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NEW METHODS FOR THE SYNTHESIS OF TRIFLUOROMETHYL ORGANOMETALLIC COMPOUNDS

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I. Introduction

As most readers will undoubtedly be aware, the study of trifluoromethyl organometallic compounds, and the initiation of this area as a field of research, began with the discovery of bis(trifluoromethyl)mercury by Emeléus and Haszeldine (*1*) in 1949 and continued with their associated research programs. Since that time, a steady, and sometimes spectacular, international research effort has continued over the past twenty-five years that has involved many laboratories (*2*).

Nevertheless, it could be fairly stated that, in the next 20-year period through the end of the sixties, preparation of even the initial bis(trifluoromethyl)mercury compound in quantity required considerable time and effort and was, in general, painstakingly laborious. Furthermore, it is quite clear from the literature that no truly general methods were known for the synthesis of trifluoromethyl organometallic compounds. Indeed, the literature contains many rationalizations, based on suppositions of instability of compounds, for the failure of certain synthetic methods to afford highly substituted trifluoromethyl compounds that are now known to be stable, in many cases to temperatures of over 100°C. Many of the more established synthetic methods in the area also have associated activation-energy problems, making it difficult or impossible to prepare trifluoromethyl organometallic compounds of marginal stability.

The state of the synthetic art in this area, in 1979, is much more satisfactory. During the past decade, several new synthetic developments have occurred such that we are closer to the point where the limitations upon synthesis of trifluoromethyl compounds are related more to stability problems in isolated cases, and are not nearly so much due to lack of widely applicable synthetic techniques. We find ourselves, for example, in a position in 1979 where the germanium compound, $Ge(CF_3)_4$, which in the past decade, was considered by many workers to be of insufficient stability to permit isolation, has been prepared by four independent methods and is known to be stable to over 100°C. Many of these new synthetic techniques have emerged from studies conducted in our laboratory at the University of Texas and previously

at the Massachusetts Institute of Technology during the past several years.

The four general areas of research discussed in this article are in some cases only vaguely interrelated with respect to methodology, even when they are capable of producing the same compounds. They range from such rather exotic approaches as elemental fluorination of alkyls, which has, surprisingly, proved to be a practical synthetic method for several trifluoromethyl organometallic compounds, to the development of an extremely general synthesis involving metal atoms and free radicals as precursors, a method that impacts not only on the area of trifluoromethyl organometallic chemistry, but on such diverse areas as the synthesis of new methyl alkyls and new classes of sigma-bonded, alkyl-like compounds both within and outside the realm of fluorine chemistry.

Perfluoroalkyl derivatives of the inorganic elements have long been known to possess properties quite different from those of their perhydrogenated analogs. Although the properties of the alkyl and perfluoroalkyl derivatives of many elements could be contrasted, one example will suffice. Bis(trifluoromethyl)mercury, the first perfluoroalkyl organometallic compound prepared (*1*), is a sublimable solid, having no known liquid phase, that is soluble in and easily recoverable from water, and *appears* to be physiologically inert, as it has been handled routinely in the open laboratory atmosphere many times without adverse effect (*3*). Additionally, it has been reported that this perfluoromethyl mercurial does not exchange ligands with other inorganic halides to yield trifluoromethyl inorganic compounds and mercuric halides (*2*). All of these properties are in marked contrast to the properties of the perhydrogen analog, dimethylmercury. They are also among the first indications that the properties and reactivities of perfluorinated organometallic compounds may be strikingly different from those of the more-usual, hydrogen-containing, organometallic compounds.

The trifluoromethyl ligand has the characteristics both of a pseudohalogen and an alkyl group. For example, the trifluoromethyl group stabilizes the highest-valence states of such elements as arsenic, e.g., $(CF_3)_3AsCl_2$, (*4*), for which even the pentachloride is unstable. One especially interesting example of the interplay of the various properties of the trifluoromethyl group concerns the ground states of pentavalent phosphoranes where, originally, it had been proposed that the site preference of different ligands is related solely to the electronegativity of the ligand (*5*). Results have, however, now been obtained that indicate that other factors predominate, and the CF_3 ligand is considered to

be located equatorially in mixed chloro(trifluoromethyl)phosphoranes (*6*).

Although a great number of trifluoromethyl-containing compounds have been prepared, one curious feature is that, until recently, almost all of these compounds had been prepared either directly from, or through, the intermediacy of only one precursor, trifluoromethyl iodide. This reagent has been found to oxidize a few elements directly, and to add oxidatively to low-valent complexes of a large number of other main-group and transition-metal elements, generating compounds containing from one to as many as three trifluoromethyl groups. The most thermally stable of these compounds are formed directly by the lighter elements of Groups 5 and 6A. Antimony, arsenic, phosphorus, and selenium all form the fully substituted, trifluoromethyl derivatives simply upon heating with trifluoromethyl iodide; elemental sulfur forms $(CF_3)_2S$ upon UV irradiation of the $(CF_3)_2S_2$ that is initially formed by reaction of trifluoromethyl iodide with the element. The mercurial, $(CF_3)_2Hg$, is, however, formed only if the element has previously been amalgamated.

Monosubstituted trifluoromethyl derivatives of the Group 4A elements have also been prepared, but by very specific reactions. The divalent halides SiF_2 and GeI_2 react with CF_3I to form CF_3SiF_2I and CF_3GeI_3 and a very small proportion of $(CF_3)_2GeI_2$, but the more stable SnI_2 is unaffected. The metal–metal bond in hexamethyldistannane is cleaved by CF_3I to form CF_3SnMe_3, but the stronger bonds in hexamethyldisilane and hexamethyldigermane are unreactive. Additionally, the reaction of $CF_3Sn(CH_3)_3$ with BF_3 has been shown (*7*) to yield $CF_3BF_3^-$. Trifluoromethyl iodide has thus proved to be an extremely versatile reagent, but it seems likely that other reagents and conditions could be found that would prove to be superior for the formation of currently unknown, per(trifluoromethyl) compounds of the main-group elements. Thus, a number of investigations have been undertaken to assess the potential of several, alternative synthetic techniques for the preparation of trifluoromethyl-containing organometallic compounds. One possible route to these compounds was the discharge reaction of hexafluoroethane to produce very reactive trifluoromethyl radicals that could react with metal halides. Another involved reinvestigation of the claim that the trifluoromethyl mercurial was much less inclined to exchange ligands than alkyl mercurials. A third possibility concerned the reaction of elemental fluorine with alkyl compounds, a technique described (*8*) as ". . . not suitable for the preparation of perfluoroalkyl-metallic derivatives." Finally, the

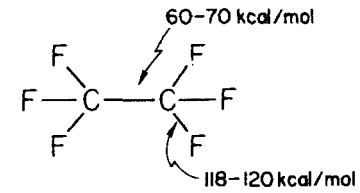
reaction of atomic metal vapors with trifluoromethyl radicals has been preliminarily surveyed.

As a test of the suitability of these potential, synthetic routes, the preparation of several molecules that had not previously been synthesized was attempted. They included the compounds $(CF_3)_2Te$ and $(CF_3)_3Bi$, the fully substituted derivatives of the lower elements in Groups 5 and 6A (which had previously been sought, but not isolated), and the tetrasubstituted compounds of Group 4A elements, e.g., $(CF_3)_4Ge$, as, with the trivial exception of perfluoroneopentane, no compound containing more than three trifluoromethyl groups attached to any element was known. Because relatively little information was available as to the chemical properties of Group 4A compounds in which one or more of the ligands was a CF_3 group, the chemical stabilities of the CF_3Ge and CF_3Sn linkages were tested by reaction of the trifluoromethylgermanium or trifluoromethyltin halides with a variety of standard reagents to determine whether the CF_3–metal bonds are reactive.

II. Plasma-Generated Trifluoromethyl Radicals as a Synthetic Reagent

Hexafluoroethane is a particularly promising precursor for trifluoromethyl-containing species, as it is relatively inexpensive, readily available, and easy to manipulate. Conceptually, if a process could be found that would preferentially cleave the carbon–carbon bond in this molecule to generate, e.g., trifluoromethyl radicals, these could then react with another substrate, such as a metal halide, to form metal or metalloid compounds highly substituted with CF_3 groups. Although the bond strengths in C_2F_6 are controversial (*9*), the best estimates currently available indicate that the carbon–fluorine bond is ~40 kcal/mole stronger than the carbon–carbon bond (*10*) (see Fig. 1). Thus, were hexafluoroethane dissociated under relatively mild conditions, it would be expected that cleavage of the weaker carbon–carbon bond to produce trifluoromethyl radicals (or ions) would predominate, and that cleavage of the carbon–fluorine bond, to produce, e.g., pentafluoroethyl radicals, would be a very minor reaction.

Low-temperature glow-discharges were utilized to cause bond rupture in hexafluoroethane (*11*). In these experiments, the power to support the discharge was supplied by a radio-frequency discharge that delivered ~25 W of power, at a frequency of 8.6 MHz, to the copper coil surrounding the Pyrex reactor (see Fig. 2). The load coil was induc-



$$CF_3^{\cdot} + MX_n \longrightarrow M(CF_3)_n + X_2$$

$$CF_3^{\cdot} + CX_n \longrightarrow C(CF_3)_n + X_2$$

(X = Br, Cl, or I)

FIG. 1. Estimated strengths of the carbon–carbon and carbon–fluorine bonds in hexafluoroethane.

tively coupled to the plasma within the reactor, and any free electrons in the discharge region were accelerated by the rapidly fluctuating magnetic field. Other ions present were too massive to gain significant kinetic energy before the polarity of the field reversed. The critical difference between this type of discharge and dc and 60-Hz discharges is that only the electrons gain appreciable translational energy from the magnetic field. As the pressure is low, little kinetic energy is transferred from the electrons to the larger species, and thus, the temperature of the gaseous molecules, T_g, is low. This is, perhaps, the key feature for the success of this synthetic method. The higher translational energies, which are associated with the generation of such high-energy reactants by thermal means, would result in pyrolysis of many marginally stable reactants, such as hydrocarbon compounds. When the apparatus is in operation, the temperatures observed immediately ad-

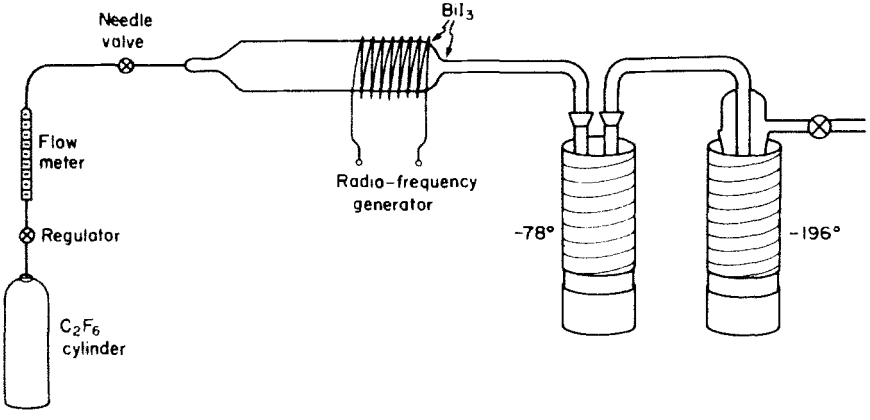


FIG. 2. Diagram of plasma apparatus.

jacent to the discharge region are ~40–50°C. In other types of discharges, quartz reactors have frequently been needed, in order to withstand the severe heat-strains encountered (*12*).

In operation, the gaseous precursor, hexafluoroethane, at a pressure of 0.1 to 1 mm Hg, flows into the discharge region (see Fig. 2), where the radicals and ions are formed. As the gas flows out of the discharge region, abstractions and recombinations quickly lower the radical concentrations to zero. In attempts to utilize these reactive species, halides of metals or metalloids were placed at the tail of the plasma, to react and afford volatile, trifluoromethyl-substituted compounds which then would be swept away from the discharge region by the gas flow and into the traps, later to be isolated, identified, and characterized by the usual techniques. Thus, the objective of the experiments was to promote such reactions as those in Eq. (1)–(3) at the expense of Eq. (4). Equations (5) and (6) indicate the observed fate of many of the halogen atoms.

$$C_2F_6 \xrightarrow{\text{discharge}} 2\cdot CF_3 \tag{1}$$

$$\cdot CF_3 + MX_n \rightarrow CF_3MX_{n-1} + X\cdot \tag{2}$$

$$\cdot CF_3 + CF_3MX_{n-1} \rightarrow (CF_3)_2MX_{n-2} + X\cdot \tag{3}$$

$$2\cdot CF_3 \rightarrow C_2F_6 \tag{4}$$

$$\cdot CF_3 + X\cdot \rightarrow CF_3X \tag{5}$$

$$2X\cdot + M \rightarrow X_2 + M^* \tag{6}$$

A. Reaction with Mercuric Halides

The reactions of mercuric iodide, mercuric bromide, and mercuric chloride with the excited species produced in the hexafluoroethane plasma were examined first, as the expected products were known to be stable and had been well characterized (*13*). Thus, these reactions constituted a "calibration" of the system. Bis(trifluoromethyl)mercury was obtained from the reaction of all of the mercuric halides, but the highest yield (95%, based on the amount of metal halide consumed) was obtained with mercuric iodide. The mole ratios of bis(trifluoromethyl)mercury to (trifluoromethyl)mercuric halides formed by the respective halides is presented in Table I, along with the weight in grams of the trifluoromethyl mercurials recovered from a typical, five-hour run.

As might have been expected, the highest ratio of disubstituted compound, as well as the largest total amount of trifluoromethyl mercurials, was formed by the reagent having the weakest metal–halogen

TABLE I

MOLE RATIOS AND WEIGHTS OF TRIFLUOROMETHYL MERCURIALS FORMED

Mercuric halide	Mole ratio $(CF_3)_2Hg/CF_3HgX$	Mercurials recovered (g) $(CF_3)_2Hg + CF_3HgX$
HgI_2	43.0	0.82
$HgBr_2$	0.85	0.55
$HgCl_2$	0.11	0.44

bond, namely, mercuric iodide. This is illustrated very clearly in Figs. 3–5, which show the ^{19}F-NMR spectra of the unseparated mixtures of products produced by the reactions of CF_3 radicals with HgI_2, $HgBr_2$, and $HgCl_2$, respectively. In Fig. 3, the small peak to the left of the central, $Hg(CF_3)_2$ resonance is due to CF_3HgI. By varying the experimental parameters, the quantity of $(CF_3)_2Hg$ produced from HgI_2 was increased to 8 g/day. These reactions indicated that plasmas could be successfully used to generate trifluoromethyl organometallic compounds in relatively large amounts. An attractive feature of the technique is that very little of the operator's time is required, as the reactions, once started, proceed virtually unattended.

B. REACTION WITH GERMANIUM TETRABROMIDE

At a point near the tail of the plasma, where the blue glow was near extinction, gaseous germanium tetrabromide was slowly admitted to the reactor from a side arm. Tetrakis(trifluoromethyl)germane, previously unknown, was prepared in 64% yield, along with smaller proportions of $(CF_3)_3GeBr$, also new, and $(CF_3)_2GeBr_2$. These species were isolated and identified by the usual techniques (*11*), and, during the course of the characterization, two noteworthy observations were made. The first was that, during the isolation of $(CF_3)_3GeBr$, or especially $(CF_3)_3GeI$ (if GeI_4 had been used as the reactant), as the compound was concentrated, all of the $(CF_3)_4Ge$, as well as the material of the formula $(CF_3)_2GeX_2$, was removed. However, if the sample containing, e.g., $(CF_3)_3GeI$, was kept at room temperature for a few days and then examined, it was found that more $(CF_3)_4Ge$ and $(CF_3)_2GeI_2$ could be isolated. Clearly, the tris(trifluoromethyl)germanes were undergoing ligand redistribution-reactions in which the CF_3 group as a unit was exchanging metal centers, a type of reaction previously reported (*14*) not to proceed, even at 180°C. Later studies (*15*) showed that neat $(CF_3)_3GeI$ does, indeed, exchange ligands, to form $(CF_3)_4Ge$ and $(CF_3)_2GeI_2$, as shown in Table II. The second observation, as yet un-

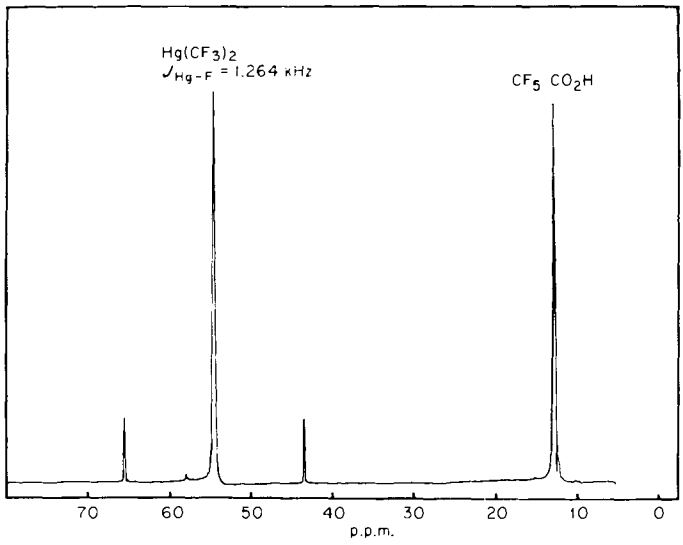


FIG. 3. ^{19}F-NMR spectrum of the mixture from the reaction of CF_3 radicals with HgI_2.

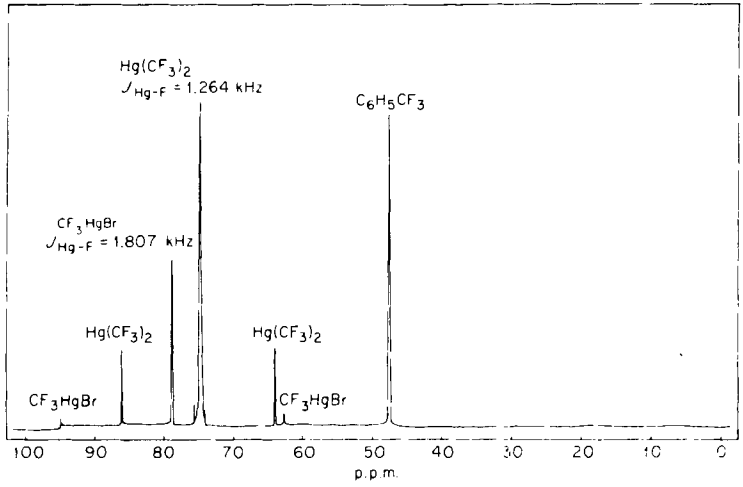


FIG. 4. ^{19}F-NMR spectrum of the mixture from the reaction of CF_3 radicals with $HgBr_2$.

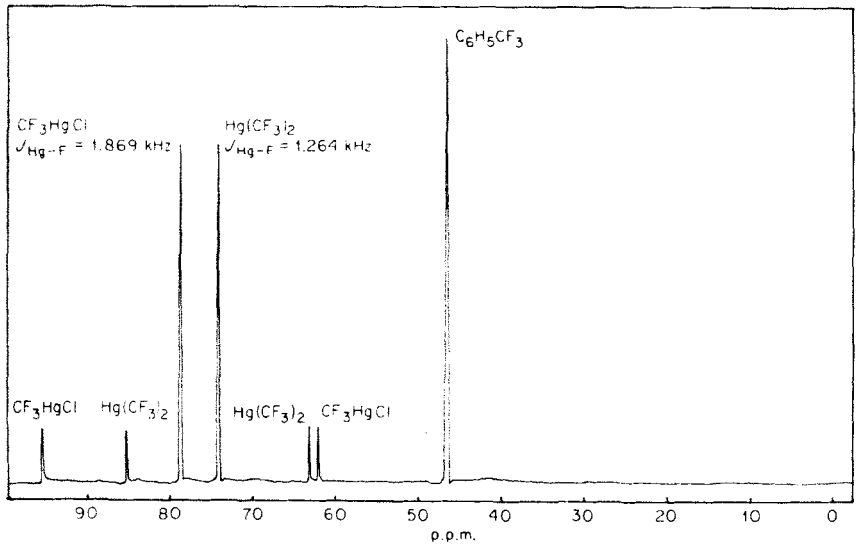


FIG. 5. ^{19}F-NMR spectrum of the mixture from the reaction of CF_3 radicals with $HgCl_2$.

exploited, was that a strong metastable ion observed in the mass spectrum of $(CF_3)_4Ge$ could be ascribed to the following decomposition.

$$Ge(CF_3)_3CF_2^+ \rightarrow :Ge(CF_3)_2 + C_2F_5^+$$

The facile elimination of the methylene-like species $(CF_3)_2Ge$: indicates that, under the appropriate conditions, $(CF_3)_4Ge$ may well serve as a useful laboratory source of trifluoromethyl-substituted Ge(II).

C. REACTION WITH TIN TETRAIODIDE

Tin tetraiodide was placed in a quartz boat which was then positioned at the tail of the plasma. Tetrakis(trifluoromethyl)tin was syn-

TABLE II

REDISTRIBUTION REACTION OF $(CF_3)_3GeI$ AT 155°

Time (h)	Amount of trifluoromethylgermane[a] (mole %)		
	$(CF_3)_2GeI_2$	$(CF_3)_3GeI$	$(CF_3)_4Ge$
0	0	100	0
15	8	86	6
30	12	77	11
90	19	71	19

[a] Sealed, 4-mm tubes; monitored by ^{19}F-NMR.

thesized in 90% yield, along with $(CF_3)_3SnI$ and $(CF_3)_2SnI_2$ which were formed in small proportions (*11*). Tetrakis(trifluoromethyl)germane and tetrakis(trifluoromethyl)tin were the first organometallic compounds prepared in which an atom of any element had more than three trifluoromethyl ligands. The preparation of $(CF_3)_4Sn$ is also an indication that this type of discharge is capable of synthesizing compounds that have only marginal thermal stability, as $(CF_3)_4Sn$ was shown to decompose totally in 24 hours at 100°C. Even at temperatures as low as 66°C, the majority of the sample decomposes within 24 hours (*15, 16*).

D. Reaction with Bismuth Triiodide

Bismuth triiodide (18 g) was introduced into the reactor, and spread out on the walls of the Pyrex vessel shown in Fig. 2. After evacuation of the reactor and introduction of hexafluoroethane at a pressure of ~1 torr, the discharge was initiated and maintained for 100 hours. Tris(trifluoromethyl)bismuthine, 0.8 g, was isolated in 32% yield (*17*), along with the previously prepared $(CF_3)_2BiI$. This reaction again demonstrates the utility of this synthetic route as a preparative tool, as several early attempts to prepare $(CF_3)_3Bi$ by more traditional routes had proved unsuccessful (*18*). In one closely related experiment, $\cdot CF_3$ radicals, generated by the pyrolysis of hexafluoroacetone, were reacted with a bismuth mirror in a Paneth type of reaction, but no trifluoromethyl-substituted bismuthines were isolated (*19*). In each of the earlier studies, temperatures over 200° were needed (*18, 19*), and yet tris(trifluoromethyl)bismuth has been shown to decompose (*17*) within a few minutes at 100°C. Thus, if $(CF_3)_3Bi$ had been prepared by, e.g., ligand exchange-reactions (*18*), it would have immediately decomposed.

E. Reaction with Tellurium Tetrabromide

Tellurium tetrabromide (2.6 g) was placed in a Vycor sample-boat which was then positioned in the tail of the plasma. After exposure to the discharge for 46 hours, 1.5 g of the $TeBr_4$ had been consumed, and three major, tellurium-containing products had been formed (*11*). Bis(trifluoromethyl)tellurium, $(CF_3)_2Te$, a new compound, was isolated in 20% yield, and later found to react with gaseous bromine to give $(CF_3)_2TeBr_2$. When $(CF_3)_2Te$ in a sealed tube was gently heated with a flame, the compound decomposed, with the evolution of fluorocarbons and $(CF_3)_2Te_2$. The second compound synthesized was bis(trifluoromethyl)ditelluride, $(CF_3)_2Te_2$, a previously known compound, which was formed in 33% yield, based on the $TeBr_4$ consumed. The final prod-

uct, formed in 36% yield, was a solid of low volatility and solubility. The mass-spectral and ^{19}F-NMR data indicated a mixed (trifluoromethyl)tellurium bromide.

This reaction provides a third indication of the usefulness of a radio-frequency discharge in the synthesis of compounds of low thermal stability. The more-stable $(CF_3)_2Te_2$ had been prepared by the interaction of CF_3 radicals, formed in the pyrolysis of $(CF_3)_2CO$, with a tellurium mirror (*19*). The less-stable $(CF_3)_2Te$ was not, however, observed in that experiment.

F. Reactions of Trifluoromethyl Radicals with Sulfur Vapor

Although belonging to a slightly different class of reactions, the reaction of trifluoromethyl radicals with sulfur vapor has been shown to provide a route to trifluoromethyl polysulfide compounds (*20*). Instead of using sulfur halides, which undoubtedly would also give positive results, elemental sulfur (S_8) was vaporized and dissociated into atomic and polyatomic sulfur species.

$$S_{8(g)} \xrightarrow{rf} S + S_2 + S_3 + S_4 + \ldots\ldots$$

The apparatus used is shown in Fig. 6. The reaction proceeds according to the equation

$$S_m + CF_3\cdot \rightarrow CF_3S_nCF_3 + C_2F_5S_nCF_3 + C_2F_5S_nC_2F_3,$$

where $m = 1\text{–}8$, and $n = 1\text{–}4$.

The primary products are the trifluoromethyl compounds. The perfluoroethyl species are considered to arise through an unusual mechanistic process (*20*), instead of being generated directly, as penta-

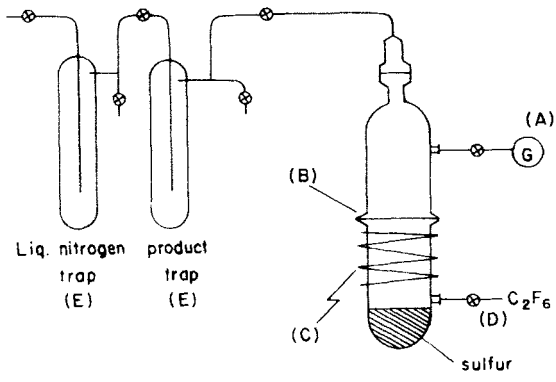


Fig. 6. Plasma apparatus.

fluoroethyl radicals, from C_2F_6. Although the majority of these species had been reported previously, several novel compounds resulted from these synthetic efforts.

G. Reactions of Trifluoromethyl Radicals with Organic Halides

For completeness, it should be mentioned that the reaction of trifluoromethyl radicals to replace halogens is extremely general, and not confined solely to metal species. Plasma-generated trifluoromethyl radicals will react with halocarbons according to the reaction (*21*)

$$CF_3\cdot + CX_n \rightarrow C(CF_3)_n + n/2\ X_2,$$

where X = Br, Cl, or I.

Specifically, the reaction of trifluoromethyl radicals with carbon tetraiodide produces perfluoro-*tert*-butyl iodide and perfluoroneopentane in the ratio of 3:1. Incomplete substitution is presumably due to steric factors around the crowded, central carbon atom.

$$\underset{}{CF_3\cdot} + \underset{}{CI_4} \rightarrow \underset{(24\%)}{C(CF_3)_4} + \underset{(73\%)}{(CF_3)_3CI} + I_2$$

Such reactions appear to be rather general in scope, since an aryl example, the substitution for bromine in bromobenzene, and for halogen in a normal alkyl halide has also been observed (*21*).

$$PhBr + CF_3\cdot \rightarrow PhCF_3 + \tfrac{1}{2}Br_2$$

$$C_7H_{15}I + CF_3\cdot \rightarrow C_7H_{15}CF_3 + \tfrac{1}{2}I_2$$

H. Summary

Hexafluoroethane has been demonstrated to be a very useful precursor to trifluoromethyl-containing compounds of the main-group elements. Previously unknown compounds in which the ligands were solely trifluoromethyl groups have been prepared in good to excellent yield by the interaction of the halides of metal or metalloid elements with the reactive intermediates produced in the radio-frequency discharge of hexafluoroethane. In several instances, the compounds formed possess very limited thermal stability, and yet they could be synthesized readily. Because the emphasis in these experiments was development of a new and more useful preparative tool, the formation of known trifluoromethyl-containing species was not attempted. For example, $(CF_3)_3As$ could be readily prepared from AsI_3 by the preceding method.

The various spectral and physical properties of the compounds prepared, including their elemental analysis, and IR, NMR, and mass spectra (which contained the appropriate ions, each of the intensity demanded by the isotopic composition of the ion), all fully supported the formulation of the species as reported. With two exceptions, all of the new compounds were found to be colorless liquids, typically having a relatively short liquid range, and they are usually very volatile for their molecular weight. The two exceptions are $(CF_3)_2Te$, which is yellow-green, and $(CF_3)_2Te_2$, which is red-brown (*11*).

Experimentally, there has been but little direct observation of the reactive intermediates present in this, or any other, type of discharge, as it is extraordinarily difficult to analyze a reactive plasma without perturbing the system.

Ideally, it would be desirable to determine many parameters in order to characterize and mechanistically define these unusual reactions. This has been an important objective that has often been considered in the course of these studies. It would be helpful to know, as a function of such parameters of the plasma as the radio-frequency power, pressure, and rate of admission of reactants, (*1*) the identity and concentrations of all species, including trifluoromethyl radicals, (*2*) the electronic states of each species, (*3*) the vibrational states of each species, and (*4*) both the rotational states of each species and the average, translational energies of, at least, the trifluoromethyl radicals.

Objective (*1*) has been the impetus for a considerable amount of contemporary research, but it has proved most difficult to design a mass-spectrometric sampling-system that does not perturb the species when they are admitted to the ionization chamber (which must necessarily be at a pressure lower than the 1 mm Hg required for plasma conditions). Only recently has convincing evidence been adduced that non-spurious results might be achieved by use of slit sampling-devices and quadrupole, mass spectrometers. To observe the excited electronic states, one option would, of course, be to examine the vacuum-ultraviolet spectrum of such species, but this has been found to be exceedingly complex because many lines arise from the multiple species. Attachment of a vacuum-ultraviolet spectrometer to a plasma device is also rather awkward. Gas-phase photoelectron spectroscopy offers some possibilities here but the attendant radio frequency and microwave generated field cause instrumental problems with currently available spectrometers. Vibrationally, the multiplicity of species and broadening of lines observed in plasmas constitute a source of some difficulty with infrared or Raman spectroscopy. In studies of rotational states by microwave spectroscopy, the microwave radiation would be

likely to cause fluctuations and variations in the plasma, since microwave sources are also capable of producing discharges.

Another technique that should eventually prove fruitful in the investigation of plasma reactions is EPR spectroscopy, by which each radical species could be observed, but not in a strictly quantitative way, and could be characterized from its EPR spectrum. Again, in this instance, there are permutations of the plasma conditions caused by the EPR klystron sources. Thus, to characterize such a seemingly simple reaction adequately, a tremendous amount of spectroscopic data should be collected simultaneously. After all of this instrumentation had been assembled, perhaps the most perplexing problem would be the fact that the radio-frequency- or microwave-generated plasma is not uniform in intensity, or with respect to any other parameter, but changes continually, from the central part of the coils towards the edge, or "tail," of the plasma. Thus, the fact that certain energy states and species were observed at one particular point would not necessarily mean that they were uniform throughout and, in fact, to characterize the plasma completely, a number of such points of observation would have to be considered. The solution to this multiple dilemma appears to lie in various types of laser spectrometers that can be focused on precise points in a plasma apparatus. It would be expected that spectroscopic information of this type would be useful in increasing the yields of known processes and in developing new syntheses.

Operationally, however, the vast majority of the metal-containing products are those expected from the reactions already presented, namely, successive exchange of trifluoromethyl for halogen. Equations (7) and (8), for example, represent the last two steps of the formation of $(CF_3)_4Ge$.

$$\cdot CF_3 + (CF_3)_2GeBr_2 \rightarrow (CF_3)_3GeBr + \cdot Br \tag{7}$$

$$\cdot CF_3 + (CF_3)_3GeBr \rightarrow (CF_3)_4Ge + \cdot Br \tag{8}$$

With the exception of the reactions of trifluoromethyl radicals with sulfur vapor, which is really a separate class of reactions, if the power supplied to the load coil surrounding the reactor (see Fig. 2) was maintained at, or near, the minimum amount needed to support the discharge, in only two cases were compounds found that clearly resulted from reactions other than replacement of halogen by trifluoromethyl. The reaction of tellurium tetrabromide (or the chloride) gave, in addition to the products just reported, very small proportions of such species as $BrCF_2TeCF_2Br$ and $(C_2F_5)_2Te$, which were isolated in *yields of*

much less than 1%. The isolation of these products was made possible by the fact that they are highly colored. Presumably, similar types of products were formed in comparable yields during the reaction of the other metal halides. The isolation of these products indicates that other reactive intermediates, e.g., $:CF_2$ or $\cdot C_2F_5$, may well be present, but, as expected, in very low concentration.

III. Bis(trifluoromethyl)mercury as a Synthetic Reagent

As noted in the Introduction, the trifluoromethyl group is a substituted alkyl species that appears to react as though it were a pseudohalogen. Somewhat surprisingly, however, ligand-exchange reactions that result in the transfer of a trifluoromethyl group from one metallic element to another appear to have been but little investigated as a synthetic procedure. The results of several earlier experiments had been summarized (*8*): "All attempts to prepare new perfluoroalkyl organometallics from the mercury compounds have been unsuccessful." In only one instance had more than one trifluoromethyl ligand been attached to another element by an exchange reaction, and, in that study, no compounds could be isolated, but the appearance of new resonances in the fluorine-NMR spectrum was postulated (*22*) to be due to the formation of $(CF_3)_2Cd$.

However, the formation of $(CF_3)_4Ge$ and $(CF_3)_2GeI_2$ in aged samples that had originally contained only $(CF_3)_3GeI$ indicated that the transfer of trifluoromethyl ligands, at least among germanium centers, must take place fairly easily. To learn more concerning the potential of ligand-exchange reactions for the preparation of trifluoromethyl-containing compounds, the interaction of bis(trifluoromethyl)mercury with the halides of several Group 4A elements was examined, as this synthetic route might nicely complement the discharge synthesis. In the discharge reaction, the yields of the compounds containing only CF_3 groups as ligands was rather high, and, consequently, the yields of such partially substituted species as $(CF_3)_2SnBr_2$ was necessarily low. Should the ligand-exchange reaction between $(CF_3)_2Hg$ and the Group 4A tetrahalides proceed to afford the (trifluoromethyl)Group 4A halides, suitable control of the reaction conditions might well result in a synthesis that preferentially resulted in compounds containing only two, or three, trifluoromethyl ligands. As little was known of the chemical stability of a CF_3 group bound to a Group 4A element, the reactivity of this linkage was assessed by exposing representative (trifluoromethyl)germanium and (trifluoromethyl)tin halides to a spectrum of common reagents, in order to determine whether the CF_3Ge or

CF_3Sn bond is stable to reaction conditions that cleave the metal–halogen bond.

The preparative reactions were conducted in sealed tubes in which ~1–3 g of the reagents had been placed. After the vessels had been maintained at the indicated temperatures for the designated times, the contents were removed, to be separated by fractional condensation and GLC. In addition to the (trifluoromethyl)Group 4A halides reported next, each sample contained unreacted $(CF_3)_2Hg$, the expected (trifluoromethyl)mercuric halide, and the mercuric halide, identified by fluorine-NMR spectroscopy and mass spectrometry.

In our laboratory, we find that the plasma reaction of trifluoromethyl radicals with mercuric iodide is an excellent source of bis(trifluoromethyl)mercury. For those laboratories that lack access to radiofrequency (rf) equipment (a 100-W, rf source can at present be purchased for less than $1,000), synthesis of bis(trifluoromethyl)mercury by the thermal decarboxylation of $(CF_3CO_2)_2Hg$ is also a functional, and quite convenient, source of bis(trifluoromethyl)mercury (*23*).

A. Reaction with Germanium Tetraiodide

Germanium tetraiodide (3 g) and sufficient $(CF_3)_2Hg$ to provide molar ratios (of mercurial to germane) of 0.55, 0.98, 1.72, and 2.00 were placed in tubes (10-mm diam.) that were then degassed, sealed, and placed in an oven held at 120°. After 120 hours, the tubes were opened, and the contents separated. The yields of the (trifluoromethyl)germanium halides formed (*16*), based on GeI_4, are presented in Table III.

As these results indicate, the reaction of $(CF_3)_2Hg$ with germanium tetraiodide provides a convenient source of the (trifluoromethyl)germanium iodides in good to excellent yields, and these yields can be varied, to increase the proportion of a particular (trifluoromethyl) germa-

TABLE III

Product Distribution for the Reaction[a] of $(CF_3)_2Hg$ with GeI_4

Molar ratio $(CF_3)_2Hg/GeI_4$	CF_3GeI_3	$(CF_3)_2GeI_2$	$(CF_3)_3GeI$	$(CF_3)_4Ge$	$(CF_3)_3GeF$
0.55	90	5			
0.98	13	53	16		
1.72			72	22	
2.00			72	15	11

[a] During 120 h at 120°.

nium halide, by appropriate selection of the proportions of the reagents employed. Presumably, the formation of the fluoride $(CF_3)_3GeF$ is acid-catalyzed, as both the mercurial $(CF_3)_2Hg$[1] and the germanes (see Table II) are stable at the temperatures employed. The fluoride is "anomalous," in that the sublimation point of this compound is normal when compared to the boiling point of the other halides, $(CF_3)_3GeX$ (X =Cl, Br, or I), but the melting point is quite abnormal, being ~125° above the melting point of the chloride; this is an indication of association in the solid state. The fluorine-NMR spectrum of the (heated) neat liquid consists of two broad singlets. In solution in diethyl ether, however, the resonances become resolved into the expected doublet and decet, again demonstrating association in the condensed phase that is broken up (on the NMR time-scale) by the intervention of solvent molecules (*15*). Similar effects have been reported for related compounds, and constitute indications that the germanium fluorides occupy a middle ground between those of carbon and silicon, which are very volatile, nonassociated fluorides, and those of tin and lead, which are essentially nonvolatile at lower temperatures and are strongly associated in the solid phase.

In order to test the generality of the synthesis, the reaction of $(C_2F_5)_2Hg$ with GeI_4 was assessed. This reaction required a higher temperature, 135°, before it proceeded measurably. (Pentafluoroethyl)germanium triiodide was the only (perfluoroethyl)germanium halide produced, in 54% yield (*15*). From this reaction, perfluoroethyl iodide was also isolated (in 30% yield). The reactions of $GeBr_4$ with $(CF_3)_2Hg$ and $(C_2F_5)_2Hg$ were similar in nature (*16*).

B. Reaction with Tin Tetrabromide

Under a variety of conditions, the reaction of $SnBr_4$ with $(CF_3)_2Hg$ results in the formation of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ as the only volatile, tin-containing products. All attempts to produce more fully substituted (trifluoromethyl)tin bromides by further reaction of $(CF_3)_2SnBr_2$ with more $(CF_3)_2Hg$ failed (*16, 17*). At 80°, there was no reaction; at 100°, the $(CF_3)_2SnBr_2$ decomposed. The nature of this reaction was further studied by determining the proportions of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ present during the course of the reaction at 112, 121, and 130°. The proportions of these compounds formed from a 2:1 molar ratio of mercurial to stannane, at the temperatures reported (*24*), are shown in Fig. 7. Although sealed-tube reactions tend to be irregular, the trends in Fig. 7 are clear. The first step is the formation of an equilibrium mixture containing CF_3SnBr_3 and CF_3HgBr in approximately

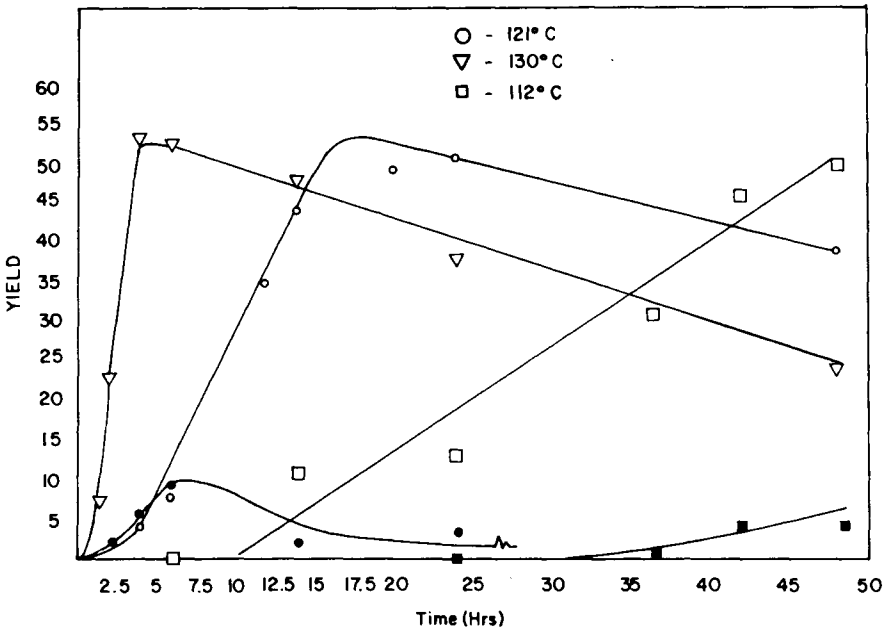


FIG. 7. The proportions of CF_3SnBr_3 formed at 112 (□), 121 (○), and 130 (▽), and of $(CF_3)_2SnBr_2$ formed at 112 (■) and 130° (●), in sealed-tube reactions.

equal proportions. The second step, the production of $(CF_3)_2SnBr_2$, results in the formation of a thermally unstable product. Thus, the formation of $(CF_3)_2SnBr_2$ is initially faster than the decomposition, but, in the later stages of the reaction, the decomposition predominates, and only small, "steady-state" concentrations of $(CF_3)_2SnBr_2$ are observed (*24*). These reactions are shown in Eqs. 9–11.

$$SnBr_r + (CF_3)_2Hg \rightarrow CF_3SnBr_3 + CF_3HgBr \quad (9)$$

$$CF_3SnBr_3 + (CF_3)_2Hg \rightarrow (CF_3)_2SnBr_2 + CF_3HgBr \quad (10)$$

$$3\ (CF_3)_2SnBr_2 \xrightarrow{\Delta} 3\ CF_3SnBr_2F + C_3F_6 \quad (11)$$

The temperature dependence of the reaction is remarkable. For a 5-h reaction, a temperature change of 18° results in a change in the yield of CF_3SnBr_3 from 0 at 112° to 55% at 130°. Alternatively, for a 35-h reaction, the yield of $(CF_3)_2SnBr_2$ is very low at both 112 and 130°; in the former, because the $(CF_3)_2SnBr_2$ has yet to be formed, whereas, in the latter, most of the $(CF_3)_2SnBr_2$ has decomposed. These results provide one explanation of the cause of the failure of the earlier study (*8*) to be productive: the temperature regime is critical.

C. Reaction with Silicon Tetrahalides

Silicon tetra-chloride, -bromide, or -iodide (~5 mmol) was similarly treated with $(CF_3)_2Hg$ (1–20 mmol) at temperatures that varied from 0 to 100°C. Although C_3F_6, SiF_4, and e.g., HgI_2 were produced, and identified by mass spectrometry, in no case were trifluoromethyl-substituted silanes discerned *under the conditions employed.*

D. Chemical Integrity of the CF_3Ge and CF_3Sn Bonds

Because the thermal stabilities of the (trifluoromethyl)germanium halides and the (trifluoromethyl)tin halides appeared to vary considerably, the chemical stability of these linkages was assessed by treating $(CF_3)_3GeI$ and, e.g., CF_3SnBr_3 with a variety of reagents (*15, 24*). The germane is remarkably resistant to chemical reaction, as, in each of the reactions reported in Equations 12–15, the new compounds were prepared in good yield by reaction of the germanium–halogen bond, leaving the CF_3Ge bond unscathed.

$$(CF_3)_3GeI + \underset{(X = F, Cl, \text{ or } Br)}{AgX} \rightarrow \underset{72, 92, \text{ or } 95\%}{(CF_3)_3GeX} \quad (12)$$

$$(CF_3)_3GeI + HgO \rightarrow (CF_3)_3GeOGe(CF_3)_3\ (100\%) \quad (13)$$

$$(CF_3)_3GeI + Na/Hg \rightarrow (CF_3)_3GeGe(CF_3)_3\ (60\%) \quad (14)$$

$$(CF_3)_3GeI + BH_4^- \rightarrow (CF_3)_3GeH\ (93\%) \quad (15)$$

Tris(trifluoromethyl)germanium iodide is unstable in 3*M* base, however, and yields fluoroform quantitatively. All of the compounds showed good thermal stability (*15*).

The trifluoromethyl–tin bond is, however, much less stable chemically (*24*). Reaction of, e.g., $(CF_3)_2SnBr_2$ with an excess of the relatively covalent, methylating agent $(CH_3)_2Cd$ results in the very slow substitution for one of the $Sn–CF_3$ bonds, but the reaction of CF_3SnBr_3 with an excess of the more powerful, more ionic reagent methyllithium results in the displacement of all of the ligands, and the formation of $(CH_3)_4Sn$ as shown in Equations 16 and 17.

$$(CF_3)_2SnBr_2 + (CH_3)_2Cd \rightarrow CF_3Sn(CH_3)_3\ (50\%) \quad (16)$$

$$CF_3SnBr_3 + CH_3Li \rightarrow (CH_3)_4Sn \quad (95\%) \quad (17)$$

A variety of reductions designed to prepare the stannane CF_3SnH_3 by reaction with, e.g., $LiAlH_4$, failed (*24*). In each instance, SnH_4 was produced, but little CF_3SnH_3 was isolated.

E. Summary

These studies have shown that $(CF_3)_2Hg$ and GeI_4, or $SnBr_4$, do exchange ligands to provide the compounds $(CF_3)_nGeI_{4-n}$, $n = 1-4$, or $(CF_3)_nSnBr_{4-n}$, $n = 1$ or 2, and that these reactions constitute convenient syntheses of trifluoromethyl-containing germanium and tin compounds (*16, 17, 22*). The method is especially effective for the more-electronegative element germanium, where the trifluoromethyl–germanium linkage is stable both thermally and chemically, a stability akin to the stabilities found for other substituted alkyl ligands (*16*). The trifluoromethyl–tin bond, a bond to a more electropositive element, is much less stable, both thermally and chemically, and is readily displaced in reactions of the (trifluoromethyl)tin halides with more powerful reagents, such as CH_3Li or $LiAlH_4$, with the CF_3 ligand reacting somewhat like a pseudohalogen (*24*). Towards more covalent, more discriminating reagents, such as $(CH_3)_2Cd$, however, the distinction between the CF_3–Sn and the Br–Sn bond is differentiable, as $(CF_3)_2Sn(CH_3)_2$ may be prepared from $(CF_3)_2SnBr_2$ in good yield. These methods, coupled with the plasma technique, have been so effective synthetically that all $Ge(CF_3)_n(X)_{4-n}$ (X = I, Br, Cl, F) compounds are now known due to a research effort by a former member of our research team (*16b*).

IV. Synthesis of Trifluoromethyl Organometallic Compounds by Direct Fluorination

A quite surprising development, even to experienced workers in elemental-fluorine chemistry, has been the synthesis of trifluoromethyl organometallic compounds by direct fluorination of metal alkyls (*25*). Even more surprising is the fact that, for certain metal and metalloid systems, such as the reaction of elemental fluorine with tetramethylgermane, this type of low-temperature synthesis is a practical method (*26*) for the laboratory preparation of the perfluoro analog.

A. Experimental Methods

This method of low-temperature, direct fluorination involves very precise control of fluorine concentrations during the reaction, and initial high dilution of the fluorine with helium. The reaction of elemental fluorine with organometallic compounds is conducted (*27*) in a cryogenic-zone reactor (see Fig. 8) at temperatures in the range of −78 to

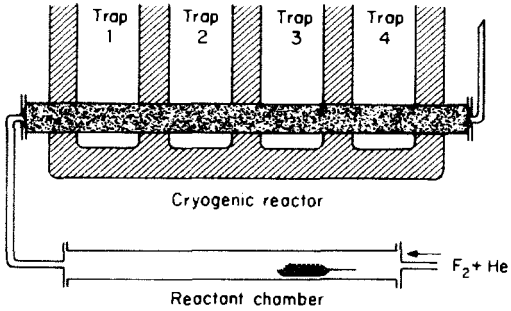


FIG. 8. Cryogenic reactor system.

−100°C. Details on methodology, and applications of these synthetic capabilities, are provided in a review article (*28*). The preservation of metal–carbon and metalloid–carbon bonds during direct fluorination is one of the most impressive cases of successful, direct fluorination described to date.

B. The Controlled Reaction of Metal Alkyls with Elemental Fluorine

Under the appropriate conditions, $Ge(CF_3)_4$ is obtained from $Ge(CH_3)_4$ in 63% yield, on a three-gram scale.

$$Ge(CH_3)_4 + F_2\text{–}He \rightarrow \underset{(63\%)}{Ge(CF_3)_4} + \text{polyfluorotetramethylgermanes} + \text{fluorocarbons}$$

That the carbon–metal or carbon–metalloid bonds are preserved at all in these reactions is quite surprising. With tetramethylgermanes, for example, this free-radical reaction must be a 24-step process. The success in preserving carbon–germanium bonds must arise from very rapid, molecular-vibrational, rotational, and translational relaxation-processes occurring on the cryogenically cooled surfaces, such that the energy from the extremely exothermic reaction is smoothly dissipated. Under milder conditions of fluorination, a range of partially fluorinated methylgermanium compounds is produced (*30*) (see Tables IV–VI).

The reaction of tetramethylsilane with fluorine led to the isolation of several, partially fluorine-substituted tetramethylsilanes (see Tables VII–IX), and preservation of over 80% of the silicon–carbon bonds in the initial, tetramethylsilane reactant. The stability of many of the partially fluorinated germanes and silanes (some are stable to over 100°C) is very surprising, for the possibility of elimination of hydrogen fluoride is obvious. Indeed, before the first reported synthesis (*12*) of

TABLE IV

FLUORINE-NMR SPECTRA OF POLYFLUOROTETRAMETHYLGERMANES

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]			
$Ge(CF_3)_2(CF_2H)(CFH_2)$	−27.6	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
$Ge(CF_2H)(CFH_2)_3$			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 p.p.m. 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.

$Ge(CF_3)_4$ and $Sn(CF_3)_4$ in 1975, many authors had given detailed reasons for the supposed instability of these species as a rationale for the failure of conventional syntheses to produce them.

The first successful, fluorine reaction observed with organometallics was the conversion of dimethylmercury into bis(trifluoromethyl)mercury (*25*).

$$Hg(CH_3)_2 \xrightarrow[-110°C]{He\text{-}F_2} \underset{(6.8\%)}{Hg(CF_3)_2}$$

It is quite probable that, were this reaction to be repeated, yields much higher than the 6.8% yield reported (*25*) could be obtained. In fact, it is even possible that this method, too, could eventually be developed into a practical synthesis for bis(trifluoromethyl)mercury.

The reaction of elemental fluorine with tetramethyltin is very different, and even more unusual (*31*). Under the conditions studied, no volatile compounds, such as $Sn(CF_3)_4$, were obtained. If fact, it appears

TABLE V

PROTON-NMR SPECTRA OF POLYFLUOROTETRAMETHYLGERMANES

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
$Ge(CF_3)_2CFH_2)_2$					
$Ge(CF_3)(CF_2H)_2(CFH_2)$		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 p.p.m. + downfield from external Me_4Si. [b] Coupling constants in Hertz. [c] OH (2.43), singlet.

TABLE VI

WEIGHT PERCENTAGE YIELDS[a] OF POLYFLUOROTETRAMETHYLGERMANIUM

Compound	Yield
$Ge(CF_3)_4$	63.5[b]
$Ge(CF_3)_3(C_2F_5)$	0.25
$Ge(CF_3)_3(CF_2H)$	0.38
$Ge(CF_3)_3(CFH_2)$	0.06
$Ge(CF_3)_2(CF_2H)_2$	6.20
$Ge(CF_3)_2(CF_2H)(CFH_2)$	4.16
$Ge(CF_3)(CF_2H)_3/Ge(CF_3)_2(CFH_2)_2/Ge(CF_3)(CF_2H)_2(CH_3)$	13.35[c]
$Ge(CF_3)(CF_2H)_2(CFH_2)/Ge(CF_3)(CF_2H)(CFH_2)(CH_3)$	13.94[d]
$Ge(CF_3)(CF_2H)(CFH_2)_2$	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 from reaction conditions designed to maximize $Ge(CF_3)_4$. When yield of $Ge(CF_3)_4$ is high, only traces of two other compounds, $Ge(CF_3)_3(C_2F_5)$ and $Ge(CF_3)_3(OH)$, appear. [b] Based on 0.87 g of $Ge(CH_3)_4$ 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.

TABLE VII

MELTING POINTS OF POLYFLUOROTETRAMETHYLSILANES

Compound	Melting point (°C)
$Si(CH_3)_3(CH_2F)$	−86.5 to −85.0
$Si(CH_3)(CH_2F)_3$	−89.5 to −84.5
$Si(CH_3)(CH_2F_2(CHF_2)$	−63.5 to −62.0
$Si(CH_2F)_4$	−18.0 to −16.6
$Si(CH_3)(CH_2F)(CHF_2)_2$	−58.7 to −56.8
$Si(CH_3)(CH_2F)_2(CF_3)$	−144 to −142.7
$Si(CH_2F)_3(CHF_2)$	−54.0 to −53.2
$Si(CH_3)(CH_2F)(CHF_2)(CF_3)$	−144 to −138
$Si(CH_2F)_2(CHF_2)_2$	−68.2 to −66.8
$Si(CH_2F)(CHF_2)_3$	−72.6 to −71.0
$Si(CH_3)_4$	−91.1

that the initial step in the reaction is cleavage of some of the tin–carbon bonds, to produce involatile, partially fluorinated, organometallic tin fluorides.

$$Sn(CH_3)_4 \xrightarrow[-100°C]{F_2\text{–}He} \underset{\text{I}}{Sn(CF_3)_2F_2} + \underset{\text{II}}{Sn(CF_3)F_3} + \underset{\text{III}}{Sn(CH_2F)F_2} + \underset{\text{IV}}{Sn(CHF_2)_2F_2} + \underset{\text{V}}{Sn(CHF_2)F_3} + \underset{\text{VI}}{SnF_4}$$

TABLE VIII

PROTON-NMR SPECTRA OF SUBSTITUTED SILANES

Compound	CH_3	CH_2F*	J_{HF}	CHF_2**	J_{HF}
$Si(CH_3)_3(CH_2F)$[a]	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	52.0
$Si(CH_3)(CH_2F)_3$	−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 p.p.m. from external Me_4Si, + downfield from Me_4Si. Coupling constants in Hertz. [a] Lit. (*29*) CH_3 (0.31), CH_2F (4.53), J_{HF} (46.8).

TABLE IX

FLUORINE-NMR SPECTRA OF SUBSTITUTED SILANES

Compound	CF_3	CHF_2*	J_{HF}	CH_2F**	J_{HF}
$Si(CH_3)_3(CH_2F)$ (*29*)				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]
$Si(CH_2F)_4$				200.13	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 p.p.m. from external TFA, + upfield from TFA. Coupling constants in Hertz. [a] J_{FF} = 1.4 (triplet). [b] J_{FF} = 1.5 (multiplet), $J_{HHF} \approx 1.0$. [c] J_{FF} = 1.8 (doublet). [d] J_{FF} = 1.4 (multiplet), $J_{HHF} \approx 0.5$. [e] J_{FF} = 3.2 (quartet of triplets), $J_{HHF} \approx 1.0$. [f] J_{FF} = 1.8 (quartet). [g] J_{FF} = 1.6 (triplet). [h] J_{FF} = 3.0 (quartet or doublet of triplets). [i] J_{FF} = 2.0 (triplet). [j] J_{FF} = 1.9 (pentet). [k] J_{FF} = 2.1. [l] J_{FF} = 2.0, $J_{HHF} \approx 0.4$.

Subsequently, exchange with dimethylcadmium produces mixed fluoromethyl compounds, according to the following reaction (*31*).

$$\text{I–VI} \xrightarrow{Cd(CH_3)_2} Sn(CF_3)_2(CH_3)_2 + Sn(CF_3)(CH_3)_3 + Sn(CH_2F)_2(CH_3)_2 + Sn(CHF_2)_2(CH_3)_2 + Sn(CHF_2)(CH_3)_3 + Sn(CH_3)_4$$

The properties of these compounds, and the relative composition of the products are shown in Table X.

Two additional areas are under study at this time. The reaction of fluorine with transition-metal alkyls appears to be quite promising.

An attempt is also being made to preserve metal–metal bonds during direct fluorination. It has been found that the reaction of fluorine with hexamethyldigermane leads primarily to tris(trisfluoromethyl)-germanium fluoride (*34*).

$$(CH_3)_3Ge\text{-}Ge(CH_3)_3 \xrightarrow[-100°C]{F_2\text{–}He} \underset{70\% \text{ (based on Ge)}}{(CF_3)_3GeF}$$

Other studies are under way, with other metal–metal bonded compounds, such as the tin and silicon alkyls.

TABLE X

COMPOSITION AND MELTING POINTS OF FLUORINATION PRODUCTS OF THE REACTION OF FLUORINE WITH $Sn(CH_3)_4$

Compound	Weight % of products	Melting point (°C)
$Sn(CH_3)_4$	48.4	−54.2 to −53.5[a]
$Sn(CH_3)_3(CF_3)$[b]	12.9	−57.0 to −53.2
$Sn(CH_3)_3(CH_2F)$	12.9	−62.5 to −59.0
$Sn(CH_3)_3(CHF_2)$[c]	3.2	−70.5 to −66.4
$Sn(CH_3)_2(CF_3)_2$	12.9	−34.5 to −32.0
$Sn(CH_3)_2(CH_2F)_2$	9.7	>80

* Cloudy until −55°. ** Cloudy until −63°. [a] Lit. m.p. −54.8°. [b] Ref. (*32*), b.p. 97–101° (745 mm Hg). [c] Ref. (*33*), b.p. 111.5°.

V. A New General Synthesis for Trifluoromethyl Organometallic Compounds and Other Sigma-Bonded Metal Compounds Based on Metal Vapor as a Reagent

A. INTRODUCTION

Just beginning to unfold in the literature is a new synthesis for metal alkyls $M(R)_n$ and sigma-bonded metal compounds that appears to be of an extremely general nature (*35*). This new method is, perhaps, the most promising development reported in the present review. It appears, at this writing, to provide an absolutely general synthesis both of trifluoromethyl, organometallic compounds and many new classes of alkyl-like, sigma-bonded, metal compounds. It employs the cocondensation of metal vapor of almost any type with free radicals under conditions where the metal is oxidized to the most stable (usually, the highest) oxidation state.

In the field of metal-vapor chemistry, since its inception by the initial papers of Timms (*36*) and Skell and Engel (*37*), the major thrust has been towards syntheses involving cocondensation of π-bonding ligands with metal vapor, with the most notable exceptions being the use of metal atoms as dehalogenation agents or in Grignard-like reactions. Most of the products formed are those in which the metal vapor is in a low-valence state, π-bonded or complexed to various ligands. Such reactions have constituted an important, major research-effort in inorganic chemistry during the past ten years (*38*).

$$M(g) + nL \xrightarrow[-196°C]{} ML_n$$

A new synthesis for sigma-bonded, metal alkyls and similar compounds, involving a reaction between metal vapor and free radicals generated in a radio-frequency glow-discharge, has been reported (*35*).

$$M(g) + n\,R\cdot \xrightarrow[-196°C]{} MR_n$$

where R = CH_3, CF_3, or SiF_3.

The radicals, such as methyl, trifluoromethyl, and trifluorosilyl, used in this work have been found to oxidize zero-valent metals to their highest oxidation-state upon cocondensation with these metals on a cold surface at −196°C.

It has been experimentally determined that a number of sources of radicals, including some generated by pyrolysis, may be used for this technique. However, the low-temperature glow-discharge is a convenient source of radicals for synthetic work.

B. Apparatus

The reactor in which the syntheses were accomplished is shown in Fig. 9. The cold finger (A) and the reactor are connected with a glass, O-ring connector (B). The base (C) is made of brass, with water-cooled, electrical feed-throughs (D) for the tungsten basket or crucible heater (E). The base and reactor are connected with an O-ring junction (F). The Pyrex reactor consists of halves separated by an O-ring (G). The radio-frequency power is supplied by a Tegal Corp., 100-W, 13.56-MHz, radio-frequency generator and matching network capacitively coupled to the reactor by two metal rings (H and I). The plasma gas (i.e., hexafluoroethane) enters at the outer jacket of the reactor (J) into a ballast volume, and proceeds through a slit (~0.5 in. wide) in the inner tubing and between the metal rings (H and I). The tungsten basket or crucible heater are resistively heated by passing current through them. Metals more volatile than bismuth are evaporated from a quartz crucible heated by tungsten wire around the outside of the crucible. Bismuth and less volatile metals are placed in a tungsten-wire basket which is coated with aluminum oxide cement.

C. Synthesis of Trifluoromethyl Organometallic Compounds by Cocondensation of Trifluoromethyl Radicals and Metals

Using this technique, it is extremely easy to prepare almost all of the trifluoromethyl organometallic compounds that have been discussed

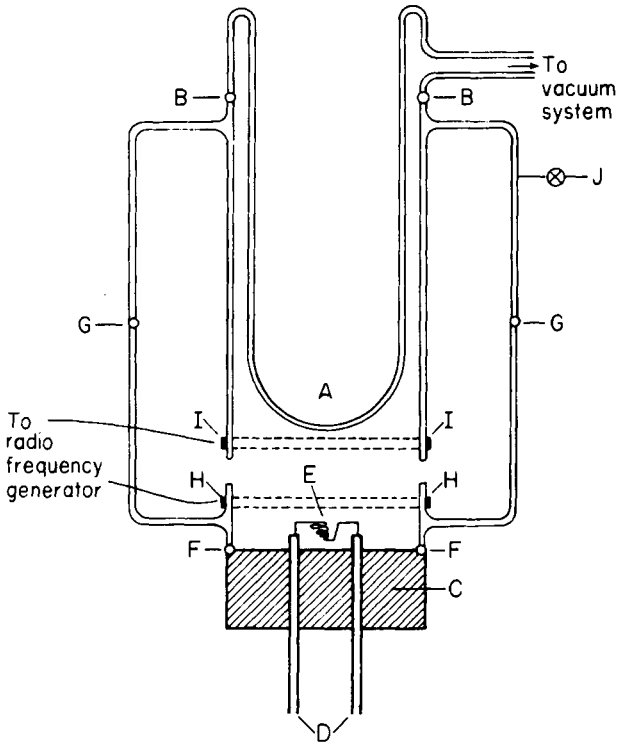


FIG. 9. Reactor for the new general metal vapor synthetic method.

in previous Sections. In each case, at least 1.5 g, and often as much as 4 g, of metal was evaporated during 2 h, and cocondensed with trifluoromethyl radicals. Although the prospects for this type of reaction appear limitless, the examples that have thus far been reported, all at −196°C, are as follows.

$$Hg(g) + n\,CF_3\cdot \rightarrow Hg(CF_3)_2\ (89\%)$$

$$Te(g) + n\,CF_3\cdot \rightarrow \underset{(10\%)}{Te(CF_3)_2} + \underset{(20\%)}{Te_2(CF_3)_2}$$

$$Bi(g) + n\,CF_3\cdot \rightarrow Bi(CF_3)_3\ (31\%)$$

$$Sn(g) + n\,CF_3\cdot \rightarrow Sn(CF_3)_4\ (8\%)$$

$$Ge(g) + n\,CF_3\cdot \rightarrow Ge(CF_3)_4\ (50\%)$$

D. Synthesis of Methyl Organometallic Compounds by Cocondensation of Methyl Radicals and Metals

This new method appears to be extremely general, and it has applications extending far outside the bounds of fluorine chemistry. With

the newer technique, it is possible to use other symmetrical molecules, such as ethane, having a relatively weak central bond to produce methyl radicals, and Si_2F_6 to produce trifluorosilyl radicals. The carbon–carbon bond in ethane has a bond strength of ~83–84 kcal/mole, and the carbon–hydrogen bond-strength (*39*) is 98–99 kcal/mole. Although this difference in bond strengths of ~15 kcal/mole is substantially smaller than with hexafluoroethane, where it is at least 40 kcal/mole, no substantial amounts (none were observed in NMR spectra) of the metal alkyls produced by the reaction of metal atoms with an ethane discharge contained ethyl groups. This result was somewhat surprising, and, initially, some experiments were conducted that employed sources (of methyl radicals) other than ethane.

A number of methyl-radical reactions with various metals have also been observed to occur in good yield on about the same, 1–4-g scale at −196°C.

$$Hg(g) + n\,CH_3\cdot \rightarrow Hg(CH_3)_2\ (9\%)$$

$$Cd(g) + n\,CH_3\cdot \rightarrow Cd(CH_3)_2\ (31\%)$$

$$Bi(g) + n\,CH_3\cdot \rightarrow Bi(CH_3)_3\ (13\%)$$

$$Sn(g) + n\,CH_3\cdot \rightarrow Sn(CH_3)_4\ (87\%)$$

$$Ge(g) + n\,CH_3\cdot \rightarrow Ge(CH_3)_4\ (16\%)$$

It is clear that the "oxidation" of metal atoms to their most stable (and, usually, highest) coordination state by radicals on a cold surface or in the gas phase should be possible for radicals of almost any type. Although it might have been predicted that such highly electronegative radicals as $CF_3\cdot$ and $SF_5\cdot$ would accomplish this oxidation, the fact that it occurs with such facility for the methyl radical (which has no particularly great oxidizing power) is an encouraging sign. Certainly, new organometallic compounds from ethyl, phenyl, and other organic radicals of most types are plausible. The fact that the reaction appears to occur primarily on the cold finger of the reactor, or in the very short time preceding condensation, offers the possibility that very unstable compounds (i.e., compounds that decompose at −50°C) might be isolated by extracting the matrix with a cold solvent or by adding other stabilizing ligands, as has become common practice in the previous metal-vapor–ligand reactions. There is a distinct possibility that the work on cocondensation of transition-metal vapors and methyl radicals that is currently in progress could establish the existence of methyl transition-metal alkyl species too unstable to be produced by the conventional routes (which often require a much higher activation-energy).

E. Synthesis of Bis(trifluorosilyl)mercury by Cocondensation of Mercury and Trifluorosilyl Radicals

The first trifluorosilyl "organometallic" compound, bis(trifluorosilyl)mercury, has been prepared by using the new, metal-vapor technique (*35*).

$$Si_2F_6 \xrightarrow{rf} 2\ SiF_3\cdot$$

$$Hg(g) + n\ SiF_3\cdot \xrightarrow[-196°C]{} Hg(SiF_3)_2\ (26\%)$$

Previously, trifluorosilyl groups have been bound to phosphorus (*40*) and silicon *via* the $SiF_2(g)$, fluorine-bond insertion-mechanism (*41*). The new compound $Hg(SiF_3)_2$ is readily hydrolyzed, but it can be stored for long periods of time in an inert atmosphere. It is a volatile, white solid that is stable up to at least 80°C. The preparation of bis(trifluorosilyl)mercury, of course, raises the possibility of (*a*) synthesis of the complete series of trifluorosilyl, "silametallic" compounds, as had previously been done for bis(trifluoromethyl)mercury by using conventional syntheses, and (*b*) transfer reactions similar to those in Section II, as well as (*c*) further exploration of the metal-vapor approach. The compound $Hg(SiF_3)_2$ appears also to be a convenient source of difluorosilane upon thermal decomposition, analogous to bis(trifluoromethyl)-mercury:

$$Hg(SiF_3)_2 \xrightarrow{\Delta} HgF_2 + 2SiF_2$$

This route could prove to be a very productive condensed phase (solution) method of generating a high concentration of SiF_2. An investigation to determine the reaction differences and similarities to the well known difluorosilane work of Margrave (*42*) is contemplated.

F. Prospects and Future Applications of This Technique

There are prospects for this type of reaction which are likely to have sweeping applications. There are a number of areas in which significant developments in the near future may be forecast. (*1*) It is quite clear that there are extensive, experimental applications of this type of metal-vapor reaction in transition-metal chemistry. (*2*) Currently, work has been successful in generating several new $M(SCF_3)_n$ compounds (*43*) from CF_3SSCF_3, and $M(SF_5)_n$ compounds (*44*) from S_2F_{10}. Work is under way on the generation of sigma-bonded-BF_2, organometallic compounds, using B_2F_4 as a source of BF_2 radicals, and with

SF_5 radicals generated from S_2F_{10} directed toward the preparation of sigma-bonded $M(SF_5)_n$. Also, $PF_2\cdot$, $SiCl_3\cdot$, and $SiH_3\cdot$ reactions are under investigation. (*3*) Furthermore, it is clear that the oxidation of many species other than pure metals is possible on cold surfaces with metal radicals. In particular, such metal halides as $SnCl_2$ are converted primarily (*45*) into $Sn(CF_3)_2Cl_2$ while PbX_2 compounds have yielded the new compound $Pb(CF_3)_4$, which is surprisingly stable. Other metal subfluorides or metal oxides that are either stable at ambient temperature, or generated solely as high-temperature species, are also oxidized. Here, a possible criterion for reaction is simply that the ionization potentials of the metal or non-metal compounds must be comparable to those of the corresponding main-group or transition metals, so that oxidation may take place. (*4*) A further ramification of the present work is the possibility of cocondensing metals and radicals in argon and other types of matrices for spectroscopic study. It would appear that an apparatus as simple as a diathermy plasma-source and metal atoms could be used to prepare, by cocondensation, many new species in matrices. Of particular interest should be the cocondensation of transition metals with such species as methyl radicals, to produce the unsaturated species (i.e., of valence lower than normal) $M(R)_{n-1}$, $M(R)_{n-2}$, etc., where the metal is not coordinatively saturated. The structures of such species would be of unusual interest in view of the fact that unsaturated metal alkyls have been proposed by many workers as being active species in homogeneous catalysis. Such spectroscopic work on the unsaturated metal carbonyls $M(CO)_{n-1}$ and $M(CO)_{n-2}$ had been performed by Ozin, Turner, and others (*46*).

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