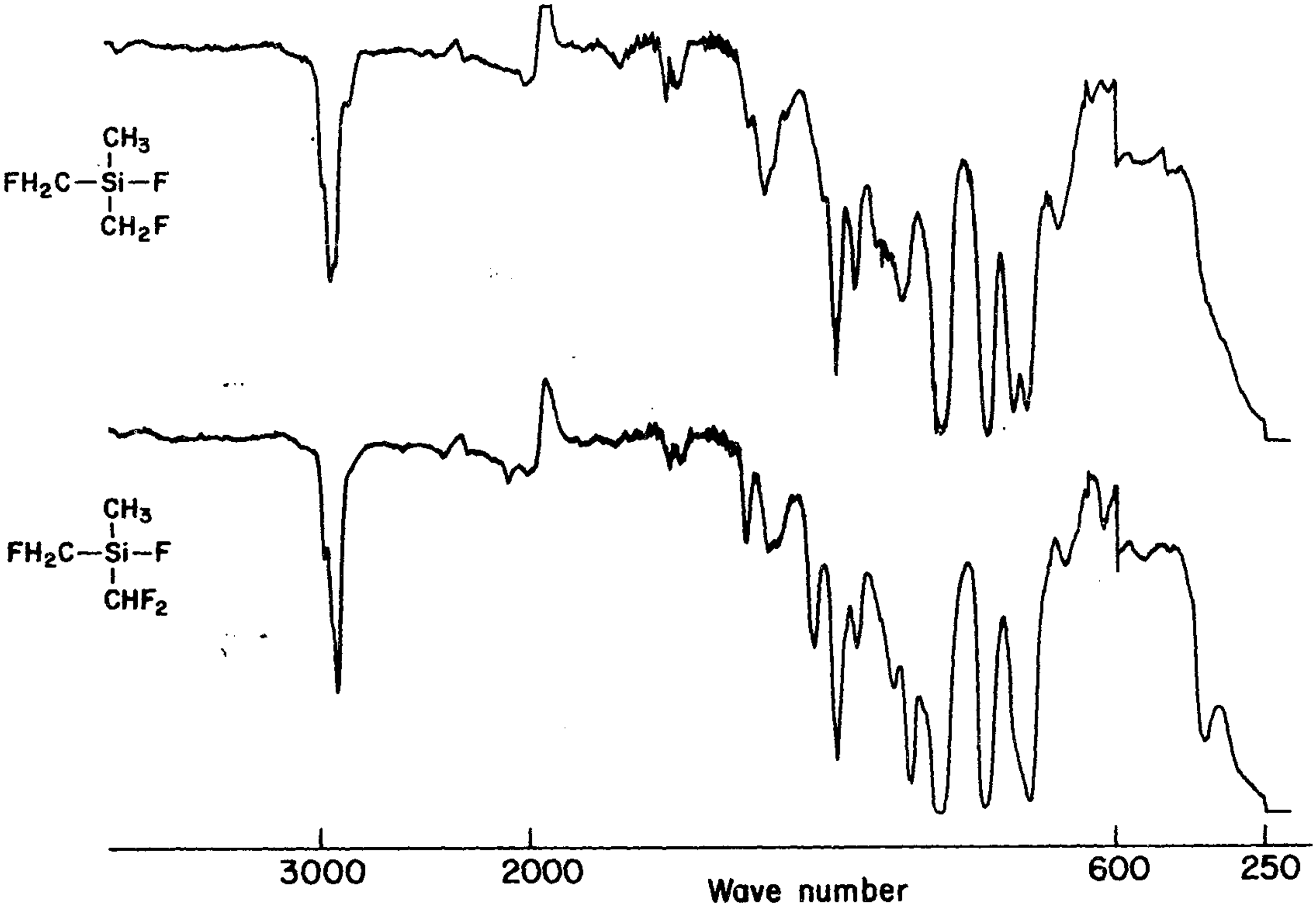


Figure 8. Infrared spectra of $Si(CH_3)(CH_2F)(CHF_2)F$ and $Si(CH_3)(CH_2F)_2F$

Table V . Melting Points of Polyfluorotetramethylsilane

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

Nuclear Magnetic Resonance. The proton and fluorine NMR's of the polyfluorotetramethylsilane compounds are summarized in Tables 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 to 47.5 hz while that for the CHF_2 group range from 45.0 to 46.2 hz. (An 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_{HF} is 52 hz.) These coupling constants were in good agreement with those obtained in the fluorine NMR.

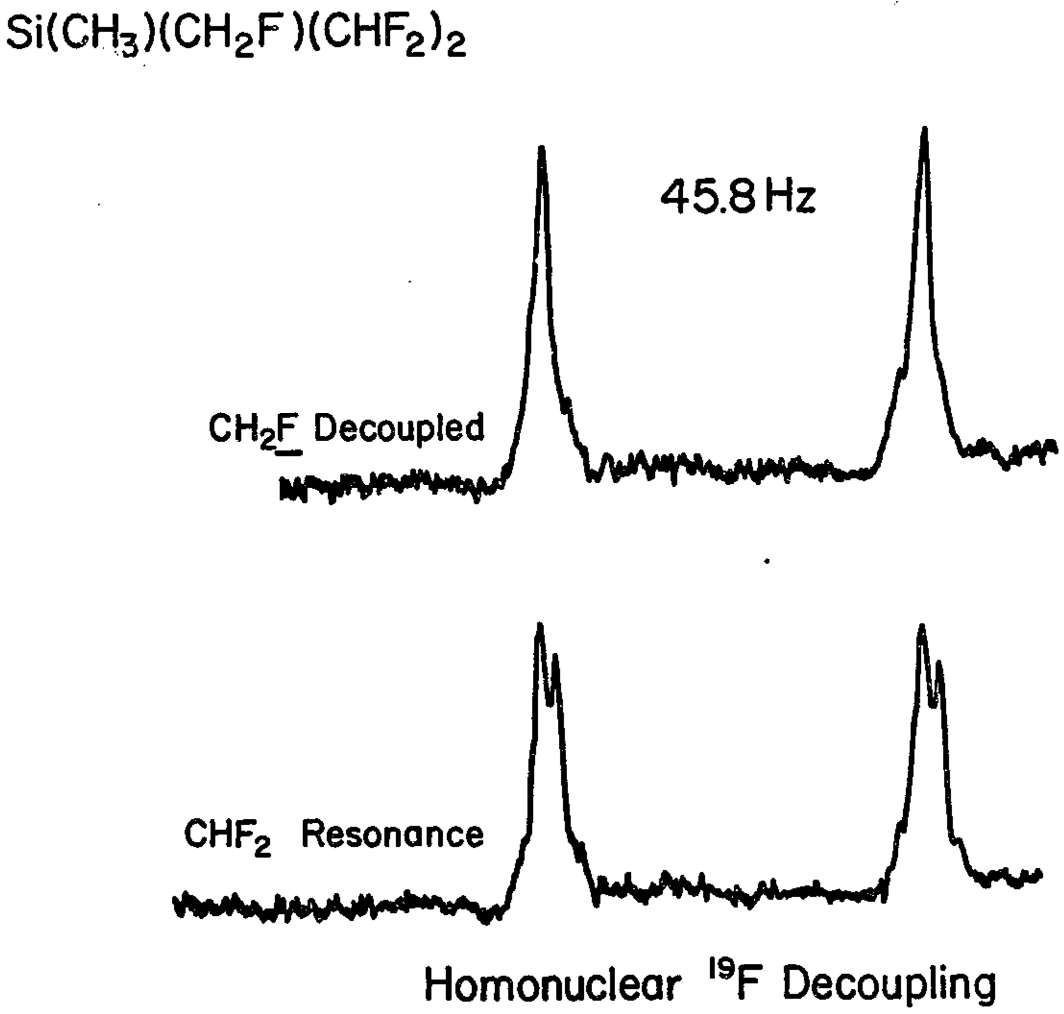
Characteristic resonances also appear in the fluorine NMR spectra. The CH_2F groups appear as triplets from H-F coupling. Coupling constants range from 46.3 - 47.1 hz, in good agreement with that obtained in the proton spectra. Chemical shifts for the CH_2F groups fall between 195.14 - 204.39 ppm upfield 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 resonances 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 chemical shifts for $M(CF_3)_4$, M = C, Ge, Sn, one can predict that the ^{19}F resonance for $Si(CF_3)_4$ will be around -21 ppm downfield from trifluoroacetic acid. For $Si(CF_3)F_3$, the CF_3 resonance is about -10 ppm downfield from TFA.[52] 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 belief. (See figures 9-12.) 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 the groups on silicon. These were not well resolved, even through fourier transform NMR spectra. 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.)[58]

If one plots chemical shifts of the groups, CH_3, CH_2F, CHF_2 and CF_3, against the total number of fluorines on the molecule, one obtains the following results:

a) ^{1}H chemical shift of CH_3 group versus number of fluorine atoms. There is a shift to more positive values with increasing number of fluorine atoms when one considers a plot versus number of CH_3 groups on the molecule.

b) There is a slight shift to more positive chemical shifts (more deshielding) for both the CH_2F and CHF_2 groups in the ^{1}H spectra.



$Si(CH_3)(CH_2F)(CHF_2)_2$
45.8 Hz
$CH_2\underline{F}$ Decoupled
CHF_2 Resonance
Homonuclear ^{19}F Decoupling

Figure 9.

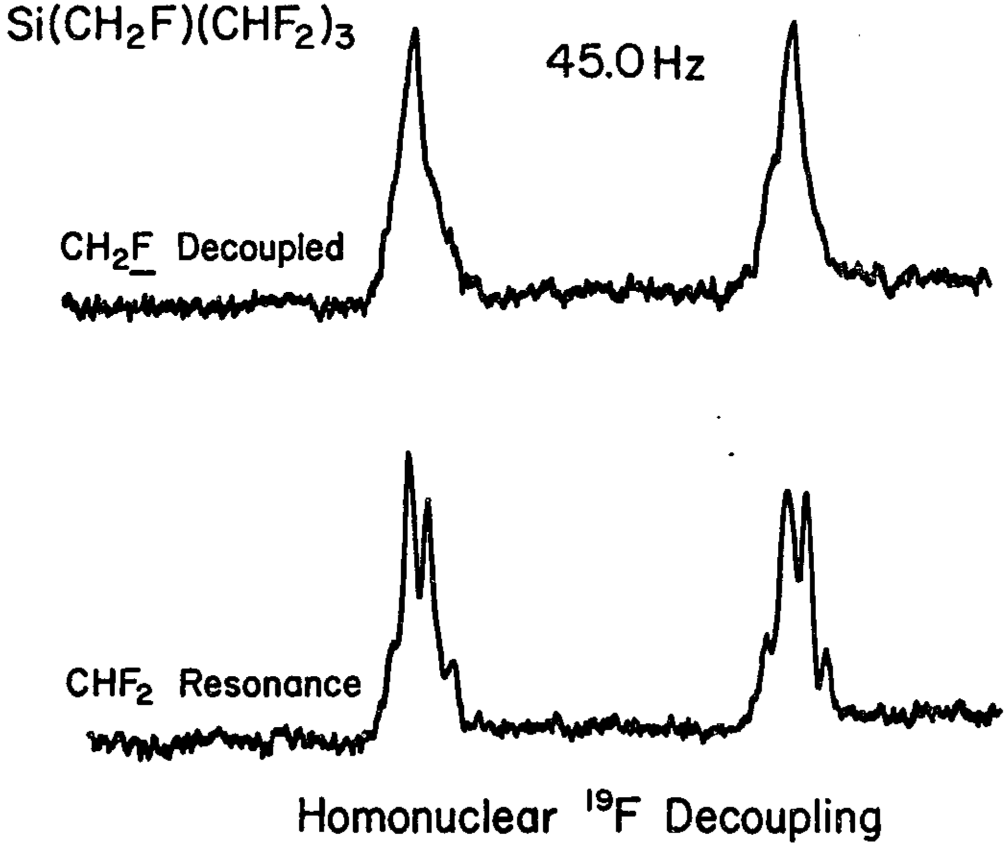

$Si(CH_2F)(CHF_2)_3$
45.0 Hz
$CH_2\underline{F}$ Decoupled
CHF_2 Resonance
Homonuclear ^{19}F Decoupling

Figure 10.

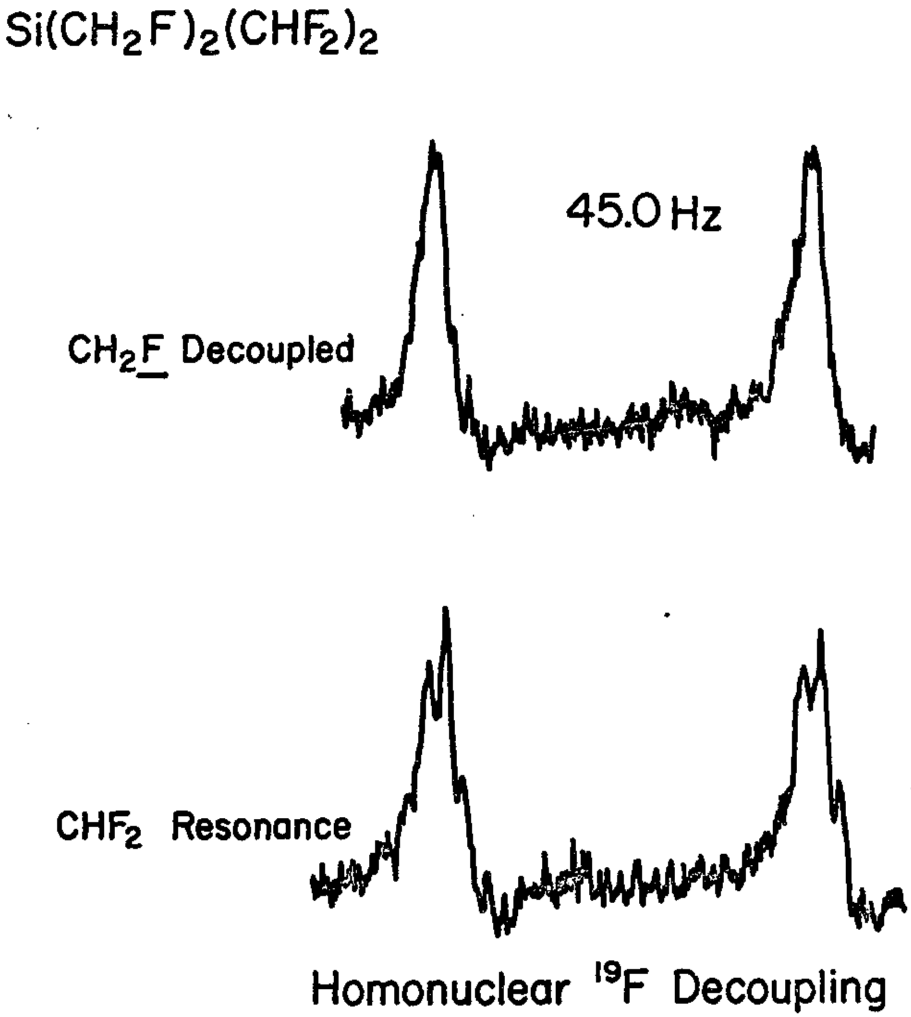

Si(CH$_2$F)$_2$(CHF$_2$)$_2$
45.0 Hz
CH$_2$F Decoupled
CHF$_2$ Resonance
Homonuclear ^{19}F Decoupling

Figure 11.

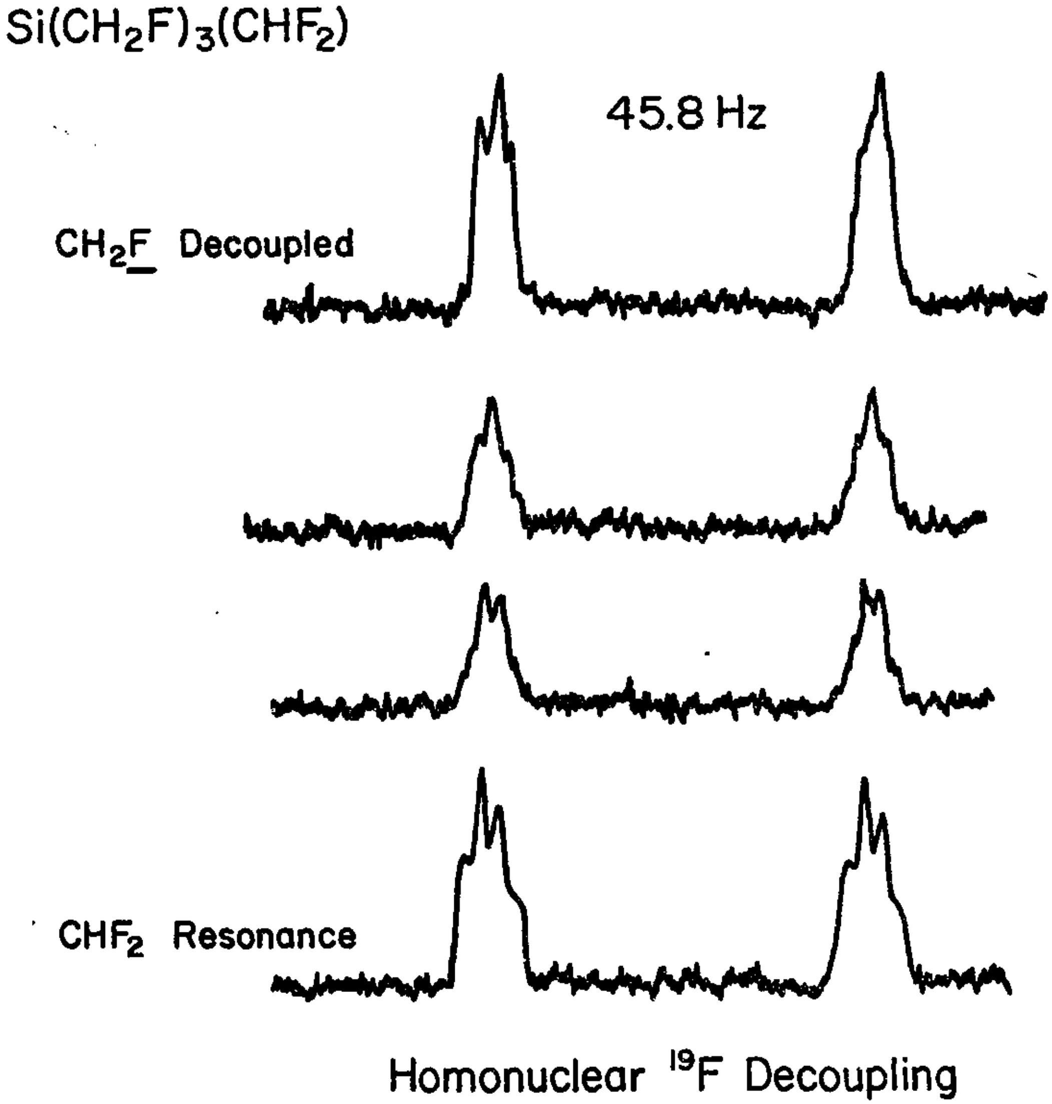
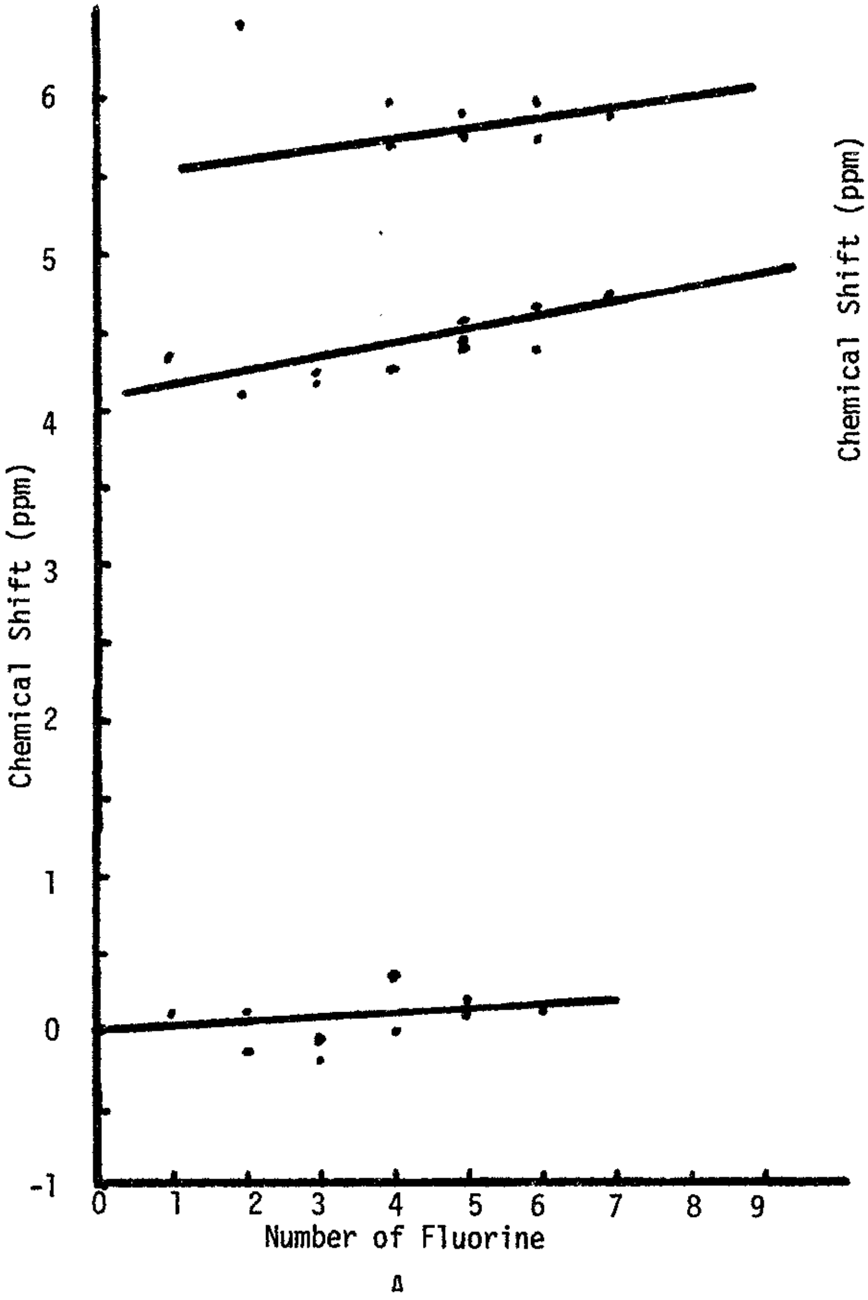

Si(CH_2F)$_3$(CHF_2)
45.8 Hz
$CH_2\underline{F}$ Decoupled
CHF_2 Resonance
Homonuclear ^{19}F Decoupling

Figure 12.



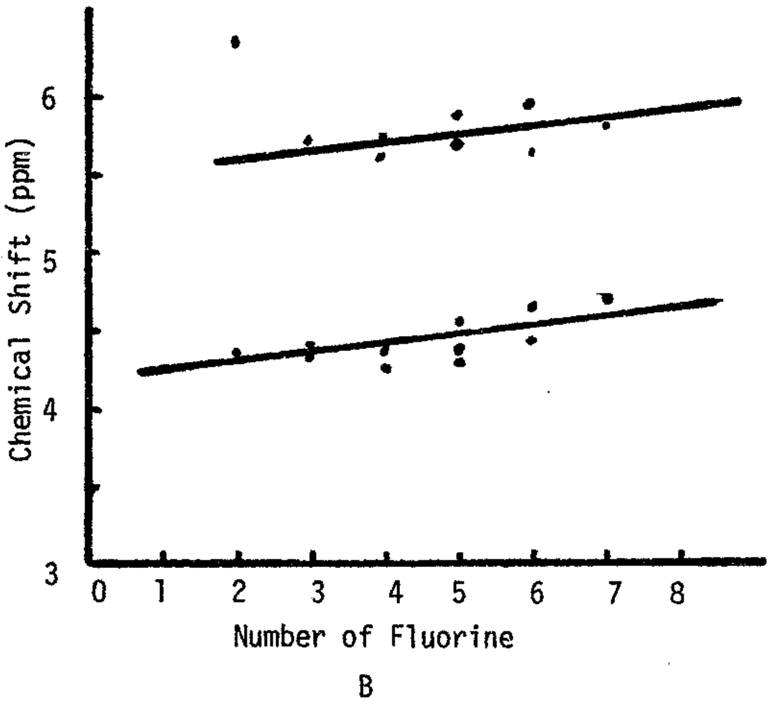
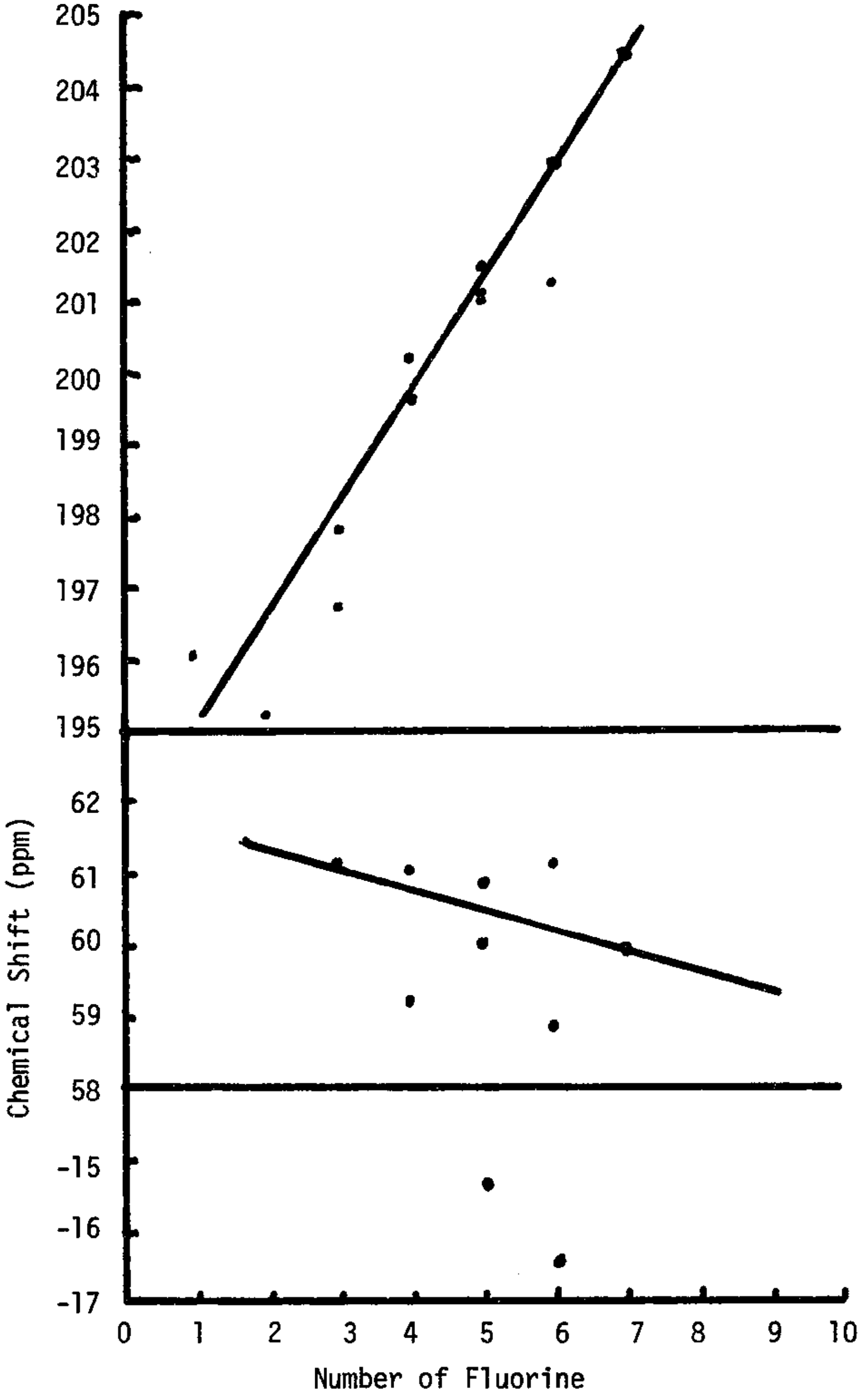


Figure 13.

^1H Chemical Shift vs. Number of Fluorine on $Si(CH_3)_4$

A Experimental chemical shifts.

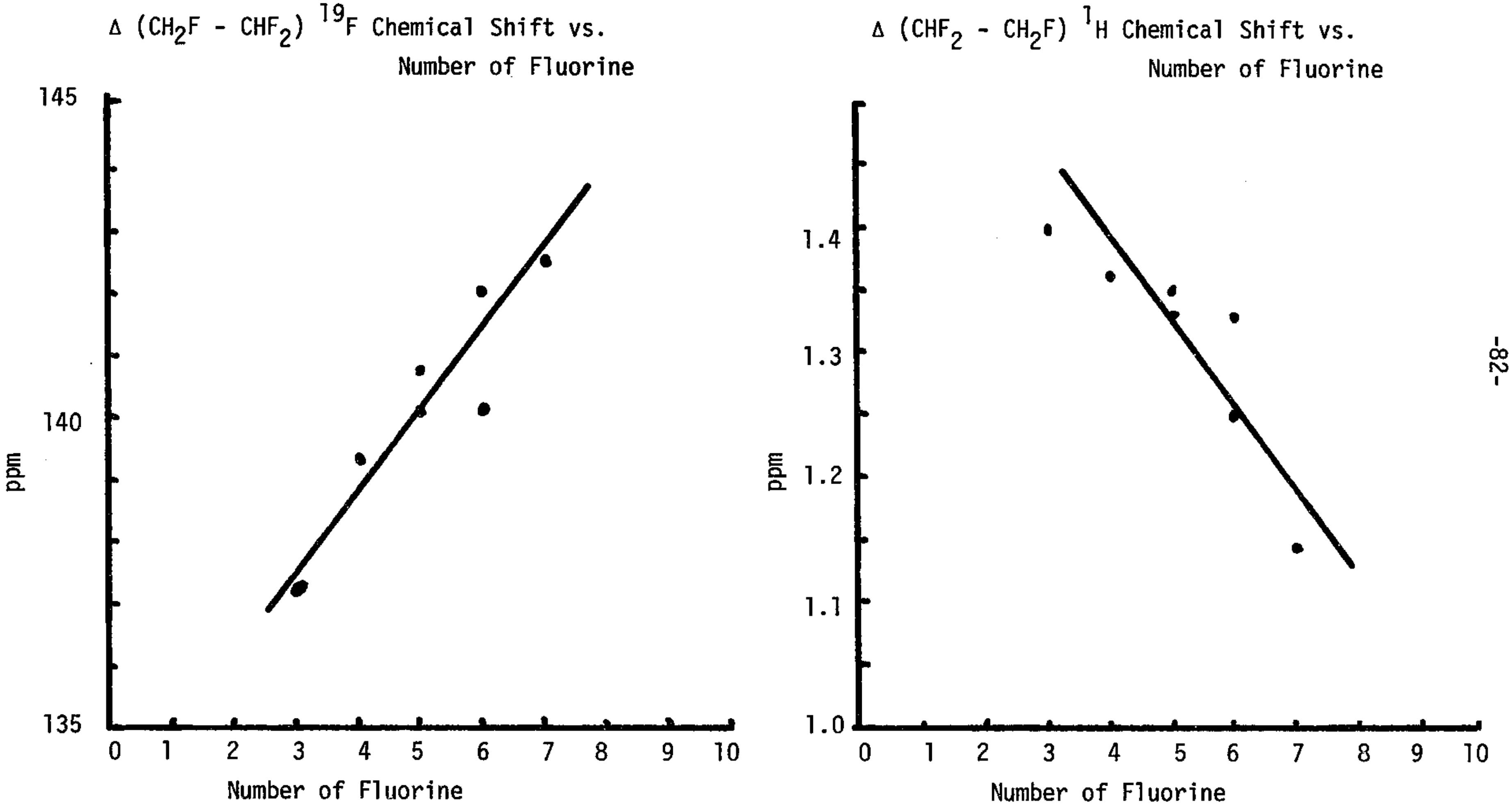
B Chemical shifts with $CH_3 = 0$.



^{19}F Chemical Shift vs. Number of Fluorine on $Si(CH_3)_4$

Figure 14.

Tetramethylsilane


Δ $(CH_2F - CHF_2)$ ^{19}F Chemical Shift vs. Number of Fluorine

Δ $(CHF_2 - CH_2F)$ ^{1}H Chemical Shift vs. Number of Fluorine

Figure 15.

c) ^{19}F chemical shifts of the CH_2F group gets larger as the total number of fluorine atoms on the molecule increases.

d) ^{19}F chemical shifts of the CHF_2 group gets smaller as the total number of fluorine atoms increases.

e) A plot of $\Delta(CH_2F - CHF_2)$ ^{19}F chemical shifts shows an increasingly larger difference as the number of fluorine atoms increase.

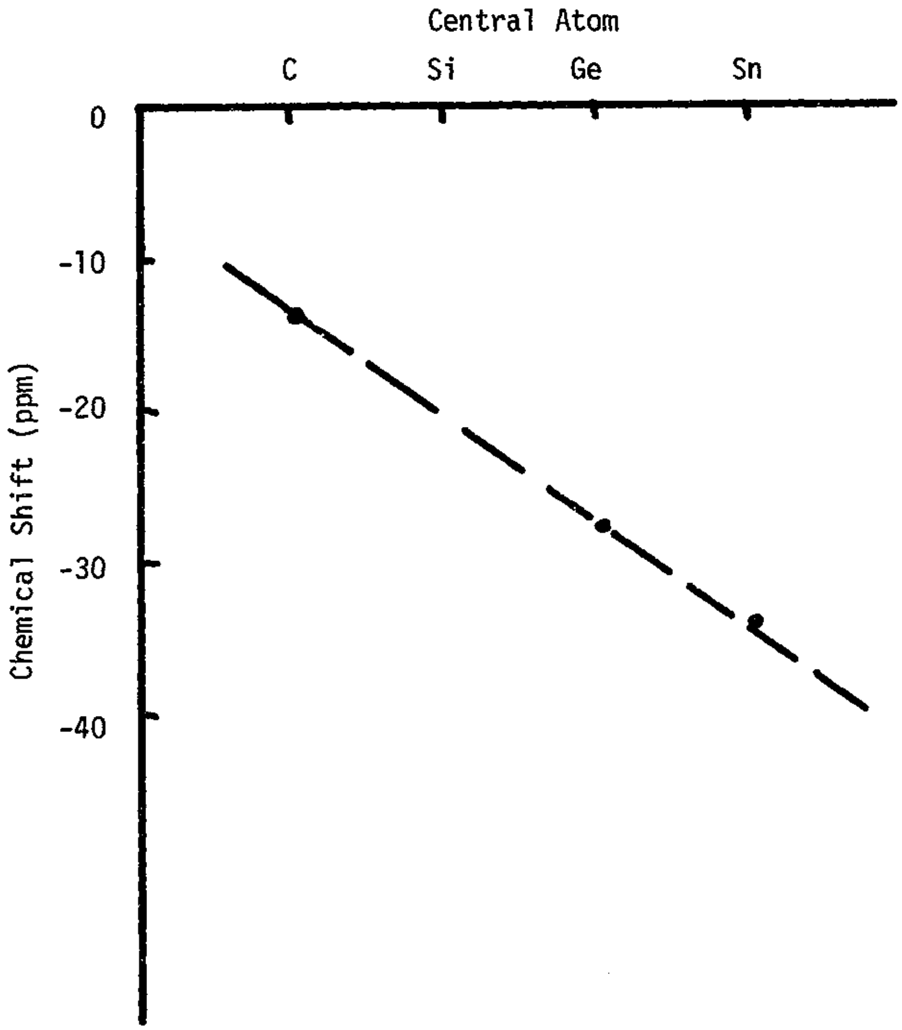
f) A plot of $\Delta(CHF_2 - CH_2F)$ ^{1}H chemical shifts versus total number of fluorine atoms shows a smaller difference with increasing number of fluorine atoms.

g) Insufficient compounds with CF_3 groups present does not render a plot of CF_3 chemical shifts versus total number of fluorine atoms meaningful.

If one were to plot the CF_3 chemical shift versus some arbitrary unit for the Group IVA compounds, one could extrapolate where a $Si\text{-}CF_3$ group would appear and more importantly, where $Si(CF_3)_4$ might appear. A plot of chemical shifts versus an arbitrary distance for C, Si, Ge, and Sn is shown on the following page. The $Si(CF_3)_4$ is predicted to come at approximately -21 ppm downfield from trifluoroacetic acid. Further comments will be given later to this prediction and its merit.

It should be noted that for the partially fluorinated tetramethylsilanes, J_{HF} for $CH_2F > CHF_2$. This is the reverse of that observed for the partially fluorinated neopentane compounds. Also J_{FF} for the two compounds with $Si\text{-}CF_3$ 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 spectral



CF_3 Chemical Shift vs. Central Atom (C, Si, Ge, Sn)

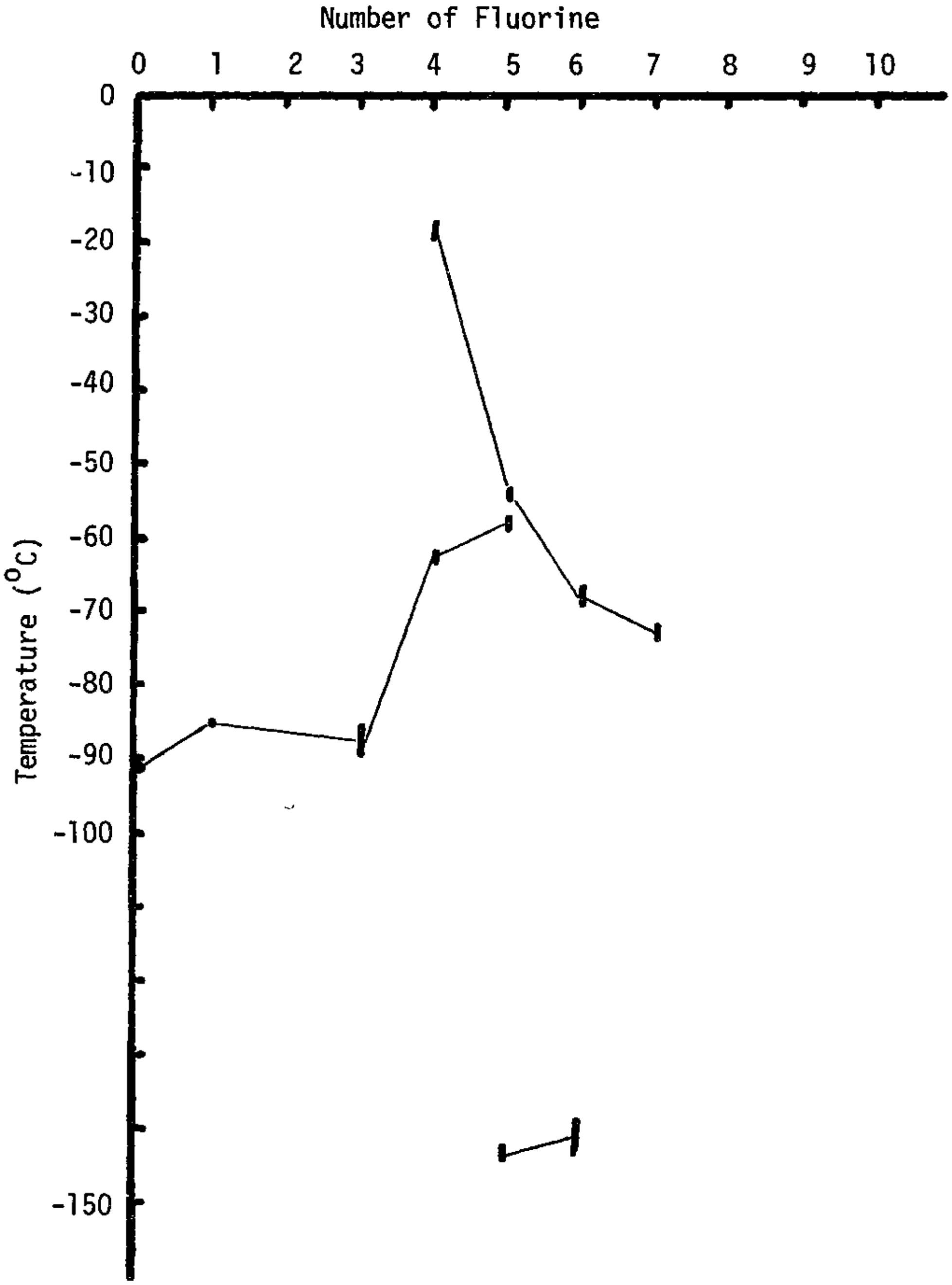
Figure 16.

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. (Extensive redistribution is not too surprising as Krause and Lampe[64] show in their study of the mass spectrometer reactions of CF_3^+ with SiH_4. They obtained CH_3^+, CH_2F^+ and CF_2H^+ ions.) 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 (CF_2H^+), and 33 (CH_2F^+). The mass spectra show the correct isotope pattern for a single silicon in the compound.

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. Similiar results are seen in the $Si(CF_3)F_3$ mass spectrum.[52]

Infrared Spectra. The infrared spectra of the polyfluorotetramethylsilane compounds have been tabulated in Table IV. All the spectra look very similiar, as to be expected. All spectra were recorded in the gas phase with a 10 cm gas cell. Figures 2 - 8 show the infrared spectra of the polyfluorotetramethylsilanes.

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 obtains 4 - 5 fluorines on $Si(CH_3)_4$. Then the melting points of the



Melting Point vs. Number of Fluorine on $Si(CH_3)_4$

Figure 17.

compounds decrease with increasing number of fluorine atoms. 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 of $Si(CF_3)_4$ would fall between those of $C(CF_3)_4$, $72.5 - 73^o$ and $Ge(CF_3)_4$, -19.7^o.

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

One would not have expected the silicon-carbon bond to survive reactions with elemental fluorine based on a reported electrochemical fluorination of $Si(CH_3)_4$. There has been a report[65] concerning the electrochemical fluorination of tetramethylsilane in an effort to prepare perfluoroalkyl derivatives of silane. The author pointed out that only fragmentation and decomposition products were observed. Methylfluorosilanes, $Si(CH_3)_3F$, $Si(CH_3)_2F_2$, and $Si(CH_3)F_3$ were produced in addition to SiF_4, CF_4, CF_3H, CF_2H_2, and CFH_3. Since considerable cleavage of the silicon-carbon bond resulted, the author attributed this to the facile nucleophilic attack on the silicon-carbon bond by the fluoride ion. One could conceivably write several mechanisms for the cleavage of the silicon-methyl bond and the formation of silicon-fluorine bond. 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.

Results can often be startling, but one needs to explain experimental results and see the extent to which one can exploit the results. As can be seen from the results, we are able to preserve the silicon-carbon bond during direct fluorination. Rapid metalloid-carbon bond vibrational and translational relaxation processes occurring at the cryogenic surfaces may account for the isolation of these compounds. The dilute fluorine concentrations also allow sufficient time between collisions for all relaxation processess to occur.

As to be 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 one went to higher temperatures, one produced more SiF_4, CF_4 and CF_3H. Higher fluorine concentrations also gave 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 fluorinated. This delicate balance of concentration and temperature demonstrated the difficulty and subtlities for the fluorination of tetramethylsilane.

As can be seen by the compounds isolated, a considerable degree of fluorination occurs on tetramethylsilane. In fact, it is only at temperatures of -140 to -150^0 that one can isolate the monofluoro compound, $Si(CH_3)_3(CH_2F)$. At such low temperatures, the activation energy for a reaction is only marginally available so most of the material remains tetramethylsilane. Occasional collisions lead to $Si(CH_3)_3(CH_2F)$ but insufficient collisional energy is present to result in further fluorination.

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 include 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 was found that product distribution was different depending on length of reaction, fluorine concentration and temperature. Often one could shift the fluorination to obtain a high degree of fluorination although for some unknown reason, the fluorination appears to stop at 7 fluorines, with $Si(CH_2F)(CHF_2)_3$ being the highest fluorinated species identified.

Aside from the uniqueness of the reaction in two respects: (1) the synthesis of polyfluorotetramethylsilanes and (2) preservation of all four of the silicon-carbon bonds, is the lack of silicon fluorides as products. 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. Although the silicon-carbon bond is quite strong, 104 kcal/mole, one would have expected a considerable amount of cleavage. One could probably attribute the absence of the three methylfluorosilanes to the low reaction temperatures employed in which there is insufficient energy for initial cleavage of the silicon-carbon bond.

Actually the silicon-carbon bond is much more stable than was expected. One can do photo-chlorination to obtain $Si(CH_3)_3(CH_2Cl)$ as in the following reaction.[63]

$$\mathrm{Si(CH_3)_4 + Cl_2 \xrightarrow[CCl_4,\ liq\ phase]{h\nu} Si(CH_3)_3(CH_2Cl) + HCl.}$$

Another method for halomethyl compounds has been the reaction of diazomethane.[66]

$$\mathrm{M\text{-}X + CH_2N_2 \longrightarrow M - CH_2X + N_2\ .}$$

$$\mathrm{X = Cl,\ Br,\ I}$$

However, the absence of methylfluorosilanes can be understood but the lack of large quantities of polyfluoromethylfluorosilanes is another puzzling observation. There are two polyfluoromethylfluorosilanes, but whether they are formed as a result of decomposition during handling or from the actual experiment is difficult to determine. But the amount is extremely low, well under 1% of the total material recovered. [$Si(CH_3)(CH_2F)(CHF_2)F$; ^1H: CH_3 (-0.06, doublet, $J_{HF'}=6.9$ hz), CH_2F (4.12, doublet of doublets, $J_{HF}=47.4$ hz, $J_{HF'}=5.5$ hz), CHF_2 (5.48, doublet of triplets, $J_{HF}=45.4$ hz); ^{19}F: CHF_2 (63.3, doublet), CH_2F (203.89, triplet), F (101.1, singlet); $Si(CH_3)(CH_2F)_2F$; ^1H: CH_3 (-0.16, doublet, $J_{HF'}=5.8$ hz), CH_2F (4.04, doublet of doublets, $J_{HF}=47.4$ hz, $J_{HF'}=4.8$ hz); ^{19}F: CH_2F (201.5, triplet), F (97.5, singlet). The assignments of the Si-F chemical shifts were with reference to $Si(CH_3)F_3$, 62.6, $J_{HF}=4.0$ hz, $Si(CH_3)_2F_2$, 56.7, $J_{HF}=6.0$ hz, and $Si(CH_3)_3F$, 82.7, $J_{HF}=7.0$ hz.[67]] The observation was made that the partially fluorinated tetramethylsilanes were low in volatility and require more activation energy for reactions to occur caused one to increase fluorine concentration and temperature for the reaction. One would certainly have expected large quantities of Si-F cleavage compounds. But this was not the case. The amount of CF_4, CF_3H and SiF_4 increased tremendously as the amount of isolable polyfluorotetramethylsilanes decreased, SiF_4, being the only Si-F compound isolated.

What apparently happens during the fluorination process is that once one silicon-carbon bond is broken, the other three also cleave leaving SiF_4 and the corresponding fluoromethanes, CF_4, CF_3H, or CF_2H_2 depending on the degree of fluorination. The amount of CF_2H_2 is always much less than that of CF_4 and CF_3H. The large quantities of CF_4 generated in several reactions indicated that we were getting a high degree of fluorination, although the fluorination went too far. However, we were still unable to isolate the desired $Si(CF_3)_4$ compound despite altering conditions. We also did not isolate any $Si(CF_3)F_3$ or any compounds with combinations of CF_3, CF_2H, and CFH_2 on silicon with Si-F bonds, except the two compounds mentioned above. 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 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 proceeds. However, this does not appear to be the case with tetramethylsilane and fluorine. As mentioned above, varying the conditions given previously gave larger quantities of SiF_4, CF_4 and CF_3H.

This leads to the last apparent unique feature of this experiment, either one obtains polyfluorotetramethylsilanes or one obtains SiF_4. This all or none feature of the reaction between fluorine and tetramethylsilane is indeed puzzling. This apparent anamolous feature leads one to believe that the two compounds mentioned above containing Si-F bonds result from decomposition of other compounds, not from reaction conditions. Whether this is the actual method of generation for the Si-F compounds can be established by decomposing the two $Si-CF_3$ compounds. However, an insufficient quantity of material was present for the $Si-CF_3$ compounds and likewise the amount, as mentioned above, of the Si-F compounds is really insignificant. However, the generation of the compounds 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 likihood, $Si(CF_3)_4$, would be excellent sources of difluorocarbene. Evidence in support of the above observation is supplied by work on $Si(CF_3)F_3$[52] and by Haszeldine on his polyfluoroalkylsilanes[55]. $Si(CF_3)F_3$ decomposes by difluorocarbene elimination to give mainly C_2F_4 and some $c-C_3F_6$. Polyfluorotetramethylsilanes appear to have similiar routes of decomposition. Decomposition of the polyfluorotetramethylsilanes, even on standing at room temperature in sealed glass tubes, generally leads to $C_2F_2H_2$ both as $CF_2=CH_2$ and CFH=CFH and a very viscous liquid assumed to be a fluorosilicon 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. Decomposition 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 $Si(CF_3)_4$ is indeed formed but is unstable at room temperature, eliminating difluorocarbene. (However, no $c\text{-}C_3F_6$ or C_2F_4 was identified as such. Therefore the amount of $Si(CF_3)_4$ had to be extremely small.)

Besides the apparent interest in $Si(CF_3)_4$ as possibly a difluorocarbene source and its unusual high symmetry of CF_3 groups on silicon, the chemical shift of the CF_3 group would be of interest. More will be said on this point in comparison of the Group IVA compounds later. However, it can be established that a plot of the chemical shift for the CF_3 group versus atomic number predicts the ^{19}F shift for $Si(CF_3)_4$ to be about -21 while a plot of the ^{19}F chemical shift versus electronegativity predicts a shift of -34 (with silicon being more electronegative than germanium).

Silicon might hold a unique position in the periodic table in the Group IVA elements in light of our inability to produce $Si(CF_3)_4$. However, direct fluorination has shown it possible to preserve the silicon-carbon bond, resulting in many new, interesting compounds, unattainable by other methods.

FLUORINATION OF TETRAMETHYLGERMANIUM, $Ge(CH_3)_4$

INTRODUCTION

The chemistry of the germanium-carbon bond has been summarized by Glocking and Hooten.[68] Little work has been described up to that point for the reaction of the halogens with tetraalkylgermaniums. It is known that Br_2 and I_2 cleave tetramethylgermanium, but the reaction stops after the first bond cleavage.[69] The reactivity of the germanium-carbon bond is quite low.

$$Ge(CH_3)_4 + Br_2 + n\text{-}C_3H_7Br \xrightarrow[\text{reflux}]{\text{20 hr}} (CH_3)_3GeBr\ (98\%).$$

However, with longer alkyl groups, not only does bond cleavage occur, but bromine react with hydrogens to give $(C_3H_6Br)_3GeBr$ from the bromination of $(C_3H_7)_4Ge$.[70] Iodination proceeds in a similiar fashion.

Due to the reactivity of Cl_2 and F_2, one would expect similiar bond cleavage. This is indeed the situation with chlorine. Tetraalkyls of germanium preferentially cleave with chlorine. However, one is able to produce chloromethylgermanium compounds by several methods. Two are listed below.

$$GeCl_4 + CH_2N_2 \xrightarrow[-60]{\text{Cu powder}} Cl_3GeCH_2Cl\ (94\%) + N_2 \tag{71}$$

$$CH_3GeCl_3 + SO_2Cl_2 \xrightarrow[(C_6H_5CO)_2O_2]{} ClCH_2GeCl_3 + Cl_2CHGeCl_3 \tag{72}$$

Under careful experimental conditions, one can chlorinate organogermanes, as demonstrated below.[73,74,75]

$$Me_3GeCl + Cl_2 \xrightarrow{<140^{o}} Me_2(ClCH_2)GeCl\ (84\%) + HCl \tag{73}$$

$$Me_4Ge + Cl_2 \longrightarrow \underset{79\%}{GeMe_3(CH_2Cl)} + \underset{6\%}{GeMe_3(CHCl_2)} + \underset{6\%}{GeMe_2(CH_2Cl)_2}$$

$$Me_3GeCH_2Cl + Cl_2 \longrightarrow \underset{45\%}{Me_2Ge(CH_2Cl)_2} + \underset{27\%}{Me_3GeCHCl_2} \tag{74}$$

The reaction of fluorine has not been studied but hydrofluoric acid cleaves the germanium-carbon bonds as in:[75]

$$R_4Ge + HF \longrightarrow R_3GeF + RH, \; R = CH_3, C_2H_5 .$$

With this in mind, we proceeded with an attempt to preserve the germanium-carbon bond during fluorination.

EXPERIMENTAL

Reaction 1.

With zone 2 at -100°, 0.67 ml of $Ge(CH_3)_4$ was syringed through a swagelok T-assembly with a helium flow of 100 cc/minute. After flushing for 2 hours with helium, fluorination began with a fluorine flow of 1 cc/minute to a helium flow of 60 cc/minute. Zone 2 was kept at -90° during the duration of the fluorination. After 64 hours, the fluorine was turned off. After purging with helium for 10 hours, the temperature controller was turned off. The reaction was flushed for 40 hours at room temperature.

The volatile materials were separated by -95°, -131° and -196° fractions. The -196° fraction contained CF_3H, CF_2H_2 and a trace of C_2F_6. There was very little CF_4 present. The -131° fraction contained $Ge(CF_3)_4$ and a little $Ge(CH_3)_4$. The -95° fraction contained partially fluorinated materials.

The $Ge(CF_3)_4$ was identified by its infrared, NMR and mass spectra. These were in excellent agreement with previously reported spectra.[8] Estimated yield based on starting material was approximately 0.5%.

A considerable amount of material stopped in the -95° trap. An NMR of the mixture showed sets of peaks in the CF_3, CF_2H and CFH_2 region of the fluorine and proton spectra, indicating the presence of these groups.

Approximately 3/4 ml of liquid was present in this fraction. A gas chromatograph separation, using the following conditions, indicated the presence of at least 12 distinct compounds.

SE-30, 3/8" x 24'
30^{o} isothermal for 30'
2^{o} per minute to 60^{o} for 15'
2.5^{o} per minute to 100^{o} for 50'
185^{o} bake.

The material was kept to be gas chromatographed for compound collection later as more samples were prepared.

Reaction 2.

1.15 ml (8.71×10^{-3} mole) of $Ge(CH_3)_4$ was syringed into the reactor with zone 2 at -100^{o} with a helium flow of 100 cc/minute. The reactor was purged for 2.5 hours with helium. Fluorination began with a fluorine flow of 1 cc/minute to a helium flow of 60 cc/minute. After 150 hours, the fluorine flow was turned off. After purging for 6 hours with helium, the temperature controller was turned off. During the entire course of the reaction, the temperature was at -100^{o}. After purging for 39 hours with helium, the volatiles were separated into -95^{o}, -131^{o} and -196^{o} fractions.

The -196^{o} fraction contained a little CF_4 but mainly CF_3H. The -131^{o} fraction contained $Ge(CF_3)_4$ and some $Ge(CH_3)_4$. After further separation, the $Ge(CF_3)_4$ was identified pure by its infrared and NMR spectra. 33.8 mg of sample gave a 1.1% yield of $Ge(CF_3)_4$. The bulk of the material stopped in the -95^{o} trap. An infrared spectra showed partially fluorinated materials present. NMR's of the sample showed peaks characteristic of CF_3, CF_2H and CFH_2 type groups. A gas chromatograph of part of the material showed the same number of peaks as that in reaction 1, but with different peak area distribution. The sample was stored for further gas chromatograph separation.

Reaction 3.

0.92 ml (6.97×10^{-3} mole) of $Ge(CH_3)_4$ was syringed into the reactor with zone 2 at -100°. A helium flow of 100 cc/minute was used. After four hours of purging with helium, the following reaction conditions were used. Zone 2 was always cooled to the temperature indicated.

F_2 (cc/minute)	He (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

The volatile materials were separated into -95°, -131° and -196° fractions. The -196° fraction contained very little material. There was very little CF_4 present. Most of the volatiles were CF_3H and C_2F_6. The material which stopped in a -131° trap showed $Ge(CF_3)_4$ and a small amount of $Ge(CH_3)_4$. After separating the $Ge(CH_3)_4$ from the $Ge(CF_3)_4$, it was found that 144.7 mg of $Ge(CF_3)_4$ was produced, equivalent to a yield of 5.96%. The material which stopped in the -95° trap showed a higher degree of fluorination than previous reactions, as indicated by the infrared spectra. NMR of the material showed again the chemical shifts characteristic of CF_3, CF_2H and CFH_2 groups. A gas chromatograph of the sample showed the same number of peaks as previous, but again in a different distribution. This reaction contained more compounds with higher volatility. The sample was stored for further gas chromatograph separation.

Reaction 4.

0.90 ml (0.8695 gm, 6.55×10^{-3} mole) of $Ge(CH_3)_4$ was syringed into the reactor with zone 2 at -100°. Using a helium flow of 100 cc/minute, the reactor was purged for 2 hours. With zone 2 being cooled to the temperature indicated, the following reaction conditions were used.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
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 $Ge(CF_3)_4$. The bulk of the material was in the -95° trap.

The NMR of the -95^{o} fraction showed the presence of only three compounds. The compounds were $Ge(CF_3)_4$ (-27.0 ppm), $Ge(CF_3)_3F$ (-21.9) and $Ge(CF_3)_3(OH)$ (-21.4).

After its separation from all impurities, 1.45 gm of $Ge(CF_3)_4$ was isolated pure. This results in a minimum yield of 63.51%. The amounts of the other compounds will be discussed later.

Reaction 5.

0.95 ml of $Ge(CH_3)_4$ was syringed into the reactor with a 100 cc/minute helium flow and with zone 2 at -100^{o}. After 2 hours of purging with helium, the following reaction conditions were used with zone 2 always cooled.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
1.0	60	-100	24 hours
1.0	30	-100	8
2.0	30	-90	18
2.0	30	-80	8
2.0	30	-70	14
2.0	30	-60	10
2.0	30	-50	12
2.0	30	-40	12
2.0	30	-30	14
0.0	30	-30	24
0.0	30	RT	28

The materials were separated into -131^{o} and -196^{o} fractions. The -196^{o} fraction contained a good quantity of CF_4 and CF_3H. However, the -131^{o} fraction contained $Ge(CF_3)_4$ in considerable amounts, with the only contaminants being $Ge(CF_3)_3F$ and $Ge(CF_3)_3(OH)$, as shown by NMR.

Separation of Compounds by Gas Chromatography

Separation of $Ge(CF_3)_4$ from impurities.

The following gas chromatograph conditions were used.

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

Depending on the amount of material injected into the gas chromatograph, the retention times varied. Generally approximately 100 µl was injected. If 75 µl was used, $Ge(CF_3)_4$ had a retention time of 3'17", $Ge(CF_3)_3(C_2F_5)$, 6'10", $Ge(CF_3)_3(OH)$, 20'43" and $Ge(CH_3)_4$, 29'16". The two major impurities comprised about 4% of the material.

Separation of polyfluorotetramethylgermane.

The following gas chromatgraph conditions were used with an average of 100 µl of liquid injected into the gas chromatograph.

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

The compounds had excellent baseline separation. 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 compounds were collected individually 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.

DISCUSSION

As can be seen from the experiments described, the synthesis of $Ge(CF_3)_4$ is very much dependent on the experimental conditions. The constant temperature reaction gave a small amount of $Ge(CF_3)_4$. Allowing the reaction to proceed for a longer period of time increased the yield only marginally. In the reaction where the temperature was increased, the yield increased dramatically. It was noted in all these experiments that the other compounds which were present were partially fluorinated tetramethylgermanes. Therefore it was felt that if one went to possibly higher temperatures, one could 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 material. One was $Ge(CF_3)_3F$, identified by its hydrolysis product of $Ge(CF_3)_3(OH)$. There were no partially fluorinated tetramethylgermanes present. If one tried other conditions to shorten the reaction time, one can obtain excellent yields of $Ge(CF_3)_4$ on the order of 50%, but many cleavage products resulted.

The crucial factor in the successful high yield was the observation that the partially fluorinated tetramethylgermanes were very much less volatile than $Ge(CH_3)_4$. (This is a general phenomenon we observe in fluorination. The volatility of the compound, compared to the starting material, decreases as fluorines replace hydrogens. Empirically, it was found that somewhere when just over half of the protons have been replaced by fluorines, the volatility begins increasing again and generally the perfluorinated material surpasses the volatility of its hydrocarbon analog.) The crucial temperature range in the synthesis of $Ge(CF_3)_4$

from $Ge(CH_3)_4$ was in the -20° to -60° range. The 40 degree increase caused an excess of 10-fold increase in yield. This decrease in volatility can be attributed to both intra- and inter- molecular interactions between protons and fluorines. Probably some bifluoride type bridges, F--H--F form to decrease the volatility of the material. This decrease in volatility also causes an apparent decrease in reactivity. Therefore more activation energy in terms of vibrational energy in the molecule or kinetic energy in the fluorine is required to cause further reactions of the proton to occur.

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 predominantly after CF_3 groups are produced on gemanium.

The spectral data for the separated compounds have been listed in tabular form on the following pages. Some spectral trends and comments will be given below.

^{19}F and ^{1}H NMR.

Together, the ^{1}H 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.

^{1}H: (1) The CH_3 resonance shifted to larger δ values as the total number of fluorine atoms on the molecule increased. The shifts

Table VI. Proton NMR Spectra of Polyfluorotetramethylgermanium

Compound	CH_3*	CH_2F**	J_{HF}	CHF_2***	J_{HF}
$Ge(CF_3)_3(CF_2H)$				6.10[a]	45.0[b]
$Ge(CF_3)_3(CFH_2)$					
$Ge(CF_3)_2(CF_2H)_2$				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
$Ge(CF_2H)_3(CFH_2)$		5.02	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		
$Ge(CF_3)_3(OH)$[c]					

* Singlet
** Doublet
*** Triplet

a Chemical shifts in ppm. + downfield from TMS (ext)

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}	CH_2F***	J_{HF}	J_{FF}
$Ge(CF_3)_4$	-27.0							
$Ge(CF_3)_3(C_2F_5)$	-27.7	2.7[a]						
$Ge(CF_3)_3(CF_2H)$	-27.2	3.0[b]	49.0	45.5	3.1[c]			
$Ge(CF_3)_3(CFH_2)$	-25.8							
$Ge(CF_3)_2(CF_2H)_2$	-27.6	3.2[d]	49.4	46.0	3.1[e]			
$Ge(CF_3)_2(CF_2H)(CFH_2)$	-26.3	3.3[f]	50.6	45.5	3.0[g]	193.2	46.5	3.3[h]
$Ge(CF_3)(CF_2H)_3$	-27.9	3.2[i]	49.7	46.0	3.1[j]			
$Ge(CF_3)_2(CFH_2)_2$	-24.8	3.4[k]				193.0	47.0	3.5[l]
$Ge(CF_3)(CF_2H)_2(CFH_2)$	-26.8	3.2[m]	50.5	45.6	3.0[n]	193.0	46.0	2.9[o]
$Ge(CF_3)(CF_2H)_2(CH_3)$	-23.5	3.4[p]	53.0	46.5	3.2[q]			
$Ge(CF_3)(CF_2H)(CFH_2)_2$	-25.2	3.2[r]	51.8	45.5	3.0[s]	192.0	46.0	2.7[t]
$Ge(CF_2H)_3(CFH_2)$			50.5	46.2	2.2[u]	192.9	46.0	2.4[v]
$Ge(CF_2H)_2(CFH_2)_2$			51.4	46.0	2.5[w]	192.5	46.6	2.5[x]
$Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$	-22.3	3.4[y]	53.7	46.0	3.0[z]	192.5	46.0	3.0

Table VII. (continued)

Compound	CF_3*	J_{FF}	CHF_2**	J_{HF}	J_{FF}	CH_2F***	J_{HF}	J_{FF}
$Ge(CF_2H)(CFH_2)_3$			52.0	46.0	2.1[aa]	191.9	46.6	1.8[bb]
$Ge(CF_2H)(CFH_2)_2(CH_3)$			53.9	46.2	2.1[cc]	192.5	46.5	2.0[dd]
$Ge(CFH_2)_4$						191.4	46.7	
$Ge(CF_3)_3(OH)$	-21.6							

* Singlet
** Doublet
*** Triplet

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

a	Basic quartet C_2F_5 group: CF_3, 6.76, multiplet CF_2, 38.4, J_{FF}=3.3, septet
b	triplet
c	4 of 10 lines
d	pentet
e	septet
f	quartet
g	6 of 8 lines
h	7 of 9 lines
i	septet
j	quartet
k	triplet
l	5 of 7 lines
m	sextet
n	pentet
o	6 of 8 lines
p	pentet
q	quartet
r	pentet
s	sextet
t	sextet
u	doublet
v	5 of 7 lines
w	pentet
x	pentet
y	quartet
z	pentet
aa	quartet
bb	triplet
cc	triplet
dd	triplet

Table VIII. Mass Spectra of Polyfluorotetramethylgermanium[a]

$Ge(CF_3)_4$* MW=350[b]	331[c](9.3), 281(54.2), 231(30.6), 182(38.1), 143(10.6), 119(83.6), 100(0.1), 93(59.2), 81(3.5), 69(100), 50(2.6), 31(8.3)
$Ge(CF_3)_3(C_2F_5)$** 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)
$Ge(CF_3)_3(CF_2H)$ 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)
$Ge(CF_3)_3(CFH_2)$* 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)
$Ge(CF_3)_2(CF_2H)_2$ 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)

Table VIII. (continued)

$Ge(CF_3)_2(CF_2H)(CFH_2)$ 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)
$Ge(CF_3)(CF_2H)_3$ [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)
$Ge(CF_3)(CF_2H)_2(CFH_2)$ [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)
$Ge(CF_3)(CF_2H)(CFH_2)_2$ 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)

Table VIII. (continued)

$Ge(CF_2H)_3(CFH_2)$ 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)
$Ge(CF_2H)_2(CFH_2)_2{}^{*f}$ 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)
$Ge(CF_2H)(CFH_2)_3$ 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(13.0)(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)

Table VIII. (continued)

a Intensities of m/e are reported for instrument at (room temperature)(150^o)
b Molecular weight calculated for Ge = 74.
c m/e containing germanium isotope pattern reported with Ge = 74.
d Sample contained 2.5% $Ge(CF_3)_2(CF_2H)_2$
e Sample contained 9% $Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$
f Sample contained 12% $Ge(CF_2H)(CFH_2)(CH_3)$
* Did not record spectrum at 150^o.
** Did not record spectrum at room temperature.

Table IX. Infrared Spectra of Polyfluorotetramethylgermanium[a]

$Ge(CF_3)_3(C_2F_5)$	1345(wsh) 1335(w) 1240(m) 1202(m) 1175(vs) 1122(vw) 972(w) 745(vw)
$Ge(CF_3)_3(CF_2H)$	2959(vw) 1329(w) 1209(m) 1175(vs) 1155(s) 1135(m) 1095(w) 1079(w) 645(vw)
$Ge(CF_3)_3(CFH_2)$	2950(vvw) 1299(w) 1259(m) 1165(vs) 1152(s) 1129(m) 1039(w) 779(vvw) 739(vvw)
$Ge(CF_3)_2(CF_2H)_2$	2970(w) 1305(m) 1197(vs) 1173(vs) 1145(vs) 1125(sh) 1090(m) 740(w)
$Ge(CF_3)_2(CF_2H)(CFH_2)$	2960(vw) 1315(w) 1300(w) 1200(s) 1180(vs) 1140(s) 1115(m) 1070(m) 1040(w) 799(vw) 765(vvw) 735(vvw)
$Ge(CF_3)(CF_2H)_3$[b]	2980(m) 1339(w) 1310(s) 1180(s) 1139(vs) 1100(vs) 1070(s) 1040(sh) 740(vw) 660(w)
$Ge(CF_3)(CF_2H)_2(CFH_2)$[c]	2980(w) 1305(m) 1190(vs) 1130(vs) 1100(s) 1060(s) 1030(m) 800(vw) 740(w)
$Ge(CF_3)(CF_2H)(CFH_2)_2$	2960(m) 1440(w) 1305(s) 1185(vs) 1119(vs) 1090(sh) 1050(s) 1021(s) 900(w) 820(m) 770(w) 660(vw)
$Ge(CF_2H)_3(CFH_2)$	2970(m) 1435(w) 1300(s) 1220(w) 1185(m) 1105(sh) 1085(vs) 1045(vs) 1015(s) 815(w) 793(vw) 620(vw)
$Ge(CF_2H)_2(CFH_2)_2$[d]	2950(w) 1305(m) 1180(m) 1160(w) 1090(s) 1040(s) 1015(s) 820(w)
$Ge(CF_2H)(CFH_2)_3$	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)

Table IX. (continued)

$Ge(CF_3)_3(OH)$	1200(w) 1181(vs) 1163(s) 950(w) 740(vw) (OH stretch at 3680 (vvw))

a Numbers in cm^{-1}

b Contains 2.5% $Ge(CF_3)_2(CFH_2)_2$

c Contains 9% $Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$

d Contains 12% $Ge(CF_2H)(CFH_2)_2(CH_3)$

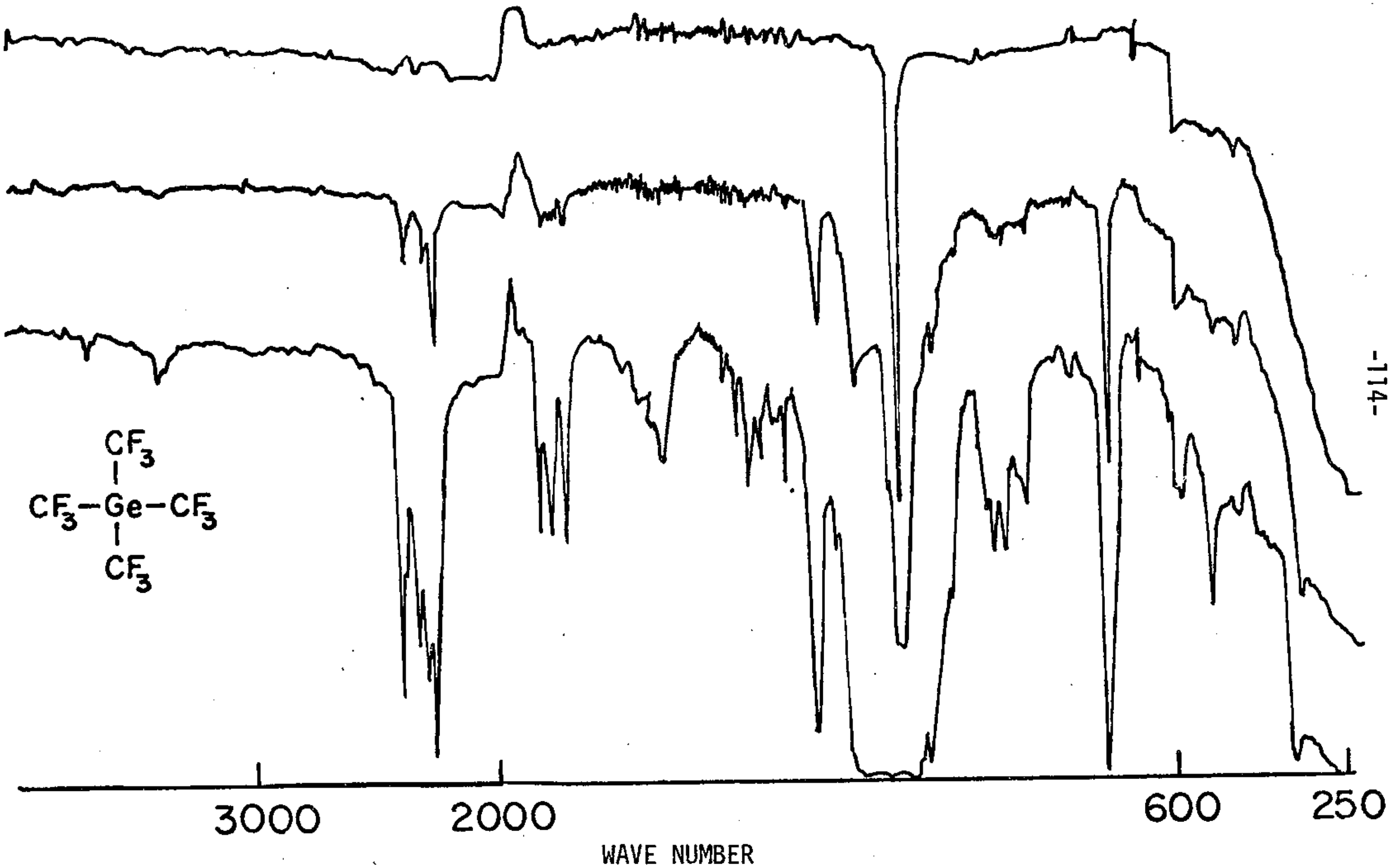


Figure 18. Infrared spectrum of $Ge(CF_3)_4$.

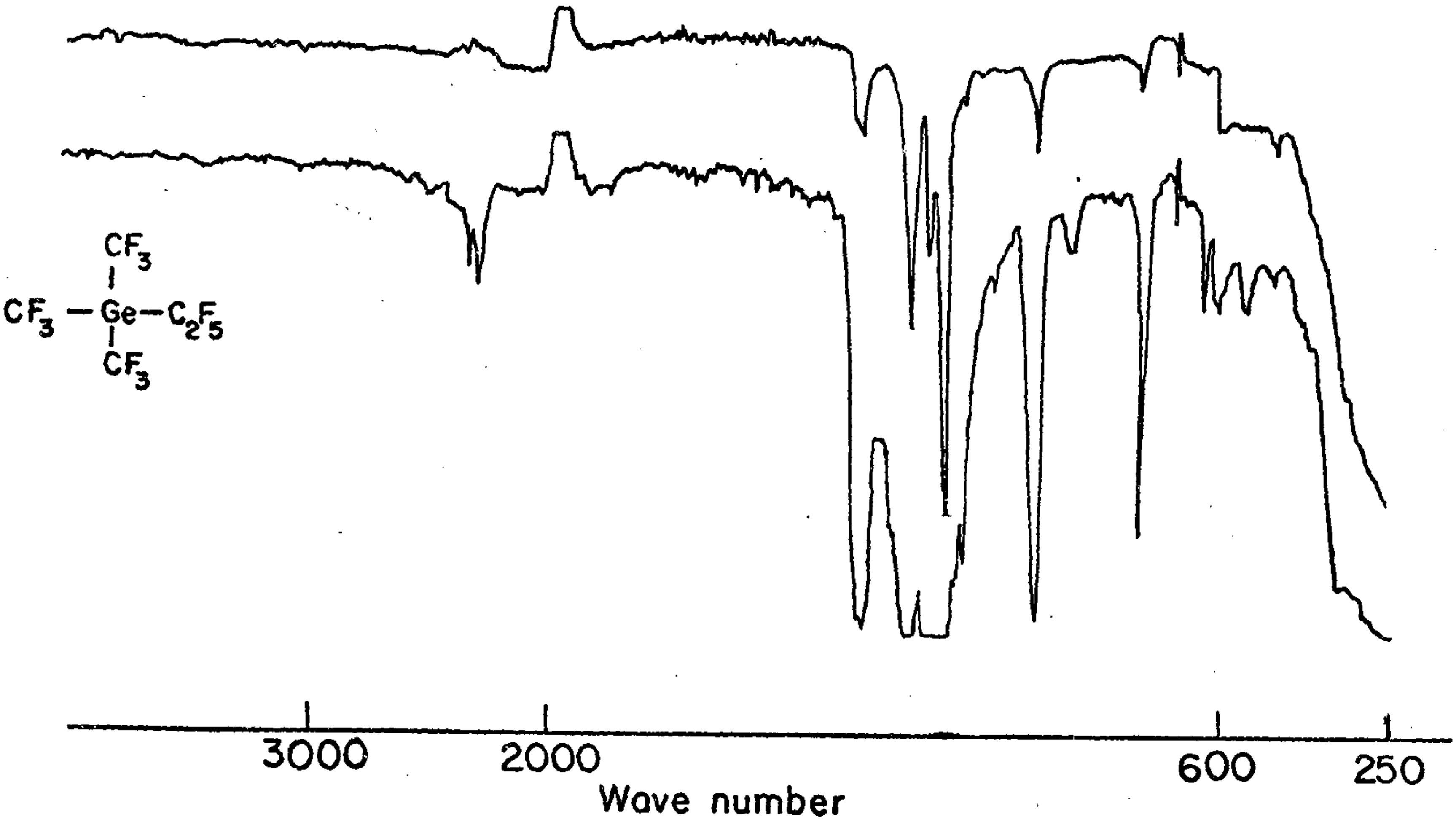


Figure 19. Infrared spectrum of $Ge(CF_3)_3(C_2F_5)$

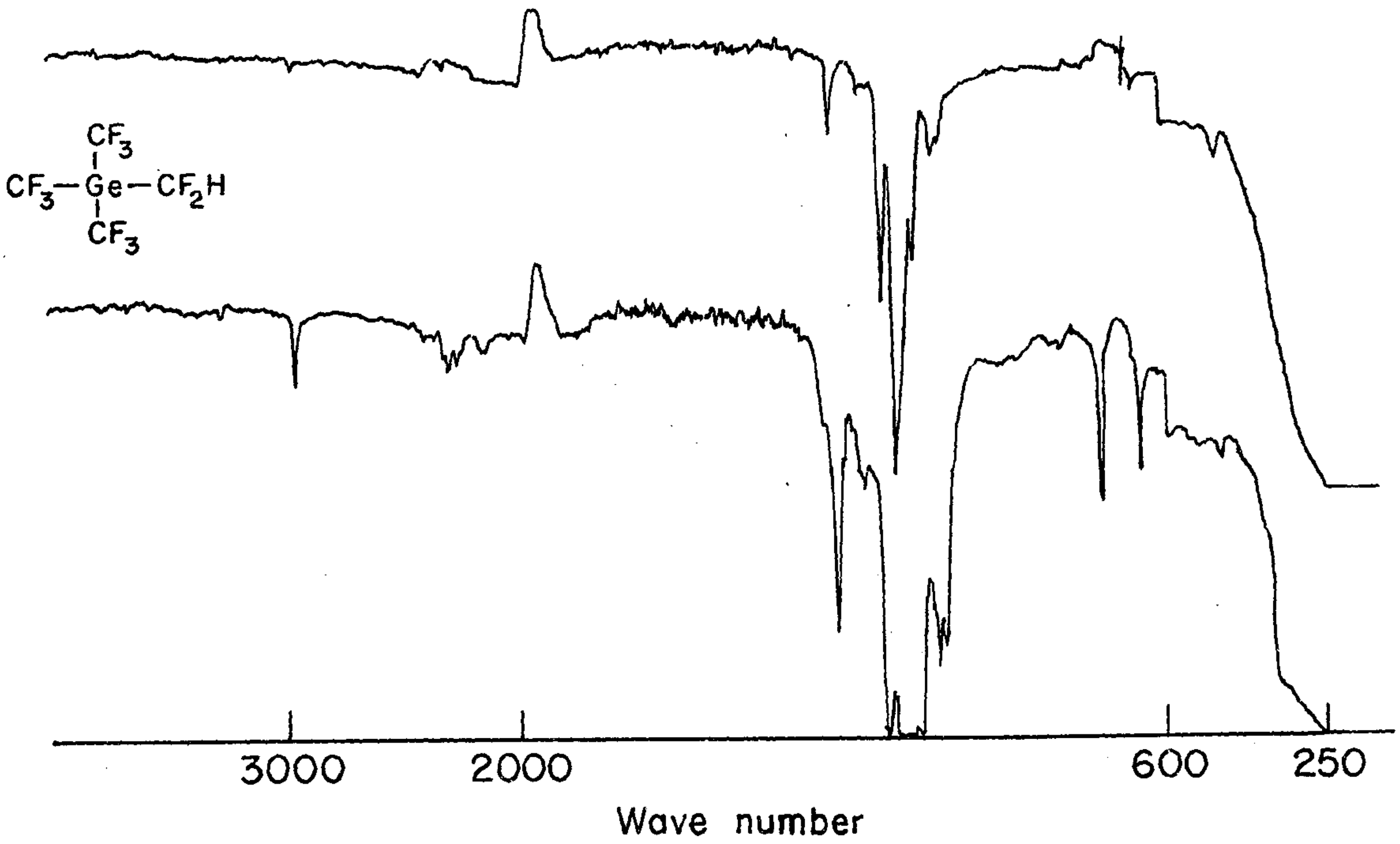


Figure 20. Infrared spectrum of $Ge(CF_3)_3(CF_2H)$

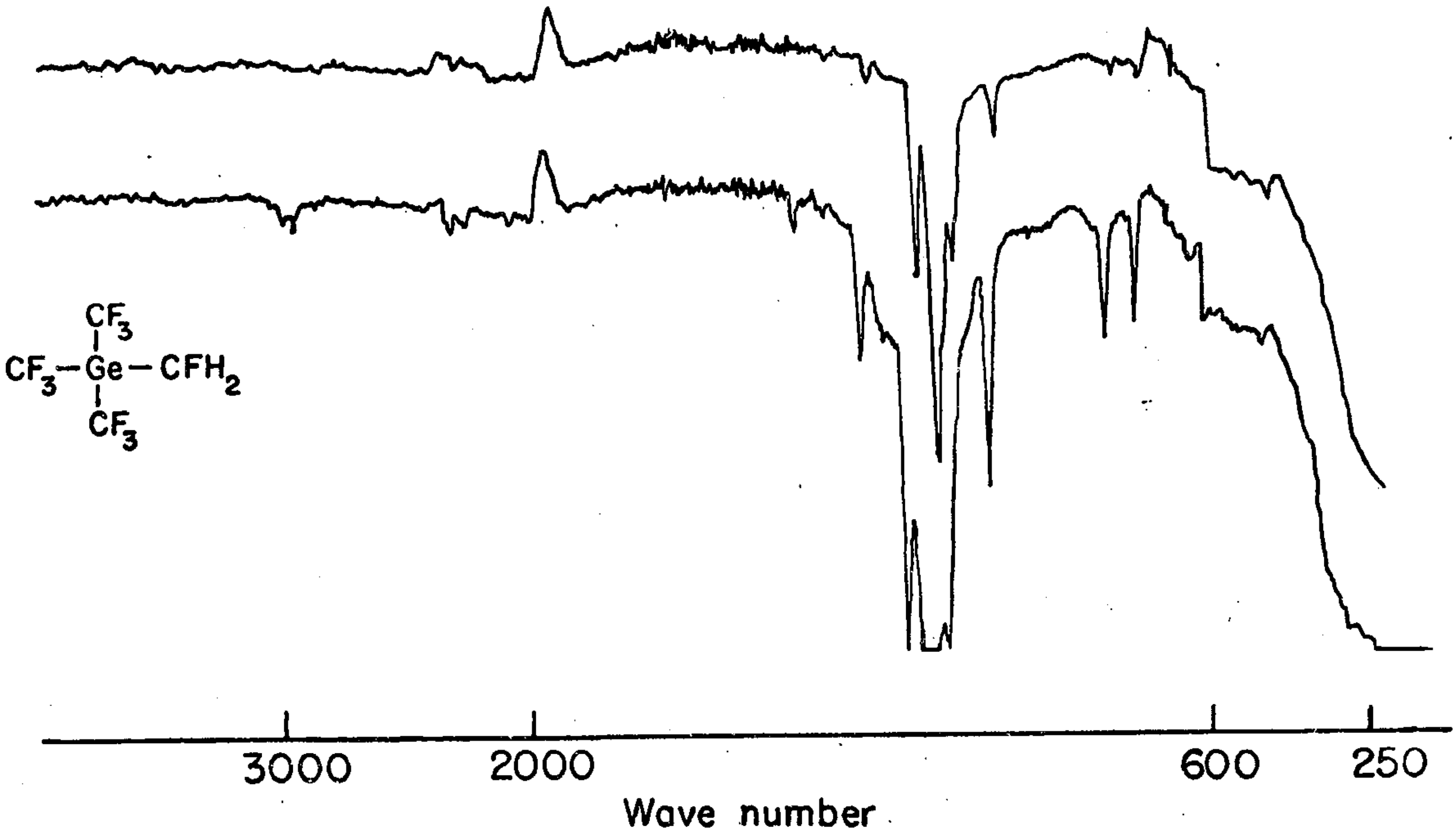


Figure 21. Infrared spectrum of $Ge(CF_3)_3(CFH_2)$

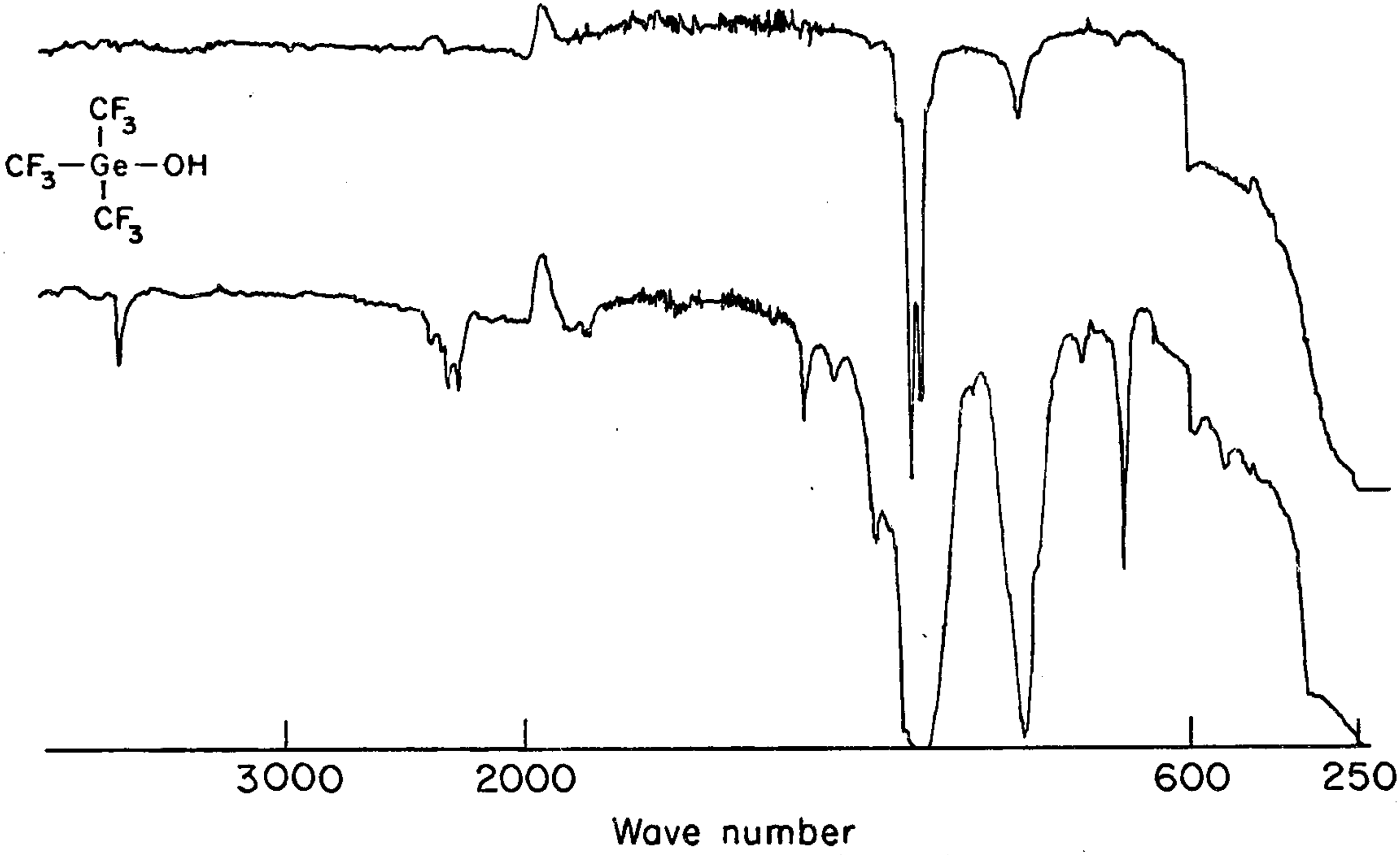


Figure 22. Infrared spectrum of Ge(CF$_3$)$_3$(OH)

Table X. Weight Percentage Yields of Polyfluorotetramethylgermanium[a]*

$Ge(CF_3)_4$	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
$Ge(CF_3)_2(CF_2)_2$	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 gm $Ge(CH_3)_4$ 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

* Total weight of fluorinated sample for three reactions upon which all yields except $Ge(CF_3)_4$ was calculated was 4.13 gm.

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 neglible. 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.

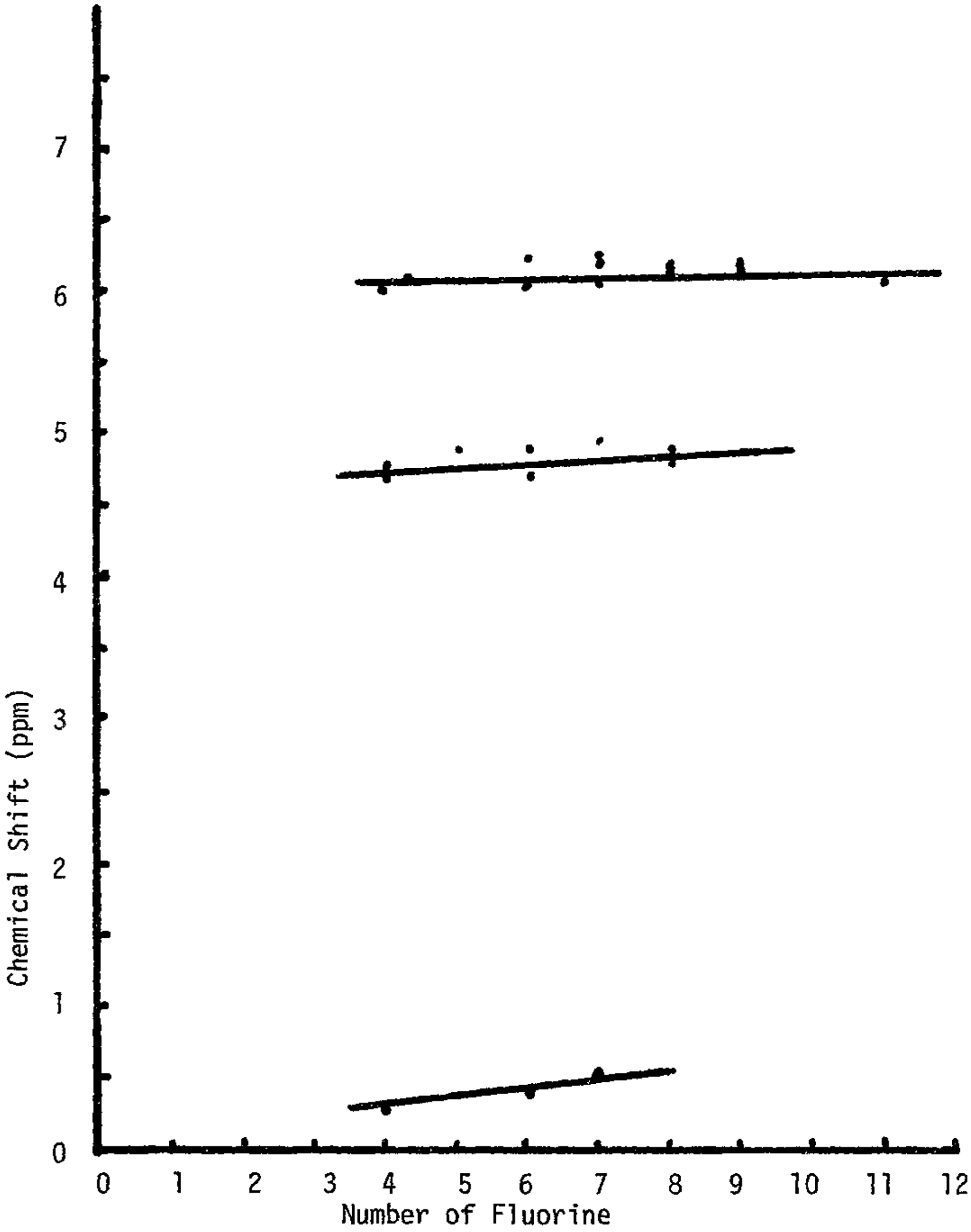
(3) The proton-fluorine coupling constants were for all practical purposes, identical for both the CH_2F and CF_2H groups.

(4) The OH chemical shift for $Ge(CF_3)_3(OH)$ was at 2.43 and was a broad singlet.

^{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. The fluorine-fluorine interactions among the various types of groups make meaningful interpretations here difficult.

(2) The CF_2H 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. In other words, as the total number of fluorines on the molecule increases, the CF_2H group gets deshielded to a greater extent, lower chemical shift.

(3) The chemical shift of the CFH_2 group has a slight trend toward increase chemical shifts with increasing total number of fluorine



^1H Chemical Shift vs. Number of Fluorine on $Ge(CH_3)_4$

Figure 23.

atoms. Shifts vary between 191.4 and 193.2.

(4) Fluorine-fluorine coupling constants were a few hertz 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 approximately 2 hz. It is curious that with CF_3 groups, the coupling constant changes by 1 hz. (The same observation was made with the silicon compounds.)

(5) The fluorine-fluorine long-range coupling led to splitting patterns which confirmed structures consistent with the integration.

Infrared Spectra.

The infrared stretching frequencies have been listed. The bands are quite broad when there are several types of groups present. Absorptions are very sharp when there are quite a few CF_3 groups on germanium. The OH stretch in $Ge(CF_3)_3(OH)$ is at 3680 cm^{-1}.

Mass Spectra.

The mass spectra of several of the compounds were recorded at two temperatures, room temperature and at 150^o, regular operating temperature of the mass spectrometer. Subtle differences can be seen by close examination of the m/e intensities. However, no detailed analysis will be given here. The general features are normally weak peaks, if any, for the parent peak 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 CH_2F groups show large m/e peaks for these groups.

The largest m/e peak intensities were 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 in the compound.

Some of the characteristic m/e values 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 1 μ vacuum. Some of the compounds leave behind a white involatile film on 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, only the hydroxide was found and characterized as $Ge(CF_3)_3(OH)$. Often moisture attacked the partially fluorinated tetramethylgermanium compounds leaving hydroxides as identified by NMR.

The relative amounts of each of the compounds is give in Table X. Of the partially fluorinated material, five compounds $Ge(CF_3)(CF_2H)_3$, $Ge(CF_3)(CF_2H)_2(CFH_2)$, $Ge(CF_3)(CF_2H)(CFH_2)_2$, $Ge(CF_2H)_3(CFH_2)$ 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. From the compound distribution in the representative gas chromatographs taken, one can follow the synthesis of more highly fluorinated species in the different conditions in going from reaction 1 to 2 to 3. A detailed careful analysis would probably shed

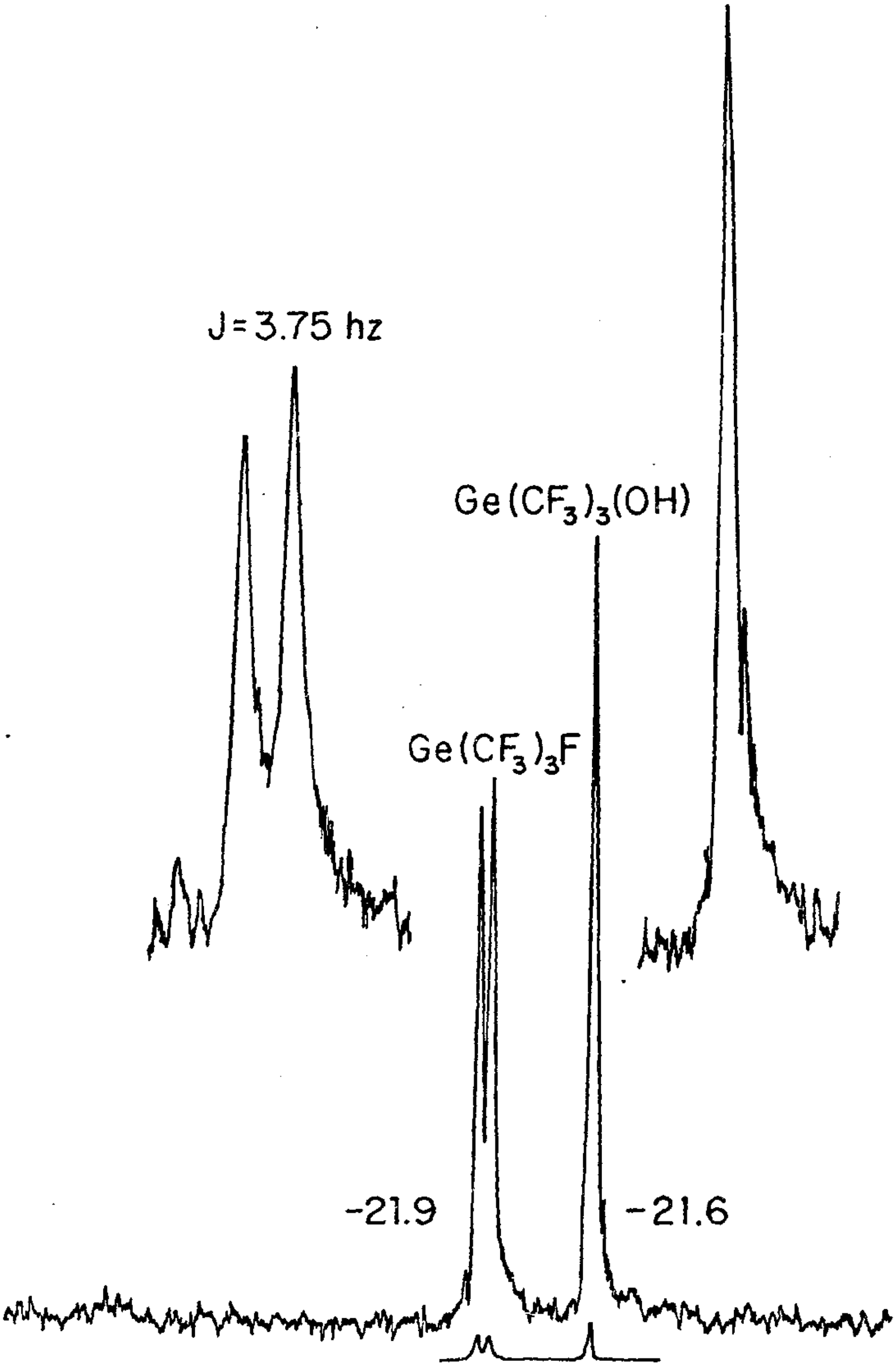


Figure 24. ^{19}F NMR of Ge(CF$_3$)$_3$F and Ge(CF$_3$)$_3$(OH).

light into whether the reactions were purely random in converting CH_3 to CF_3 or that there is some selectivity. 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 $Ge(CF_3)_3(OH)$ 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 apparent that bond cleavage in the fluorination of $Ge(CH_3)_4$ to $Ge(CF_3)_4$ occurs predominantly 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 $Ge(CF_3)_4$ if the conditions are correct. If the fluorination conditions are too vigorous, as in reaction 5, cleavage occurs more rapidly, thus the yield of $Ge(CF_3)_4$ decreases and the amount of CF_4 increases.

One factor which is favorable for higher yields of $Ge(CF_3)_4$ than $C(CF_3)_4$ under similiar reaction conditions is that there is much more interaction between the partially fluorinated groups on neopentane than there is on tetramethylgermanium. Since germanium is larger than carbon, (covalent radii 1.22 A^o vs. 0.77 A^o)[76], the interaction of CH_3, CH_2F, CHF_2 and CF_3 groups is expected to be less in germanium than in carbon. Therefore a higher activation energy may be required to remove the last few protons in neopentane than in tetramethylgermanium. This increase in "energy" can be obtained in many ways, one of which is by increasing the temperature of the reaction. At -78°, the fluorination of neopentane gives only 10% of the perfluoro material. It is expected that upon raising the temperature, the yield of perfluoroneopentane should increase. Reaction conditions have been developed recently which give yields as high as 90% on a 3 gram scale for perfluoroneopentane.

One apparent advantage it appears in this reaction is the surprising thermal stability of $Ge(CF_3)_4$. It is stable at 165^0 for several days.

FLUORINATION OF TETRAMETHYLTIN, $Sn(CH_3)_4$

INTRODUCTION

The statement by Coates, Green and Wade,[77]

> "Noteworthy features of the organic chemistry of tin include ... (f) relative ease of cleavage of some organic, particularly unsaturated, groups from tin allows certain organotin compounds to be used as intermediates in the preparation of other organometallic compounds by transmetalation."

would almost certainly predict rapid cleavage of the Sn-C bonds by the halogens. This is indeed the case. Bromine reacts rapidly.[78,79] So does chlorine as shown below.[79,80]

$$Sn(CH_3)_4 + Cl_2 \xrightarrow{0^o} Me_3SnCl\ .$$

In fact, it is quite difficult to stop the cleavage at just one alkyl group. This extreme ease of carbon-tin cleavage does not allow side-chain chlorination on halomethyltin compounds as is the case for halomethylsilanes.[81]

Lüyten and van der Kerk[82] make a more dramatic statement.

> "Cleavage by fluorine is never practiced; with the other halogens, the ease of cleavage is in the order Cl > Br > I."

However, there are methods of preparation of halomethyltin compounds.[66,81] One example is given below.[83]

$$R_nSnX_{4-n} + CH_2N_2 \longrightarrow R_n(XCH_2)SnX_{3-n}\ .$$

Only two fluoromethyltin compounds have been prepared (not considering CF_3).

$$Sn(CH_3)_3(CH_2Cl) \xrightarrow[170\ -\ 180^o]{KF} Sn(CFH_2)(CH_3)_3 \qquad (84)$$

(ethylene glycol/diethylene glycol)

$$Sn(CH_3)_3H + Sn(CH_3)_3(CF_3) \xrightarrow{150^o} Sn(CH_3)_3(CF_2H) + Sn(CH_3)_3F \qquad (85)$$

An interesting observation is that chlorine cleaves a methyl group rather than a trifluoromethyl group from tin.[86]

$$Sn(CH_3)_3(CF_3) + Cl_2 \xrightarrow{CHCl_3} Sn(CH_3)_2(CF_3)Cl + CH_3Cl \ .$$

EXPERIMENTAL

Reaction 1.

0.95 ml (1.25 gm, 6.98×10^{-3} mole) of $Sn(CH_3)_4$ was syringed into the reactor through a swagelok T-assembly with zone 2 at -80^0 and a helium flow of 100 cc/minute. After several hours, fluorination began with a fluorine flow of 1.0 cc/minute to a helium flow of 60 cc/minute. After 163 hours, the fluorine flow was terminated. After purging for 8 hours, the temperature controller was turned off and the reactor allowed to warm to room temperature. After flushing for 34 hours, the contents in the liquid nitrogen trap were fractionated into -131^0 and -196^0 fractions. The -196^0 fraction contained mainly CF_4, CF_3H, CF_2H_2 and CH_3F. Very little material was in the -131^0 fraction. The ^{19}F NMR of the -131^0 fraction in benzene showed no peaks of interest.

Reaction 2.

0.88 ml of $Sn(CH_3)_4$ was syringed into the reactor with zone 3 at -78^0. After flushing for an hour, zone 2 was also cooled to -78^0. The following fluorinations were used with zone 2 and 3 cooled to -78^0.

F_2 (cc/minute)	He (cc/minute)	Time
1.0	60	48 hours
2.0	60	24
5.0	60	24

F_2 (cc/minute)	He (cc/minute)	Time
(cont.)		
10.0	60	24
0.0	60	10
0.0	60	14 (purged at room temp.)

The volatile materials in the liquid nitrogen trap were fractionated at -131° and -196°. During the separation, a white solid formed in the glass trap. This involatile compound was not readily identifiable. Infrared spectra of the material stopping in the -131° fraction showed broad absorptions in the CH and CF regions of the spectrum. These appeared to be fluorocarbons of varying lengths. No further workup was done due to the small amount of material present.

Reaction 3.

0.875 ml of $Sn(CH_3)_4$ was syringed into the reactor with a 100 cc/minute helium flow and with zone 2 cooled to -110°. After purging for an hour with helium, a fluorine flow of 1 cc/minute to a helium flow of 60 cc/minute was used for 240 hours. Fluorine was flushed from the reactor for 8 hours after which the reactor was allowed to warm to room temperature. The reactor was flushed with helium for 3 days to carry out in the vapor stream any material of low volatility.

The contents of the liquid nitrogen trap were separated into -131° and -196° fractions. The -196° fraction contained CF_4, CF_3H, and CF_2H_2. Very little material stopped in the -131° trap. Approximately 20 μl of liquid showed a broad infrared stretch in the CH and CF regions of the spectrum and the ^1H and ^{19}F NMR showed patterns attributable to CF_2H and

CFH_2 type groups. Of interest were peaks in the proton NMR around 10 τ, indicative of methyl groups on a metal. Insufficient quantity of material made it impossible to identify the possible types of $Sn\text{-}CH_3$ compounds which might be present.

Reaction 4.

0.65 ml of $Sn(CH_3)_4$ was syringed into the reactor with a helium flow of 100 cc/minute and with zone 4 at -78^{0}. After 1 hour of purging with helium, zones 1, 2, 3 and 4 were all cooled to -78^{0}. The following fluorination conditions were used with zones 1, 2, 3, and 4 held at -78^{0}.

F_2 (cc/minute)	He (cc/minute)	Time
1.0	60	44 hours
1.0	30	13
2.0	30	30
2.0	15	45
0.0	30	12
0.0	30	16 (room temperature)

Separation of the volatile materials showed mainly CF_4 and CF_3H in the -196^{0} fraction. Very little material was in the -131^{0} trap. The only unusual item of the -131^{0} fraction was in the ^{19}F NMR in which a singlet appeared at approximately 50 ppm upfield from TFA, indicating possibly a Sn-F.

Reaction 5 (a, b, c).

Due to the small amount of volatile materials present, we decided to take a look at the material left in the reactor which was at first believed to be only tin fluorides. The following three experiments were done to the off-white colored powder scrapped out of the reactor and off the copper turnings.

(a) To approximately 1/2 ml volume of the powder was added 0.28 ml of $Cd(CH_3)_2$ in a vacuum system. Upon contact at room temperature, the material turned gray and the volatiles were subsequently removed.

Infrared spectra of the volatile materials showed no $Cd(CH_3)_2$ present but absorptions characteristic of CH_3 and CF_3 on metals. An NMR was taken of the mixture, whereby two strong resonances at -34.1 and -31.6 ppm from TFA were observed. Also present in the spectrum were what was believed to be tin 117,119 satellites. (This material was kept and its disposition will be discussed after 5c.)

(b) To another portion of the off-white powder was added 0.30 ml of $Cd(CH_3)_2$, again in a vacuum system. Analogous results were observed as that of (a), except the two resonances were in different ratios. (The disposition of this material will be discussed after 5c.)

(c) To approximately 1/2 ml volume of $Sn(CH_3)_2F_2$ was added 0.25 ml of $Cd(CH_3)_2$. The resultant infrared and NMR spectra showed the sample to be $Sn(CH_3)_4$, quantitatively converted. There was no $Cd(CH_3)_2$ present.

(a) and (b) samples, prepared by the reaction of the powder with $Cd(CH_3)_2$ were then separated by chromatography. Each of the compounds was analyzed by infrared, NMR and mass spectra. Elemental analysis on several of the samples proved satisfactory while some samples produced violent reactions in the analyzer. The following pages show the data for the compounds separated.

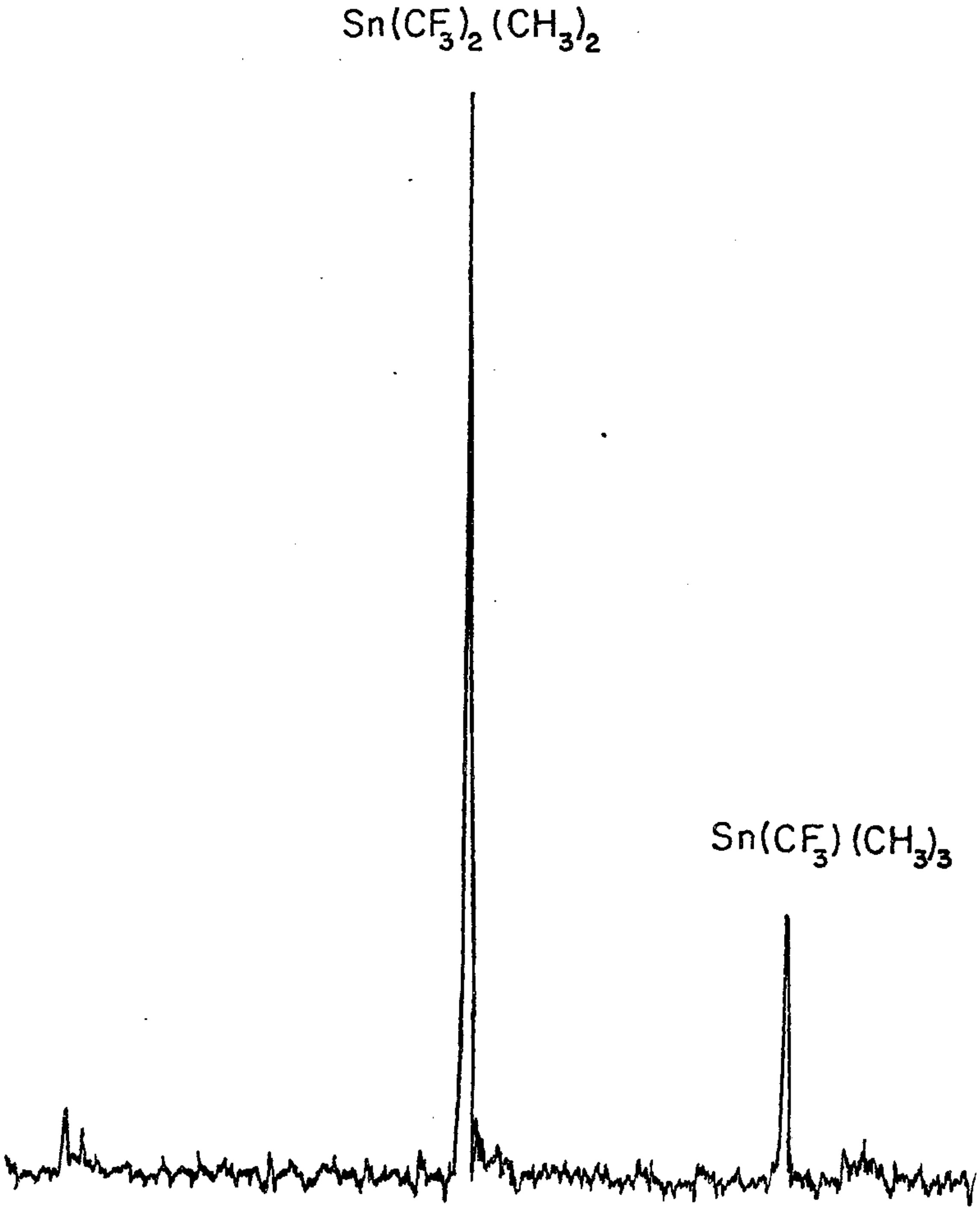


Figure 25. ^{19}F NMR of a mixture of $Sn(CF_3)(CH_3)_3$ and $Sn(CF_3)_2(CH_3)_2$ as seen from reaction 5(a).

Reaction 6.

0.757 gm of $Sn(CH_3)_2F_2$ was placed in a nickel boat and placed in a nickel reactor. The following fluorination conditions were used.

F_2 (cc/minute)	He (cc/minute)	Time
1.0	60	6 hours
2.0	30	18
4.0	15	24
0.0	30	22

$Hg(CH_3)_2$ was added to a portion of the material in the boat after the fluorination. ^1H NMR showed only $Hg(CH_3)_2$. If $Cd(CH_3)_2$ was used, one obtains $Sn(CH_3)_4$ only. The mass spectrum showed only starting material. No apparent reaction seemed to have occurred under the above conditions.

The "off-white" tin fluorides here etch glass slowly, as most tin fluorides do. The compounds are also hydroscopic and the loose powder tends to adhere together after remaining at room temperature for days. A KBr pellet of the material shows the following absorptions.

2960 (broad-m), 2400 (broad-w), 1260 (m), 1200 (m), 1160(vs), 1080 (vs), 1040 (broad-s), 800 (m), 750 (m), 570 (m), 380 (broad-s) (also present was the characteristic broad water peaks)

Table XI. Proton NMR Spectra for Polyfluorotetramethyltin Compounds

Compound	CH_3	$J_{117/119_{SnH}}$	CH_2F[1]	J_{HF}	CHF_2[2]	J_{HF}
$Sn(CH_3)_4$	0.047	53.1				
$Sn(CH_2F)(CH_3)_3$[a]	-0.037	53.9/56.0	4.75	48.0		
$Sn(CH_2F)_2(CH_3)_2$	0.10	55.9	4.93	47.9		
$Sn(CHF_2)(CH_3)_3$[b]	-0.028	56.7			6.08	45.8
$Sn(CF_3)(CH_3)_3$	0.09	57.7/60.0				
$Sn(CF_3)_2(CH_3)_2$	0.39	64.1/66.4				

1 Doublet

2 Triplet

All samples ran as neat liquids.
^1H shifts in ppm. + downfield from TMS (ext.)
J in hz.

a Ref. 84 CH_3 (-0.015) CH_2F (4.85) J_{HF}=48 hz

b Ref. 85 CH_3 (+0.18) $J_{117/119_{SnH}}$=53.5/57.5 CHF_2 (6.25) J_{HF}=45.5 hz

Table XII. Fluorine NMR Spectra for Polyfluorotetramethyltin Compounds

Compound	CF_3	$J_{^{117/119}SnF}$	CHF_2[1]	J_{HF}	CH_2F[2]	J_{HF}
$Sn(CH_3)_4$						
$Sn(CH_2F)(CH_3)_3$					190.73	48.0
$Sn(CH_2F)_2(CH_3)_2$					190.85	47.3
$Sn(CHF_2)(CH_3)_3$[a]			48.15	46.0		
$Sn(CF_3)(CH_3)_3$	-29.14[b]	263.2/276.2				
$Sn(CF_3)_2(CH_3)_2$	-31.46	333.0/348.6				
$Sn(CF_3)_4$[c]	-33.8	503/531				

1 Doublet

2 Triplet

All samples ran as neat liquids.
^{19}F shifts in ppm. + upfield from TFA (ext.)

J in hz.

a Ref. 85 CHF_2 (49.5) J_{HF}=45.0 hz $J_{^{117/119}SnF}$=254.5/265.5

b Ref. 86 CF_3 (-29.05)

c Chemical shift taken from Ref. 8, 10.

Table XIII. Mass Spectra of Polyfluorotetramethyltin Compounds

$Sn(CHF_2)(CH_3)_3$ MW=214

14	9.1	CH_2
15	30.3	CH_3
51	18.2	CHF_2
* 118	32.3	Sn
* 133	100.0	$Sn(CH_3)$
* 148	40.4	$Sn(CH_3)_2$
* 163	68.7	$Sn(CH_3)_3$
* 167	25.2	$Sn(CH_3)_2F$
* 199	9.1	$Sn(CH_3)_2(CH_2F)$

$Sn(CH_2F)(CH_3)_3$[a] MW=196

14	6.3	CH_2
15	24.0	CH_3
33	21.5	CH_2F
* 118	40.5	Sn
* 133	100.0	$Sn(CH_3)$
* 148	35.4	$Sn(CH_3)_2$
* 163	98.7	$Sn(CH_3)_3$
* 181	22.8	$Sn(CH_3)_2(CH_2F)$

$Sn(CH_2F)_2(CH_3)_2$ MW=214

14	24.6	CH_2
15	78.0	CH_3
33	34.7	CH_2F
51	31.4	CHF_2
* 118	44.1	Sn
* 133	100.0	$Sn(CH_3)$
* 137	69.5	SnF
* 148	14.4	$Sn(CH_3)_2$
* 163	15.2	$Sn(CH_3)_3$
* 171	11.0	$Sn(CH_3)F_2$
* 181	66.1	$Sn(CH_3)_2(CH_2F)$
* 199	13.6	$Sn(CH_3)(CH_2F)_2$

* Sn isotope pattern

a Ref. 87 m/e 45, 118, 133, 148, 163, 181

Table XIV. Infrared Spectra of Polyfluorotetramethyltin Compounds

$\mathrm{Sn(CH_2F)(CH_3)_3}$[a]	3070(m) 3010(s) 2960(sh) 2940(s) 2860(sh) 2400(w) 1740(vw) 1717(vw) 1450(w) 1269,1260, 1255 pqr(m) 1215,1205,1200 pqr(m) 1078(m) 989(vs) 779(vs) 531(vs) $\mathrm{cm^{-1}}$
$\mathrm{Sn(CH_2F)_2(CH_3)_2}$	3000(w) 2960(sh) 2940(m) 1745(vw) 1455(vw) 1380(vw) 1320(vw) 1275(m) 1221(m) 1151(m) 1081(m) 1045(w) 1015(w) 989(s) 951(m) 920(m) 878(w) 820(m) 770(m) 530(m) $\mathrm{cm^{-1}}$
$\mathrm{Sn(CHF_2)(CH_3)_3}$[b]	3060(w) 3010(m) 2910(s) 2400(w) 1745(vw) 1725(vw) 1480(vw) 1400(vw) 1330(w) 1285(s) 1205(m) 1155(m) 1124(s) 1090(s) 1055(vs) 1011(vs) 780(vs) 725(s) 535(vs) 510(sh) $\mathrm{cm^{-1}}$
$\mathrm{Sn(CF_3)(CH_3)_3}$	3080(vw) 3010(m) 2940(m) 1330(vw) 1220,1210, 1205 pqr(m) 1160(vs) 1075(vs) 810(sh) 785(s) 730(m) 541(s) 520(sh) $\mathrm{cm^{-1}}$
$\mathrm{Sn(CF_3)_2(CH_3)_2}$	3010(vw) 2930(vw) 1330(vw) 1220(m) 1165(vs) 1140(vs) 1095(vs) 1075(vs) 979(vw) 810(sh) 771(m) 735(w) 715(w) 550(m) 525(m) $\mathrm{cm^{-1}}$

w = weak
vw = very weak
m = medium
s = strong
vs= very strong
sh = shoulder

[a] Ref. 84 2950, 2900, 1450, 1400, 1250, 1150, 980, 790, 530 $\mathrm{cm^{-1}}$

[b] Ref. 85 3043(w) 2993(w) 2910(m) 1282(m) 1200(m) 1120(w) 1085(w) 1052(s) 775(s) $\mathrm{cm^{-1}}$

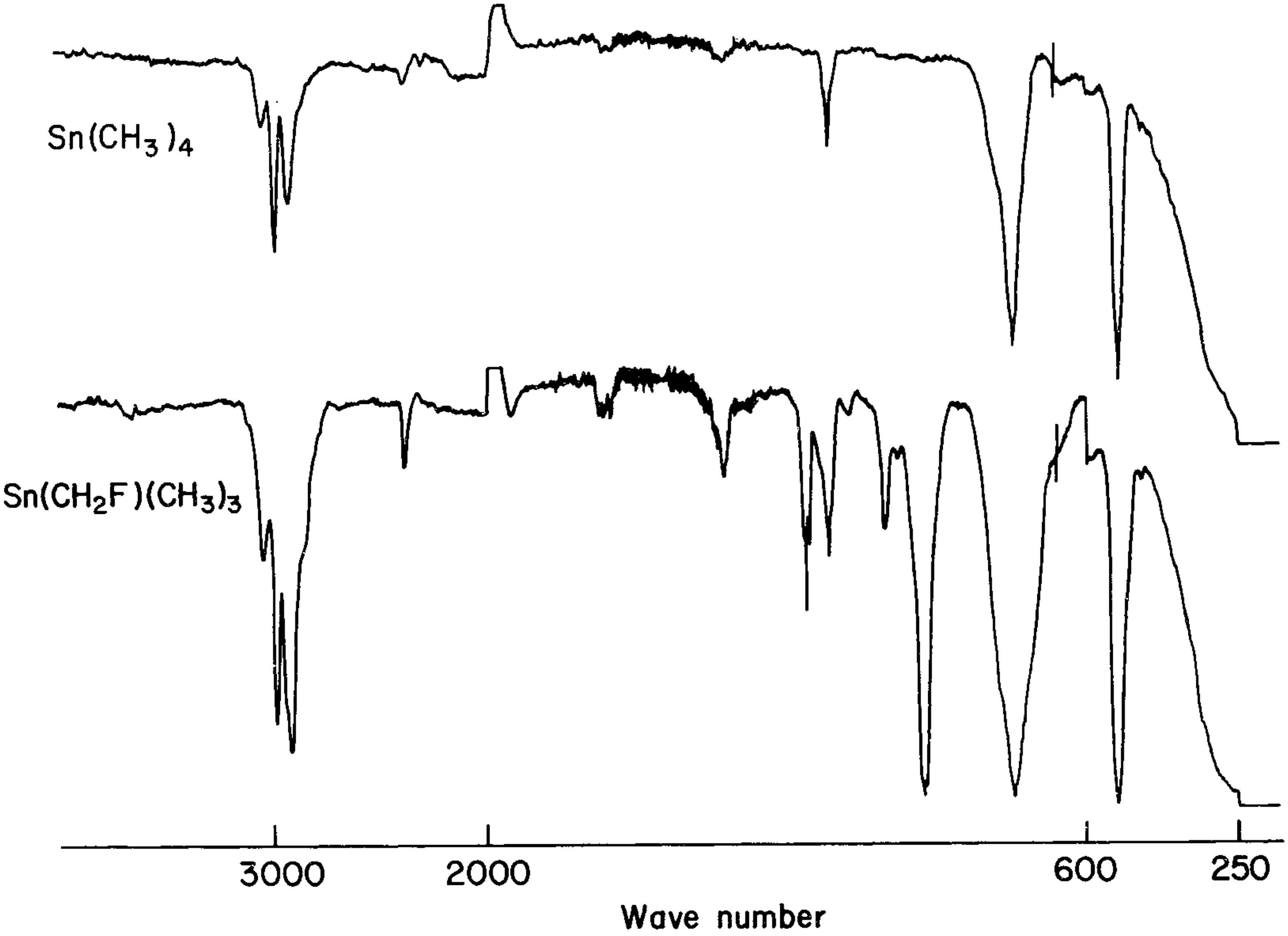


Figure 26. Infrared spectra of $Sn(CH_3)_4$ and $Sn(CH_3)_3(CH_2F)$

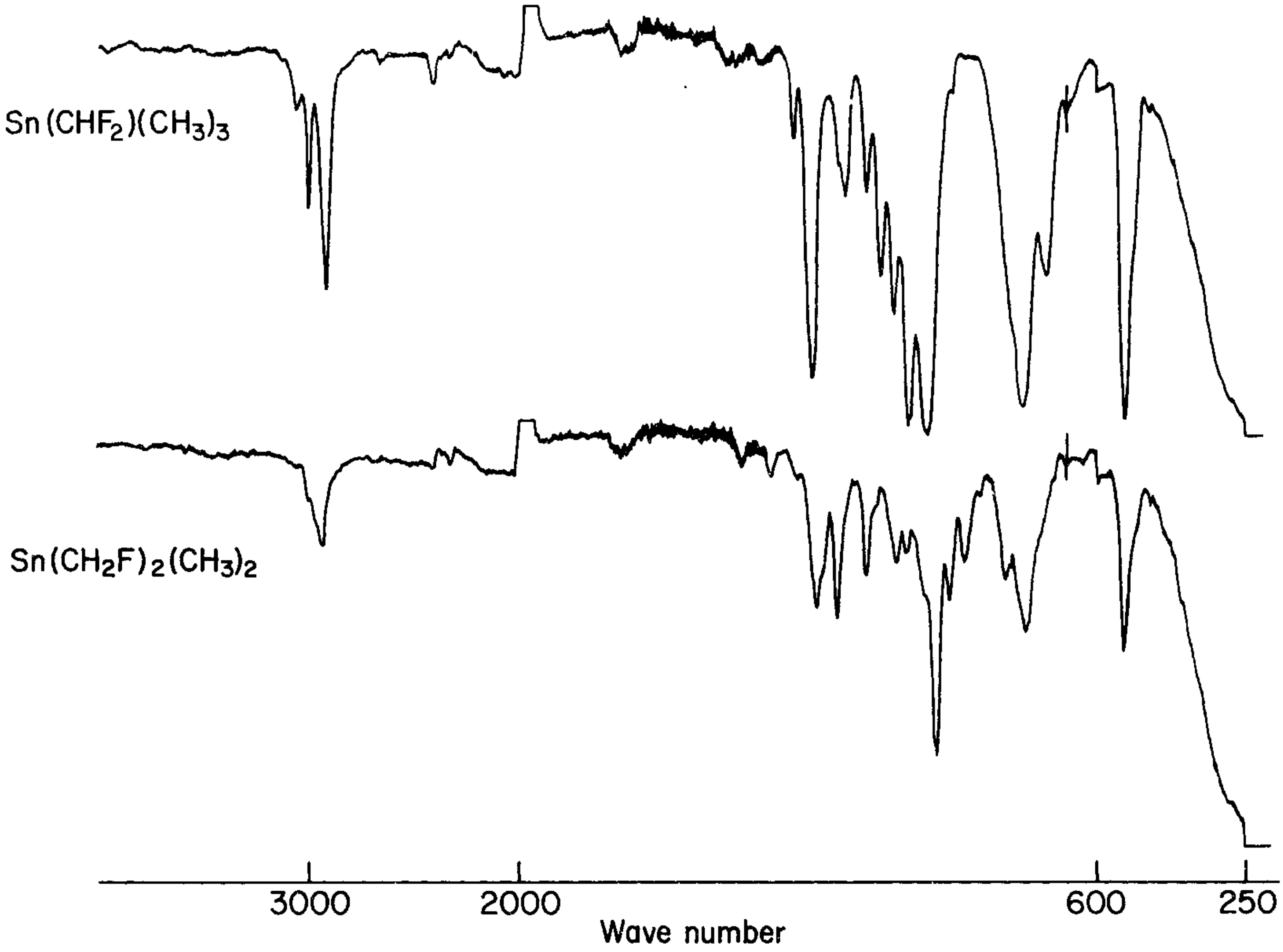


Figure 27. Infrared spectra of Sn(CH$_3$)$_3$(CHF$_2$) and Sn(CH$_3$)$_2$(CH$_2$F)$_2$

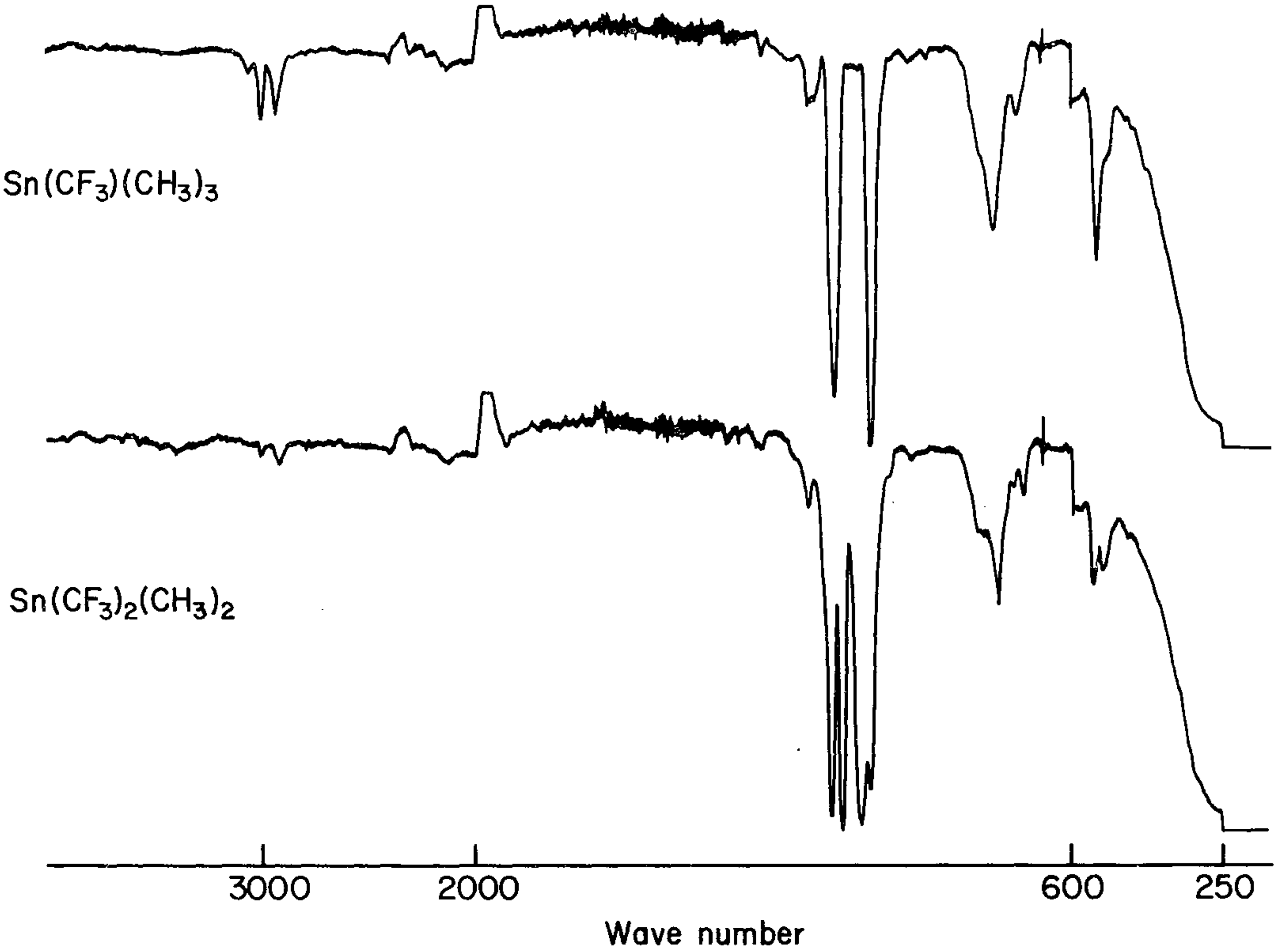


Figure 28. Infrared spectra of $Sn(CH_3)_3(CF_3)$ and $Sn(CH_3)_2(CF_3)_2$

Table XV. Melting Points of Polyfluorotetramethyltin Compounds

Compound	Melting Point (°C)
$Sn(CH_3)_4$	-54.2 - -53.5[1]
$Sn(CH_2F)(CH_3)_3$[a]	-62.5 - -59.0
$Sn(CH_2F)_2(CH_3)_2$*	< -80
$Sn(CHF_2)(CH_3)_3$**[b]	-70.5 - -66.4
$Sn(CF_3)(CH_3)_3$	-57.0 - -53.2
$Sn(CF_3)_2(CH_3)_2$	-34.5 - -32.0

* cloudy until -63

** cloudy until -55

[1] Literature: -54.8°

[a] Ref. 84 b.p. 97-101°(745mm)

[b] Ref. 85 b.p. 111.5°

Table XVI. Solvent Effect on ^{19}F Chemical Shift of CF_3 Groups on $Sn(CF_3)(CH_3)_3$ and $Sn(CF_3)_2(CH_3)_2$

Solvent	$Sn(CF_3)(CH_3)_3$	$Sn(CF_3)_2(CH_3)_2$
neat	-29.14	-31.46
pyridine	-28.10	-29.25
$Sn(CH_3)_4$	-29.51	-32.36
$Cd(CH_3)_2$	-31.61	-34.11
CCl_4	-29.05[a]	

Chemical shifts in ppm downfield from external TFA.

[a] Ref. 86.

Table XVII. Percent Products of Polyfluorotetramethyltin Compounds. Gas Chromatographic Retention Time.

Compound	% of Products	GC* Retention Time (min-sec)
$Sn(CH_3)_4$	48.4	38'47"
$Sn(CH_3)_3(CF_3)$	12.9	67' 0"
$Sn(CH_3)_3(CH_2F)^a$	12.9	69'55"
$Sn(CH_3)_3(CHF_2)$	3.2	74'40"
$Sn(CH_3)_2(CF_3)_2{}^b$	12.9	77'13"
$Sn(CH_3)_2(CH_2F)_2$	9.7	98'15"

* Gas Chromatograph Conditions

10% fluorosilicon on Chromosorb P
3/8" x 25' Cu tubing
0^o isothermal/15 minutes
2.5^o/minute → 50^o/15 minutes
2.5^o/minute → 80^o/50 minutes

Elemental Analysis

a	Calculated:	C(24.40)	H(5.59)	F(9.66)
	Found:	C(24.31)	H(6.07)	F(9.40)
b	Calculated:	C(16.74)	H(2.09)	F(39.76)
	Found:	C(16.51)	H(2.28)	F(40.13)

DISCUSSION

From the experiments described, it is evident that the cleavage of the tin-carbon bond is the limiting factor toward the synthesis of $Sn(CF_3)_4$. It appears that during the fluorination process, a considerable number of Sn-C bonds are cleaved to produce Sn-F bonds. The methyltinfluorides produced are involatile and this may account for the relatively small amount of volatile materials recovered with tin present in the reaction of $Sn(CH_3)_4$ with fluorine. From the volatile materials, it is apparent that fluorination is occurring in that one obtains CF_4, CF_3H, and CF_2H_2 in considerable amounts. The various experiments described were intended to keep to a minimum these cleavage products in hope of obtaining $Sn(CF_3)_4$. However, it is apparent that one did not produce $Sn(CF_3)_4$ in the reaction or that if $Sn(CF_3)_4$ did form, it was unstable in the fluorine atmosphere.

The question whether fluorination can convert methyl groups on tin to trifluoromethyl groups can be answered by looking at the results of reaction 5. The reaction of the "off-white" powder with $Cd(CH_3)_2$ (this reaction does not work at room temperature with $Hg(CH_3)_2$) is most encouraging in that the following products formed, $Sn(CH_3)_4$, $Sn(CH_2F)(CH_3)_3$, $Sn(CH_2F)_2(CH_3)_2$, $Sn(CHF_2)(CH_3)_3$, $Sn(CF_3)(CH_3)_3$, and $Sn(CF_3)_2(CH_3)_2$. In that the compounds form only after the addition of $Cd(CH_3)_2$ implies that all existed as a tin fluoride, although it is not possible to report with confidence the number of fluorines bonded directly to the tin. No effort was made to separate and study the physical properties of the tin fluorides formed here. Also no effort was made to study the thermodynamics of the CH_3 exchange of $Cd(CH_3)_2$ with the Sn-F to see if any redistribution had occurred. No $Cd(CF_3)(CH_3)$ or $Cd(CF_3)_2$ formed in the addition of the

$Cd(CH_3)_2$ to the "off-white" powder. Therefore no redistribution in that respect occurred although this could be a consequence of an excess of "off-white" powder used and no solvent present. Speculation on the number of fluorines bonded to tin itself can proceed by first listing the possible fluorides that could result.

$Sn(CH_3)_4$: $Sn(CH_3)_3F$, $Sn(CH_3)_2F_2$, $Sn(CH_3)F_3$, SnF_4
$Sn(CH_2F)(CH_3)_3$: $Sn(CH_2F)(CH_3)_2F$, $Sn(CH_2F)(CH_3)F_2$, $Sn(CH_2F)F_3$
$Sn(CH_2F)_2(CH_3)_2$: $Sn(CH_2F)_2(CH_3)F$, $Sn(CH_2F)_2F_2$
$Sn(CHF_2)(CH_3)_3$: $Sn(CHF_2)(CH_3)_2F$, $Sn(CHF_2)(CH_3)F_2$, $Sn(CHF_2)F_3$
$Sn(CF_3)(CH_3)_3$: $Sn(CF_3)(CH_3)_2F$, $Sn(CF_3)(CH_3)F_2$, $Sn(CF_3)F_3$
$Sn(CF_3)_2(CH_3)_2$: $Sn(CF_3)_2(CH_3)F$, $Sn(CF_3)_2F_2$.

Since the tin fluorides would be non-volatile and ionic in nature,[77] it is possible that for each of the compounds any of the fluorides are possible or a combination of several fluorides. However, it is probable that the only important fluorides are $Sn(CH_3)_3F$, $Sn(CH_2F)(CH_3)_2F$, $Sn(CH_2F)_2(CH_3)F$, $Sn(CHF_2)(CH_3)_2F$, $Sn(CF_3)(CH_3)_2F$ and $Sn(CF_3)_2(CH_3)F$. Once one tin-carbon bond is replaced with a tin-fluorine bond, these compounds appear to be very much unreactive toward fluorine at low temperatures and appear to remain unfluorinated under these conditions. This conclusion is based on the results of reaction 6 described above. Under the conditions used, no CF_3, CF_2H, or CFH_2 groups formed on the dimethyltindifluoride. Therefore one can conclude that methyltinfluorides are quite unreactive toward fluorine at both ambient and subambient temperatures. Higher temperatures are probably required to fluorinate the methyl groups.

To summarize the reaction of fluorine with $Sn(CH_3)_4$, the following schematic is presented.

$$Sn(CH_3)_4 + F_2/He \xrightarrow[\text{low temp}]{} SnR_x(CH_3)_yF + CF_4 + CF_3H + CF_2H_2 + HF,$$

$$R = CH_3,\ CH_2F\ (x = 1,\ 2),\ CHF_2\ (x = 1),$$

$$CF_3\ (x = 1,\ 2)$$

$$x + y = 3.$$

$$SnR_x(CH_3)_yF + Cd(CH_3)_2 \longrightarrow Sn(CH_3)_4 + Sn(CH_2F)(CH_3)_3 +$$

$$Sn(CH_2F)_2(CH_3)_2 + Sn(CHF_2)(CH_3)_3 +$$

$$Sn(CF_3)(CH_3)_3 + Sn(CF_3)_2(CH_3)_2\ .$$

It is interesting to note that there was no $Sn(CF_3)_3(CH_3)$ formed in the reaction. This could imply that during the fluorination process there was too much energy present after two CF_3 groups form on tin. As a result, a tin fluoride forms. This can be represented as:

$$Sn(CH_3)_4 + F_2/He \longrightarrow Sn(CF_3)(CH_3)_3$$

$$Sn(CF_3)(CH_3)_3 + F_2/He \longrightarrow Sn(CF_3)_2(CH_3)_2$$

$$Sn(CF_3)_2(CH_3)_2 + F_2/He \longrightarrow Sn(CF_3)_2(CH_3)F\ .$$

It is apparent, as mentioned earlier, that a major process in the reaction of $Sn(CH_3)_4$ with fluorine is the cleavage of the tin-carbon bond. This can be seen in Table XVII which lists the percentage of products obtained in the reaction with $Cd(CH_3)_2$. Assuming no redistribution, almost half the amount of material formed is $Sn(CH_3)_4$. However, enough material survives initial stages of fluorination to give equal amounts of $Sn(CF_3)(CH_3)_3$ and $Sn(CF_3)_2(CH_3)_2$, which comprise approximately 25% of the products. This may indicate that it might be possible to synthesize $Sn(CF_3)_4$ from $Sn(CH_3)_4$ and fluorine under conditions other than those employed here. In that $Sn(CF_3)(CH_3)_3$ and

$Sn(CF_3)_2(CH_3)_2$ form as the major fluorination products, one can say the reaction of fluorine with $Sn(CH_3)_4$ appears to occur on one CH_3 group at a time.

The infrared spectra of CF_3 containing compounds are very characteristic and lead to ready identification of the number of CF_3 groups on the compound. This can be seen in figure 28 for $Sn(CF_3)(CH_3)_3$ and $Sn(CF_3)_2(CH_3)_2$.

The mass spectra of $Sn(CH_2F)(CH_3)_3$, $Sn(CH_2F)_2(CH_3)_2$ and $Sn(CHF_2)(CH_3)_3$ are given in Table XIII. The highest m/e in each of the spectrum corresponds to parent minus a methyl group, $P^+ - 15$ (CH_3). Also, the largest m/e for each is $Sn(CH_3)^+$. $Sn(CH_2F)_2(CH_3)_2$ gives some apparent rearrangements resulting in a m/e of 51 for CHF_2^+ and 163 for $Sn(CH_3)_3^+$. The mass spectra for $Sn(CF_3)_2(CH_3)_2$ and $Sn(CF_3)(CH_3)_3$ are what is expected from halide exchange with bromine and chlorine in the mass spectrometer as observed in our laboratory.[88]

Both ^1H and ^{19}F NMR lead to conclusive identification of the tin compounds. Also present are the very characteristic tin 117/119 isotope satellites. Table XI and XII give the proton and fluorine NMR data for the compounds. Although the number of compounds are few,several trends can be seen:

(1) Increasing the number of CF_3 groups from one to two causes a large deshielding of the proton to cause the CH_3 resonance to drop from 0.09 to 0.39.

(2) When there are no CF_3 groups, the CH_3 chemical shift is near 0.0 ($Sn(CH_3)_2(CH_2F)_2$ appears to be an anomaly).

(3) $J_{^{117/119}Sn-H}$ increases with the number of fluorines on the

molecule.

(4) J_{HF} for a Sn-CH_2F group is greater than J_{HF} for a Sn-CHF_2 group.

(5) $J_{^{117/119}Sn-F}$ are much greater than $J_{^{117/119}Sn-H}$ and appear to be dependent on the number of fluorines on the molecule.

(6) Increase number of CF_3 groups causes a shift to lower chemical shifts.

Besides the characteristic doublet and triplet patterns as a result of proton - fluorine coupling, the chemical shift leads to ready identification of the groups, for protons CH_3 (~ 0), CH_2F (~ 4.8), CHF_2 (~ 6.0), and for fluorine CF_3 (~ -30), CHF_2 (~ 48) and CH_2F (~ 190). Integration of the partially fluorinated species gives the number of CH_3 groups on tin.

The observation[86] that chlorine cleaves a methyl group rather than trifluoromethyl group from $Sn(CH_3)_3(CF_3)$ is intriguing for this reaction. If fluorine behaves in a similiar manner, then once the groups CH_2F, CHF_2 and CF_3 form, they remain on the tin and a methyl group is cleaved. Schematically, the following is possible.

$$\begin{array}{llll}
Sn(CH_3)_4 + F_2/He \longrightarrow & Sn(CH_3)_3(CH_2F) & & Sn(CH_3)_2(CH_2F)F \\
& + Sn(CH_3)_2(CH_2F)_2 & & Sn(CH_3)(CH_2F)_2F \\
& + Sn(CH_3)_3(CHF_2) & + F_2/He \longrightarrow & Sn(CH_3)_2(CHF_2)F \\
& + Sn(CH_3)_3(CF_3) & & Sn(CH_3)_2(CF_3)F \\
& + Sn(CH_3)_2(CF_3)_2 & & Sn(CH_3)(CF_3)_2F\ .
\end{array}$$

FLUORINATION OF TETRAMETHYLLEAD, $Pb(CH_3)_4$

INTRODUCTION

The lead - carbon bonds are expected to be the weakest in Group IVA compounds. Tetraalkyllead compounds are thermally less stable than other members of Group IVA and thus they are more reactive than their tin analogues.[89] In fact, tetramethyllead is proven as an excellent source of CH_3 radicals. Therefore any CF_3 type compound would probably prove equally well as a source of CF_3 radicals and thus be of value in synthesis.

Chlorine reacts with lead tetraalkyls extremely rapidly and often it is difficult to stop the reaction at the monochloride stage.[89] The reactivity of tetramethyllead with chlorine at -60^o to give Me_3PbCl[90] indicates that fluorine will undoubtedly react producing bond cleavage even at lower temperatures. Reaction with other halogens and acids is also quite rapid and difficult to stop at the monohalide stage.[91]

However, there have been reports of the synthesis of CF_3 lead compounds by other methods.

a. $PbMe_4 + CF_3I \xrightarrow{h\nu} PbMe_3CF_3$ (infrared and hydrolysis)[92]

b. CF_3 radical from pyrolysis of CF_3COCF_3 onto lead mirror to yield $Pb(CF_3)_4$, colorless, involatile liquid, hydrolysis to CF_3H analysis[93]

The above compounds are not very well characterized. Two new lead CF_3 compounds have been recently synthesized, isolated and characterized, $Pb(CH_3)_3(CF_3)$ and $Pb(CH_3)_2(CF_3)_2$.[13]

EXPERIMENTAL

Reaction 1.

0.82 ml (6.12×10^{-3} mole) of $Pb(CH_3)_4$ was syringed into the low temperature reactor with zone 3 at -78° and a helium flow of 100 cc/minute. After flushing for 1 hour, zones 1 and 2 were also cooled to -78°. The following fluorination conditions were used.

F_2 (cc/minute)	He (cc/minute)	Temperature	Time
1.0	60	1,2,3 (-78)	54 hours
1.0	60	2,3 (-78)	15
1.0	60	3 (-78)	10
0.0	60	3 (-78)	12
0.0	100	1,2,3,4 (RT)	72

The volatile materials in the liquid nitrogen trap were fractionated into -131° and -196° fractions. There was approximately 1.5 ml of liquid that passed a -131° slush. Infrared spectra showed this mainly to contain CF_4 and CF_3H with a trace of SiF_4. Approximately 20 μl of liquid stopped in the -131° slush. Both the ^1H and ^{19}F NMR of the material were inconclusive. There was no starting material present but what appeared to be fluorocarbons and partially fluorinated hydrocarbons. However, what was curious was a material that appeared to comprise approximately half of the sample which had a doublet centered at 61.7 ppm upfield from TFA with a coupling constant of 56.4 hz in the fluorine NMR. Each of the doublet peaks appeared to be further split into doublets with J = 0.6 hz. This material remained unidentified.

Reaction 2.

With zone 3 cooled to -78^0 and a helium flow of 100 cc/minute, 1.15 ml of $Pb(CH_3)_4$ was syringed into the reactor. After purging with helium for ½ hour, zones 1 and 2 were also cooled to -78^0. 2 hours later, the fluorine flow was initiated with 1.0 cc/minute of fluorine metered in a stream of helium at 60 cc/minute. After six hours, the fluorine flow was terminated and the reactor flushed for 18 hours before the reactor was brought to room temperature. The contents of the liquid nitrogen trap were separated into -131^0 and -196^0 fractions. The -196^0 fraction contained only CF_4 and CF_3H. That which stopped in a -131^0 trap contained only starting material and no fluorinated material.

Reaction 3.

0.36 ml of $Pb(CH_3)_4$ was syringed into the reactor with a helium flow of 100 cc/minute and with zone 2 at -100^0. After one hour, the fluorine flow was started with 1 cc/minute of fluorine to 60 cc/minute of helium. After 29 hours, the fluorine flow was terminated and the reactor purged with helium for 10 hours before the temperature controller was turned off. The volatile materials which collected after 24 hours of flushing at room temperature were separated into -131^0 and -196^0 portions. The -196^0 fraction contained mainly CF_4, CF_3H and SiF_4. There was very little material present in the -131^0 fraction. Toluene was added to this fraction for a ^{19}F NMR. Three peaks were present at -51.0 (apparent singlet), -14.0 (broad singlet) and 59.2 (doublet, J = 60 hz) (referenced to external TFA).

Reaction 4.

With zone 2 cooled to -50°, 0.30 ml (2.14×10^{-3} mole) of $Pb(CH_3)_4$ was syringed into the reactor with a helium flow of 100 cc/minute. After six hours, the temperature of the reactor was lowered to -90°. Fluorination was allowed to occur for 20 hours with a fluorine flow of 0.5 cc/minute to a helium flow of 60 cc/minute. After flushing for 7 hours to remove all the fluorine from the system, the reactor was allowed to warm. The volatiles in the liquid nitrogen trap were fractionated into -95°, -131° and -196° portions, after purging for 21 hours at room temperature. Upon separation, a white material was deposited in the glass trap and on the vacuum line. The material in the -196° trap showed CF_3H and CF_2H_2 as its main components with no CF_4. The -131° fraction showed a decomposition product on the windows of the gas infrared cell. Broad bands were present in the 3000 and 1200 cm^{-1} regions of the infrared spectrum, attributable to poly CH and CF moieties. The material that stopped in a -95° trap was only starting material.

Reaction 5.

0.85 ml (6.34×10^{-3} mole) of $Pb(CH_3)_4$ was syringed into the reactor with zone 2 at -90° and a helium flow of 100 cc/minute. Fluorination was initiated with a fluorine flow of 0.5 cc/minute to a helium flow of 60 cc/minute. After 45 hours, the fluorine flow was increased to 1.0 cc/minute. The fluorine flow was terminated after 36 hours. After purging the reactor with helium for 6 hours, the temperature of the reactor was brought to room temperature. The volatile materials were fractionated into -95°, -131° and -196°. There was approximately

½ ml of liquid in the -196° fraction which consisted of CF_4 and CF_3H. There was very little sample in both the -95° and -131° fractions. That which stopped in a -131° fraction contained mainly higher fluorocarbons and partially fluorinated hydrocarbons. The material in the -95° trap seemed to decompose and deposited on the KBr windows an apparent polymer containing both CH and CF. Its mass spectrum showed peaks beyond 500 mass units.

Reaction 6.

0.79 ml of $Pb(CH_3)_4$ was syringed into the reactor which was at -70° with a helium flow of 60 cc/minute. After 4 hours of purging with helium, a fluorine flow of 0.5 cc/minute to a helium flow of 60 cc/minute was initiated. 55 hours later the fluorine flow was terminated. After 12 hours of flushing with helium, the temperature controller was turned off and the helium flow continued for 14 hours at room temperature. Extremely volatile materials which passed a -131° trap contained mainly CF_3H and CF_2H_2 with very little CF_4. Unidentified fluorocarbons were present in the -131°trap that had passed a -95°trap. The material in the -95° trap again deposited a polymer-type material of CH and CF content on the gas cell windows.

Reaction 7.

With zone 2 at -50° and zone 3 at -90°, 0.88 ml of $Pb(CH_3)_4$ was syringed into the reactor with a helium flow of 100 cc/minute. After 6 hours of purging with helium, both zones 2 and 3 were brought to -100°. Fluorination began with a flow of 0.5 cc/minute of fluorine to 60 cc/

minute of helium. After 50 hours, the fluorine flow was terminated. After 14 hours of purging with helium, the reactor was brought to room temperature and continued purging for 14 hours was allowed. Approximately 3/4 ml of material passed a -95^{o} slush bath. This material contained mainly CF_3H and CF_2H_2, with more CF_2H_2 than CF_3H, but very little CF_4. The material which stopped in a -95^{o} trap showed broad CH and CF bands in the infrared spectrum with little decomposition. Although the material was not identified, the interesting features of the ^{19}F NMR were a doublet at -15.6 (J = 4.5 hz), a doublet at 54.2 (J = 54 hz) split into quartets with J = 15.9 hz and a doublet at 61.8 (J = 55.5 hz). One portion of the ^{1}H spectrum of interest was a doublet with J = 48 hz at 5.4 ppm downfield from TMS. Several of the peaks can be attributed to groups such as CF_2H and CFH_2, whether on lead or not. Mass spectra gave inconclusive results as to whether lead was present or not.

Reaction 8.

With zone 2 at -30^{o} and zone 3 at -80^{o}, 0.65 ml of $Pb(CH_3)_4$ was syringed into the reactor with a helium flow of 100 cc/minute. After 6 hours, both zones 2 and 3 were cooled to -120^{o}. A fluorine flow of 0.5 cc/minute and a helium flow of 60 cc/minute was used for 18 hours. After flushing for eight hours, the temperature controller was turned off. After purging for 17 hours with helium at room temperature, the material was fractionated into -95^{o}, -131^{o} and -196^{o}. No CF_4 was present. Very little material was present in the other traps, however, one sample did show an interesting feature in the ^{19}F NMR, as an unresolved singlet at -34.7 ppm from TFA. This small amount of material did not make it possible to identify the compound further. Some of the starting material was also recovered.

Reaction 9.

To the yellowish-white powder, scrapped out of the reactor and off the copper turnings, $Hg(CH_3)_2$ was added. The NMR showed only $Hg(CH_3)_2$. There was no apparent reaction at room temperature. However, if $Cd(CH_3)_2$ was added, one obtained $Pb(CH_3)_4$ as the only compound. There appeared to be no fluorinated material present.

If the methylleadfluoride powder was heated in a thermal gradient sublimer at about 100^{o}, one obtained only $Pb(CH_3)_4$. This is what is to be expected if only methylleadfluorides were present.[91]

DISCUSSION

From the reactions attempted (of which a representative selection have been given) it does not appear that any $Pb(CF_3)_4$ was ever synthesized by direct fluorination. Several of the experiments were encouraging with ^{19}F chemical shifts in the correct region of the spectrum, but insufficient material made it difficult to tell conclusively what the compound was.

There has been a report of $Pb(CF_3)_4$[93] but the compound has not been well characterized. From the tentative NMR data, there appears to be groups of the following type, $Pb-CF_2H$ and $PbCFH_2$ formed but in small quantities. The preferred mode of the reaction appears to be the cleavage of the lead-carbon bond during direct fluorination leading to large quantities of CF_3H and CF_2H_2.

It is possible that any partially fluorinated material might be unstable with facile decomposition occurring to leave a polymer and lead fluorides. As to be expected, when the amounts of CF_4, CF_3H and CF_2H_2 increase, the amount of material of low volatility decreases considerably and the amount of lead fluorides increases.

Analogous to the reaction of $Sn(CH_3)_4$, it is possible that one could be forming compounds of the following type, PbR_3F, PbR_2F_2 and $PbRF_3$, where $R = CH_3, CH_2F, CHF_2, CF_3$. The lead fluorides would not be volatile and would not be expected to leave the reactor. When the reactor was opened after the lead reactions, a white to cream-white powder can be scrapped out and shaken off the copper turnings. KBr pellets of the material were inconclusive whether there was any CF present. However, upon addition of $Cd(CH_3)_2$, one obtained only $Pb(CH_3)_4$, no fluorine was present as evidenced by the ^{19}F NMR. Therefore one is inclined to think that the lead-carbon bond is readily cleaved by fluorine to yield methyllead-fluorides which are not expected to be reactive toward fluorine at such low temperatures. Schematically, the following appears to result.

$$Pb(CH_3)_4 + F_2/He \longrightarrow Pb(CH_3)_3F + Pb(CH_3)_2F_2 + Pb(CH_3)F_3 \qquad (1)$$

It is also possible that the methyl groups are fluorinated and as more fluorines replace protons, the lead-carbon bond becomes susceptible to cleavage by fluorine.

$$Pb(CH_3)_4 + F_2 \longrightarrow Pb(CH_3)_3(CH_2F) + HF \qquad (2)$$

$$Pb(CH_3)_3(CH_2F) + F_2 \longrightarrow Pb(CH_3)_3F + CH_2F_2 \qquad (3)$$

$$Pb(CH_3)_3(CH_2F) + F_2 \longrightarrow Pb(CH_3)_3(CHF_2) + HF \qquad (4)$$

$$Pb(CH_3)_3(CHF_2) + F_2 \longrightarrow Pb(CH_3)_3F + CHF_3 \qquad (5)$$

$$Pb(CH_3)_3(CHF_2) + F_2 \longrightarrow Pb(CH_3)_3(CF_3) + HF \qquad (6)$$

$$Pb(CH_3)_3(CF_3) + F_2 \longrightarrow Pb(CH_3)_3F + CF_4 \qquad (7)$$

Reactions (3), (5) and (7) are probable in light of the amounts of CF_4, CF_3H and CF_2H_2 present. It was curious that there were not very many fluoroethanes or propanes. A small percentage of the time one isolates C_2F_3H but there was no C_2F_6.

One possible route to the synthesis of CF_3 lead compounds is to fluorinate methylleadfluorides and then convert the fluorides to an alkyl group by a methylating agent. However, this is a another project in itself. That this is indeed feasible is shown by reaction 9.

REACTION OF FLUORINE WITH $C(CH_3)_4$, $Si(CH_3)_4$, $Ge(CH_3)_4$, $Sn(CH_3)_4$, and $Pb(CH_3)_4$

Direct fluorination of group IVA tetramethyl compounds can be summarized as follows:

I. $C(CH_3)_4 + F_2 \xrightarrow[-78]{} C(CF_3)_4 + C(CF_3)_w(CF_2H)_x(CFH_2)_y(CH_3)_z$, $w + x + y + z = 4$.

a. Dilute fluorine with no increase to pure fluorine leads to no $C(CF_3)_4$.

b. Dilute fluorine with an increase to pure fluorine leads to 10-90% $C(CF_3)_4$.[111]

II. $Si(CH_3)_4 + F_2 \xrightarrow[-150]{} Si(CH_3)_3(CH_2F)$

$\xrightarrow[-110]{} Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$.

a. Only small yields of $Si\text{-}CF_3$ compounds.

III. $Ge(CH_3)_4 + F_2 \xrightarrow[-100]{} Ge(CF_3)_4 + Ge(CF_3)_x(CF_2H)_y(CFH_2)_z$, $x + y + z = 4$.

a. Increase in temperature from -100° to -60° leads to low yields of $Ge(CF_3)_4$, 1 - 6 %.

b. Increase in temperature from -100° to -20° leads to high yields of $Ge(CF_3)_4$, 63.5%, but no $Ge(CF_3)_x(CF_2H)_y(CFH_2)_z$ is produced.

IV. $Sn(CH_3)_4 + F_2 \xrightarrow[\text{low temp}]{} Sn(CH_3)_3F + Sn(CH_3)_2(CH_2F)F +$
$Sn(CH_3)(CH_2F)_2F + Sn(CH_3)_2(CHF_2)F +$
$Sn(CH_3)_2(CF_3)F + Sn(CH_3)(CF_3)_2F$

a. Compounds analyzed by methyl exchange with $Cd(CH_3)_2$.

V. $Pb(CH_3)_4 + F_2 \xrightarrow[\text{low temp}]{} Pb(CH_3)_3F$.

The fluorination of the tetramethyl compounds of Group IVA leads to some quite interesting results. Previously it has been shown that neopentane smoothly fluorinates to perfluoroneopentane.[16] High fluorine concentrations are required to obtain $C(CF_3)_4$, otherwise one obtains only partially fluorinated materials at low temperatures. The fluorination appears to be totally random in nature. A high degree of fluorination occurs. The fluorination of tetramethylsilane leads to only partially fluorinated materials of the following type, $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$, with only a small percentage of the products with CF_3 groups. For some unknown reason, the fluorination does not proceed to as high a degree as that for neopentane. Besides no $Si(CF_3)_4$ being isolated, there appears to be some reluctance to form CF_3 groups on silicon. Although the fluorination again appears to be random, it behaves a little different from chlorination reactions. Chlorination tends to activate the same carbon leading from CH_2Cl to $CHCl_2$ to CCl_3 before another CH_3 group is chlorinated in neopentane[94,95] or tetramethylsilane[61,96]. This is obviously not the case for fluorination as one would obtain much more $Si\text{-}CF_3$ compounds.

Tetramethylgermanium fluorinates extremely well, possibly as well as neopentane. The yield of tetrakis(trifluoromethyl)germanium is quite dependent on the temperature of the reaction. When the yield of $Ge(CF_3)_4$ is low, one can isolate the partially fluorinated materials of the following composition, $Ge(CF_3)_x(CF_2H)_y(CFH_2)_z$, $x + y + z = 4$. In fact there is a high degree of fluorination on tetramethylgermanium, leading to many compounds with CF_3 groups. Tetramethylgermanium appears to behave very much like neopentane as opposed to tetramethylsilane in its reaction with fluorine. Fluorination of tetramethyltin is in one respect similiar to that of other halogen reactions with tin alkyls.

Cleavage of the tin-carbon bond by fluorine is quite dominant. However, fluorination to some extent does also occur to yield CF_3 groups on tin. Here it appears that there is some selectivity in the fluorination process to yield CF_3, rather than a purely random-type reaction. The fluorination of tetramethyllead behaves in an analogous manner to that of the other halogens with lead alkyls. Facile lead-carbon bond cleavage occurs with fluorine, even at low temperatures.

Whether there is any true selectivity in the fluorination process for the reactions described above can only be answered by very careful experiments, which are beyond the scope of this thesis. Tedder[97] has pointed out that there might indeed be some selectivity in fluorination, but it is not the same extent observed for chlorination. This has been attributed to the low dissociation energy of fluorine and thus its radical reactivity is not temperature sensitive. However, there does appear to be some selectivity toward fluorinating another group rather than one with a fluorine already present. Numbers for this reactivity difference as given by Tedder are:

$$\begin{array}{ccccccc} CH_2F & - & CH_2 & - & CH_2 & - & CH_3 \\ <0.3 & & 0.8 & & 1.0 & & 1.0 \end{array}$$

But nevertheless, the fluorination of tetramethylsilane is quite different from that of neopentane, tetramethylgermanium, and tetramethyltin in that there is an apparent reluctance to form CF_3 groups on silicon, while CF_3 groups form readily on carbon, germanium and tin.

The infrared spectra are hard to interpret but it is apparent that with more CF_3 groups present, the spectra simplify tremendously. With CF_2H, CFH_2 and CH_3 groups present, the bands are quite broad. However,

CF_3 groups tend to sharpen the absorptions.

The mass spectra for the tin compounds are quite simple while those for the silicon and germanium are quite a bit more complex. This complexity arises due to the interactions of the various groups present on the molecule.

A point which should be made clear is that with neopentane one obtains all four types of groups CF_3, CF_2H, CFH_2 and CH_3 quite randomly. With tetramethylsilane, the groups which predominate are CF_2H, CFH_2 and CH_3. With tetramethylgermanium, very few compounds have CH_3 groups, mainly CF_3, CF_2H and CFH_2 groups.

The carbon-13 NMR for several CF_3 compounds are shown on the following pages. Unfortunately the compounds $Si(CF_3)_4$ and $Pb(CF_3)_4$ do not yet exist for their ^{13}C NMR would be of much interest. The shift to further deshielding from $Ge(CF_3)_4$ to $Sn(CF_3)_4$ is what to be expected.

^{13}C Data

	δ[100]	$J_{^{13}C-H}$		δ	$J_{^{13}C-H}$[c]
$C(CH_3)_4$	-31.9[a]	120[98,99] 124[100-102]	$C(CF_3)_4$		
$Si(CH_3)_4$	0.0	120[98,99] 119[100]	$Si(CF_3)_4$		
$Ge(CH_3)_4$	1.4	126[100]	$Ge(CF_3)_4$	126.2[b]	331[b] (329.5)[13]
$Sn(CH_3)_4$	8.6	128[100,102] 126[98]	$Sn(CF_3)_4$	132.7[b]	349[b]
$Pb(CH_3)_4$	2.6	133[100]	$Pb(CF_3)_4$		

a. methyl carbon, center carbon at -27.9.

b. this work.

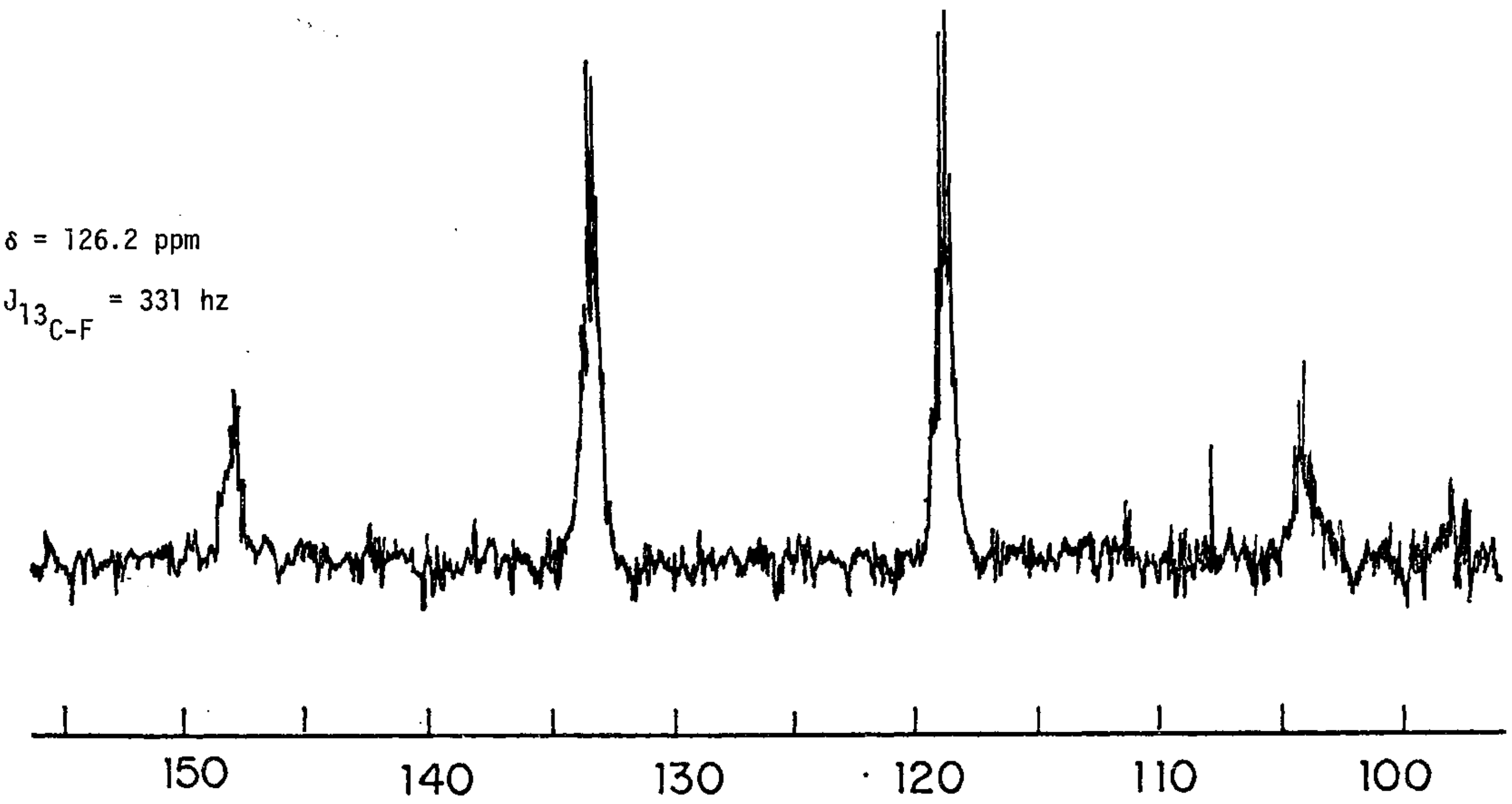
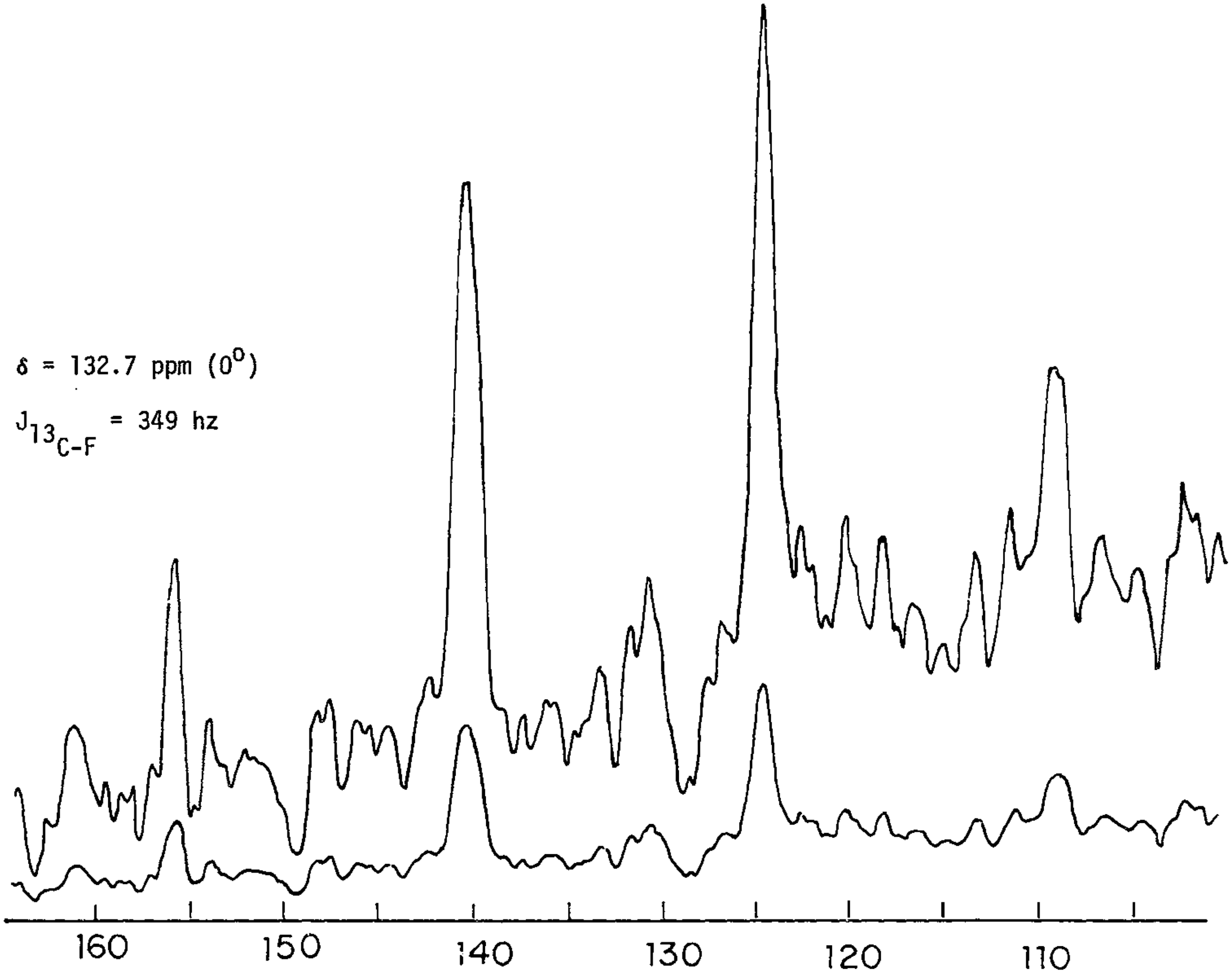


Figure 29. Carbon-13 spectrum of $Ge(CF_3)_4$



δ = 132.7 ppm (0^{o})

$J_{^{13}C-F}$ = 349 hz

Figure 30. Carbon-13 spectrum of $Sn(CF_3)_4$

c. $CF_3Ge(CH_3)_3$[103] J = 338

$CF_3Sn(CH_3)_3$[103] J = 356

CF_3HgCF_3[104] J = 356.3

CF_3SeCF_3[104] J = 331.3

Shifts relative to TMS. Coupling constants in hertz.

Another interesting feature is the J_{HF} coupling contants of the fluorinated tetramethyl compounds.

				CHF_2	CH_2F
carbon	CHF_2	$>$	CH_2F	≈ 52	≈ 47
silicon	CHF_2	$<$	CH_2F	≈ 45.5	≈ 47
germanium	CHF_2	≈	CH_2F	≈ 46	≈ 46
tin	CHF_2	$<$	CH_2F	≈ 46	≈ 48

The long-range fluorine - fluorine coupling constants are:

carbon 8-9.5 hz

silicon 1.4-2.1 hz (no CF_3 groups) 3.0-3.2 (with CF_3 groups)

germanium 2.1-2.5 hz (no CF_3 groups) 2.9-3.5 (with CF_3 groups)

If electronegativity can be correlated with coupling constants, this would put silicon less electronegative than germanium and tin, which is what several authors have contended.[105,106,107]

The range of chemical shifts for the groups on the Group IVA elements is given on the following page. Whether the silicon compounds give anomalous shifts is difficult to determine. What is of interest is whether Si-CF_3 chemical shift is in the proper place. A plot of the expected chemical shift of $Si(CF_3)_4$ versus electronegativity indicates the chemical shift may be approximately -35 ppm rather than -21 ppm

	^{1}H			^{19}F		
	CH_3	CH_2F	CHF_2	CF_3	CF_2H	CFH_2
Carbon	0.7 - 0.9	4.0 - 4.7	6.0 - 6.1	-8.8 - -13.5	49.7 - 51	157 - 167.5
Silicon	-0.2 - 0.3	4.2 - 4.7	5.6 - 5.9	-15.5 - -16.5	59 - 61	195 - 204
Germanium	0.3 - 0.5	4.8 - 5.0	6.1 - 6.3	-21.1 - -27.9	49 - 53.9	191 - 193
Tin	0.0 - 0.4	4.7 - 4.9	6.1	-29.1 - -33.8	48.1	190 - 191
Lead				-35.6 - -39.0		

TABLE XVIII. Approximate Chemical Shifts of Various Groups predicted by a plot of chemical shift versus atomic number. Both the ^{19}F and ^{13}C NMR of the compound would be of interest in this respect to see if silicon is anomalous or not. However, since electronegativities are not directly related to chemical shifts, a plot of chemical shifts versus atomic number would be more reliable.

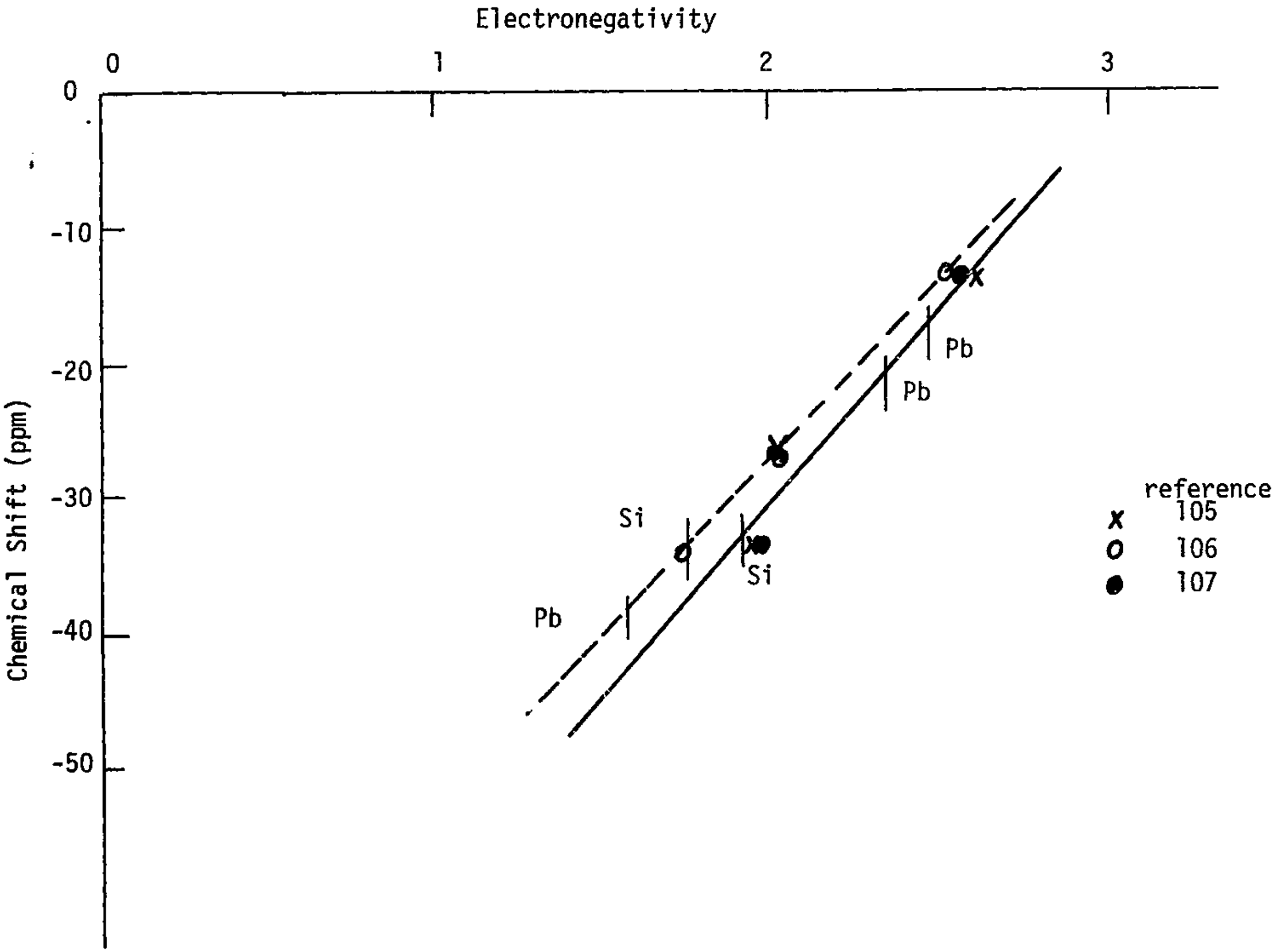


Figure 31. Chemical shift of CF_3 groups on group IVA elements versus electronegativity.

a. in CCl_4
b. in $CFCl_3$
c. -30.6 in CCl_4
d. in pyridine
e. -30.8 in benzene
f. in benzene, -40.5 in ether[31]

All chemical shifts given are for neat samples unless otherwise noted. Chemical shifts relative to external TFA.
- downfield from TFA.

						HCF_3[108] + 8	
			$C(CF_3)_4$[16] -13.9[a]	$N(CF_3)_3$[108] -17.6	$O(CF_3)_2$[108] -14.6	FCF_3[108] -7.6	
				$P(CF_3)_3$[109] -25.8[b]	$S(CF_3)_2$[104] -38[b]	$ClCF_3$[108] -43.6	
			$Ge(CF_3)_4$[9] -27.0[c]	$As(CF_3)_3$	$Se(CF_3)_2$[104] -44.7[b]	$BrCF_3$[108] -55.6	
	$Cd(CF_3)_2$[27] -46.7[d]		$Sn(CF_3)_4$[10] -33.8[e]	$Sb(CF_3)_3$	$Te(CF_3)_2$[10 -54	ICF_3[108] -71.6	
	$Hg(CF_3)_2$[9] -42.1[f]			$Bi(CF_3)_3$[110] -45.9			

Figure 32. ^{19}F Chemical Shifts of Trifluoromethyl Compounds

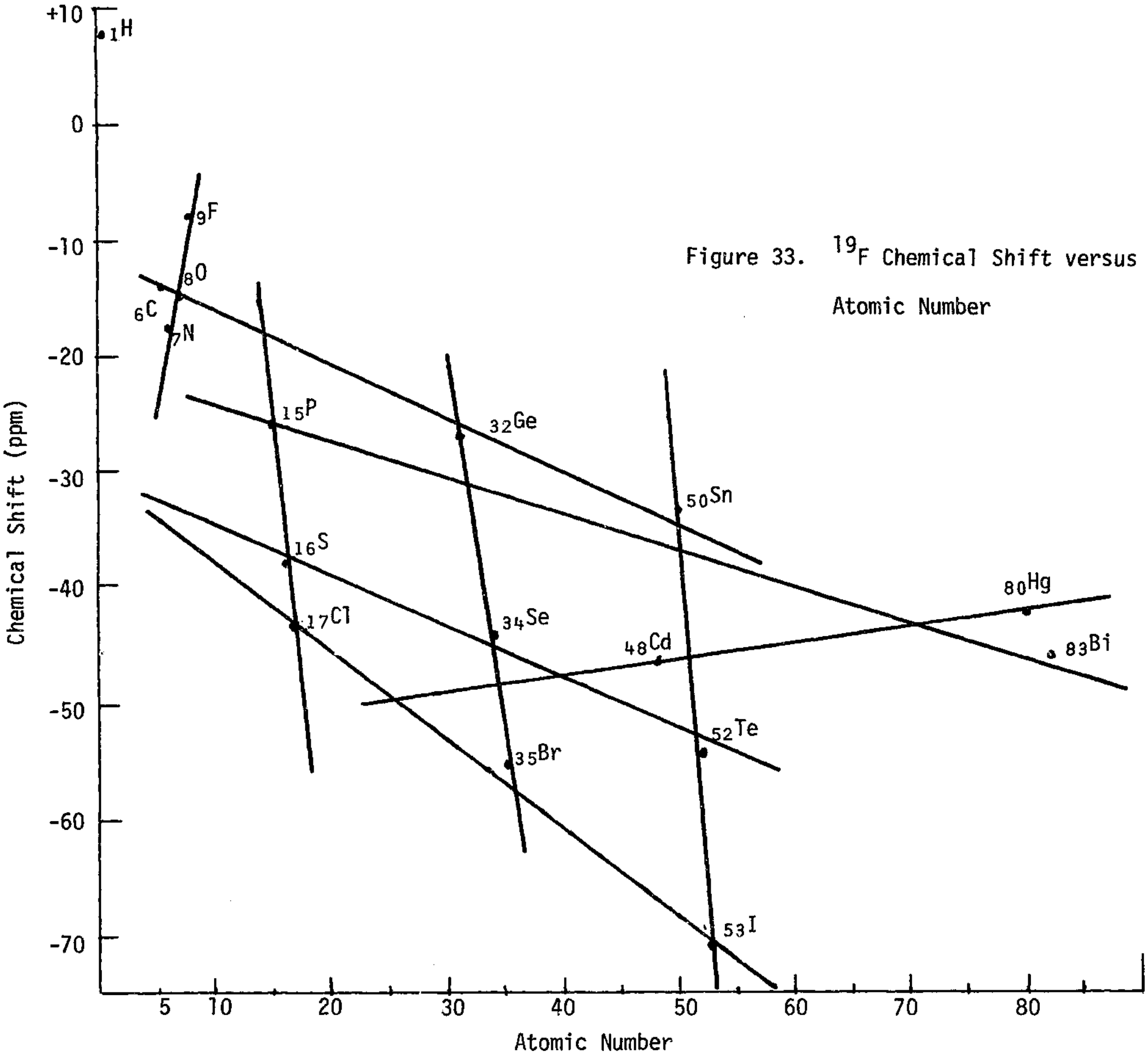


Figure 33. ^{19}F Chemical Shift versus Atomic Number

CHAPTER IV

SUMMARY

As stated in the introduction, the goal of this research was to explore the fluorination technique as an alternative method for the synthesis of trifluoromethyl compounds. One can certainly conclude from the work presented here that a very promising new synthetic method has been discovered. Obviously the fluorination of many more compounds should be studied before the final value of the method is established. Although it is true that no $Sn(CF_3)_4$ or $Pb(CF_3)_4$ were synthesized, there is only one other method presently available to make $Sn(CF_3)_4$[8] and none for $Pb(CF_3)_4$. Direct fluorination is certainly an excellent method for the synthesis of $Ge(CF_3)_4$. The yield is only marginal at best for $Hg(CF_3)_2$, but the technique works, which is a result anyone would have agreed was unexpected. $Si(CF_3)_4$ has still evaded the synthetic methods presently known.

We have been able to show that metal - carbon and metalloid - carbon bonds can remain intact during direct fluorination as one is converting C-H bonds to C-F bonds. We are able to produce many interesting partially fluorinated species of tetramethylsilane and tetramethylgermanium, unattainable by other methods. What has to be done is to evaluate direct fluorination as a synthetic tool on individual compounds or groups of compounds rather than in general. A good example is the synthesis of $Hg(CF_3)_2$. One would not use direct fluorination to produce large quantities of $Hg(CF_3)_2$ from $Hg(CH_3)_2$. There are other methods which give much higher yields.[32] However, it is of synthetic utility to produce large quantities of $Ge(CF_3)_4$ by direct fluorination. One should also not overlook the possibility of future refinements in our direct fluorination technology.

We have gained some valuable information concerning the Group IVA tetramethyl compounds by studying the direct fluorination of $M(CH_3)_4$, M = C, Si, Ge, Sn, Pb. New trifluoromethyl compounds will undoubtedly be produced by direct fluorination but many more experiments need to be attempted.

In the section on preparation of perfluoroalkyl compounds, Clark[1] mentioned direct fluorination of alkyl compounds as a method for the preparation of perfluoro compounds. However, he pointed out that at the time of the review, direct fluorination was used only for the preparation of nitrogen derivatives. The reason given was:

> "Owing to the ease of cleavage of most metal - carbon bonds on fluorination, it is not suitable for the preparation of perfluoroalkylmetallic derivatives."

We would like to suggest that direct fluorination is a suitable method for the preparation of certain perfluoroalkylmetallic derivatives.

CHAPTER V

MISCELLANEOUS REACTIONS

Fluorination of Dimethyldichlorosilane, $Si(CH_3)_2Cl_2$

Experimental. 2.0 ml of $Si(CH_3)_2Cl_2$ was syringed into the low temperature reactor with zone 2 cooled to -100^0 and a helium flow of 100 cc/minute. For 48 hours, fluorination was done with a fluorine flow of 1.0 cc/minute to a helium flow of 60 cc/minute.

Fractionation was done on the volatile materials at -95^0, -131^0, -160^0 and -196^0. The -196^0 fraction contained a considerable amount of material, approximately 1.0 ml of liquid. Present were mainly CF_4, CF_3H, CF_2H_2, SiF_4, CF_3Cl and HCl. Material which stopped in the -160^0 trap contained mainly CH_3SiF_3 with some $(CH_3)_2SiF_2$. There was approximately 0.5 ml of CH_3SiF_3. Freons and chlorocarbons made up most of the material which stopped in the -95^0 and -131^0 traps. Chlorine was also present but not in large quantities.

Discussion. The fluorination of $Si(CH_3)_2Cl_2$ was attempted in an effort to produce either $Si(CF_3)_2F_2$ or $Si(CF_3)F_3$. Since $Si(CF_3)F_3$ was known to be stable, it was felt that direct fluorination might be a suitable method for the synthesis of that compound. Although a lot of $Si(CH_3)_2F_2$ and $Si(CH_3)F_3$ were produced, no $Si-CF_3$ compounds were isolated. This was disappointing in like of our failure with the fluorination of tetramethylsilane to produce large quantities of $Si-CF_3$ compounds. However, the fluorination of $Si(CH_3)_2Cl_2$ demonstrated how unanticipated problems can result. This will be discussed in the next paragraph.

From the compounds readily identifiable by infrared, mass spectra and NMR, one see that the chlorine radical formed is indeed quite reactive and appears to be as competitive as fluorination. Compounds such as HCl, $CHCl_3$, CH_2Cl_2 and $CFCl_3$ give an idea of the reactivity of the chlorine radical formed during the fluorination process. It is possible that the chlorination inhibits, or at least complicates, the fluorination process and prevents the formation of Si-CF_3. The mass spectra showed the presence of compounds containing more than two carbons with up to four chlorines present.

Unfortunately $Si(CH_3)_2F_2$ and $Si(CH_3)F_3$ were not kept for further fluorination for these would be ideal starting materials for preparing $Si(CF_3)_2F_2$ and $Si(CF_3)F_3$ without the interference of the chlorine radical. However, a reactor problem occurs for these two compounds are quite volatile. Extremely low reaction temperatures are thus required. At such low temperatures as -120 to -150, fluorination does not occur as well. The fluorination conditions described here led to mainly $Si(CH_3)F_3$, approximately 0.5 ml with some $Si(CH_3)_2F_2$. Other fluorination conditions give different amounts of the two methylfluorosilanes. One can isolate more $Si(CH_3)_2F_2$ than $Si(CH_3)F_3$ if one uses the following conditions: -110, F_2/He ratio of 0.5/60 cc/minute.

This reaction demonstrated that halogens can quite possibly complicate a fluorination process. This is probably true with both chlorine and bromine since both radicals are quite reactive. With iodine the problem will not be too serious due to the low reactivity of the radical and the size of the atom. Therefore the fluorination of chlorinated compounds can lead to quite interesting results.

Reaction of $Hg(CF_3)_2$ with $Si(CH_3)_3Cl$

Into a 4 mm glass tube was condensed $Hg(CF_3)_2$ and $Si(CH_3)_3Cl$. The reaction was monitored by proton and fluorine NMR.

After remaining at room temperature for one day, the ^{19}F NMR showed no reaction, only a small amount of $Hg(CF_3)_2$ had dissolved in the $Si(CH_3)_3Cl$. Heating the tube at 100° for 1 day gave $Hg(CF_3)Cl$, $Si(CH_3)_3F$ and c-C_3F_6 as new resonances. [$Hg(CF_3)_2$, -41.79, J_{HgF}=1210 hz, $Hg(CF_3)Cl$, -45.42, J_{HgF}=1860 hz, $Si(CH_3)_3F$, +76.77, J_{HF}=7.3 hz, c-C_3F_6, +78.54] The ratio of $Hg(CF_3)_2$ to $Hg(CF_3)Cl$ was approximately 2 to 1. Heating the sample at 100° for an additional day gave the $Hg(CF_3)_2$/$Hg(CF_3)Cl$ ratio of 1/1. An additional day of heating at 80° gave a $Hg(CF_3)_2$/$Hg(CF_3)Cl$ ratio of 4/5. An additional three days at 100° gave a $Hg(CF_3)_2$/$Hg(CF_3)Cl$ ratio of 1/2.

8 of 10 lines for the proton-fluorine coupling pattern of $Si(CH_3)_3F$ were resolved in the ^{19}F NME. c-C_3F_6 was a sharp singlet. The amount of $Si(CH_3)_3Cl$ can be monitored in the proton NMR by comparison with the amount of $Si(CH_3)_3F$ present. $Si(CH_3)_3F$ gives a characteristic doublet upfield from $Si(CH_3)_3Cl$.

Discussion. No Si-CF_3 compounds were identified. This is possible in light of the temperature at which the experiment was run. At 100°, the half-life of $Si(CF_3)F_3$ is reported to be only 7 minutes. Therefore, any Si-CF_3 compounds formed under these conditions would undoubtedly eliminate :CF_2 to give Si-F and c-C_3F_6 or C_2F_4, which is what is seen.

However, there is CF_3 transfer with the chloride. Formation of $Hg(CF_3)Cl$ is a promising sign for one does not expect fluoride transfer from $Hg(CF_3)_2$ to Si-Cl. Therefore one could speculate that Si-CF_3 did indeed form and was not stable at the temperature of the experiment.

Fluorination of 1-adamantamine.

Experimental. Two boats, each containing 1.0 grams of 1-adamantamine, were placed in a nickel reactor for the reaction to occur at room temperature. A glass trap was placed downstream from the NaF scrubber. Dry ice was used to trap any volatile material. The following fluorination conditions were used.

F_2 (cc/minute)	He (cc/minute)	Time (hrs)
1.0	60	24
1.0	30	24
1.0	15	24
3.0	15	24
5.0	15	24
5.0	0	24
0.0	30	22
0.0	60	26
(removed sample in boat, reground sample and placed back in boat for fluorination)		
2.0	30	24
2.0	15	24
2.0	0	96
2.0	30	24
0.0	30	24
(removed sample in boat, reground sample and placed back in boat for fluorination)		
2.0	30	24
2.0	15	24
2.0	0	168
0.0	60	168

The volatile material in the dry ice trap was transferred out into a glass storage tube. The sample in the boat was scrapped out and stored in a glass vessel. The material was slightly tacky.

The volatile material in the glass trap was transferred to a glass vessel to which CCl_4 was added. The fluorinated material was only very slightly soluble. Upon warming the CCl_4 solution, more of the material dissolved. The material was syringed warm into the gas chromatograph.

With 60 µl of CCl_4 solution, the peaks of interest had the following retention times, 15'45", 25'20" and 38'20". The gas chromatograph program used was: 50^{0} isothermal until the second peak of interest was off the column, then 10^{0}/minute to 100^{0}, isothermal at 100^{0} until the third peak of interest was out. CCl_4 had a retention time of approximately 33 minutes with this program. 10% SE-30 on chromosorb P was used in a 24' x 3/8" column.

Infrared, mass spectrum and NMR led to the identification of the following compounds.

15'45"

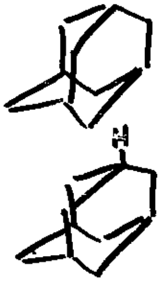
1375(w), 1350(sh), 1341(s), 1329(s), 1311(s), 1285(s) 1269(m), 1245(m), 1205(m), 1170(w), 1151(w), 1080(w), 1051(m), 1021(w), 1000(w), 981(sh), 975(s), 932(s), 877(m), 855(w), 730(m), 651(w), 629(w), 540(w)

^{19}F NMR:	+59.3	+113.7	+122.0	+124.4	+221.8
	CF_3	CF_2	CF_2	CF_2	CF
	6 :	4 :	4 :	2 :	2

(referenced to $CFCl_3$)

Mass Spectrum: MW = 500, $C_{10}F_{20}$

481(0.071), 459(0.028), 443(0.13), 424(9.68), 405(17.10), 355(8.06), 343(0.58), 336(1.54), 317(2.77), 305(4.51), 293(3.22), 286(2.90), 281(0.84), 274(2.58), 267(8.71), 255(29.35), 243(7.10), 236(12.26), 224(16.45), 205(40.65), 193(2.90), 186(8.71), 181(26.45), 155(14.19), 143(3.54), 131(48.39), 119(10.32), 100(3.87),69(100)



R_f

25'20"

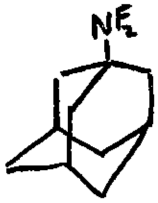
1340(w), 1311(s), 1300(sh), 1293(vs), 1271(m), 1242(w), 1215(w), 1190(w), 1152(vw), 1140(vw), 1110(vw), 1009(w), 980(vs), 915(vs), 851(w), 729(w), 669(w)

^{19}F NMR:	121.5	224.1
	CF_2	CF
	4 :	1.0

Mass Spectrum: MW = 424, $C_{10}F_{16}$

443, 424, 405

(Appears to be two compounds. Possibly $C_{10}F_{16}$ and $C_{10}F_{15}H$, ^1H: 1.38 (singlet))



R_f

38'20"

1350(w), 1321(sh), 1310(s), 1300(s), 1260(m), 1241(w), 1205(w), 1165(vw), 1109(vw), 1079(vw), 1041(m), 1010(m), 990(s), 945(m), 890(w), 841(m), 805(s), 790(w), 780(w), 775(w), 730(vw), 659(m)

^{19}F NMR:	-37.4	+112.8	+121.4	+220.9
	NF_2	CF_2	CF_2	CF
	2.2 :	6 :	6 :	3.2

Mass Spectrum: MW = 457, $C_{10}F_{17}N$

457(6.49), 438(4.67), 421(0.480), 405(9.35), 355(2.60), 336(0.91), 317(4.93), 305(2.08), 293(0.91), 286(3.90), 267(6.89), 245(9.61), 236(22.73), 186(15.06), 181(23.38), 155(10.91), 143(2.99), 131(33.77), 100(1.67), 69(100)

The fluorination of adamantane previously produced only monohydroperfluoroadamantane as the highest fluorinated adamantane compound. It was a puzzle why no perfluoroadamantane was produced despite very vigorous reaction conditions. The fluorination of 1-adamantamine was attempted to see if this bridgehead phenomenon was a general one, i.e. that there will always be one bridgehead proton unfluorinated. From this work it appears not to be the case for isolated compounds appear to be perfluoro. Maximum infrared intensities produced no CH stretches. ^{19}F NMR integration tells that there are no protons present. What is interesting is that it appears that we are able to preserve the C-N bond during fluorination to produce $C-NF_2$ from $C-NH_2$.

Fluorination of Tetramethylammonium Halides.

The following compounds were fluorinated: $N(CH_3)_4Cl$, $N(CH_3)_4Br$, $N(CH_3)_4I$, and $N(CH_3)_4PF_6$. In no cases were any fluorination noticed on the methyl groups. No compounds of the type $N-CF_3$, $N-CF_2H$ or $N-CFH_2$ were isolated. Fluorination was attempted mainly at room temperature and higher with very high fluorine concentrations.

Fluorination of $N(CH_3)_4Cl$ led to a 40/60 mixture of $N(CH_3)_4Cl/N(CH_3)_4HF_2$ as identified by elemental analysis on fluorine and carbon. It was observed that room temperature fluorination led to much chlorine production. Reactions at higher temperatures, up to 100^o, led to increased chlorine production, but not fluorination of the methyl groups. When the fluorinated products were dissolved in water, one can observe the formation of HF as the F^- ion fluorinates the water. In time, the HF_2^- resonance grows in and the F^- and HF resonances disappear. It was felt that $N(CH_3)_4F$ was formed anhydrous if all the moisture from the starting material was removed. Traces of moisture led to $N(CH_3)_4F.nHF$. Upon sitting, the fluorinated material picks up moisture, which is characteristic of the fluorides. One normally obtains commercially

$N(CH_3)_4F.5H_2O$. It is very difficult to obtain $N(CH_3)_4F$ anhydrous due to the small F^- counterion, and thus its affinity to pick up water or HF. (^{19}F NMR resonances were F^-, ≈54, HF_2^-, ≈86, and HF, ≈127) ($N(CH_3)_4F.5H_2O$, ≈43.1)

Fluorination of $N(CH_3)_4Br$ gave essentially the same results as that for $N(CH_3)_4Cl$ except that the amount of $N(CH_3)_4F$ was less. Conversion of the bromide ion to bromine appears more difficult than the conversion of the chloride ion to chlorine, and thus lower fluoride production.

Fluorination of $N(CH_3)_4I$ also produced $N(CH_3)_4F$, but in even less quantity than for the bromide. Iodine production was correspondingly lower. Upon sitting in glass tubes, the fluorinated material appears to evolve I_2 in time, indicating the possible HF formation of the F^- attack on the glass and subsequent attack on the iodide counterion.

Fluorination of $N(CH_3)_4PF_6$ led to no different fluorinated products. No fluorides were formed as PF_6^- could not be converted to PF_5, PF_3 or any other phosphorous fluorides. However, upon heating, still no fluorination occurred on the methyl groups.

Several times it was possible to burn the ammonium salts but no fluorinated material of interest was isolated. If one heated the mixture of $N(CH_3)_4Cl/N(CH_3)_4HF_2$ (40/60) in vacuum to about 100^0, one obtains the following volatile materials, $N(CH_3)_3$, CH_3F, CH_3Cl, and HF.

This apparent reluctance to fluorinate can be explained on as an electronic factor. With the positive charge on nitrogen, one can assume that any fluorinated material would have to withdraw more electron density from an already electron deficient source. However, this is not to say that $N(CF_3)_4^+$ cannot be produced by some other method. Evidently the fluorination process, being slow controlled collisional processes, is not rapid enough to allow CF_3 to form.

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APPENDIX

Regeneration of NaF Pellets from $NaHF_2$

The used sodium bifluoride pellets, after loose $NaHF_2$ powder has been removed by screening, are placed in an iron tube which has a copper turning plug in the bottom. The iron tube should be equippped for heating from 200 - 300°C.

Dry nitrogen is used to purge the iron tube with a flow of at least 150 cc/minute. An exit tube should aerate from the iron tube into either a NaOH or KOH water bath.

Upon heating the tube, the first material removed from the pellets is water. HF comes off after most of the water has been removed. The water solution containing the KOH should be slightly basic to start with. As HF is generated, the water bath should become acidic, at which time more KOH should be added. This should continue until no more HF is generated and the solution remains slightly basic.

After the heat is turned off, continued flushing with dry nitrogen should ensue. The pellets should then be placed in a suitable container(s) and placed in an oven which is at a temperature of at least 100°C. The pellets are very hygroscopic at this stage. Prolonged exposure to air will result in considerable moisture adsorption.

An X-ray powder pattern of the pellets should be taken to see if the pellets are pure NaF. The powder pattern of $NaHF_2$ is quite different from that of NaF. In this manner, the purity of the regenerated pellets can be checked.

The regenerated pellets should not crush easily. If this is the case, do not use the pellets. This generally occurs when the pellets have been overheated. Pellets which crush easily will tend to fuse and probably plug the NaF scrubber upon contact with a large quantity of HF.

The Preservation of Metal–Carbon Bonds and Metalloid–Carbon Bonds during Direct Fluorination: a Surprise Even to Fluorine Chemists

Sir:

Occasionally chemical experiments prove successful which surprise even the researchers initiating the work. Such is the case with the preservation of metal–carbon bonds during direct fluorination.

Before the fact, one could have written general logical mechanisms for elimination of methyl groups or cleavage of all metal–carbon bonds such that certain failure would be projected. These pathways still contribute to the overall reaction even under the reported conditions but are not catastrophic.

We have demonstrated preservation of mercury-carbon and silicon–carbon bonds during the process of direct fluorination by the fluorination of dimethylmercury to give bis(trifluoromethyl)mercury and of tetramethylsilane to give a series polyfluoro-tetramethylsilanes. The versatility of the method of direct fluorination has been previously demonstrated by the fluorination of structurally unusual hydrocarbons,[1] polymers,[2] and inorganic compounds[3] to mention just a few.

Dimethylmercury can be fluorinated to its perfluoro analogue, bis(trifluoromethyl)mercury, 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 using a mixture of 1 cm^3/min fluorine to 60 cm^3/min helium, was used for 5 days in the cryogenic zone reactor.[1] The bis(trifluoromethyl)mercury was separated from fluorocarbons and unreacted dimethylmercury on a vacuum line. The reaction can be represented as follows.

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

The physical properties and ^{19}F NMR agree with authentic samples prepared by alternative methods.[4] It has been found that $Hg(CF_3)_2$ does not react with 3% F_2 at −78 °C. It has also been found that $Hg(CF_3)_2$ does react slowly with 3% fluorine at 0 °C and appreciably at room temperature, forming HgF_2 and CF_4.

Table I[a]

	^1H[b]					^{19}F[c]				
	CH_3	CH_2F	J_{HF}	CHF_2	J_{HF}	CH_2F	J_{HF}	CHF_2	J_{HF}	J_{FF}
$Si(CH_3)(CH_2F)_2(CHF_2)$	−0.06	4.32	47.3	5.68	45.9	199.60	47.0	61.08	45.8	1.5
$Si(CH_2F)_2(CHF_2)_2$		4.66	46.6	5.91	45.4	202.87	46.4	59.88	45.4	2.0
$Si(CH_2F)_3(CHF_2)$		4.54	46.6	5.87	45.4	201.41	46.6	60.03	45.4	1.7
$Si(CH_2F)(CHF_2)_3$		4.68	46.2	5.82	45.0	204.39	46.6	59.57	45.0	2.4
$Si(CH_2F)_4$		4.24	47.0			200.13	46.9			

[a] All samples were run as neat liquids. Shifts are in parts per million. Coupling constants are in hertz. [b] + downfield from external Me_4Si. [c] + upfield from external TFA.

We have found it possible to preserve silicon–carbon bonds under low temperature direct fluorination and are able to isolate many polyfluorotetramethylsilanes produced by controlled low temperature fluorination of tetramethylsilane. Using 1.67% fluorine, obtained by combining flows of 1 cm^3/min fluorine and 60 cm^3/min helium, in a cryogenic zone reactor[1] in which 1.65 g of tetramethylsilane has been frozen at −110 °C, one can recover up to 75% of the fluorine substituted starting material containing all four silicon–carbon bonds intact. Varying degrees of fluorination are observed. Compounds of the type $Si(CH_3)_x(CH_2F)_y(CHF_2)_z$, $x + y + z = 4$, have been isolated and characterized (see Table I). Under the above conditions, we did not isolate any fluoromethylsilanes of the type $Si(CH_3)_3F$, $Si(CH_3)_2F_2$, and $Si(CH_3)F_3$. Several of the compounds are listed below along with their proton and fluorine NMR's. A considerable degree of fluorination results under the above conditions. In fact, only at −150 °C can one slow the fluorination process to allow the isolation of a single partially fluorinated species, $Si(CH_3)_3(CH_2F)$ (55% yield), as the sole product along with unreacted tetramethylsilane. The infrared, mass spectrum, and NMR of $Si(CH_3)_3(CH_2F)$ agree with that reported in the literature.[5]

Rapid metal-carbon bond vibrational and translational relaxation processes occurring at cryogenic surfaces may account for the isolation of these compounds. Obviously, the formation of three hydrogen fluoride molecules and three carbon fluorine bonds per methyl group is so exothermic that one could not explain the retention of metal–carbon bonds on energetic grounds. Work is now underway on the tungsten hexamethyl system and successful preliminary results have been achieved with a number of metal alkyl systems such as cadmium and tin.

Acknowledgments. We are grateful for the research support from the Office of Naval Research (N00014-75-C-0994).

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Received August 13, 1976