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CHEMICAL STUDIES WITH ORGANOTIN HYDRIDES

by

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of the requirements for the degree of
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Faculty of Graduate Studies
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ABSTRACT

The reactions of trimethyltin hydride and dimethyltin dihydride with perfluorovinyl compounds of Group IVB elements have been investigated. Under thermal conditions trimethyltin hydride reacts with compounds of the type $(CH_3)_3MCF = CF_2$ and $(CH_3)_2M(CF = CF_2)_2$, M = Si, Ge, to give fluorovinyl derivatives of $(CH_3)_3M$- and $(CH_3)_2M$- containing the cis-$CF = CFH$, trans-$CF = CFH$, $-CH = CF_2$ and $-C_2H_2F$ groups. However, under ultraviolet irradiation or by heating with the free radical initiator azobisisobutyronitrile, trimethyltin hydride adds across the vinylic C = C bond to give the following products;

(i) 1:1 addition compounds with $(CH_3)_3MCF = CF_2$, i.e.
$(CH_3)_3MCFHCF_2Sn(CH_3)_3$ and $(CH_3)_3MCF(Sn(CH_3)_3)CF_2H$,
(M = Si, Ge, Sn).

(ii) 1:2 addition compounds with $(CH_3)_2M(CF = CF_2)_2$, i.e.
$(CH_3)_2M(CFHCF_2Sn(CH_3)_3)_2$, $(CH_3)_2M(CF(Sn(CH_3)_3)CF_2H)_2$
and $(CH_3)_2M(CFHCF_2Sn(CH_3)_3)(CF(Sn(CH_3)_3CF_2H)$,
(M = Si, Ge).

Evidence is presented which shows that these addition products are formed by a free radical chain mechanism, and their decomposition to organotin fluorides and to appropriate fluorovinyl derivatives proceeds *via* a β-fluorine elimination.

Dimethyltin dihydride reacts with compounds of the type $(CH_3)_3MCF = CF_2$ or $(CH_3)_2M(CF = CF_2)_2$, (M = Si, Ge), under ultraviolet irradiation as well as under thermal reaction conditions to give fluorovinyl derivatives of $(CH_3)_3M$- and $(CH_3)_2M$- containing the <u>cis</u>-CF = CFH, <u>trans</u>-CF = CFH, $-CH = CF_2$ and $-C_2H_2F$ groups. These reactions where the stable addition products of dimethyltin dihydride could not be isolated indicate the greater reactivity of the dihydride as compared with trimethyltin hydride and its facile conversion to dimethyltin difluoride.

Trimethyltin hydride and dimethyltin dihydride react with pentacarbonyl-perfluorovinylrhenium to give fluorovinyl derivatives of $(CO)_5Re$- containing the <u>cis</u>-CF = CFH, <u>trans</u>-CF = CFH and $-CH = CF_2$ groups. In the reactions of trimethyltin hydride with $(CO)_5ReCF = CF_2$ under free radical generating conditions, evidence for the existence of the unstable intermediate addition products $(CO)_5ReCFHCF_2Sn(CH_3)_3$ and $(CO)_5ReCF(Sn(CH_3)_3)CF_2H$ is presented.

The compounds were characterized by detailed spectroscopic studies. The proton and fluorine magnetic resonance spectra and infrared spectra ($4000 - 400\ cm^{-1}$) of the new compounds are discussed.

The reactions of trimethyltin hydride and dimethyltin dihydride with phosphonitrilic halides do not lead to the exchange between the halogen on the phosphonitrilic halide molecule and the hydrogen on an organotin hydride. The initiation of polymerization limits such reduction reactions.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Professor Howard C. Clark for his guidance and kind encouragement throughout this work. I am also indebted to Mr. Brian K. Hunter for the valuable discussions regarding the nuclear magnetic resonance studies and to Dr. J. David Ruddick for the help given during the preparation of this manuscript.

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CHAPTER I

INTRODUCTION

The addition of organotin hydrides (hydrostannation) to terminal olefins was first discovered by van der Kerk and co-workers in 1956 (1-3). They showed that, when heated, organotin hydrides add to olefins and acetylenic compounds. Since then many studies have been made of the non-catalyzed addition of the Sn-H group across olefins and vinylmetallic compounds. Henry and Noltes in 1960 described the non-catalyzed reactions of organotin hydrides with various vinyl derivatives of silicon, germanium, tin and lead (4). Such addition reactions proceed at 80-100°, in good yield in the absence of any catalyst or solvent, especially when the vinylic double bond is activated by the presence of electron attracting substituents. This type of reaction has been applied to the preparation of functionally substituted organotin compounds and organometallic polymers (5,6). Thus far, most work had been concerned with the preparation and characterization of new derivatives, and no systematic studies had yet been made to elucidate the mechanism of these addition reactions. From the qualitative evidence available, it had been concluded that (i) the mechanism was ionic, (ii) predominantly steric factors determined the course of the reaction, and (iii) polar effects only influenced the rate of the addition. It was at this stage that the detailed study of organotin hydride chemistry was started.

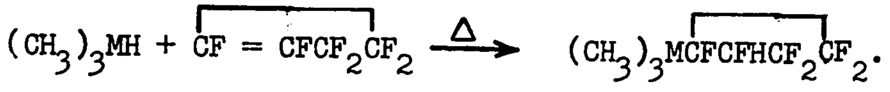
In 1961 Neumann and co-workers concluded that the addition reactions proceed by a free radical mechanism, and can be efficiently catalyzed by free radical sources which decompose at low temperatures (7,8). They showed that it was possible to add not only organotin monohydrides but also di- and tri-hydrides to a large number of olefins. Azobisisobutyronitrile (AIBN), benzyl hyponitrite, phenylazoisobutyronitrile and other free radical generating sources were shown to be useful catalysts. The most favorable reaction temperatures usually lie between 30 and 80°. These catalysts and also $ZnCl_2$, also promote addition of organotin hydrides to azomethines and carbonyl compounds (7,9);

$$(C_2H_5)_3SnH + C_6H_5N = CHC_6H_5 \xrightarrow{\text{Catalyst}} (C_2H_5)_3Sn\text{-}N(C_6H_5)CH_2C_6H_5.$$

$$(C_2H_5)_3SnH + O = CHC_6H_5 \xrightarrow{\text{Catalyst}} (C_2H_5)_3Sn\text{-}O\text{-}CH_2C_6H_5.$$

Some addition reactions are also made possible by the use of ultraviolet light (10). Recently it has been shown that organotin hydrides add to double bonds of simple internal olefins and also to terminal olefins, using light initiation, e.g. as provided by a mercury lamp at 10-15° (11,12).

In 1963, Clark et al. showed that the simple hydrocarbon and fluorocarbon olefins such as C_2H_4 and C_2F_4 do add to organotin hydrides under mild reaction conditions (13-15). At this time the only other reported addition of a tin hydride to a simple olefin was that of dibutyltin dihydride with tetrafluoroethylene, forming $(C_4H_9)_2Sn(C_2F_4H)_2$ (16). Clark and co-workers reported that, although such additions take place under mild conditions, ultraviolet irradiation always accelerated the reaction considerably. Moreover, it was shown that the addition took place in a stepwise fashion, such that for the addition of $R_2C = CR_2$ to R_2SnH_2, both $R_2SnH(C_2R_2R_2H)$ and $R_2Sn(C_2R_2R_2H)_2$ could either be isolated and characterized, or else there was good evidence of their transient existence. Convincing arguments were presented for the involvement of a free radical mechanism in such reactions, where the formation of radicals from the tin hydride was probably the rate determining step (13-15). Cullen and Styan have described addition reactions of Group IV B hydrides with various perhalocyclobutenes, fluoroacetylenes and hexafluoroacetone (17). Such additions take place easily under mild conditions <u>e.g.:</u>



$$(CH_3)_3MH + \overline{CF = CFCF_2CF_2} \xrightarrow{\Delta} (CH_3)_3M\overline{CFCFHCF_2CF_2}.$$

M = Si, Ge, Sn.

$$R_3SnH + CF_3C \equiv CCF_3 \xrightarrow{\Delta} R_3SnC(CF_3) = C(CF_3)H.$$

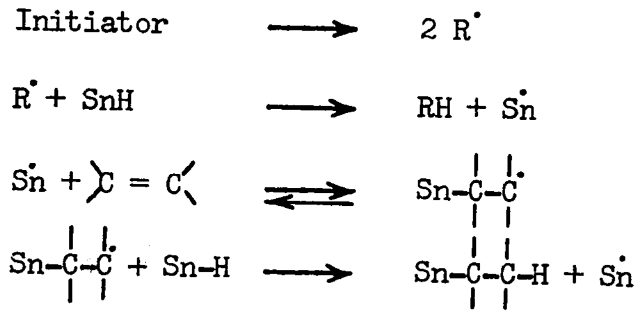
$R = CH_3,\ C_2H_3,\ \underline{n}\text{-}C_4H_9$

$$(C_4H_9)_2SnH_2 + CF_3C \equiv CCF_3 \xrightarrow{\Delta} (C_4H_9)_2Sn(C(CF_3) = C(CF_3)H)_2.$$

$$(CH_3)_3SnH + HC \equiv CCF_3 \xrightarrow{\Delta} (CH_3)_3SnCH = CHCF_3 + H_2C = C(CF_3)Sn(CH_3)_3$$

$$+ ((CH_3)_3Sn)_2CHCH_2CF_3.$$

Although detailed studies on the mechanism of organotin hydride addition reactions to olefins remain to be explored, a few conclusions can, however, be drawn on the basis of the information available at present. The acceleration of the reaction by free radical initiators and retardation by free radical inhibitors demonstrates that the reaction most likely proceeds by a free radical mechanism, since only a small amount of the initiator is needed in many cases for complete reaction (7,8,18). The following mechanism has been proposed by Kuivila, where R is a carbon free radical and Sn is a trisubstituted tin radical (19);



$$\text{Initiator} \longrightarrow 2\,\text{R}^{\bullet}$$
$$\text{R}^{\bullet} + \text{SnH} \longrightarrow \text{RH} + \text{Sn}^{\bullet}$$
$$\text{Sn}^{\bullet} + {>}\text{C}=\text{C}{<} \rightleftharpoons \text{Sn–C–C}^{\bullet}$$
$$\text{Sn–C–C}^{\bullet} + \text{Sn–H} \longrightarrow \text{Sn–C–C–H} + \text{Sn}^{\bullet}$$

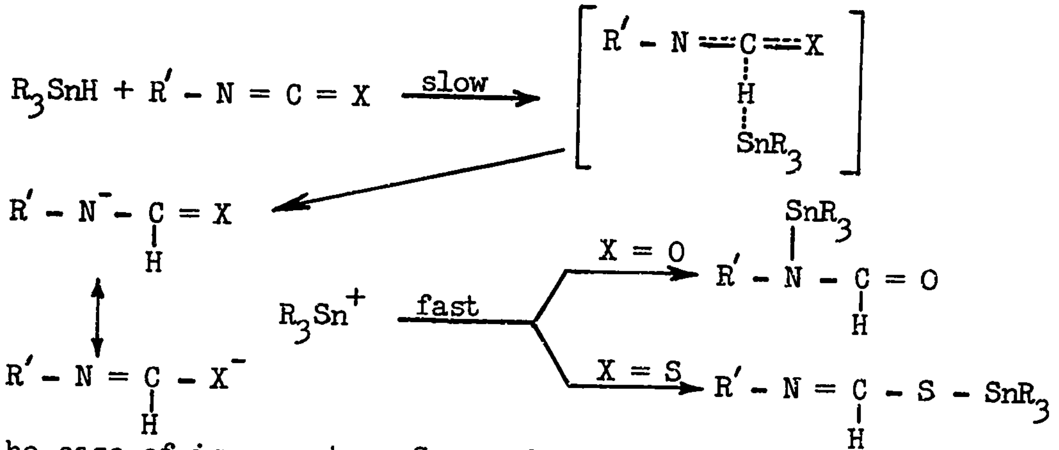
Most of the organotin hydride addition reactions can be explained in this way. Kuivila has also suggested a similar radical mechanism for the reduction of alkyl and aryl halides by organotin hydrides (19).

Recently it has been shown that the organotin hydride additions to the C = N bond of isocyanates and to the C = S bond of isothiocyanates proceed by a polar mechanism, even in the presence of AIBN (20,21). The polarity of the Sn–H bond plays an important part in such ionic reactions of organotin hydrides. In these reactions, a transition state is formed in which under the influence of a strong electrophile, E, the Sn–H bond will become polarized according to (I), and under

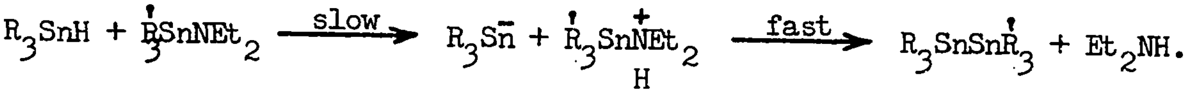
$$R_3\overset{\delta+}{\text{Sn}}\text{-----}\overset{\delta-}{\text{H}}\text{-----E} \qquad\qquad R_3\overset{\delta-}{\text{Sn}}\text{----}\overset{\delta+}{\text{H}}\text{----N}$$

(I) (II)

the influence of a strong nucleophile, N, according to (II). Electron attracting groups on tin allow delocalization of partial negative charge and thus favor electrophilic attack by the hydride according to (II). Electron donating alkyl groups increase the electron density on tin and thus promote the nucleophilic attack by the hydride according to (I). Thus the nucleophilic addition of organotin hydrides to isocyanates and isothiocyanates has been described by the following polar mechanism (20-21):



In the case of isocyanates, Sommer had reported that the tin atom becomes attached to the oxygen (22). However, Noltes et al. have presented conclusive evidence, on the basis of UV and IR spectra, for the presence of a Sn-N bond in the adducts with isocyanates, and of an Sn-S bond in the adducts with isothiocyanates (23,24). The electrophilic hydrostannolysis of tin-nitrogen bonds has also been described by Noltes et al. (25);



$$R_3SnH + R'_3SnNEt_2 \xrightarrow{slow} R_3\bar{Sn} + R'_3Sn\underset{H}{\overset{+}{N}}Et_2 \xrightarrow{fast} R_3SnSnR'_3 + Et_2NH.$$

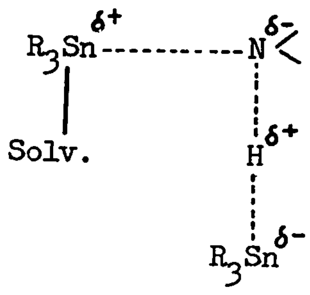
Although the possibility of the free radical nature of these reactions has not been excluded, the polar course has been strongly preferred for the following reasons.

(1) The rate of addition increases considerably with increasing polarity of the solvent. Additions in butyronitrile ($\varepsilon = 30.3$) are much faster than in cyclohexane ($\varepsilon = 2.0$).

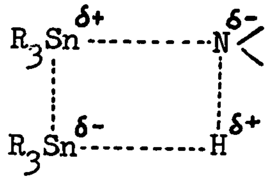
(2) Neither the presence of initiator, AIBN, nor that of inhibitor phenoxyl, affects the rate of reaction (26).

(3) Electron releasing substituents attached to the tin hydride, and electron withdrawing groups, e.g. bound to the isocyanate accelerate the addition.

But for hydrostannolysis reactions in non-polar solvents, a four centre type reaction could be involved.

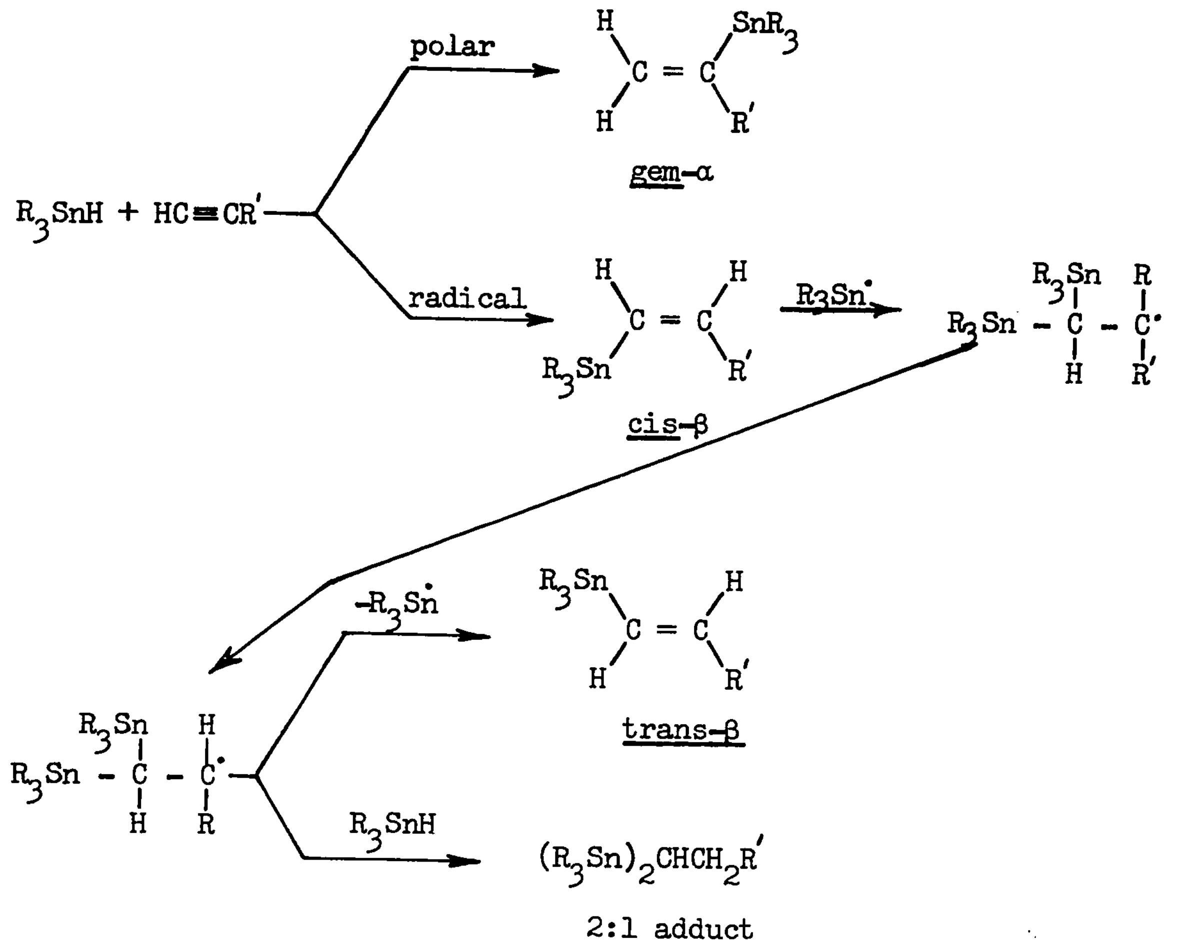


Polar solvents



Non-polar solvents

Similar mechanisms have been proposed for the reactions of tin tetraalkyls with halogens and for the cleavage of the tin-tin bond in hexaalkylditin compounds by iodine (27,28). The partial positive charge may be stabilized by solvent e.g. butyronitrile, but the stabilization of a negatively charged tin species by an electron donating solvent does not seem to be a likely process. Marsman et al. have presented convincing evidence that the addition of trialkyltin hydrides to carbon-carbon triple bonds can proceed via a polar mechanism leading to α-adducts, as well as via a radical mechanism leading to β-adducts (29,30). Secondary reactions involving organotin radicals may convert the cis-addition products into trans-isomers or into 2:1 adducts (29,30). In their studies concerning the reactions of trimethyltin hydride with methyl propiolate, they find that the rate of formation of the gem-adduct is not affected by the addition of the free radical inhibitor phenoxyl, or the free radical initiator



$R = CH_3$, $R' = COOCH_3$

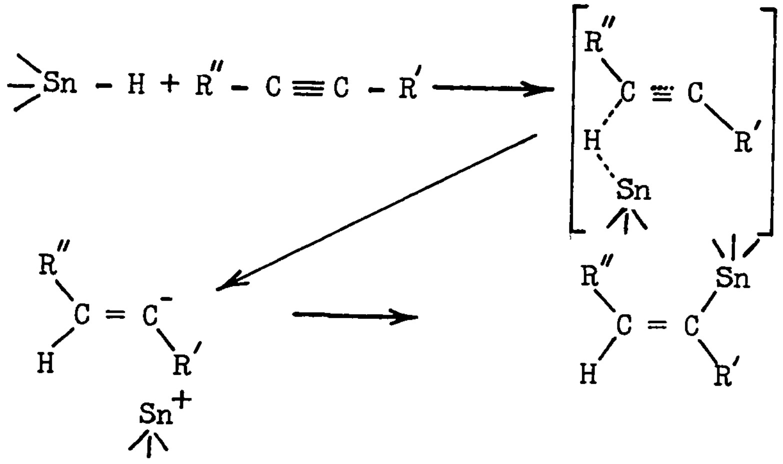
AIBN. However, the rate of formation of the gem-adduct is much greater in the polar solvent butyronitrile ($\varepsilon = 20.3$) than in decane ($\varepsilon = 1.95$). Moreover, in the formation of the gem-adduct only, trans-addition occurs in the reactions involving triethyltin deuteride, hence a four-centre mechanism can be excluded. Thus, the formation of the non-terminal gem-adduct proceeds via a polar trans-mechanism. Addition of AIBN increases the yield chiefly of the cis-adduct, while at the same time some trans-adduct is formed. Obviously the cis-adduct is formed via a free radical trans-addition, whereas the trans-adduct is formed via a free radical isomerization of the cis-adduct. The free radical trans-addition and isomerization has been studied using 1-hexyne, ethyl 1-propynecarboxylate and ethoxyethyne as the unsaturated partners. The mechanism of the polar reactions with cyanoethyne and diethyl acetylenedicarboxylate was studied by measuring the extinction of the Sn-H absorption band in the infrared spectrum (29,30). These studies showed that;

(1) Electron-withdrawing substituents attached to the carbon-carbon triple bond accelerate the addition considerably.

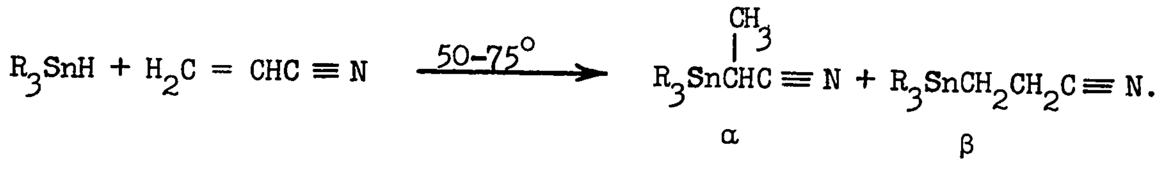
(2) The order of reactivity of the tin hydrides is:-
$Ph_3SnH \ll Me_3SnH < Et_3SnH, Bu_3SnH$.

(3) The reaction is first order in both the hydride and acetylene.

These data are in agreement with a nucleophilic attack of the hydrogen bound to tin on carbon, as the rate determining step;



Similar observations concerning the addition of organotin hydrides across the C = C bond in acrylonitrile have been made by Leusink and Noltes (31). They identified the α- and β- adducts by nuclear magnetic resonance spectroscopy;



$$R_3SnH + H_2C = CHC \equiv N \xrightarrow{50\text{-}75^\circ} \underset{\alpha}{R_3Sn\overset{\overset{CH_3}{|}}{C}HC \equiv N} + \underset{\beta}{R_3SnCH_2CH_2C \equiv N}.$$

isomerization of the <u>cis</u>-adduct. The free radical <u>trans</u>-addition and isomerization has been studied using 1-hexyne, ethyl 1-propynecarboxylate and ethoxyethyne as the unsaturated partners. The mechanism of the polar reactions with cyanoethyne and diethyl acetylenedicarboxylate was studied by measuring the extinction of the Sn-H absorption band in the infrared spectrum (29,30). These studies showed that;

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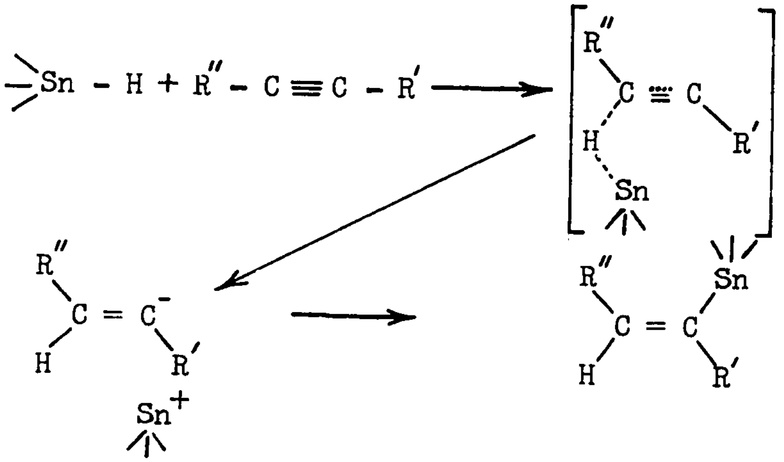

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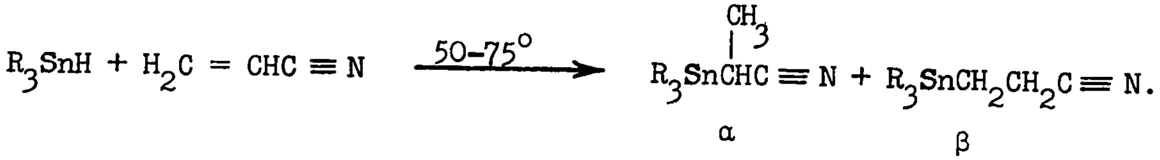


$$R_3SnH + H_2C = CHC \equiv N \xrightarrow{50\text{–}75^{\circ}} \underset{\alpha}{R_3Sn\overset{CH_3}{\overset{|}{C}}HC \equiv N} + \underset{\beta}{R_3SnCH_2CH_2C \equiv N}.$$

Addition of AIBN enhances considerably the rate of formation of the β-adduct only. The rate of formation of the α-adduct increases with increasing polarity of the solvent. This makes a four-centre type transition state in the formation of the α-adduct less probable (5). Thus, the involvement of a polar mechanism in the formation of α-adduct and of a radical mechanism in the formation of the β-adduct is supported.

Although there is sufficient evidence for the involvement of a free radical mechanism involving the hydrostannation reactions of various olefins and acetylenes, the possibility of a polar mechanism cannot be completely ruled out. The fact that the hydrostannation of carbonyl derivatives and azomethines is not only accelerated by ultraviolet light and free radical-forming species, but also by a non-radical-forming catalyst, zinc chloride, again shows that reaction modes other than free radical processes should not be completely rejected (7,9).

Thus far, most of the work involving the reactions of organotin hydrides has been concerned with the behaviour of the Sn-H group towards unsaturated, purely organic systems. However, there are other areas where the nature of the reactions of the Sn-H group needs to be explored. An exchange reaction could also occur between organotin hydrides and organotin compounds containing a tin-element bond;

$$R_3SnX + \overset{\prime}{R}_3SnH \rightleftharpoons R_3SnH + \overset{\prime}{R}_3SnX$$

Many examples of this type of reaction have been mentioned in the literature, <u>e.g.</u> where X = halogen (32,33), RCOO (34), OR, SR (35), D (36), $OSnR_3$, $SSnR_3$, CN or PR_2 (37). Similarly, the fluorine atoms on pentavalent phosphorus are easily replaced by the hydrogen of an organotin hydride at room temperature (38,39);

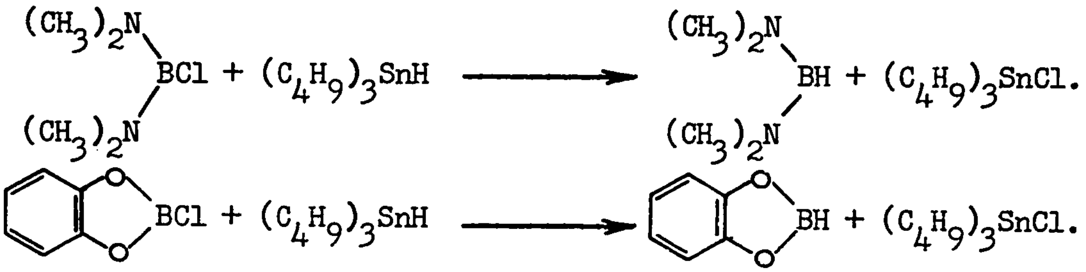
$$PF_5 + (CH_3)_3SnH \longrightarrow HPF_4 + (CH_3)_3SnF.$$

$$PF_5 + x(CH_3)_3SnH \longrightarrow H_2PF_3 + x(CH_3)_3SnF.$$

$$CH_3PF_4 + (CH_3)_3SnH \longrightarrow CH_3PF_3H + (CH_3)_3SnF.$$

$$C_2H_5PF_4 + (CH_3)_3SnH \longrightarrow C_2H_5PF_3H + (CH_3)_3SnF.$$

Nothing is yet known about the mechanism involved in these reactions. The reductions of chloroboranes by tributyltin hydride at 90° to give the corresponding hydrides, in addition to other unidentified products, have also been observed (40);



These reactions are not catalyzed by AIBN and are not inhibited by phenoxyl. The effect of the polarity of the solvent, although small, is consistent with a polar mechanism involving some kind of charge separation. However, a direct displacement cannot be ruled out by the data available, because quantitative reductions take place between neat reactants as well (40).

One suitable system to study the mechanistic aspects of organotin hydride reactions is the investigation of the reactions of the Sn-H group with the vinyl and perfluorovinyl compounds of different elements. Seyferth _et al._ have described the reaction of triphenyltin hydride with triphenylperfluorovinyltin (41);

$$(C_6H_5)_3SnH + (C_6H_5)_3SnCF = CF_2 \xrightarrow{70^\circ} (C_6H_5)_3SnSn(C_6H_5)_3 + C_2F_3H.$$

Instead of addition to the vinylic C = C bond, they obtained hexaphenylditin. This result is surprising, and the reaction needs further investigation. Clark *et al*. have reported the reactions of trimethyltin hydride and dimethyltin dihydride with perfluorovinyltin compounds (42). In the reactions of trimethyltin hydride with $(CH_3)_3SnCF = CF_2$ under heat or ultraviolet irradiation, the main reaction product obtained was *cis*-$CFH = CFSn(CH_3)_3$. They had suggested the possibility of addition across the vinylic C = C bond, followed immediately by trimethyltin fluoride elimination. However, no conclusive evidence could be presented about the reaction mechanism involved, hence further investigation of this type of reaction was desirable.

The present work was undertaken to investigate the mechanism involved in the reactions of organotin hydrides with perfluorovinyl compounds of different elements. Group IV B elements silicon, germanium and tin were selected. In vinylsilanes, the occurrence of π-bonding ($\underline{d}\pi - \underline{p}\pi$), that is the overlap of the olefinic π-electron cloud from filled carbon $\underline{sp}^n$ hydrid orbital or from a carbon *p* orbital with *d* orbitals of silicon in the ground state, Fig. I., has been discussed by a number of workers and used to explain certain anomalies of vinylsilane reactivity (4,43-52). Qualitative spectroscopic investigations have been cited in support of such π-bonding.

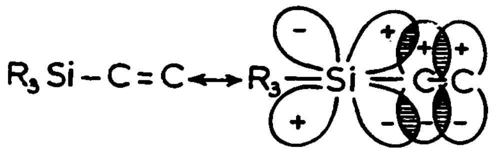


Fig. 1.

$\underline{d}\pi - \underline{p}\pi$ Bonding in Vinylsilanes

Petrov et al. have investigated the absorptions in the Raman spectra for the compounds $(CH_3)_3MCH = CH_2$, where M = C, Si, Ge and Sn (53). The data for C = C stretching frequencies are given in Table I. The intensities are relative to the cyclohexane line at 802 $cm.^{-1}$ taken as 250 units.

TABLE I.

Raman Spectral Data for Trimethylvinyl Compounds of Group IV B Elements.

Compound	C = C Stretch ($cm.^{-1}$)	Intensity
$(CH_3)_3CCH = CH_2$	1648	70
$(CH_3)_3SiCH = CH_2$	1595	50
$(CH_3)_3GeCH = CH_2$	1594	33
$(CH_3)_3SnCH = CH_2$	1581	27

They also found that the reactivity of the double bond in $(CH_3)_3MCH = CH_2$ compounds towards the addition of thiocyanogen increases in the order $M = C < Si < Ge < Sn$. Thus the essential difference in the reactivities was attributed to the central atom M. The increase in the metallic properties of the atom is connected with the high lability of the external electron shells i.e. an increase in polarizability, and consequently with a high intensity of the Raman spectra. Thus a decrease in the intensity of ν (C = C) in going from C to Si, Ge and Sn was unexpected. Moreover, these authors also found that in the compounds of the type $R_3MCH_2CH = CH_2$ the intensity of ν (C = C) increases as M changes from C to Si, Ge and Sn, in the approximate ratio of 1:2:4:8. Thus it was supposed that the decrease of intensity of ν (C = C) in the vinyl compounds is explained by the complex structure of the electron cloud in the M–C bond, whose formation involves the d orbitals of the atom M, as also described by Craig et al. (54). This M–C bond will have the properties of a double bond and the d orbitals of atom M will overlap the π-orbitals of the multiple bond in the vinyl position. Thus, the anomalous intensity changes in the vinyl derivatives were ascribed to $d\pi - p\pi$ bonding.

Proton magnetic resonance studies also provide evidence for $d\pi - p\pi$ bonding in vinylsilanes (46, 48, 55). Substitution of a proton of ethylene by an $Si(CH_3)_3$ group decreases the shielding of all ethylenic protons, and especially of the protons in the β-position, which are shifted 1 p.p.m. below the resonances of the corresponding protons in 3,3-dimethylbutene (48,55). This shift is usually interpreted as a manifestation of the $d\pi - p\pi$ dative bond between the vinyl group and silicon.

Again, vinylsilanes usually have absorptions due to $\nu(C = C)$ at 1590-1595 cm^{-1} in their infrared spectra. This is about 50-55 cm^{-1} below the $\nu(C = C)$ of unsubstituted olefins. Such shifts have been attributed to the occurrence of $d\pi - p\pi$ bonding (56). However, Egorov et al. have discussed the vibrational spectra of $Cl_3MCF = CF_2$ compounds (M = Si, Ge, Sn), and have attributed the decrease in the intensity of $\nu(C = C)$ in going from silicon to tin primarily to the inductive effects of M (57).

In the present work the reactions of organotin hydrides with perfluorovinyl compounds of Group IV B elements were studied. By using different perfluorovinyl compounds subtle changes can be made in the nature of the vinylic C = C bond, not only because of differences between the inductive effects of say, R_3M groups, but also because of variations in $\underline{d}\pi - \underline{p}\pi$ interactions in the M-C = C group, where M changes from Si to Ge and Sn (44).

Perfluorovinyl compounds of various transition metals have recently been prepared (58,59). It was of interest to investigate the reactivity of the perfluorovinyl group attached to a transition metal towards the organotin hydrides and to compare it with that of the perfluorovinyl compounds of Group IV B elements. Thus the reactions of organotin hydrides with pentacarbonyl-perfluorovinylrhenium and pentacarbonyl-perfluoropropenylrhenium were investigated.

The reactions of organotin hydrides with phosphonitrilic halides were investigated. Since the initial work of Stokes on phosphonitrilic chlorides an extensive amount of work has been done in this field within the last 20 years (60). It is known that the exchange between the halogen on PF_5 and the hydrogen on an organotin hydride takes place easily in the gas phase (38-40). Hence an attempt was made to prepare phosphonitrilic hydrides or mixed phosphonitrilic halide hydrides by the exchange reactions between organotin hydrides and phosphonitrilic halides.

CHAPTER II

DISCUSSION

1. The Reactions of Organotin Hydrides with Perfluorovinyl Silicon Compounds.

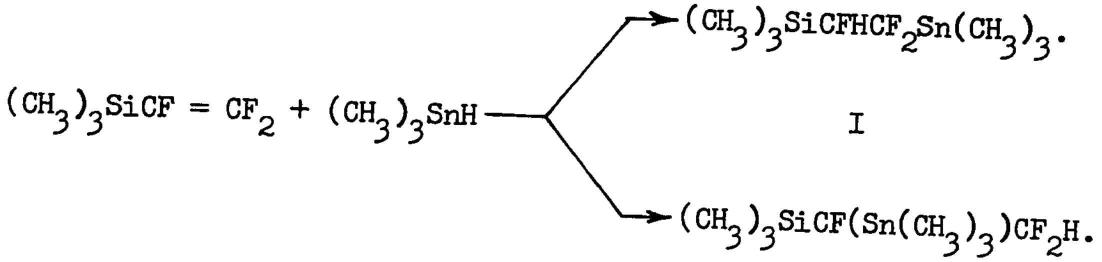
Trimethyltin hydride did not react with $(CH_3)_3SiCF = CF_2$ at room temperature, even over a long period, but at 55° reaction occurred readily with the deposition of trimethyltin fluoride and formation of fluorovinyl silanes, notably $(CH_3)_3SiCH = CF_2$, <u>cis</u>-$CFH = CFSi(CH_3)_3$, <u>trans</u>-$CFH = CFSi(CH_3)_3$ and $(CH_3)_3SiC_2H_2F$; these being listed in the order of decreasing yield. When the hydride and the perfluorovinylsilane were heated at 55° for 40 hours in butyronitrile, the same reaction products as above were obtained in approximately the same ratio. These reactions apparently differ from others reported for organotin hydrides. Thus triphenyltin hydride adds across the C = C bond of vinylsilanes readily (4),

$$(C_6H_5)_3SnH + (C_6H_5)_3SiCH = CH_2 \xrightarrow{70^\circ} (C_6H_5)_3SiCH_2CH_2Sn(C_6H_5)_3,$$

although no evidence was obtained which would distinguish between the two possible isomers, that above and $(C_6H_5)SiCH(Sn(C_6H_5)_3)CH_3$. Such addition reactions of perfluorovinylsilanes are also known, although frequently the elimination of a fluoride occurs readily. Thus triphenylsilyllithium adds to $(C_2H_5)_3SiCF = CF_2$ and the resulting adduct loses lithium fluoride (61).

$$(C_2H_5)_3SiCF = CF_2 + (C_6H_5)_3SiLi \longrightarrow (C_2H_5)_3SiCF = CFSi(C_6H_5)_3 + LiF.$$

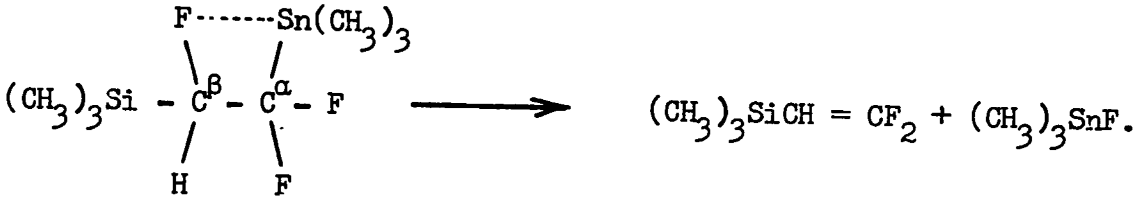
In the present instance, although addition products were not formed under thermal conditions, such products were formed under other conditions. When trimethyltin hydride and trimethylperfluorovinylsilane were exposed to ultraviolet irradiation at room temperature, a high yield of the two possible addition products, I and II in the ratio 3:2, was obtained with virtually no formation of trimethyltin fluoride.

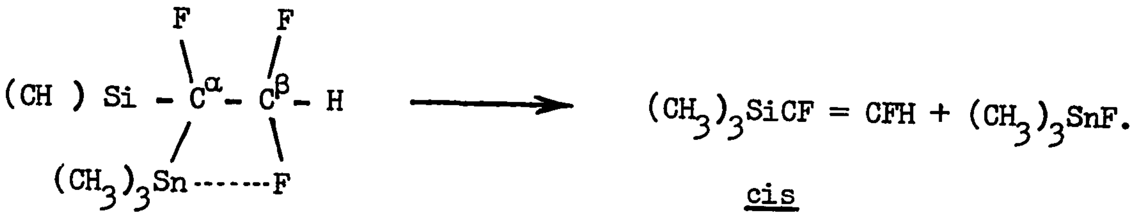


$$(CH_3)_3SiCF = CF_2 + (CH_3)_3SnH \longrightarrow (CH_3)_3SiCFHCF_2Sn(CH_3)_3. \quad \text{I}$$

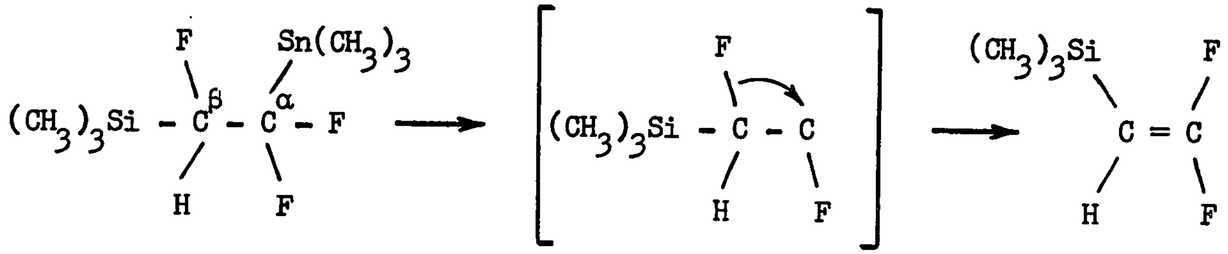
$$(CH_3)_3SiCF = CF_2 + (CH_3)_3SnH \longrightarrow (CH_3)_3SiCF(Sn(CH_3)_3)CF_2H. \quad \text{II}$$

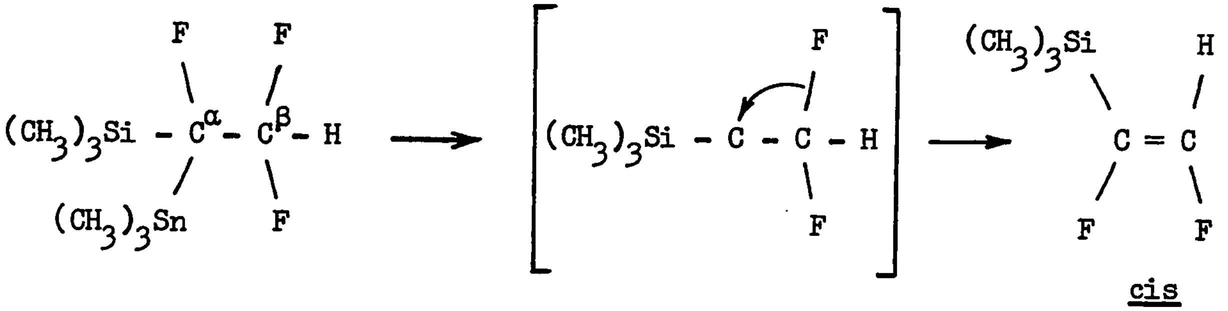
Although this mixture is stable for at least four hours at room temperature, trimethyltin fluoride is deposited to leave $(CH_3)_3SiCH = CF_2$ and <u>cis</u>- $CFH = CFSi(CH_3)_3$ in a 2:1 ratio. This latter ratio, together with the above ratio of the addition products, could indicate that $(CH_3)_3SiCH = CF_2$ has been formed from the adduct $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$ and <u>cis</u>- $CFH = CFSi(CH_3)_3$ from the other adduct, $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$, in both cases by a β-fluorine elimination leading to the formation of trimethyltin fluoride.





The reasonable nature of this type of elimination can be readily established by the use of molecular models, from which it can be seen that the p-orbitals of the β-fluorine are directed more toward the tin than are the p-orbitals of the α-fluorine, and that the Sn-F_β distance is the smaller. This evidence for β-elimination is particularly significant with respect to the addition of fluoro-olefins across metal-metal bonds. Thus, a reaction occurs between trifluoroethylene and $(CH_3)_3SnMn(CO)_5$ to give trimethyltin fluoride and cis- and trans- $CFH = CFMn(CO)_5$ (62). It was suggested that these reaction products were formed by a decomposition of $(CO)_5MnC_2F_3HSn(CH_3)_3$, although it could not be isolated. The similarity of this hypothetical addition product to the addition products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF$, and the above evidence for β-elimination, strongly suggest that the same type of process is involved in all these reactions, where the high lattice energy of trimethyltin fluoride favors its elimination (63,64). The alternative process would be an α-elimination followed by a fluoride ion migration.



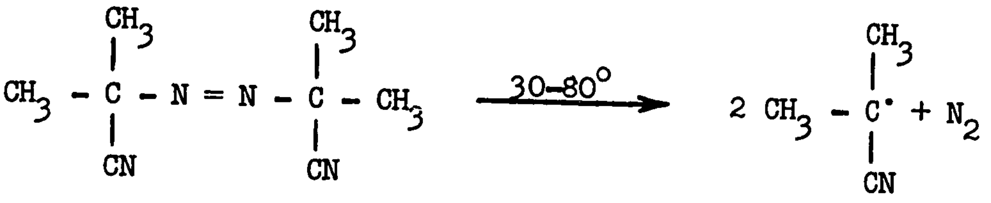


This type of elimination requires a high energy intermediate, as well as a fluoride ion shift, which seems less likely from energetic grounds alone (65). However, it has been shown that α-elimination, followed by chloride ion migration occurs in some pyrolysis reactions (65);

$$CFClHCF_2SiCl_3 \longrightarrow CFH = CFCl + FSiCl_3.$$

$$CFCl_2CF_2SiCl_3 \longrightarrow CFCL = CFCl + FSiCl_3.$$

There is good evidence that the additions of organotin hydrides to various olefins proceed <u>via</u> a free radical mechanism (9,13-15,19). One argument supporting this is the fact that ultraviolet irradiation and free radical sources readily initiate, and free radical inhibitors retard these reactions. It is known that azobisisobutyronitrile (AIBN) decomposes by heat to generate free radicals (26,66).

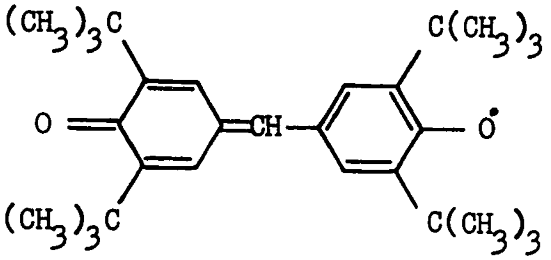


$$CH_3 - \underset{CN}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - N = N - \underset{CN}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_3 \xrightarrow{30\text{–}80^{\circ}} 2\ CH_3 - \underset{CN}{\overset{CH_3}{\underset{|}{\overset{|}{C^{\cdot}}}}} + N_2$$

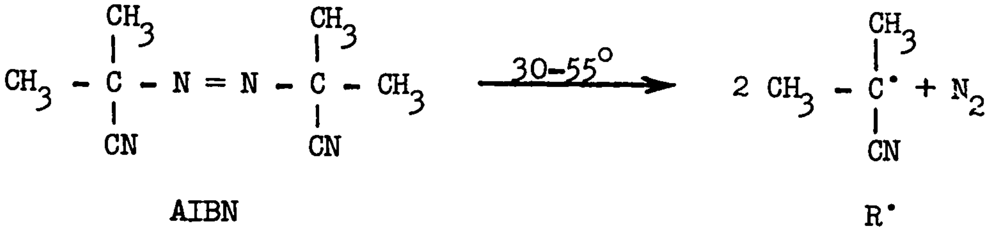
AIBN

R$^{\cdot}$

Such free radicals initiate the formation of organotin radicals when in contact with organotin hydrides, which then attack the olefinic C = C bond. Therefore, the reaction of trimethyltin hydride with $(CH_3)_3SiCF = CF_2$ was studied in the presence of AIBN. The same mixture of addition products I and II was isolated, in approximately the same ratio, although for extensive reaction a temperature of 50° was necessary, so that considerable yields of the fluorovinyl decomposition products were also obtained. It seems that AIBN certainly initiates the addition process, although less effectively than for other olefins (67). This is consistent with the generally lower reactivity of the perfluorovinylic C = C bond. A similar reaction of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$ under ultraviolet irradiation in which the effect of hydroquinone on the formation of the addition product was studied, led to a high yield of the addition products I and II. This supports earlier arguments that hydroquinone does not inhibit radical addition reactions of organotin hydrides (5,19). A more effective inhibitor, which has been extensively used in mechanistic studies of organotin hydride addition reactions is phenoxyl (18).



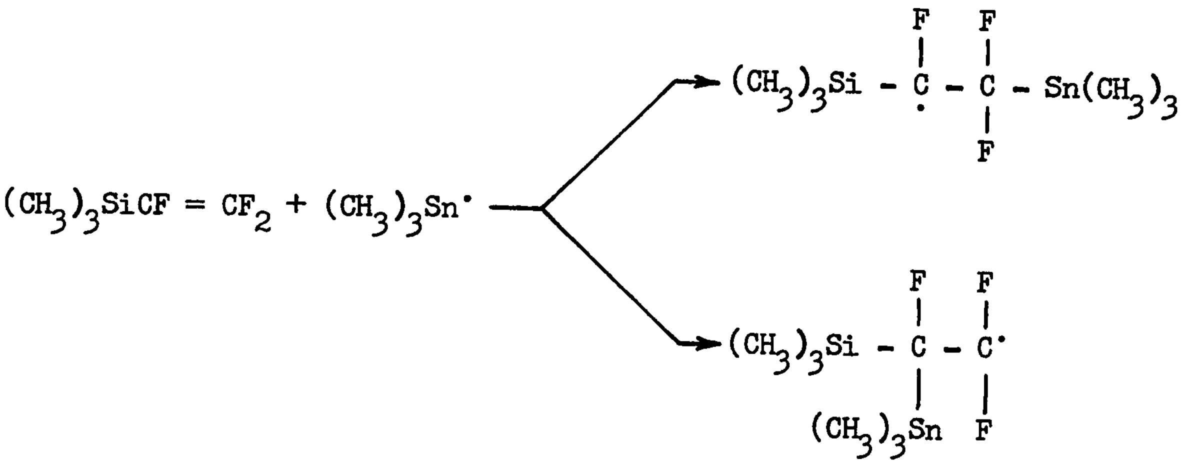
It is known that phenoxyl quenches the free radicals generated by AIBN by coupling rather than by hydrogen abstraction (26). In a reaction of trimethyltin hydride with $(CH_3)_3SiCF = CF_2$ in the presence of AIBN, phenoxyl completely stopped the addition reaction. This contrasts with certain other reactions of organotin hydrides where phenoxyl had no effect on the rate of addition reactions, and the nature of the reaction was controlled by the polar effects of the solvent (20,21). Thus there is no doubt that the addition of trimethyltin hydride to the perfluorovinylic C = C bond, which only takes place under free radical generating conditions <u>e.g.</u> by ultraviolet irradiation or by heating with AIBN, is indeed a free radical process. The following chain reaction mechanism could be responsible for such reactions:



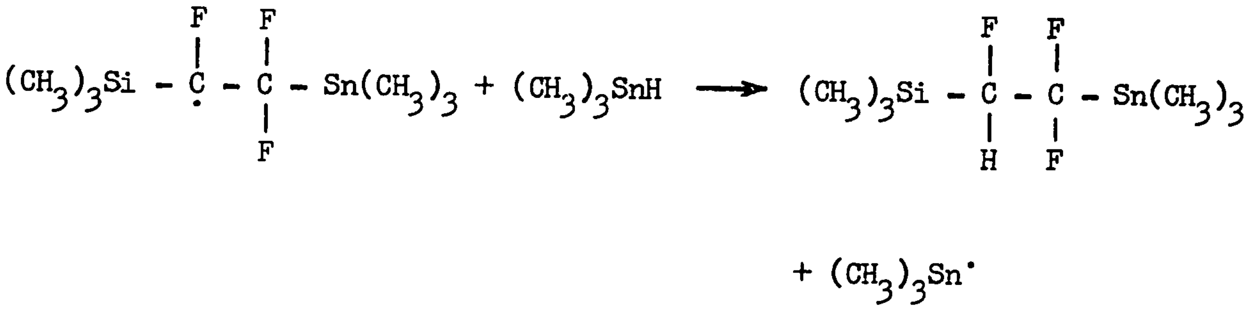
$$CH_3-\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}-CH_3 \xrightarrow{30\text{-}55^\circ} 2\ CH_3-\overset{CH_3}{\underset{CN}{C^\bullet}}+N_2$$

$$R^\bullet + (CH_3)_3SnH \longrightarrow (CH_3)_3Sn^\bullet + RH$$

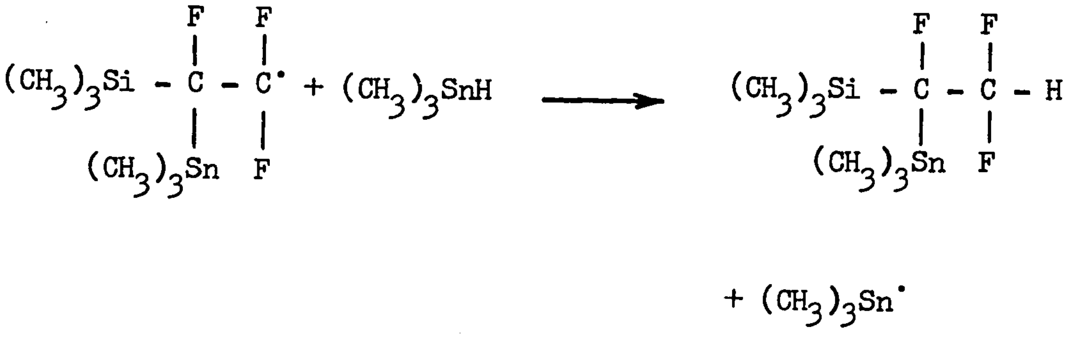
<u>or</u> $(CH_3)_3SnH \xrightarrow[\text{Light}]{\text{UV}} (CH_3)_3Sn^{\cdot} + H^{\cdot}$



$$(CH_3)_3SiCF=CF_2 + (CH_3)_3Sn^{\cdot} \longrightarrow (CH_3)_3Si-\underset{\cdot}{C}F-CF_2-Sn(CH_3)_3 \quad \text{or} \quad (CH_3)_3Si-CF(Sn(CH_3)_3)-CF_2^{\cdot}$$



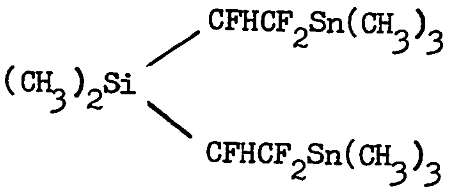
$$(CH_3)_3Si-\underset{\cdot}{C}F-CF_2-Sn(CH_3)_3 + (CH_3)_3SnH \longrightarrow (CH_3)_3Si-CFH-CF_2-Sn(CH_3)_3 + (CH_3)_3Sn^{\cdot}$$



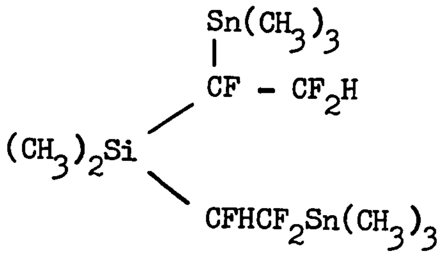
$$(CH_3)_3Si-CF(Sn(CH_3)_3)-CF_2^{\cdot} + (CH_3)_3SnH \longrightarrow (CH_3)_3Si-CF(Sn(CH_3)_3)-CF_2-H + (CH_3)_3Sn^{\cdot}$$

The behavior of dimethyltin dihydride with $(CH_3)_3SiCF = CF_2$ was next investigated. At 60°, little reaction occurred, but under ultraviolet irradiation at 25°, there was extensive conversion to dimethyltin difluoride and the fluorovinyl silanes, with $(CH_3)_3SiCH = CF_2$ again being the major volatile product.

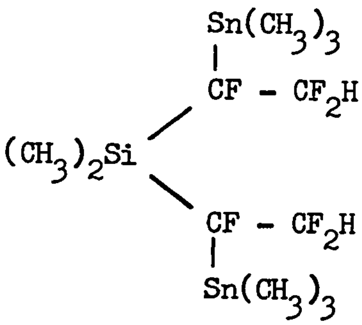
Trimethyltin hydride and $(CH_3)_2Si(CF = CF_2)_2$ do not react at room temperature, and at 55° only a limited reaction takes place. However, the reaction does take place easily under ultraviolet irradiation at room temperature, with the formation of an involatile addition product, which was identified spectroscopically as a mixture of the addition products I, II and III.



I



II

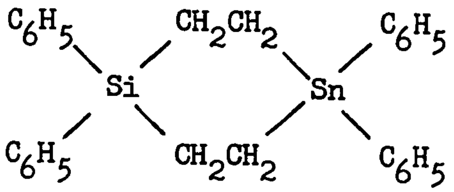


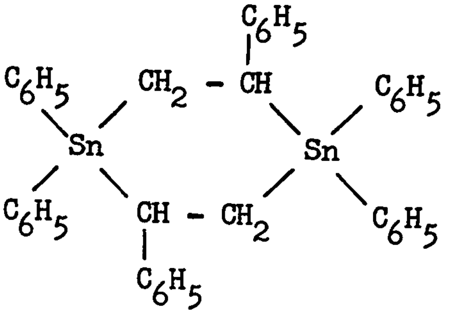
III

The proton n.m.r. spectrum of this involatile liquid showed the presence of two closely spaced sets of eight lines each, corresponding to two $-CFHCF_2-$ groups, and two other sets of eight lines each, corresponding to two $>CFCF_2H$ groups. This indicated the presence of two $-CFHCF_2Sn(CH_3)_3$groups in slightly different chemical environments, the proton spectrum of which overlapped badly. Similarly there were two overlapping $-CF(Sn(CH_3)_3)CF_2H$ groups in slightly different chemical environments. Thus, the proton n.m.r. spectrum is consistent with the existence of three different molecules I, II and III in the addition product. This mixture was unstable at room temperature, slowly eliminating trimethyltin fluoride accompanied by the formation of $-CF = CFH$ (cis) and $-CH = CF_2$ groups, thus again supporting a β-fluorine elimination process. It was not possible to separate individual compounds from the mixture chromatographically due to their instability.

In the presence of AIBN the addition of trimethyltin hydride to $(CH_3)_2Si(CF = CF_2)_2$ apparently occurred at 55°, but the addition products were unstable under these conditions since only compounds containing $-CF = CFH$, $-CH = CF_2$ and $-C_2H_2F$ groups were obtained.

The behavior of dimethyltin dihydride with $(CH_3)_2Si(CF = CF_2)_2$ was next examined. It was of particular interest, since with dihydrides cyclic compounds could result similar to that obtained from the reactions of diphenyltin dihydride with $(C_6H_5)_2Si(CH = CH_2)_2$ and $C_6H_5C \equiv CH$ (4);





Dimethyltin dihydride also easily adds across the C = C bond of simple olefins and fluoro-olefins <u>e.g.</u> (13,15);

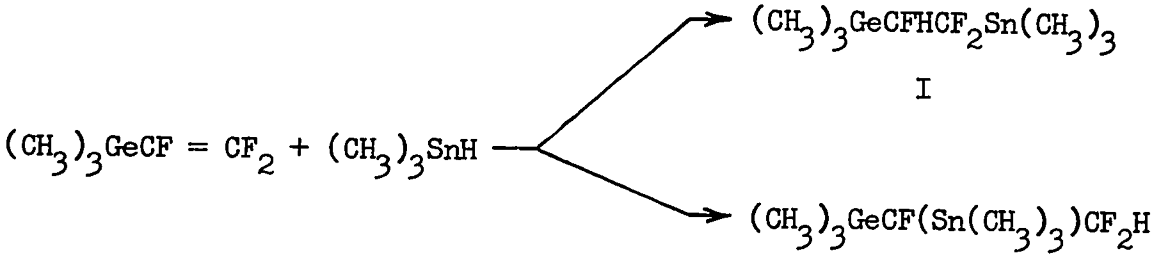
$$(CH_3)_2SnH_2 + C_2F_4 \longrightarrow (CH_3)_2SnH(C_2F_4H).$$

$$(CH_3)_2SnH(C_2F_4H) + C_2F_4 \longrightarrow (CH_3)_2Sn(C_2F_4H) \, .$$

Dimethyltin dihydride and $(CH_3)_2Si(CF = CF_2)_2$ did not react extensively at room temperature, but at 55°, or under ultraviolet irradiation at 25°, considerable amounts of dimethyltin difluoride and volatile silanes containing $- CF = CFH$ (<u>cis</u> and <u>trans</u>), $- CH = CF_2$ and $- C_2H_2F$ groups were formed. In neither case could any addition product be separated or detected. This may be due to the fact that the favorable energy release accompanying the formation of solid dimethyltin difluoride in the reactions of dimethyltin dihydride with perfluorovinyl silicon compounds is sufficient to make the intermediate cyclic addition products too unstable to be detected. The stability of this dimethyltin difluoride lattice is illustrated by the isolation of $(CH_3)_2SnF_2$ as the product when attempts were made to prepare the $B\overline{F}_4$, $P\overline{F}_6$, $As\overline{F}_6$ and $Sb\overline{F}_6$ salts of the cation $(CH_3)_2Sn^{2+}$ (68,69).

2. The Reactions of Organotin Hydrides with Perfluorovinyl Germanium and Tin Compounds.

Trimethyltin hydride did not react with $(CH_3)_3GeCF = CF_2$ at room temperature, even over long periods, but at 55° reaction occurred readily with the deposition of trimethyltin fluoride and formation of fluorovinyl germanes, notably cis-$CFH = CFGe(CH_3)_3$, $(CH_3)_3GeCH = CF_2$, $(CH_3)_3GeC_2H_2F$ and trans-$CFH = CFGe(CH_3)_3$, these being listed in the order of decreasing yield. When the hydride and $(CH_3)_3GeCF = CF_2$ were exposed to ultraviolet irradiation at room temperature, a high yield of a mixture containing the two possible addition products, I and II in the ratio 5:2 was obtained.



$$(CH_3)_3GeCF = CF_2 + (CH_3)_3SnH \rightarrow (CH_3)_3GeCFHCF_2Sn(CH_3)_3 \quad \text{I}$$

$$(CH_3)_3GeCF = CF_2 + (CH_3)_3SnH \rightarrow (CH_3)_3GeCF(Sn(CH_3)_3)CF_2H \quad \text{II}$$

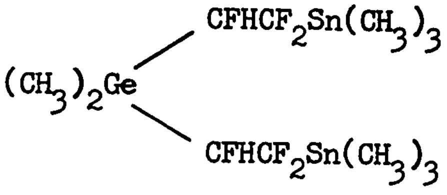
II

This mixture is unstable at room temperature and eliminates trimethyltin fluoride with the preferential formation of cis-$CFH = CFGe(CH_3)_3$ and with the more rapid disappearance of $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$. A sample of the mixture of addition products containing $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ and $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ in the ratio 2:5 is completely decomposed at 55° after 24 hours to give cis-$CFH = CFGe(CH_3)_3$ and $(CH_3)_3GeCH = CF_2$ in the ratio of approximately 1:2, with the simultaneous formation of trimethyltin fluoride. This confirms the formation of cis-$CFH = CFGe(CH_3)_3$

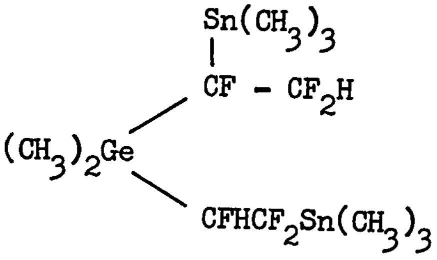
from $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ and of $(CH_3)_3GeCH = CF_2$ from $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ by β-fluorine elimination. The facile nature of this type of elimination is analogous to that in the corresponding compounds of silicon. It again supports the arguments already given in favor of the preferential elimination of β-fluorine in these compounds, compared to an α-fluorine elimination process followed by a fluoride ion migration.

The reaction of trimethyltin hydride with $(CH_3)_3SiCF = CF_2$ was shown earlier to proceed by a free radical mechanism under ultraviolet irradiation, as well as in the presence of free radical sources, e.g. AIBN. This reaction was also completely inhibited by the free radical inhibitor, phenoxyl. In the present case, the addition of trimethyltin hydride to $(CH_3)_3GeCF = CF_2$ apparently occurred at 55° in the presence of AIBN, but the thermal instability of the addition products at 55° probably explains why only cis-$CFH = CFGe(CH_3)_3$, $(CH_3)_3GeCH = CF_2$ and $(CH_3)_3GeC_2H_2F$ were obtained. It certainly seems reasonable to assume that here, and in the reactions under ultraviolet irradiation, a free radical process is again involved.

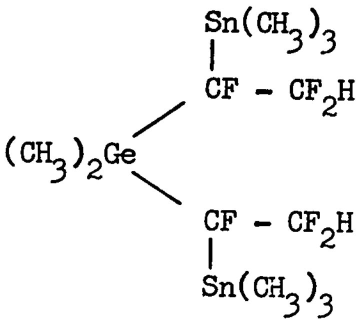
Trimethyltin hydride and $(CH_3)_2Ge(CF = CF_2)_2$ do not react at room temperature, and at 55° only a limited reaction takes place. However, the reaction does take place easily under ultraviolet irradiation at room temperature, with the formation of an involatile product, which was identified spectroscopically as a mixture of the addition compounds I, II, and III.



I



II



III

The proton n.m.r. spectrum of this product consisted of two closely spaced sets of eight lines each, corresponding to two $-CFHCF_2-$ groups, and two other closely spaced sets of eight lines each, corresponding to two $>CFCF_2H$ groups. Thus the proton spectrum indicated that there were two $-CFHCF_2Sn(CH_3)_3$ groups in slightly different chemical environments, and two other $-CF(Sn(CH_3)_3)CF_2H$ groups also in slightly different chemical environments, present in the product. Thus the proton spectrum is consistent with the presence of three different molecules I, II and III in the addition product. This mixture of addition compounds was unstable at room temperature, slowly eliminating trimethyltin fluoride accompanied by the formation of $-CF=CFH$ (cis) and $-CH=CF_2$ groups. It was not possible to separate individual compounds from the mixture chromatographically due to their instability.

The behavior of dimethyltin dihydride with $(CH_3)_3GeCF = CF_2$ and also with $(CH_3)_2Ge(CF = CF_2)_2$ was next investigated. In each case little reaction occurred at room temperature, but by heating at 55° and also under ultraviolet irradiation considerable reaction took place with the formation of fluorovinyl germanes having $- CF = CFH$ (cis and trans), $- CH = CF_2$ and $- C_2H_2F$ groups together with dimethyltin difluoride. Since dihydrides are more reactive and unstable as compared with the monohydrides, and also in view of the high lattice energy of dimethyltin difluoride in the reactions of dimethyltin dihydride with perfluorovinyl germanes, it is not too surprising that the addition products were not isolated (19,68,69).

Since trimethyltin hydride forms addition products with $(CH_3)_3SiCF = CF_2$ and $(CH_3)_3GeCF = CF_2$ under free radical generating conditions, it is of interest to compare these reactions to that of $(CH_3)_3SnH$ with $(CH_3)_3SnCF = CF_2$. Clark et al. have investigated the reactions of $(CH_3)_3SnH$ and $(CH_3)_2SnH_2$ with $(CH_3)_3SnCF = CF_2$ and $(CH_3)_2Sn(CF = CF_2)_2$ (42). In the reactions of trimethyltin hydride with $(CH_3)_3SnCF = CF_2$, the main reaction product was always cis-$CFH = CFSn(CH_3)_3$, and the possibility of addition followed immediately by trimethyltin fluoride elimination was suggested (42). These reactions were repeated, and in the reaction of trimethyltin hydride with an excess of $(CH_3)_3SnCF = CF_2$ in cyclohexane, under ultraviolet irradiation at 25°, the formation of addition products $((CH_3)_3Sn)_2CFCF_2H$ and $(CH_3)_3SnCFHCF_2Sn(CH_3)_3$ was established from the proton n.m.r. spectrum. The addition products could not be isolated due to their instability: at room temperature they quickly eliminate trimethyltin fluoride with the formation of cis-$CFH = CFSn(CH_3)_3$, this again being consistent with a β-fluorine elimination, whereby both the products $((CH_3)_3Sn)_2CFCF_2H$ and $(CH_3)_3SnCFHCF_2Sn(CH_3)_3$ can give cis-$CFH = CFSn(CH_3)_3$. The reason that these addition products were not observed previously is apparently due to the long irradiation period of 18 hours then involved, in contrast to only one hour in the present study (42). In the former case, decomposition had obviously occurred by the end of the irradiation period.

The formation of trans-$CFH = CFSn(CH_3)_3$ and $(CH_3)_3SnC_2H_2F$ in the above reactions has been suggested as due to secondary reactions of the type (42);

$$\underset{\text{cis}}{(CH_3)_3SnCF = CFH} + (CH_3)_3SnH \xrightarrow[\text{Light}]{\text{UV}} \underset{\text{trans}}{(CH_3)_3SnCF = CFH} + (CH_3)_3SnC_2H_2F + (CH_3)_3SnF.$$

This type of reaction has now also been observed, though under thermal conditions, for the germanium series;

$$\underset{\text{cis}}{(CH_3)_3GeCF = CFH} + (CH_3)_3SnH \xrightarrow{55^\circ} \underset{\text{trans}}{(CH_3)_3GeCF = CFH} + (CH_3)_3GeC_2H_2F + (CH_3)_3SnF.$$

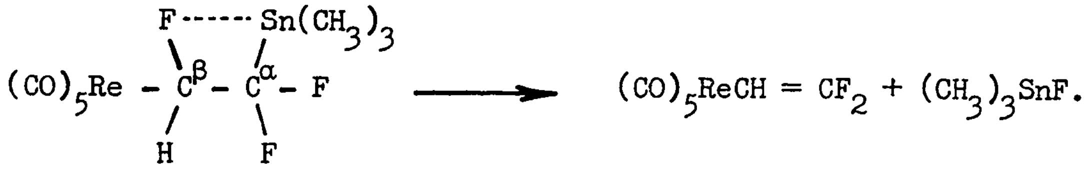
This indicates that $(CH_3)_3GeC_2H_2F$ is formed by the reaction of hydride with cis-$CFH = CFGe(CH_3)_3$, but at the same time cis-$CFH = CFGe(CH_3)_3$

rearranges to the trans-$CFH = CFGe(CH_3)_3$ form under thermal conditions.

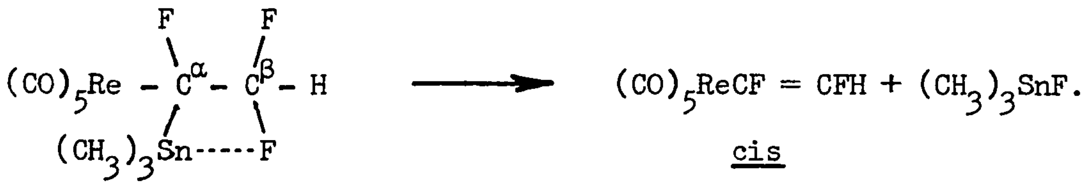
3. The Reactions of Organotin Hydrides with Pentacarbonyl-perfluorovinylrhenium and Pentacarbonyl-perfluoropropenylrhenium.

Trimethyltin hydride did not react with $(CO)_5ReCF = CF_2$ in benzene at room temperature, even over a long period. When the hydride and pentacarbonyl-perfluorovinylrhenium were heated at 45° for 48 hours in butyronitrile, only a limited reaction took place with the formation of cis-$CFH = CFRe(CO)_5$ and $(CO)_5ReCH = CF_2$, in approximately equal amounts. This reaction is in contrast to the reactions of trimethyltin hydride with perfluorovinyl compounds of silicon and germanium, where considerable yields of the corresponding fluorovinyl compounds were obtained under thermal reaction conditions.

When trimethyltin hydride and $(CO)_5ReCF = CF_2$ were exposed to ultraviolet irradiation at 35° for 36 hours in benzene, considerable reaction occurred with the deposition of trimethyltin fluoride and formation of trans-$CFH = CFRe(CO)_5$ as the main product, and cis-$CFH = CFRe(CO)_5$ and $(CO)_5ReCH = CF_2$ in smaller but approximately equal amounts. Similarly, reaction occurred readily, when the hydride and pentacarbonyl-perfluorovinylrhenium were heated in benzene in the presence of AIBN. Here again a considerable amount of trimethyltin fluoride was deposited and fluorovinyl derivatives of rhenium were formed, notably trans-$CFH = CFRe(CO)_5$, $(CO)_5ReCH = CF_2$ and cis-$CFH = CFRe(CO)_5$; these being listed in the order of decreasing yield. These reactions apparently differ from the reactions of trimethyltin hydride with perfluorovinyl compounds of silicon, germanium and tin, where additions to the vinylic C = C bond easily take place under similar free radical generating conditions. However, in the reactions of trifluoroethylene with germanium-manganese and tin-manganese bonded compounds, the products obtained were cis-CFH = CFMn(CO)$_5$ and trans-CFH = CFMn(CO)$_5$, along with trimethylfluorogermane or trimethyltin fluoride (62,63). Hence, it was suggested that these reaction products were formed by the decomposition of unstable hypothetical addition products $(CO)_5MnC_2F_3HGe(CH_3)_3$ and $(CO)_5MnC_2F_3HSn(CH_3)_3$. Thus, it certainly seems reasonable to assume that in the reactions of trimethyltin hydride with $(CO)_5ReCF = CF_2$, the high lattice energy of trimethyltin fluoride makes the existence of the following hypothetical addition products unlikely and is also consistent with a β-fluorine elimination process.



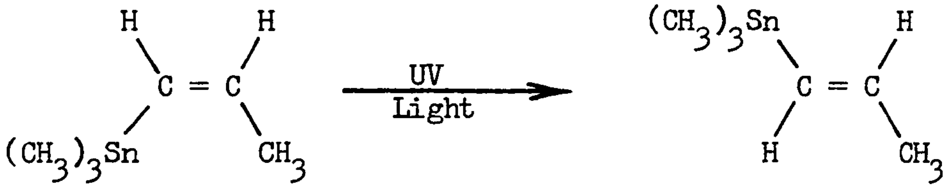
$$(CO)_5Re-C^{\beta}(F)(H)-C^{\alpha}(F)_2Sn(CH_3)_3 \longrightarrow (CO)_5ReCH=CF_2 + (CH_3)_3SnF.$$



$$(CO)_5Re-C^{\alpha}(F)(Sn(CH_3)_3)-C^{\beta}(F)(F)-H \longrightarrow \underset{\text{cis}}{(CO)_5ReCF=CFH} + (CH_3)_3SnF.$$

Although such addition products could not be isolated, the formation of $(CO)_5ReCH = CF_2$ and cis-CFH = CFRe(CO)$_5$ along with trimethyltin fluoride, strongly suggests their intermediate existence.

However, in the reactions of trimethyltin hydride with $(CO)_5ReCF = CF_2$, under free radical generating conditions e.g. by irradiation under ultraviolet light or by heating with AIBN, the main reaction product was always trans-CFH = CFRe(CO)$_5$. Similarly, trans-CFH = CFMn(CO)$_5$ was always formed along with the cis isomer in the reactions of trifluoroethylene with germanium-manganese and tin-manganese compounds under ultraviolet irradiation (62,63). Hence, to investigate the formation of trans-CFH = CFRe(CO)$_5$, a sample containing cis-CFH = CFRe(CO)$_5$ was exposed to ultraviolet irradiation in benzene. After 6 hours, 75% of the cis isomer had rearranged to the trans form. Seyferth and Vaughan have also reported that the following cis-β-adduct from trimethyltin hydride and propyne did not rearrange thermally or in the presence of either AIBN or benzoyl peroxide, but did so upon ultraviolet irradiation (70);



cis-β trans-β

However, similar rearrangements of cis- into trans adducts are also known to proceed under the influence of a triorganotin radical (71). Therefore it seems likely that in the reactions involving ultraviolet irradiation or AIBN, the primary reaction product is cis-CFH = CFRe(CO)$_5$ which rearranges to the trans isomer under these reaction conditions.

Dimethyltin dihydride did not react with (CO)$_5$ReCF = CF$_2$ in benzene at room temperature, but considerable reaction took place under ultraviolet irradiation at 25°. Dimethyltin difluoride was readily deposited accompanied by the formation of trans-CFH = $CFRe(CO)_5$, cis-CFH = $CFRe(CO)_5$ and $(CO)_5ReCH = CF_2$, here again trans-CFH = $CFRe(CO)_5$ being the major product. Such reactions are consistent with the behavior of the dihydride with perfluorovinyl compounds of silicon, germanium and tin, where fluorovinyl compounds are always obtained readily (42). The greater reactivity of the dihydride as compared to the monohydride and the lattice energy of dimethyltin difluoride, makes the isolation of the addition products unlikely in such reactions (19,68,69).

The behavior of trimethyltin hydride with $(CO)_5ReCF = CFCF_3$ was next investigated. Little reaction occurred at 45° in butyronitrile, but in the presence of AIBN in benzene, there was complete decomposition of the hydride to hexamethylditin. The hydride and $(CO)_5ReCF = CFCF_3$ did not react, even when exposed to ultraviolet irradiation in benzene at 40°. It appears that $(CO)_5ReCF = CFCF_3$ is so stable that trimethyltin radical can not activate the vinylic C = C bond.

4. The Reactions of Organotin Hydrides with Phosphonitrilic Halides.

In recent years, much experimental and theoretical work has been done on the chemistry of phosphonitrilic halides (72-74). These cyclic units $(NPX_2)_n$ are quite large e.g. n = 3-8 when X = Cl, Br and n = 3-17 when X = F (72-74). The physical and chemical properties of phosphonitrilic derivatives depend upon their electronic structures, and theoretical studies show that although these cyclic structures are formally the same as the Kekulé structures of benzene, there is an essential difference, in that d-orbitals are necessarily involved in the formation of double bonds between quinquevalent phosphorus and nitrogen (72-74). The formulae have so far been written as if single and double bonds alternate in the ring, although in fact in all the structures determined so far the ring bonds are equal in length within experimental error (72-74). To a first approximation, a system of π-electrons, which is at least partly delocalized, is formed by overlap of alternate 3*d* -orbitals (on phosphorus) and 2*p* -orbitals (on nitrogen). Some properties of these systems follow from the nature of localised $p\pi - d\pi$ bonds.

A major field of study is the question of substitution in these compounds. Some of the nucleophilic replacements of Cl by different substituents in $N_3P_3Cl_6$ are listed below (75);

Substituent	Replacement Pattern
NMe_2	predominantly non-geminal + some geminal
NC_5H_{10}	predominantly non-geminal + some geminal
NC_2H_4	predominantly geminal + some non-geminal
OPh	non-geminal
OEt	non-geminal and geminal
SEt	geminal
F	geminal

The nucleophilic replacements *e.g.* on trimeric and tetrameric chlorophosphonitriles often result in the formation of products with only a portion of the chlorine atoms replaced, and different patterns of substitution are obtained, depending upon the nature of the substituents. The substituents alter the electron density at the reaction site, but steric effects due to the size of the substituent cannot be ignored. There is experimental evidence of steric hindrance between substituents on adjacent phosphorus atoms (72). The relative basicity of the nucleophile would have to be considered in reactions where more than a single nucleophilic species is competing for the reaction site.

Although cyclic phosphonitrilic derivatives with various substituents have been prepared, cyclic phosphonitrilic hydrides or mixed halide hydrides have not been described so far. One useful reagent to prepare such hydrides is an organotin hydride. It is known that PF_5, or its organo derivatives, exchange the halogen atoms for the hydrogen atoms on organotin hydrides (38,39). Such reactions suggest the possibility of exchange of halogens from phosphonitrilic halides for hydrogen atoms or organotin hydrides.

The reactions of $(CH_3)_3SnH$ and $(CH_3)_2SnH_2$ with $N_3P_3Cl_6$ and $N_3P_3F_6$ were tried in an attempt to replace halides by the hydrogen atoms in these cyclic compounds. Trimethyltin hydride and dimethyltin dihydride reacted only slightly with $N_3P_3F_6$ in the gas phase at 50°, with the formation of hydrogen, a little $(CH_3)_3SnF$ or $(CH_3)_2SnF_2$ and $(CH_3)_2SnFH$ and a rubber-like polymer. When $(CH_3)_3SnH$ or $(CH_3)_2SnH_2$ was allowed to react with $N_3P_3F_6$ or with $N_3P_3Cl_6$ at 45° for 4 hours in benzene, cyclohexane or butyronitrile, considerable reaction occurred in each case, but again only hydrogen, the respective methyltin halide and a rubber-like polymer could be detected among the large amounts of unreacted starting materials.

In the reactions of hydrides with $N_3P_3Cl_6$ and $N_3P_3F_6$ in benzene under ultraviolet irradiation or in the presence of AIBN, an extensive polymerization of the phosphonitrilic halides occurred along with the formation of hydrogen and the methyltin halides.

At this stage it is not clear why stable phosphonitrilic hydrides could not be prepared by the reactions between organotin hydrides and the phosphonitrilic halides. One of the limitations in the chemistry of phosphonitrilic halides is the occurrence of polymerization under thermal or free radical generating conditions (72-74). Moreover, it is known that the reduction of alkyl and aryl halides by organotin hydrides proceeds by a free radical chain mechanism (19). Hence, it is perhaps not too surprising that phosphonitrilic hydrides could not be prepared by the reactions involving organotin hydrides and phosphonitrilic halides, and that polymerization appears to have been induced.

CHAPTER III

SPECTROSCOPIC STUDIES

IIIA. Infrared Studies

The results of the infrared examination of the new compounds obtained from the various reactions are discussed in this section. The assignments of the infrared bands, made on the basis of the assignments for related compounds given in the literature, are listed in appropriate tables, along with a brief discussion. Such assignments, though only made on a relative basis, are useful in the identification of the new compounds. However, unambiguous assignments are not possible without a more complete, detailed analysis. Characteristics of infrared bands (cm^{-1}) listed in tables are:- s, strong; m, medium; w, week; sh, shoulder; v, very; b, broad.

1. Infrared Spectra of Trimethylfluorovinyl and Dimethylbis(fluorovinyl) Compounds of Silicon and Germanium.

The infrared absorption frequencies of trimethylfluorovinyl silanes and of dimethylbis(fluorovinyl) silanes are given in Table 2 and 3 respectively. The assignments for methyl-silicon vibrations are in agreement with those made by Smith, Bellamy and others (76-80). The infrared spectra of trimethylfluorovinyl germanes and of dimethylbis-(fluorovinyl) germanes are given in Table 4 and 5 respectively. The assignments for methyl-germanium vibrations are made according to Rochow _et al._ and are in good agreement with similar assignments for other germanium compounds containing methyl groups (81).

The C-F stretching frequencies for the fluorovinyl compounds of silicon and germanium are assigned relative to such assignments of perfluorovinyl compounds of the main group elements made by Stone _et al._ (82). Such fluorocarbon groups produce very strong and characteristic C-F absorptions in the 900-1400 cm^{-1} region of the infrared spectrum, which are of great importance for the identification of such derivatives. A consideration of the spectra of fluoroethylenes also permits a reasonable assignment of the C-F stretching frequencies in the fluorovinyl derivatives. In the spectra of 1:1 difluoroethylenes a band due to C-F absorptions is present in the region 926-1053 cm^{-1}; which is in good agreement with the strong absorptions in the region 1030-1145 cm^{-1} in the spectra of compounds having -CF = CFH groups (82). The -CF = CFH groups also show a very strong absorption at about 1270 cm^{-1} which is probably due to the stretching mode of the C-F bond _gem._ to the metal atom (82). Barnes et al. have suggested that the = CF_2 group shows characteristic bands near 1200 and 1340 cm^{-1}, and indeed fairly strong absorptions are present at 1290-1300 cm^{-1} in the spectra of compounds having $-CH = CF_2$ groups (83). The compounds containing $-C_2H_2F$ groups showed a strong absorption which varied from 1040 to 1080 cm^{-1} but did not agree closely with the C-F absorption at 1186 cm^{-1} in the spectra of 1-fluoro-1-chloroethylene (84).

The C = C stretching vibrations lie in the range 1695-1732 cm^{-1} for perfluorovinyl derivatives of B, Si, Ge, Sn and As (82). These values for C = C stretching frequencies are a little lower in comparison with free fluoro-olefins and have been attributed to π interactions with the metallic atom (82). Further decrease in the frequency of C = C stretching vibrations occurs as fluorine is replaced by hydrogen from a perfluorovinyl group on silicon and germanium. Thus, the C = C stretching absorption is at 1725 and 1730 cm^{-1} in $(CH_3)_3SiCF = CF_2$ and $(CH_3)_2Si(CF = CF_2)_2$ respectively, while it varies from 1722 to 1625 cm^{-1} in fluorovinyl silanes. Similarly, the C = C stretching absorption is at 1730 cm^{-1} in $(CH_3)_3GeCF = CF_2$ and $(CH_3)_2Ge(CF = CF_2)_2$, while it varies from 1725 to 1625 cm^{-1} in fluorovinyl germanes. A similar lowering of the C = C stretching frequency has already been observed in tin compounds; it is at 1712 and 1711 cm^{-1} in $(CH_3)_3SnCF = CF_2$ and $(CH_3)_2Sn(CF = CF_2)_2$ respectively and varies from 1683 to 1608 cm^{-1} in the corresponding fluorovinyl derivatives of tin (42).

The behavior of olefinic bonds with multiple fluorine substitution is not yet well understood. Vinylidine fluoride absorbs at 1728 cm^{-1}, and the frequency rises steadily with further substitution to 1872 cm^{-1}

(Raman) in tetrafluoroethylene (85). This rise is accompanied by a shortening in the C = C bond lengths of these ethylenes (86). Such effects have been attributed to the strong inductive effects of the fluorine atoms which increase the polarity of the C = C bond due to the ionic forms e.g. $\bar{F}(FC = CH_2)^+$, and chemical evidence has been cited in the support of this (87-89). Thus, the FCF angle of $CF_2 = CH_2$ closes down by as much as 10° to 110°, this would be expected if the orbital of the fluorinated carbon atom which forms the C-C σ-bond were taking an increased s character (87,90). This will result in a shorter C = C bond and a higher frequency (87). Another example of similar effects is the changes in the stretching frequency of the carbonyl group with the electronegativity of the substituent (91). In formaldehyde (COH_2) the $\nu(C = O)$ is at 1745 cm^{-1} and in phosgene ($COCl_2$) it rises to 1827 cm^{-1}. The corresponding vibration is at 1928 cm^{-1} in COF_2, and the rise in frequency has been attributed to the contribution from the form $\bar{F}(FC\equiv O)^+$ (87,91).

Although no definite conclusions have been made about the frequencies associated with multiple bonds, there is enough evidence to show that such frequencies are not particularly sensitive to mass effects of the substituents, unless these happen to be hydrogen or deuterium atoms (87). However, the frequencies vary widely due to inductive and mesomeric effects of the substituents (92).

TABLE 2

Infrared Spectra of Trimethylfluorovinyl Silanes

<u>cis</u>-$CFH = CFSi(CH_3)_3$ I
<u>trans</u>-$CFH = CFSi(CH_3)_3$ II
$(CH_3)_3SiCH = CF_2$ III
$(CH_3)_2SiC_2H_2F$ IV

(Gas phase)

I	II	III	IV	Assignment
620 m	618 m	619 m	619 w	Si-C stretch
660 m	665 w	660 m	660 m	
705 m	708 m	700 m	700 m	CH_3(-Si) rock
760 s	755 s	760 s	760 s	
850 vs,b	850 vs,b	850 vs,b	850 vs,b	
920 s			950 s,b	C-F stretch
	1010 m		1000 w	
1075 s		1065 s	1070 m	
1135 s	1125 m			
1255 vs	1258 s	1260 s	1256 m	CH_3(-Si) sym. defn.
1290 s	1270 s	1295 s		C-F stretch
1404 w	1405 vs	1405 w	1406 w	CH_3(-Si) asym. defn.
1695 s	1720 s	1665 s	1625 s	C = C stretch
2690 s	2690 s	2692 m	2692 m	C-H sym. stretch
2990 s	2990 s	2992 s	2992 s	C-H asym. stretch

TABLE 3

Infrared Spectra of Dimethylbis(fluorovinyl) Silanes

<u>cis</u>-$(CFH = CF)_2Si(CH_3)_2$ I

<u>trans</u>-$(CFH = CF)_2Si(CH_3)_2$....... II

$(CH_3)_2Si(CH = CF_2)_2$ III

$(CH_3)_2Si(C_2H_2F)_2$ IV

(Gas phase)

I	II	III	IV	Assignment
655 m	654 m	655 m	655 m	Si-C stretch
692 s	690 m	692 m	692 m	
800 s	800 m	725 w	730 w	CH_3(-Si) rock
820 vs	822 vs	820 vs	822 vs	
840 vs	840 vs	842 vs	840 vs	
900 s				
			905 m	C-F stretch
	1000 vw	1050 s		
1145 m	1130 vs	1175 m	1140 s,b	
1260 s	1258 s	1260 s	1256 m	CH_3(-Si) sym. stretch
1270 s	1272 s			C-F stretch
1295 s		1300 vs		C-F stretch
1408 w	1408 w	1410 vw	1408 w	CH_3(-Si) asym. stretch
1700 s	1722 s	1665 s	1625 s	C = C stretch
2890 w				
2950 w	2952 w	2950 m	2950 w	C-H sym. stretch
2990 s	2990 s	2990 s	2992 s	C-H asym. stretch

TABLE 4

Infrared Spectra of Trimethylfluorovinyl Germanes

cis-CFH = $CFGe(CH_3)_3$ I
trans-CFH = $CFGe(CH_3)_3$......... II
$(CH_3)_3GeCH = CF_2$............... III
$(CH_3)_3GeC_2H_2F$ IV

(Gas phase)

I	II	III	IV	Assignment
		535 m	535 m	
565 w	570 vw	570 w	565 vw	Ge–C stretch
600 s	600 s	605 m	600 m	
770 m	765 m	760 m	770 m	CH_3(–Ge) rock
		815 sh.m		
830 s	830 s	830 s	825 s	
930 w			925 w	C–F stretch
			975 m	
	1025 w	1020 w		
1080 m	1070 s	1070 b.s	1060 vs	
1110 vs		1120 vs	1120 w	
			1180 m	
1250 m	1250 s	1245 m	1245 m	CH_3(–Ge) sym defn.
1280 m	1270 w	1300 w		C–F stretch
1360 w				
1410 vw	1408 w	1410 w	1400 vw	CH_3(–Ge) asym. defn.
1700 vs	1725 s	1665 s	1625 vs	C = C stretch
2910 s	2908 s	2910 s	2915 s	C–H sym. stretch
2995 s	2995 s	2995 s	2994 s	C–H asym. stretch

TABLE 5

Infrared Spectra of Dimethylbis(fluorovinyl) Germanes

cis-$(CFH = CF)_2Ge(CH_3)_2$ I
trans-$(CFH = CF)_2Ge(CH_3)_2$ II
$(CH_3)_2Ge(CH = CF_2)_2$ III
$(CH_3)_2Ge(C_2H_2F)_2$ IV

(Gas phase)

I	II	III	IV	Assignment
590 w	590 w	590 w	590 w	Ge–C stretch
620 m	610 m	620 w	620 m	
650 vw			650 vw	
768 m	765 m	760 w	765 m	CH_3(-Ge) rock
820 vs	820 s	815 s	810 vs	
835 m	840 m	840 m	840 m	
940 m	920 w	930 vw	940 w	C–F stretch
			1000 m	
1065 m	1050 s	1085 s	1080 m	
1125 vs		1130 vs	1170 s	
1252 m	1250 w	1250 m	1255 m	CH_3(–Ge) sym. defn.
1280 s	1272 s	1290 w		C–F stretch
1410 w	1412 vw	1410 w	1408 w	CH_3(–Ge) asym. defn.
1700 vs	1722 s	1665 vs	1628 vs	C = C stretch
2940 s	2940 m	2942 s	2938 s	C–H sym. stretch
3000 s	3000 s	3000 s	2998 s	C–H asym. stretch

2. Infrared Spectra of the Addition Products of Trimethyltin Hydride with Trimethylperfluorovinyl and Dimethylbis(perfluorovinyl) Compounds of Silicon and Germanium.

Trimethyltin hydride forms 1:1 addition products with $(CH_3)_3MCF = CF_2$, (M = Si and Ge) i.e. $(CH_3)_3MCFHCF_2Sn(CH_3)_3$ and $(CH_3)_3MCF(Sn(CH_3)_3)CF_2H$, and the following 2:1 addition products with $(CH_3)_2M(CF = CF_2)_2$ compounds; $(CH_3)_2M(CFHCF_2Sn(CH_3)_3)_2$, $(CH_3)_2M(CF(Sn(CH_3)_3)CF_2H)_2$ and $(CH_3)_2M(CFHCF_2Sn(CH_3)_3)(CF(Sn(CH_3)_3)CF_2H)$. These addition products could not be separated by chromatography due to their instability, but were characterized by their nuclear magnetic resonance spectra.

The infrared absorption frequencies of these addition products are given in Tables 6 and 7. The bands at 505-535 cm^{-1} were assigned to the Sn-C stretching vibrations, and are in good agreement with Sn-C stretching frequencies observed in compounds where a methyltin group is σ-bonded to fluorocarbon groups (13,93). The bands at 945-1360 cm^{-1} were assigned to C-F stretching vibrations because such assignments have been made in this region of the spectrum for C-F stretching frequencies in $(CH_3)_2Sn(CF_2CF_2H)_2$ and $(CH_3)_3SnCF_2CF_2H$ (13,93). The CH_3 symmetrical deformation bands for CH_3-Sn group usually occur at 1180-1200 cm^{-1}, but these could not be assigned to the individual vibrations due to the overlapping in the C-F stretching region (81,94,95).

In the addition products of $(CH_3)_3SnH$ with silicon compounds the strong and broad bands at 700-875 cm^{-1} were assigned to CH_3-Si and CH_3-Sn rocking modes, based on the similar assignments for these vibrations in other compounds of silicon and tin containing methyl groups (77,81,95). In these addition compounds the C-H stretching frequencies occur at 2795-2995 cm^{-1}; and the CH_3 deformation bands for CH_3-Si groups occur at 1255 and 1250 cm^{-1} (sym.) and at 1415 and 1405 cm^{-1} (asym.).

In the addition products of $(CH_3)_3SnH$ with germanium compounds the strong and broad bands in the region 715-840 cm^{-1} were assigned to CH_3-Sn and CH_3-Ge rocking modes based on the occurrence of similar vibrations in this region in tin and germanium compounds containing methyl groups (81, 94-96). In these compounds the C-H stretches occur at 2910 and 2990 cm^{-1}, while the CH_3 deformation bands for CH_3-Ge sym. deformation occur at 1240 cm^{-1} and for asym. deformation (usually a weak band) at 1410 cm^{-1}.

TABLE 6

Infrared Spectra of the Addition Products of
$(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$ and $(CH_3)_2Si(CF = CF_2)_2$

(Liquid films)

$(CH_3)_3SiCF = CF_2$ + $(CH_3)_3SnH$	$(CH_3)_2Si(CF = CF_2)_2$ + $2(CH_3)_3SnH$	Assignment
510 s	505 s	Sn-C stretch
535 vs	525 vs	
620 w		Si-C stretch
	675 sh,m	
700 m	715 s	CH_3(-Sn) and CH_3(-Si) rock
770 s,b	770 vs,b	
845 vs	830 s,b	
860 sh,s	860 sh,m	
875 sh,m		
950 vs	945 vs	
985 s	982 vs	C-F stretch
1030 s	1030 vs	
1040 s		
1065 m	1060 sh,s	
1110 sh,m	1110 sh,s	C-F stretch
1130 s	1125 vs	
1190 w	1190 w	
1225 m	1225 m	

TABLE 6 (continued)

$(CH_3)_3SiCF = CF_2$ + $(CH_3)_3SnH$	$(CH_3)_2Si(CF = CF_2)_2$ + $2(CH_3)_3SnH$	Assignment
1255 vs	1250 vs	CH_3(-Si) sym. defn.
1300 w	1300 m	C-F stretch
1335 m	1330 m	
1360 w	1360 m	
1415 w	1405 m	CH_3(-Si) asym. defn.
2360 w	2360 w	
2810 w	2795 w	C-H stretch
2920 s	2910 s	
2970 s	2995 s	

TABLE 7

Infrared Spectra of the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_3GeCF = CF_2$ and $(CH_3)_2Ge(CF = CF_2)_2$.

(Liquid films)

$(CH_3)_3GeCF = CF_2$ + $(CH_3)_3SnH$	$(CH_3)_2Ge(CF = CF_2)_2$ + $2(CH_3)_3SnH$	Assignment
508 m	510 s	Sn-C stretch
530 s	530 vs	
562 w	570 m	Ge-C stretch
600 s	605 m	
715 sh,w	730 vs	CH_3(-Sn) and CH_3(-Ge) rock
770 b,s	770 vs,b	
825 s	825 sh,s	
	840 sh,s	
945 s	945 s	C-F stretch
985 s	985 s	
1030 s	1030 s	
1060 m	1060 s	
1110 sh,m	1110 sh,s	
1125 s	1130 vs	
1190 w	1190 m	
1215 w	1210 sh,w	
1240 m	1240 m	CH_3(-Ge) sym. defn.
1260 w		

TABLE 7 (continued)

$(CH_3)_3GeCF = CF_2$ + $(CH_3)_3SnH$	$(CH_3)_2Ge(CF = CF_2)_2$ + $2(CH_3)_3SnH$	Assignment
1300 vw	1305 w	C-F stretch
1330 w	1335 m	
1355 w	1355 m	C-F stretch
1390 vw	1385 w	
1410 m	1410 m	CH_3(-Ge) asym. defn.
2910 m	2910 s	C-H stretch
2990 s	2990 s	

IIIB. Nuclear Magnetic Resonance Studies

The results of ^{1}H and ^{19}F nuclear magnetic resonance studies are discussed in this section. In compounds containing tin the spin-spin coupling to the ^{119}Sn and ^{117}Sn nuclei (spin $\frac{1}{2}$) has been observed.

1. Proton Magnetic Resonance Spectra of Trimethylfluorovinyl and Dimethylbis(fluorovinyl) Compounds of Silicon and Germanium

The fluorovinyl derivatives of silicon and germanium were separated from the reaction mixture by gas chromotagraphy. Their infrared spectra (Tables 2-5) provided qualitative information about their structure, because the presence of a C = C stretching absorption in these spectra is of considerable help for preliminary identification, The assigned configuration for each fluorovinyl derivative of silicon and germanium is based on the combined infrared and proton magnetic resonance studies.

The known spin-spin coupling constants (*J*) in some halogenated olefins are listed in Table 8. The values of the H-F coupling constants fall into the following ranges;

$$J_{(H-F)\ \underline{gem}} = 72\text{–}87\ \mathrm{Hz}$$

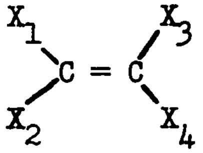
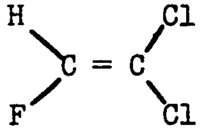
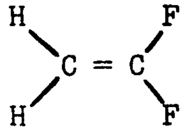
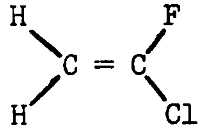
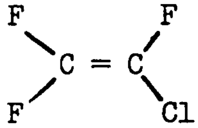
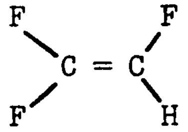
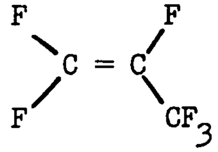
$$J_{(H-F)\ \underline{trans}} = 12\text{–}34\ \mathrm{Hz}$$

$$J_{(H-F)\ \underline{cis}} = 1\text{–}8\ \mathrm{Hz}$$

These values of H-F coupling constants thus serve as a good reference to correlate the observed values of $J_{(H-F)}$ gem, $J_{(H-F)}$ cis and $J_{(H-F)}$ trans in the fluorovinyl derivatives of silicon and germanium. The complete proton magnetic resonance data for the fluorovinyl derivatives of silicon and germanium are given in Tables 9 and 10. The proton magnetic resonance spectrum of each *cis*-CF = CFH group on silicon or germanium consists of a quartet (arising from two different coupling constants) centred around -6.0 p.p.m. and the similar multiplet arising from *trans*-CF = CFH groups is centred around -7.0 p.p.m. Similarly, a

TABLE 8

Spin-Spin Coupling Constants (Hz) in Halogenated Olefins (97).

	J_{12}	J_{13}	J_{23}	J_{14}	J_{24}	J_{34}
	81					
	4	1	34	34	1	37
	3	8	40			
	78	58	115			
	87	33	119	12	3	72
	57	39	116	8	22	13

quartet due to the proton of the $-CH=CF_2$ groups is centred at -3.0 to -4.0 p.p.m. The observed values of the coupling constants shown in Tables 9 and 10 fall into the ranges;

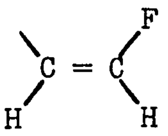
$\underline{J}_{(H-F)}$ gem = 73-82 Hz

$\underline{J}_{(H-F)}$ trans = 22-42 Hz

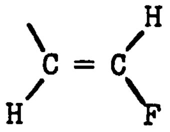
$\underline{J}_{(H-F)}$ cis = 6-15 Hz

The values of H-F coupling constants in the proton magnetic resonance spectra of the fluorovinyl derivatives of silicon and germanium are quite close to the values of such coupling constants in halogenated olefins listed in Table 8, and are also in good agreement with the proton magnetic resonance data of fluorovinyl tin compounds analysed by Clark et al. which are given in Table 11 for comparison (42).

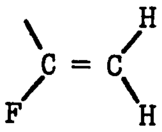
In addition to the resonances associated with the protons of cis-CF = CFH, trans-CFH and $-CH=CF_2$ groups on silicon or germanium, there was in each case another set of two quartets centred around -4.8 and -6.8 p.p.m. respectively. In this set of two quartets, there was always one common coupling constant of 5-7 Hz and one different coupling constant in each quartet of about 80 and 96 Hz. Thus, due to the occurrence of one common coupling constant in the two quartets the following configuration is the most probable one.



The coupling constant of 5-7 Hz was assigned to $\underline{J}_{(H-H)}$ cis and the coupling constant of about 80 Hz to $\underline{J}_{(H-F)}$ gem. Such an assignment required the $J_{(\text{H-F})}$ *trans* 96 Hz, which is at least twice as much as any other known value (97,98). The following two other configurations for the $-C_2H_2F$ group, could not be correlated with the observed coupling constant data.



and



A similar order of coupling constants has also been observed in $-C_2H_2F$ groups on tin (42).

TABLE 9

Proton N.M.R. Assignments for Fluorovinyl Silanes*

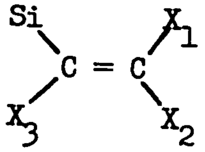
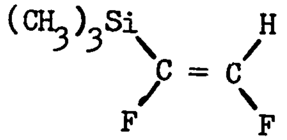
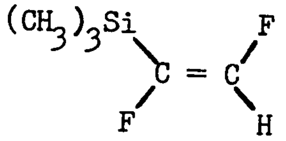
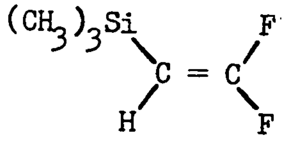
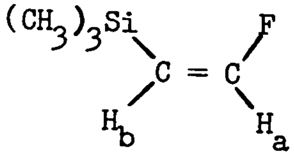
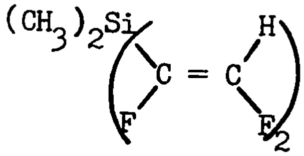
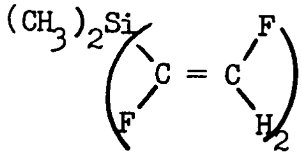
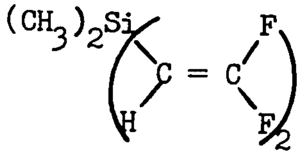
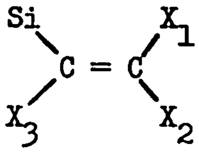
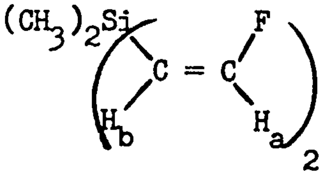
	δ_{CH_3}	$\delta_{H\ vinyl}$	J_{12}	J_{23}	J_{13}
	-0.18	-6.18	75	-	22
	-0.32	-6.88	78	12	-
	-0.04	-3.18	-	7	40
	‡	-6.2 (H_b) -5.4 (H_a)	82	6	96
	-0.14	-5.95	74	-	21
	-0.21	-6.14	74	15	-
	-0.05	-3.39	-	7	30

TABLE 9 (continued)

	δ_{CH_3}	$\delta_{H\ vinyl}$	J_{12}	J_{23}	J_{13}
	‡	$-6.2\ (H_b)$ $-5.81(H_a)$	76	5	95

*Chemical shifts (p.p.m.) are with respect to external TMS.

Coupling constants are in Hz.

‡ not distinguished

TABLE 10

Proton N.M.R. Assignments for Fluorovinyl Germanes.*

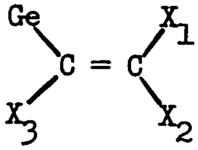
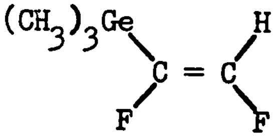
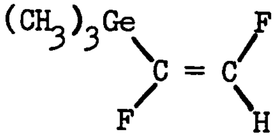
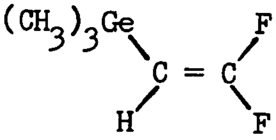
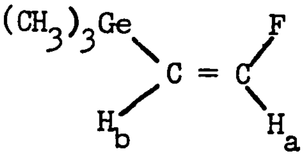
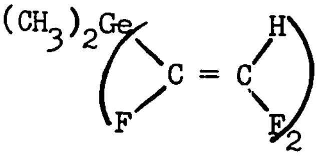
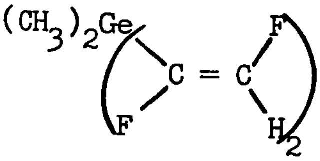
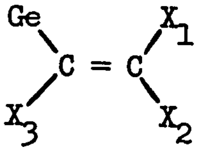
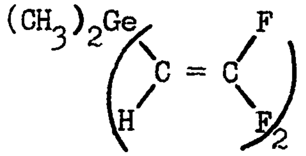
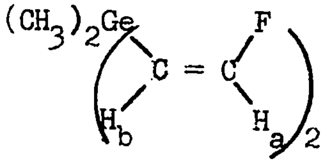
	δ_{CH_3}	$\delta_{H\ vinyl}$	J_{12}	J_{23}	J_{13}
	-0.51	-6.1	76	-	23
	-0.38	-7.5	74	15	-
	-0.45	-3.72	-	9	42
	‡	-6.5 (H_b) -4.8 (H_a)	78	6	96
	-0.42	-6.12	75	-	22
	-0.28	-7.42	73	15	-

TABLE 10 (continued)

	δ_{CH_3}	$\delta_{H\ vinyl}$	J_{12}	J_{23}	J_{13}
	-0.30	-3.82	-	7	42
	-0.32	-6.8 (H_b) -4.88(H_a)	78	7	95

* Chemical shifts are in p.p.m. with respect to external TMS.

Coupling constants are in Hz.

‡ Not distinguished

TABLE 11

Proton N.M.R. Assignments for Fluorovinyl Tin Compounds (42).*

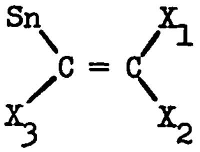
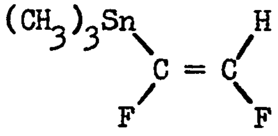
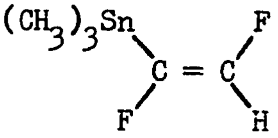
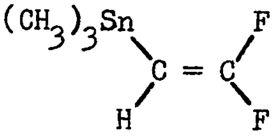
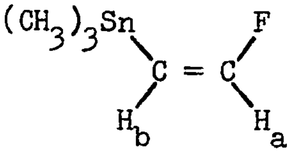
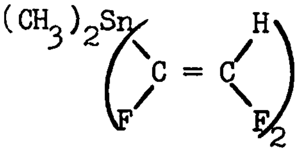
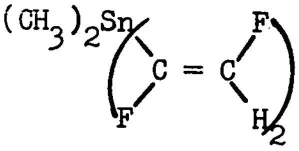
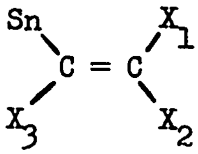
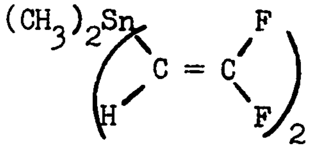
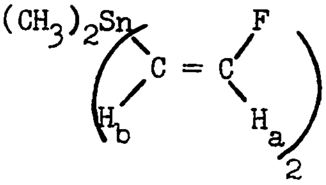
	δ_{CH_3}	$\delta_{H\ vinyl}$	$\underline{J}_{12}$	$\underline{J}_{23}$	$\underline{J}_{13}$
	-0.26	-5.93	77	-	25.5
	-0.32	-7.60	78	15	-
	‡	-3.92	-	9	46
	-0.20	-4.97 (H_a) -6.91 (H_b)	76	5.5	100
	-0.53	5.93	75.5	-	25
	‡	-7.53	76.5	15	-

TABLE 11 (continued)

	δ_{CH_3}	$\delta_{H\ vinyl}$	$\underline{J}_{12}$	$\underline{J}_{23}$	$\underline{J}_{13}$
	‡	-4.03	-	-	45
	-0.47	-5.13 (H_a) -7.04 (H_b)	72	5.5	98

* Chemical shifts are in p.p.m. with respect to external TMS.

Coupling constants are in Hz.

‡ not distinguished

2. Proton and Fluorine Magnetic Resonance Spectra of the Addition Products of Trimethyltin Hydride with Trimethylperfluorovinyl Compounds of Silicon, Germanium and Tin.

Trimethyltin hydride forms colourless liquid products with $(CH_3)_3SiCF = CF_2$ and $(CH_3)_3GeCF = CF_2$ under free radical generating conditions. The infrared spectra of these products, given in Table 6 and 7 showed the presence of C-F, methyl-tin, methyl-silicon and methyl-germanium vibrations in the respective compounds. The addition product of $(CH_3)_3SnH$ with $(CH_3)_3SnCF = CF_2$, formed under ultraviolet irradiation, was unstable at room temperature. Its analytical data and infrared spectrum could not be obtained but the proton n.m.r. spectrum recorded immediately after its formation characterized it unambiguously.

The proton magnetic resonance spectrum of the addition product of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$ consisted of two sets of eight lines, one centred at -4.72 p.p.m. and the other at -6.5 p.p.m. relative to external TMS. In addition to these lines there were signals from the methylsilicon and methyltin protons. The proton spectrum shown in Fig. 2 implies the presence of two protons in two different chemical environments, indicating the presence of two different molecules in the addition product. For one molecule the H-F coupling constants were 44, 37 and 10 Hz respectively and for the other molecule of 62, 56 and 10 Hz respectively. There are only two ways by which $(CH_3)_3SnH$ could form addition products with $(CH_3)_3SiCF = CF_2$; the $(CH_3)_3Sn$ group could be bound to the carbon α or β with respect to the silicon atom.

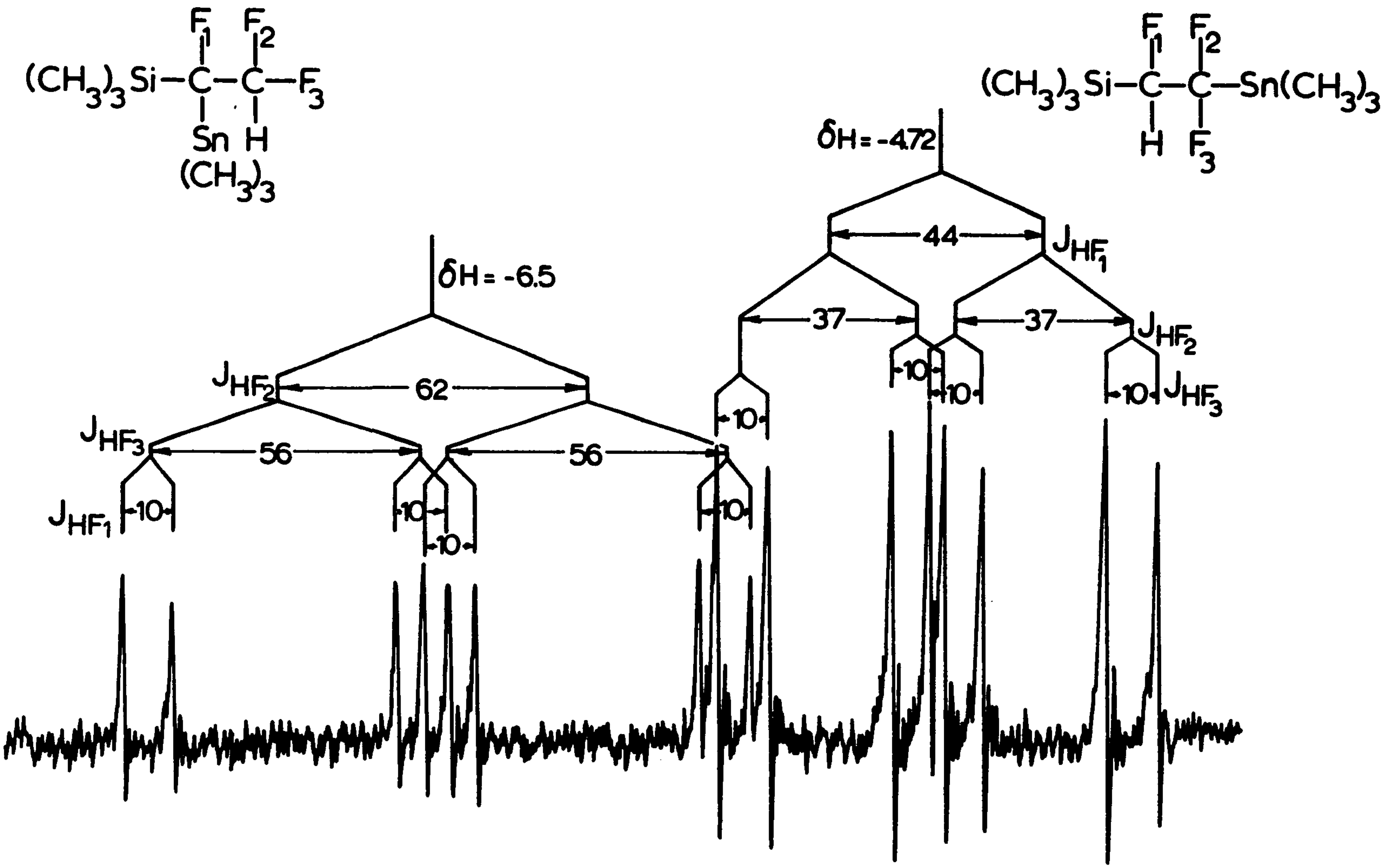
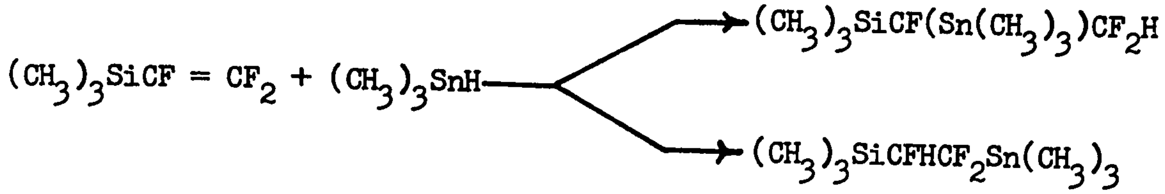


Fig. 2.

^{1}H N.M.R. Spectra of the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$.



$$(CH_3)_3SiCF=CF_2 + (CH_3)_3SnH \longrightarrow (CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$$
$$(CH_3)_3SiCF=CF_2 + (CH_3)_3SnH \longrightarrow (CH_3)_3SiCFHCF_2Sn(CH_3)_3$$

Thus, the observed proton spectrum should correspond to the spectra of $>CFCF_2H$ and $-CFHCF_2-$ groups. The parameters for J_{H-F} in the spectrum of the addition product were compared with the spectra of similar groups in other compounds. In Tables 12 and 13 the coupling constants in some compounds containing $-CFHCF_2-$ and $-CF_2CF_2H$ groups are listed. In compounds containing $-CFHCF_2-$ groups the values for $J_{(H-F)\ gem.}$ vary from 43 to 52 Hz and that of $J_{(H-F)\ vic.}$ vary from 5 to 22 Hz. The observed coupling constants of the order 44, 37 and 10 Hz compare favorably with J_{H-F} values in compounds containing $-CFHCF_2-$ groups and were assigned to the $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$ molecule. The proton signal is first split by the geminal fluorine with J_{H-F} being 44 Hz and twice again by two magnetically non-equivalent vicinal fluorine atoms giving J_{H-F} values of 37 and 10 Hz respectively. In compounds containing $-CF_2CF_2H$ groups the values of $J_{(H-F)\ gem.}$ vary from 53 to 58 Hz, which are comparable with $J_{(H-F)\ gem.}$ of 62 and 56 Hz, found in one set of the proton spectrum of the addition product. Hence, the values of 62, 56 and 10 Hz were assigned to the $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$ molecule, where the proton signal is twice split by two magnetically non-equivalent geminal fluorine atoms with $J_{(H-F)\ gem.}$ being of 62 and 56 Hz and then by the vicinal fluorine atom with $J_{(H-F)\ vic.}$ being 10 Hz. The two sets of eight lines can be attributed to the two ethane protons of $AC^{\alpha}F_2C^{\beta}FHB$ and $ABC^{\beta}FC^{\alpha}F_2H$ molecules, where the non-equivalence of the two α-fluorine atoms arises from the fact that there are three different substituents on the β-carbon

TABLE 12

Coupling Constants (Hz) in Compounds Containing $-CFHCF_2-$ Group

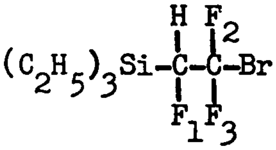
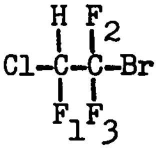
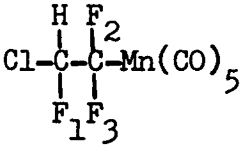
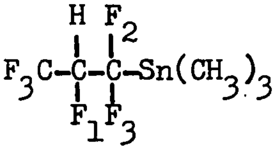
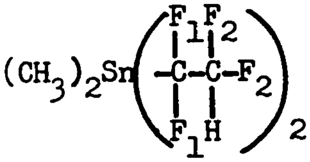
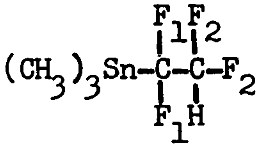
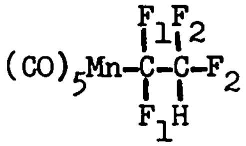
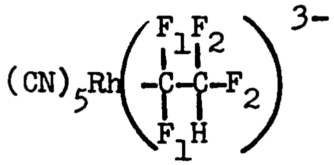
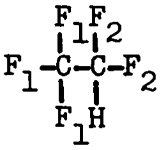
Compound	J_{H-F_1}	J_{H-F_2}	J_{H-F_3}	$J_{F_1-F_2}$	$J_{F_2-F_3}$	$J_{F_1-F_3}$	Ref.
 $(C_2H_5)_3Si-\overset{H}{\underset{F_1}{C}}-\overset{F_2}{\underset{F_3}{C}}-Br$	43.5	22	10	22	168	33	(99)
 $Cl-\overset{H}{\underset{F_1}{C}}-\overset{F_2}{\underset{F_3}{C}}-Br$	48	35	6.3	18	177	18	(100)
 $Cl-\overset{H}{\underset{F_1}{C}}-\overset{F_2}{\underset{F_3}{C}}-Mn(CO)_5$	52	12.4	5.7	16.4		12.4	(101)
 $F_3C-\overset{H}{\underset{F_1}{C}}-\overset{F_2}{\underset{F_3}{C}}-Sn(CH_3)_3$	45.9	13.9	11.3	7.1	340	6.5	(102)

TABLE 13

Coupling Constants (Hz) in Compounds Containing $-CF_2CF_2H$ Group

Compound	J_{H-F_2}	J_{H-F_1}	$J_{F_1-F_2}$	Ref.
 $(CH_3)_2Sn\left(-\overset{F_1}{\underset{F_1}{C}}-\overset{F_2}{\underset{H}{C}}-F_2\right)_2$	56.7	5.1		(103)
 $(CH_3)_3Sn-\overset{F_1}{\underset{F_1}{C}}-\overset{F_2}{\underset{H}{C}}-F_2$	57.5	5.5		(102)
 $(CO)_5Mn-\overset{F_1}{\underset{F_1}{C}}-\overset{F_2}{\underset{H}{C}}-F_2$	58	5.3		(101)
 $(CN)_5Rh\left(-\overset{F_1}{\underset{F_1}{C}}-\overset{F_2}{\underset{H}{C}}-F_2\right)^{3-}$	54	7.4	6.6	(104)
 $F_1-\overset{F_1}{\underset{F_1}{C}}-\overset{F_2}{\underset{H}{C}}-F_2$	53	3	3	(101)

atom. Thus, each molecule consists of a four spin system according to the ABMX pattern, where the three fluorines are magnetically non-equivalent.

The ^{19}F spectrum of the addition product, shown in Fig. 3., could be divided into two sets of 24 lines. In each set there were two large coupling constants of 290 and 312 Hz, which are in agreement with the values of $\underline{J}_{(F-F)\ \underline{gem}.}$ given in Table 12. Assignments for the ^{19}F spectrum were made by matching with the proton spectrum. Thus, for the molecule $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$ the three fluorine absorptions were observed at 192.7, 205.9 and 220.9 p.p.m. relative to external CCl_3F. Each of these fluorine atoms was split twice by two magnetically non-equivalent fluorine atoms and once by one proton. The values of the coupling constants for different assignments are given in Fig. 3. The assignments for the two geminal fluorines, which occur at 192.7 and 205.9 p.p.m. were made by the occurrence of $\underline{J}_{F-F}$ of 290 Hz, this leaves the third fluorine in the molecule at 220.9 p.p.m. Similarly, the geminal fluorines in $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$ were assigned at 203.7 and 216.6 p.p.m., with $\underline{J}_{(F-F)\ \underline{gem}.}$ being 312 Hz. This leaves the third fluorine atom in this molecule at 233.3 p.p.m. Here again each fluorine was split twice by two magnetically non-equivalent fluorine atoms and once by one proton, as shown in Fig. 3. The matching of ^{1}H and ^{19}F spectra showed the coincidence of H-F coupling constants. The complete ^{1}H and ^{19}F magnetic resonance data obtained by this first order analysis are given in Table 14. However, the intensities in the ^{19}F spectrum corresponding to the parameters given in Table 14 show that although these assignments are satisfactory, the spectrum is not strictly first order.

The ^{1}H and ^{19}F spectra were integrated and in each case the ratio

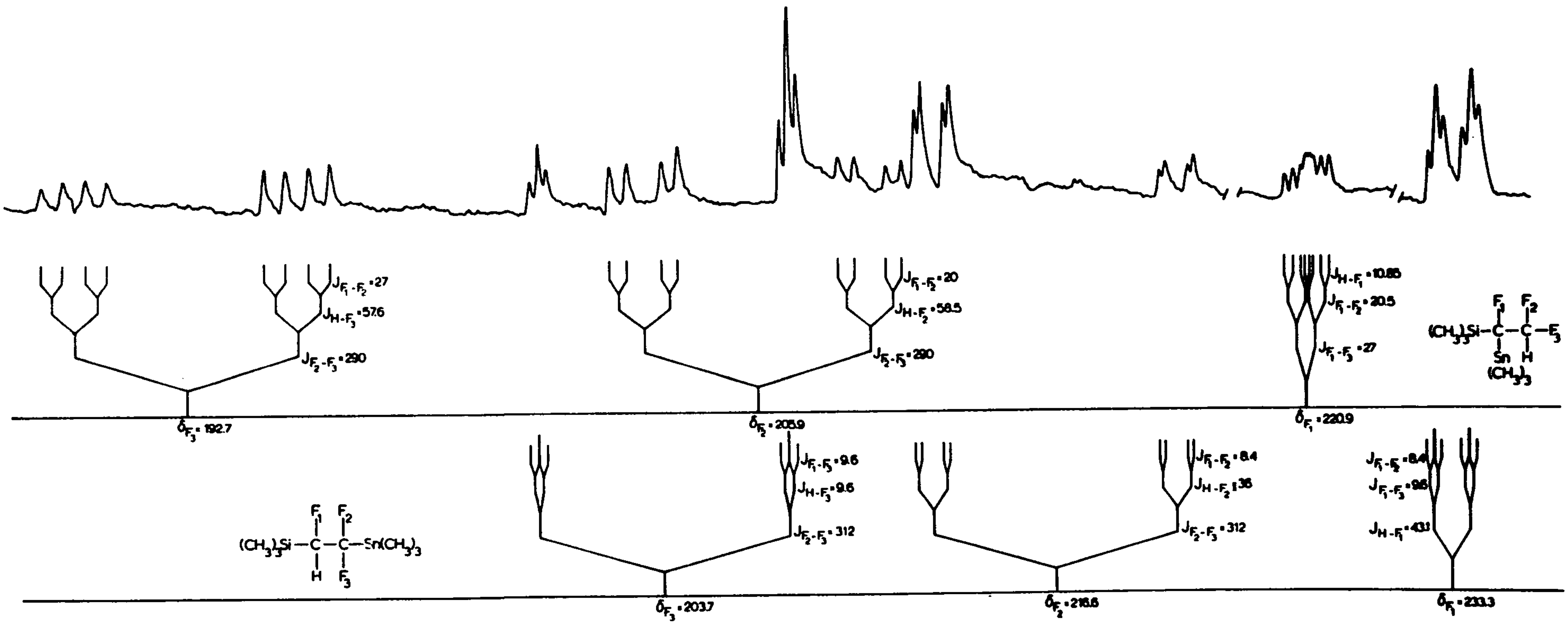


Fig. 3.

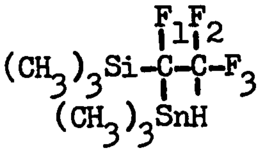
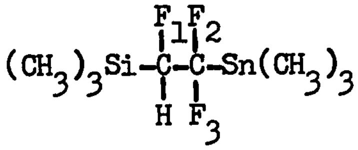
^{19}F N.M.R. Spectra of the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$.

$(CH_3)_3SiCFHCF_2Sn(CH_3)_3$: $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$ was 3:2. The resonance associated with methyl groups on silicon atoms in both molecules overlapped and was at -0.08 p.p.m. Similarly, the methyl-tin groups present in both molecules overlapped and were observed at -0.15 p.p.m. The satellites arising from coupling with ^{119}Sn and ^{117}Sn nuclei were observed; with $J_{^{119}Sn-CH_3}$ and $J_{^{117}Sn-CH_3}$ being 57.5 and 55 Hz. respectively. These values of coupling constants between the magnetically active Sn nuclei and the protons of methyl groups are in good agreement with the observed values for such splittings in other methyl-tin compounds containing fluorocarbon groups (102, 103). Since the coupling constant between two nuclei is proportional to the product of the gyromagnetic ratio of the two nuclei, the couplings $J_{^{119}Sn-CH_3}$ to $J_{^{117}Sn-CH_3}$ are in the ratio of the gyromagnetic ratio of the two tin isotopes, which is 1.046 (98). The larger coupling constant (57.5 Hz) results from 8.86% ^{119}Sn and the smaller (55 Hz) from 7.67% ^{117}Sn. Intensities of the appropriate side bands were found to be proportional to the isotopic abundances, and the ratio of coupling constants to gyromagnetic ratio within experimental error.

The ^{1}H and ^{19}F magnetic resonance spectra of the addition products of $(CH_3)_3SnH$ with $(CH_3)_3GeCF = CF_2$ were completely analogous to those of the addition products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$. There were 8 lines for the ethane proton in the ^{1}H spectrum and 24 lines in the ^{19}F spectrum for each of the molecules $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ and $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$. The ^{1}H and ^{19}F spectra for these molecules were similar to those of the corresponding silicon compounds which are shown in Fig. 2 and 3 respectively. Each molecule consisted of a four

TABLE 14

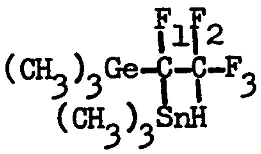
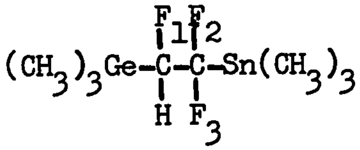
^1H and ^{19}F N.M.R. Data for the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$ *

	 $(CH_3)_3Si-\overset{F_1}{\underset{(CH_3)_3Sn}{C}}-\overset{F_2}{\underset{H}{C}}-F_3$		 $(CH_3)_3Si-\overset{F_1}{\underset{H}{C}}-\overset{F_2}{\underset{F_3}{C}}-Sn(CH_3)_3$	
	^1H spectrum	^{19}F spectrum	^1H spectrum	^{19}F spectrum
δ_{Si-CH_3}	-0.08		-0.08	
δ_H	-6.5		-4.72	
δ_{Sn-CH_3}	-0.5		-0.15	
$\underline{J}_{^{119}Sn-CH_3}$	57.5		57.5	
$\underline{J}_{^{117}Sn-CH_3}$	55		55	
δ_{F_1}		220.9		233.3
δ_{F_2}		205.9		216.6
δ_{F_3}		192.7		203.7
$\underline{J}_{H-F_1}$	10	10.9	44	43.1
$\underline{J}_{H-F_2}$	62	58.5	37	36
$\underline{J}_{H-F_3}$	56	57.6	10	9.6
$\underline{J}_{F_1-F_2}$		20		8.4
$\underline{J}_{F_1-F_3}$		27		9.6
$\underline{J}_{F_2-F_3}$		290		312

* Chemical shifts are in p.p.m. and coupling constants in Hz. Neat liquid samples were used with external CCl_3F and external TMS as references.

TABLE 15

^1H and ^{19}F N.M.R. Data for the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_3GeCF = CF_2$ in Cyclohexane.*

	 $(CH_3)_3Ge-\overset{F_1}{\underset{Sn(CH_3)_3}{C}}-\overset{F_2}{\underset{H}{C}}-F_3$		 $(CH_3)_3Ge-\overset{F_1}{\underset{H}{C}}-\overset{F_2}{\underset{F_3}{C}}-Sn(CH_3)_3$	
	^1H spectrum	^{19}F spectrum	^1H spectrum	^{19}F spectrum
δ_{Ge-CH_3}	-0.15		-0.15	
δ_H	-6.12		-4.6	
δ_{Sn-CH_3}	-0.2		-0.2	
$J_{^{119}Sn-CH_3}$	56		56	
$J_{^{117}Sn-CH_3}$	55		55	
δ_{F_1}		217.7		229
δ_{F_2}		118		111.2
δ_{F_3}		108		98.6
J_{H-F_1}	10	9.7	45	46.3
J_{H-F_2}	63	62.4	40	39.4
J_{H-F_3}	58	58	8	8
$J_{F_1-F_2}$		19.2		11
$J_{F_1-F_3}$		24		13
$J_{F_2-F_3}$		277.6		271.3

* Chemical shifts (p.p.m.) are relative to external TMS and internal CCl_3F for ^1H and ^{19}F spectrum respectively. Coupling constants in Hz.

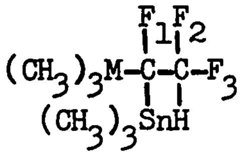
spin system according to the ABMX pattern, where the three fluorines are magnetically non-equivalent. From the closely coincident values of H-F coupling constants, the ^{1}H and ^{19}F spectra were matched. The first order analysis then gave the values shown in Table 15.

The integration of ^{1}H as well as of ^{19}F spectra gave the ratio $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$: $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ as 2:5. In both molecules the resonance due to the methyl groups on germanium overlapped and occurred at -0.15 p.p.m. Similarly, only one peak was obtained at -0.2 p.p.m. for the methyl groups on tin in both molecules with $\underline{J}_{^{119}Sn-CH_3}$ and $\underline{J}_{^{117}Sn-CH_3}$ being 56 and 55 Hz respectively.

The proton magnetic resonance spectrum of the addition product of $(CH_3)_3SnH$ with $(CH_3)_3SnCF = CF_2$ was completely analogous to the spectrum of corresponding addition products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF = CF_2$ and $(CH_3)_3GeCF = CF_2$. One set of eight lines centred at -6.3 p.p.m. and with $\underline{J}_{H-F}$ values of 62,60 and 12 Hz was assigned to $((CH_3)_3Sn)_2CFCF_2H$ molecule, and the other set of eight lines centred at -5.0 p.p.m. and with $\underline{J}_{H-F}$ values of 47, 45 and 6 Hz was assigned to $(CH_3)_3SnCFHCF_2Sn(CH_3)$. The complete proton n.m.r. data are given in Table 16, which show the many similarities among the n.m.r. parameters of the addition products of trimethyltin hydride with trimethylperfluorovinyl compounds of silicon, germanium and tin.

TABLE 16

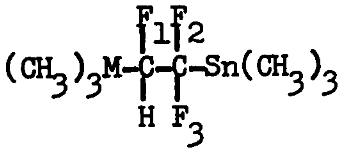
^1H N.M.R. Data for the Addition Products of $(CH_3)_3SnH$ with Trimethylperfluorovinyl Compounds of Group IVB Elements.*



$(CH_3)_3M-\overset{F_1}{\underset{(CH_3)_3Sn}{\overset{|}{\underset{|}{C}}}}-\overset{F_2}{\underset{H}{\overset{|}{\underset{|}{C}}}}-F_3$

M	Si	Ge	Sn
δ_H	-6.5	-6.12	-6.3
δ_{M-CH_3}	-0.08	-0.15	-0.22
δ_{Sn-CH_3}	-0.15	-0.2	-0.22
$J_{^{119}Sn-CH_3}$	57.5	56	55
$J_{^{117}Sn-CH_3}$	55	55	54
J_{H-F_1}	10	10	12
J_{H-F_2}	62	63	62
J_{H-F_3}	56	58	60

TABLE 16 (continued)



$(CH_3)_3M\text{-}\overset{F_1}{\underset{H}{C}}\text{-}\overset{F_2}{\underset{F_3}{C}}\text{-}Sn(CH_3)_3$

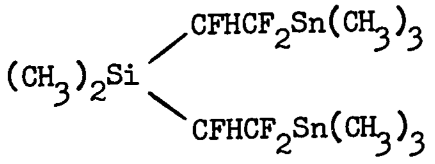
M	Si	Ge	Sn
δ_H	-4.72	-4.6	-5.0
δ_{M-CH_3}	-0.08	-0.15	-0.22
δ_{Sn-CH_3}	-0.15	-0.2	-0.22
$J_{^{119}Sn-CH_3}$	57.5	56	55
$J_{^{117}Sn-CH_3}$	55	55	54
J_{H-F_1}	44	45	47
J_{H-F_2}	37	40	45
J_{H-F_3}	10	8	6

* Chemical shifts (p.p.m.) are relative to external TMS.

Coupling constants in Hz.

3. Proton Magnetic Resonance Spectra of the Addition Products of Trimethyltin Hydride with Dimethylbis(perfluorovinyl) Compounds of Silicon and Germanium.

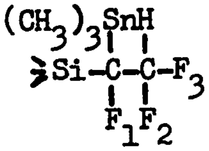
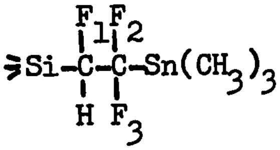
Trimethyltin hydride forms colourless involatile liquid products with $(CH_3)_2Si(CF = CF_2)_2$ and $(CH_3)_2Ge(CF = CF_2)_2$ under ultraviolet irradiation. The proton n.m.r. spectrum of the addition product of $(CH_3)_3SnH$ with $(CH_3)_2Si(CF = CF_2)_2$ showed the presence of two closely spaced $-CF(Sn(CH_3)_3)CF_2H$ groups at about -6.06 p.p.m. These groups overlapped so badly that it was not possible to assign a separate chemical shift to each ethane proton present in these groups. The H-F coupling constants in both groups were 61, 55 and 10 Hz respectively. In this spectrum there was an other set of two overlapping signals due to $-CFHCF_2Sn(CH_3)_3$ groups, centred at -4.46 p.p.m., with $\underline{J}_{H-F}$ values being 44, 38 and 8 Hz respectively. The assignments for these two different types of groups were made relative to the spectra of similar groups, and this has been discussed in detail in the preceeding section. The complete numerical data are given in Table 17. Thus, the presence of two $-CF(Sn(CH_3)_3)CF_2H$ groups and two $-CFHCF_2Sn(CH_3)_3$ groups indicates the existence of the following three molecules in the addition product of $(CH_3)_3SnH$ with $(CH_3)_2Si(CF = CF_2)_2$.



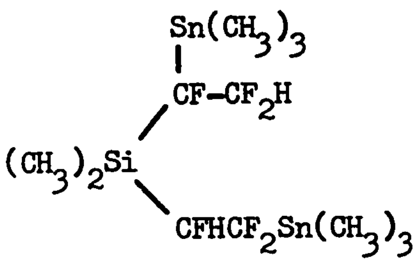
I

TABLE 17

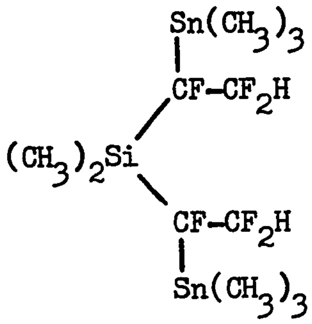
^1H N.M.R. Data for the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_2Si(CF=CF_2)_2$ in Cyclohexane.*

	 $\geqslant Si-\underset{F_1}{\overset{(CH_3)_3Sn}{C}}-\underset{F_2}{\overset{H}{C}}-F_3$	 $\geqslant Si-\underset{H}{\overset{F_1}{C}}-\underset{F_3}{\overset{F_2}{C}}-Sn(CH_3)_3$
δ_{Si-CH_3}	-0.18	-0.18
δ_H	-6.06	-4.46
δ_{Sn-CH_3}	-0.15	-0.15
$J_{^{119}Sn-CH_3}$	56	56
$J_{^{117}Sn-CH_3}$	55	55
J_{H-F_1}	10	44
J_{H-F_2}	61	38
J_{H-F_3}	55	8

* Chemical shifts (p.p.m.) are relative to external TMS. Coupling constants in Hz.

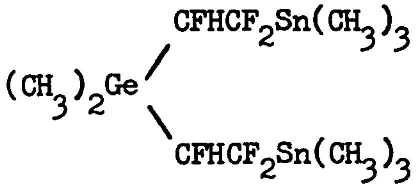


II

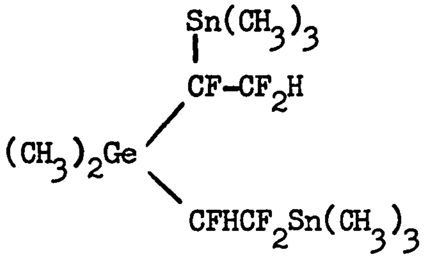


III

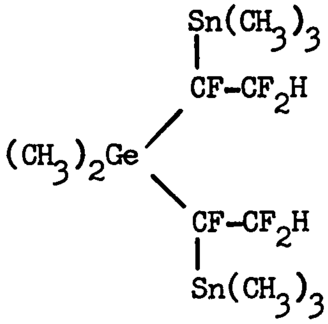
The proton n.m.r. spectrum of the addition product of $(CH_3)_3SnH$ with $(CH_3)_2Ge(CF = CF_2)_2$ also showed the presence of two $-CF(Sn(CH_3)_3)CF_2H$ groups placed at -6.36 and -6.30 p.p.m., with J_{H-F} being 65, 58, 10 Hz and 60, 56, 10 Hz respectively. There was an other set of signals due to two $-CFHCF_2Sn(CH_3)_3$ groups placed respectively at -4.98 and -4.92 p.p.m., and each having J_{H-F} values of 45, 42 and 5 Hz. These similar groups in each set, although closely spaced did not overlap each other as badly as the corresponding silicon compounds discussed above. The numerical data with the possible assignments are given in Table 18 and are completely consistent with the data already given for other addition products. Thus, the proton spectrum is consistent with the presence of the following three molecules in the addition product.



I



II



III

TABLE 18

^{1}H N.M.R. Data for the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_2Ge(CF = CF_2)_2$ in Cyclohexane.*

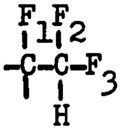
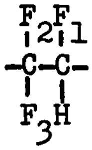
	Signals from Molecules	
	Containing  $-\overset{F_1}{\underset{\vert}{C}}-\overset{F_2}{\underset{H}{C}}-F_3$ Groups	
δ_{Ge-CH_3}	-0.58	-0.58
δ_{Sn-CH_3}	-0.35	-0.35
δ_H	-6.36	-6.30
$\underline{J}_{^{119}Sn-CH_3}$	56	56
$\underline{J}_{^{117}Sn-CH_3}$	55	55
$\underline{J}_{H-F_1}$	10	10
$\underline{J}_{H-F_2}$	65	60
$\underline{J}_{H-F_3}$	58	56

TABLE 18 (Continued)

^1H N.M.R. Data for the Addition Products of $(CH_3)_3SnH$ with $(CH_3)_2Ge(CF = CF_2)_2$ in Cyclohexane.*

	Signals from Molecules Containing  $-\overset{F_2}{\underset{F_3}{C}}-\overset{F_1}{\underset{H}{C}}-$ Groups	
δ_{Ge-CH_3}	-0.58	0.58
δ_{Sn-CH_3}	-0.35	0.35
δ_{H}	-4.98	-4.92
$J_{^{119}Sn-CH_3}$	56	56
$J_{^{117}Sn-CH_3}$	55	55
J_{H-F_1}	45	45
J_{H-F_2}	42	42
J_{H-F_3}	5	5

* Chemical shifts (p.p.m.) are relative to external TMS. Coupling constants in Hz.

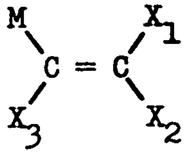
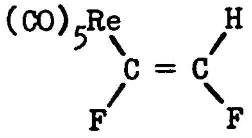
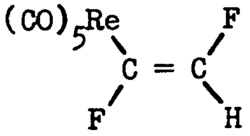
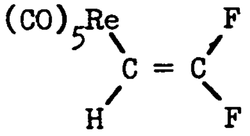
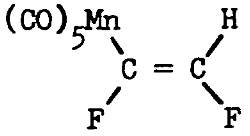
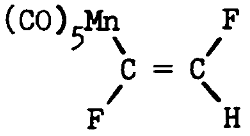
4. Proton Magnetic Resonance Spectra of Fluorovinyl Derivatives of Pentacarbonylrhenium.

The fluorovinyl derivatives of pentacarbonylrhenium were characterized by their C = C stretching absorptions combined with the values of H-F coupling constants observed in their proton n.m.r. spectra. The configurations assigned to these compounds are based on the values of H-F coupling constants in fluoro-olefins and fluorovinyl compounds of silicon, germanium and tin, given in Tables 8-11.

The compound with a C = C stretching absorption at 1675 cm^{-1}, showed a quartet at -7.57 p.p.m. with $\underline{J}_{H-F}$ 87 and 10 Hz. The value of 87 Hz corresponds to a geminal H-F coupling constant and the value of 10 Hz corresponds to a cis H-F coupling constant. These values indicate that the $(CO)_5Re-$ group is trans to the vinylic proton. Thus the configuration trans-CFH = $CFRe(CO)_5$ was assigned to this compound. The compound with a C = C stretching absorption at 1625 cm^{-1} gave rise to a quartet at -5.78 p.p.m. with $\underline{J}_{H-F}$ 82 and 26 Hz. The value of 82 Hz corresponds to a geminal H-F coupling constant and the other value of 26 Hz corresponds to trans H-F coupling constant. This indicates that in this compound the $(CO)_5Re-$ group is cis to the vinylic proton and the configuration cis-CFH = $CFRe(CO)_5$ was assigned to this compound. Similarly, the compound $(CO)_5ReCH = CF_2$ with a C = C stretching absorption at 1615 cm^{-1}, gave rise to a quartet at -3.8 p.p.m. with $\underline{J}_{(H-F)}$ trans 46 Hz and $\underline{J}_{(H-F)}$ cis 12 Hz. The complete spectroscopic data for the fluorovinyl derivatives of pentacarbonylrhenium and pentacarbonylmanganese are given in Table 19.

TABLE 19

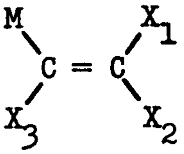
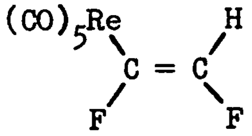
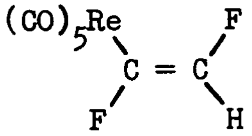
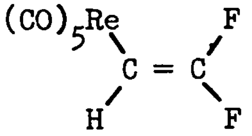
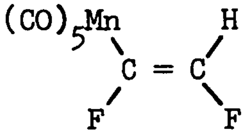
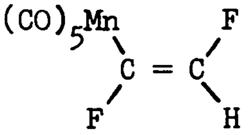
Proton N.M.R. Assignments for Fluorovinyl Derivatives of $-Re(CO)_5$ and $-Mn(CO)_5$.*

	δ H vinyl	J_{12}	J_{23}	J_{13}
	-5.78	82	-	26
	-7.57	87	10	-
	-3.8	-	12	46
	-5.7	80	-	25
	-8.1	86.5	10.2	-

* Chemical shifts (p.p.m.) with respect to internal TMS and coupling constants in Hz. The data for manganese compounds are taken from reference (62).

TABLE 19

Proton N.M.R. Assignments for Fluorovinyl Derivatives
of $-Re(CO)_5$ and $-Mn(CO)_5$.*

	$\delta_{\text{H vinyl}}$	J_{12}	J_{23}	J_{13}
	-5.78	82	-	26
	-7.57	87	10	-
	-3.8	-	12	46
	-5.7	80	-	25
	-8.1	86.5	10.2	-

* Chemical shifts (p.p.m.) with respect to internal TMS and coupling constants in Hz. The data for manganese compounds are taken from reference (62).

CHAPTER IV

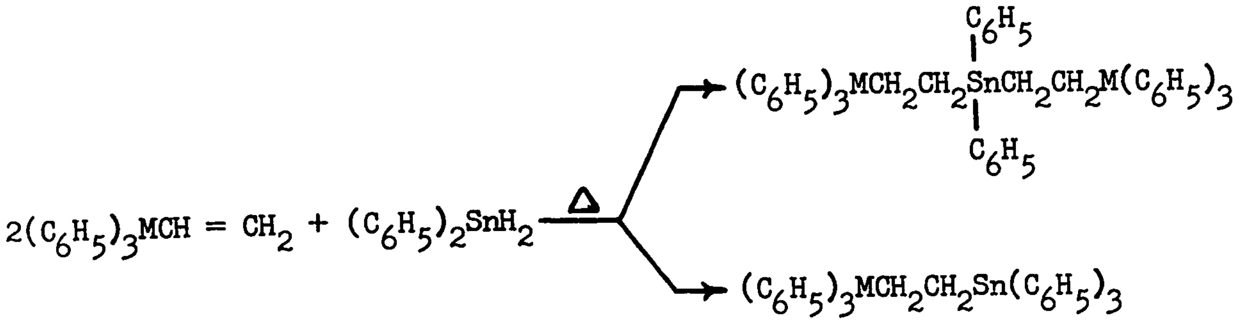
CONCLUSION

The present work establishes that the additions of trimethyltin hydride to the C = C bonds of perfluorovinyl compounds of silicon, germanium and tin are indeed free radical processes. These reactions differ from the addition reactions of organotin hydrides with acetylenes where the involvement of both a polar as well as a radical mechanism is probably involved, and particularly from the non-terminal additions with electrophilic acetylenes which are controlled mainly by the polar effects (29,30). The reactions of perfluorovinyl compounds can be compared with some addition reactions of organotin hydrides to the C = C bonds of vinyl derivatives of Group IVB elements, for example (4);

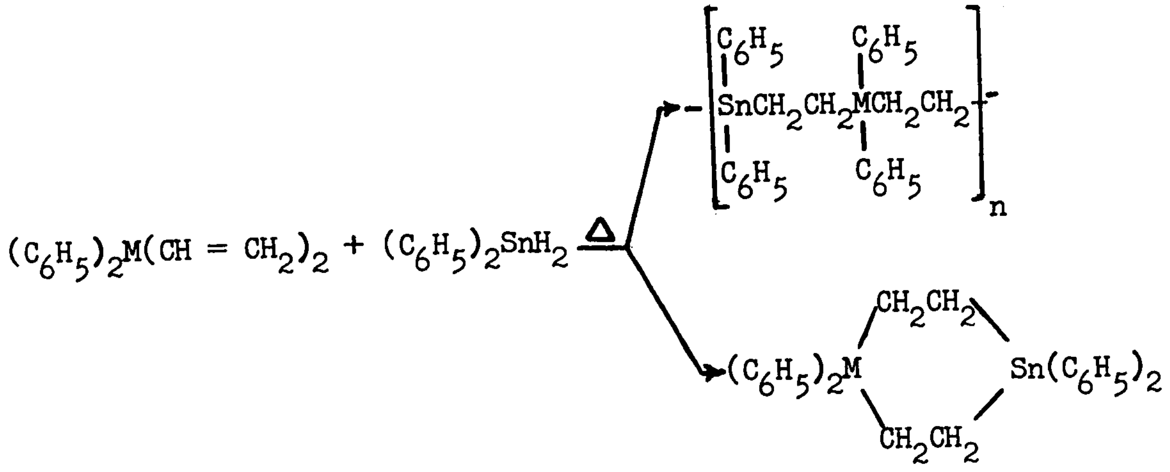
$$(C_6H_5)_3MCH = CH_2 + (C_6H_5)_3SnH \xrightarrow{\Delta} (C_6H_5)_3MCH_2CH_2Sn(C_6H_5)_3$$

$$M = Si, Ge, Sn.$$

However, the other possible addition product $(C_6H_5)_3MCH(Sn(C_6H_5)_3)CH_3$, could not be ruled out, nor could anything be said with certainty concerning the mechanism of this reaction. Dihydrides also form such addition products, which may be cyclic compounds when the reactions involve divinyl derivatives. In these reactions $(C_6H_5)_2SnH_2$ can disproportionate (4);



M = Si, Ge, Sn.



M = Si, Ge, Pb.

Perfluorovinyl-metal compounds differ from vinyl-metal derivatives in a number of respects (44). Generally, perfluorovinyl compounds are less stable thermally and kinetically than their vinyl analogs (44). But the main factor which should be taken into account regarding the reactions of organotin hydrides with perfluorovinyl and vinyl compounds is the possible formation of organotin fluorides in the former case.

Thus, the elimination of organotin fluorides in the reactions of organotin hydrides with perfluorovinyl compounds may well make the isolation of the addition products difficult, especially under thermal conditions, whereas the addition products have been isolated in the similar reactions involving the vinyl compounds (4).

It is particularly interesting to note the difference in the stability of the addition products of trimethyltin hydride with $(CH_3)_3SiCF = CF_2$, $(CH_3)_3GeCF = CF_2$ and $(CH_3)_3SnCF = CF_2$. The addition products with $(CH_3)_3SiCF = CF_2$ are the most stable, although $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$ decomposes more readily than its isomer $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$. This mixture can be handled for short periods under vacuum without decomposition, and can even be prepared at 55° using AIBN to initiate the addition reaction, while the analogous addition products with $(CH_3)_3GeCF = CF_2$ start decomposing at room temperature after a very short time and cannot be prepared under thermal conditions, even in the presence of AIBN. Here again $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ decomposes more readily than $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$. The greater steric interactions in the molecules $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$ and $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ where the two heavy groups are attached to one carbon atom could be responsible for their comparative instability. The addition products of trimethyltin hydride with $(CH_3)_3SnCF = CF_2$ are the least stable; they cannot even be separated from the reaction mixture and decompose rapidly at room temperature.

Seyferth et al. have investigated the reactions of vinyl derivatives of Group IVB elements with phenyllithium (105,106). In these reactions, a sharp difference exists between the Si and Ge compounds on the one hand and Sn and Pb compounds on the other;

$$(C_6H_5)_3MCH = CH_2 + C_6H_5Li \longrightarrow (C_6H_5)_3MCHLiCH_2C_6H_5$$

M = Si, Ge.

$$(C_6H_5)_3MCH = CH_2 + C_6H_5Li \longrightarrow (C_6H_5)_4M + LiCH = CH_2$$

M = Sn, Pb.

Although the mechanism of these reactions is not yet known with certainty, the results for Si and Ge have been explained in terms of stabilization of the transition state or of the final product by $\underline{d}\pi - \underline{p}\pi$ bonding between Si or Ge and an adjacent carbanionic centre.

It appears that the formation of the addition products of trimethyltin hydride with perfluorovinyl compounds of Si, Ge and Sn could probably be promoted by the involvement of $\underline{d}\pi - \underline{p}\pi$ bonding within the M–C = C group (M = Si, Ge, Sn). Such effects seem to be at a maximum in the silicon compounds and at a minimum in the tin compounds. The facile elimination of trimethyltin fluoride from all the addition products makes quantitative comparison of the relative stabilities of these products difficult.

There are various other cases where the involvement of $\underline{d}\pi - \underline{p}\pi$ bonding in vinylic derivatives of Group IVB elements has been emphasized. Thus, the rate of radical-initiated polymerization of the compounds $R_3MCH = CH_2$, where M = C, Si, Ge and Sn, has been found to decrease in the order $Si > C > Ge > Sn$ (107). Electron-attracting substituents on

M accelerate the reaction. The silicon compound polymerizes faster than expected. This has been interpreted on the basis of an electron-attracting effect of the R_3Si group due to $\underline{d}\pi - \underline{p}\pi$ bonding. Again, for the addition reactions of organotin hydrides to the vinyl derivatives of Group IVB elements, it has been suggested that the double bond in the vinyl compounds is activated by the neighbouring phenylmetal groups, presumably by a conjugative mechansim involving $\underline{d}\pi - \underline{p}\pi$ bonding of the metal-to-carbon bond (4). Neumann _et al._ have also found that the Sn-H group forms a stable addition product with α-olefins if C_6H_5 groups are present on tin instead of CH_3 groups, again supporting the suggestion of this conjugative mechanism (108).

A stable addition product of $(CH_3)_3SnH$ with $(CO)_5ReCF = CF_2$ could not be isolated. However, in the reactions of trimethyltin hydride with $(CO)_5ReCF = CF_2$ under free radical generating conditions, _e.g._ in the reactions involving AIBN and under ultraviolet irradiation, evidence for the existence of unstable intermediate addition products $(CO)_5ReCFHCF_2Sn(CH_3)_3$ and $(CO)_5ReCF(Sn(CH_3)_3)CF_2H$ was obtained. It has already been shown that the hypothetical products such as $(CO)_5MnC_2F_3HSn(CH_3)_3$ and $(CO)_5MnC_2F_3HGe(CH_3)_3$ are unstable, but their existence as intermediates has been shown in the reactions of trifluoroethylene with tin-manganese and germanium-manganese bonded compounds (62,63).

Although most work has been concerned with the addition reactions of organotin hydrides across a variety of unsaturated bonds, they can undergo other types of reaction _e.g._ as reducing agents. The reductions of alkyl and aryl halides by organotin hydrides generally take place by a free radical process and there are various examples where organotin hydrides have proved good hydrogen donors (19). However, phosphonitrilic hydrides could not be isolated by the reactions of organotin hydrides with phosphonitrilic halides. These reactions also differ from the reactions of organotin hydrides with phosphorus pentafluoride and some chloroboranes where the halogen atoms can be replaced by hydrogen atoms from tin (38-40). Probably the initiation of polymerization limits the reduction of phosphonitrilic halides by organotin hydrides.

CHAPTER V

EXPERIMENTAL

1. General Experimental and Physical Techniques.

Experimental work was done on a general purpose, pyrex glass vacuum line, using standard high vacuum techniques (109). The vacuum line consisted of six 25 ml. cold traps, connected by quick-fit high vacuum stopcocks. Apiezon N grease was used to lubricate the stopcocks. Three mercury manometers and one glass bulb of known volume (620 c.c.) were attached to the vacuum line to measure the volatile materials by pressure and volume. A Welch Duo-Seal mechanical pump Model 1400 was used to evacuate the apparatus. All reactions were done under strictly anhydrous conditions. The glass apparatus was evacuated and carefully dried by baking with a nonluminous flame before use. The solvents were dried and distilled immediately before use.

Reactions under thermal conditions were performed in pyrex Carius tubes, whereas those involving ultraviolet irradiation were conducted in silica tubes under a 200 watt Hanovia ultraviolet lamp in a fume hood. The volatile compounds were purified and separated from the reaction mixture by gas chromatography, using an Aerograph model A-700 Autoprep instrument with helium as a carrier gas. Microanalyses of products were carried out by Dr. A. B. Gygli, Microanalytical Laboratory, 329 George Street, Toronto, Ontario or by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. 11377, U.S.A.

Although chemical analysis is a preliminary to the identification of a compound, unambiguous characterization is often only possible after physical examination. Molecular weight measurements, infrared spectroscopic examination and nuclear magnetic resonance spectroscopy are particularly valuable. Of these infrared spectroscopy can provide immediate qualitative structural information, and this together with nuclear magnetic resonance spectroscopic data can confirm the structure unambiguously.

Molecular weights of involatile compounds were determined with an Hitachi-Perkin Elmer 115-Molecular Weight Apparatus and by the Regnault method for gases. Infrared spectra were recorded (4000-400 cm^{-1}) with a Beckman IR 10 double beam spectrophotometer, using a 10 cm cell for vapor samples, liquid films for liquids and nujol mulls for the spectra of solid compounds. Potassium bromide windows were used in each case. Proton n.m.r. spectra were obtained with a Varian A60 spectrometer and ^{19}F spectra with a Varian DP 60 spectrometer operating at 56.4 McS^{-1}.

2. Preparation of Organotin Hydrides.

In 1922, Kraus and Greer first prepared $(CH_3)_3SnH$ in low yield by the reaction of $(CH_3)_3SnNa$ and NH_4Cl (or NH_4Br) in liquid ammonia (110). The organotin anion is converted to the hydride by proton abstraction from the ammonium ion.

$$(CH_3)_3SnNa + NH_4Cl \longrightarrow (CH_3)_3SnH + NH_3 + NaCl.$$

In 1947, Finholt <u>et al.</u> discovered that organotin halides could be reduced to organotin hydrides by lithium aluminum hydride (111). The other methods used to prepare the various organotin hydrides are (i) the reactions of organotin halides with $NaBH_4$ (112), or dialkylaluminum hydrides (113), (ii) the reactions of organotin oxides with hydrosilanes (114), $LiAlH_4$ (115), and dialkylaluminum hydrides (113), and (iii) the thermal decomposition of organotin formates (116).

$$R_3SnOCHO \xrightarrow{\Delta} R_3SnH + CO_2.$$

The reduction with sodium borohydride is a suitable method for the preparation of high boiling and relatively involatile organotin hydrides (112), but only one of the hydrogens of the borohydride is used, the remainder being wasted as diborane, which is a problem to dispose off.

$$2\ R_3SnCl + 2\ NaBH_4 \xrightarrow[\text{monoglyme}]{\text{diglyme or}} 2\ R_3SnH + 2\ NaCl + B_2H_6.$$

The reduction with $LiAlH_4$ is generally the most convenient method, gives high yields and can be extended to a wide variety of organotin hydrides (19, 111).

$$\frac{1}{4-n} R_nSnCl_{4-n} + \frac{1}{4} LiAlH_4 \longrightarrow \frac{1}{4-n} R_nSnH_{4-n} + \frac{1}{4} LiAlCl$$

Trimethyltin hydride and dimethyltin dihydride were prepared by this method.

(a) Trimethyltin Hydride, $(CH_3)_3SnH$.

$(CH_3)_3SnCl$ (30 g, 0.15 mole) was dissolved in 100 ml. of n-butyl ether. This solution was added slowly, under nitrogen atmosphere, to a slurry of $LiAlH_4$ (7 g, 0.2 mole) in n-butyl ether in a three necked quick-fit flask fitted with a stirrer and a -78° condenser. The reaction mixture was stirred for two more hours after the complete addition of trimethyltin chloride. The mixture was fractionated under vacuum, thus pure $(CH_3)_3SnH$ (20 g, 80 % yield) collected in a -78° trap, while n-butyl ether collected in the -23° and -45° traps. The molecular weight was 165 (Regnaults method). (Calcd. M.W. 164.7).

(b) Dimethyltin Dihydride, $(CH_3)_2SnH_2$.

By a similar procedure as (a) above $(CH_3)_2SnCl_2$ (33 g, 0.15 mole) was added to $LiAlH_4$ (10.5 g, 0.3 mole) in n-butyl ether. Fractionation of the reaction mixture under vacuum gave $(CH_3)_2SnH_2$ (20.5 g, 82 % yield), which collected in a -126° trap. The molecular weight was 150 (Calcd. 150.7)

The samples of the hydrides were stored under vacuum in pyrex tubes. The infrared spectral data for the hydrides are given in Table 20.

TABLE 20

Infrared Spectra of $(CH_3)_3SnH$ and $(CH_3)_2SnH_2$.

(Gas phase)

$(CH_3)_3SnH(C_{3v})$	$(CH_3)_2SnH_2(C_{2v})$	Assignment (117).
	506 sh,s	
509 sh,s 516 sh,s	514 s	Sn-C sym. stretch
	526 s	
535 sh,s	536 s	Sn-C asym. stretch
	574 s	Sn-H_2 rock
659 w 671 m 681 w		C_3SnH bend
	712 vs	Sn-H_2 wag
	726 vs	Sn-H_2 defn.
	749 vs	
764 vs	760 vs	CH_3 rock
	776 vs	
803 sh,s		
1140 vw		
1191 w 1200 m 1209 w	1205 w	CH_3 sym. defn.

TABLE 20 (continued)

$(CH_3)_3SnH(C_{3v})$	$(CH_3)_2SnH_2(C_{2v})$	Assignment (117).
1410 w,b	1418 vw	CH_3 asym. defn.
1730 vw	1730 vw	
1841 vs	1869 vs	Sn-H stretch
2400 vw		
	2833 w	
2925 s	2926 s	CH_3 sym. stretch
3000 vs	3003 s	CH_3 asym. stretch
3060 w	3058 w	
	3676 vw	

3. Preparation of Perfluorovinyl Compounds of Silicon, Germanium and Tin.

Perfluorovinyl compounds of various elements have been prepared by the reactions of perfluorovinyl Grignard reagents, $CF_2 = CFMgI$ and $CF_2 = CFMgBr$, with the appropriate halides (41, 44, 118-120). Perfluorovinyl lithium, at low temperatures, has also been used to prepare such compounds (121).

For the present work perfluorovinyl compounds of silicon were prepared by the method described by Tarrant and Oliver, utilizing a two step reaction in which bromotrifluoroethylene reacted with methyllithium to give trifluorovinyllithium, which was then allowed to react with the appropriate methylchlorosilane (122). Perfluorovinyl compounds of germanium and tin were prepared by the perfluorovinyl Grignard reagent (82, 123).

(a) Trimethylperfluorovinylsilane, $(CH_3)_3SiCF = CF_2$.

Trimethylchlorosilane (28 g, 0.26 mole) was added dropwise to a stirred solution of trifluorovinyllithium (0.26 mole) in ethyl ether at -78° under a nitrogen atmosphere. The reaction mixture was allowed to come to room temperature slowly. This mixture was hydrolysed with water, and the ethereal solution was separated and dried over calcium chloride. Distillation gave $(CH_3)_3SiCF = CF_2$ (20 g, 50 % yield), boiling point 67-68°. Spectroscopic data are given in Tables 21 and 24.

(b) Dimethylbis(perfluorovinyl)silane, $(CH_3)_2Si(CF = CF_2)_2$.

Dimethyldichlorosilane (65 g, 0.5 mole) was added to trifluorovinyllithium (1.0 mole) in ethyl ether at -78°. The reaction mixture was allowed to come to room temperature slowly. Lithium chloride was filtered off. Distillation of the filtrate gave $(CH_3)_2Si(CF = CF_2)_2$ (24.5 g, 44 % yield), boiling point 98°. Spectroscopic data are given in Tables 21 and 24.

(c) Trimethylperfluorovinylgermane, $(CH_3)_3GeCF = CF_2$.

Trimethylbromogermane (22 g, 0.11 mole), magnesium chips (2.7 g, 0.11 mole) and 400 ml of tetrahydrofuran were placed in a three necked quick-fit flask, which was fitted with a condenser and a Teflon stirrer. Bromotrifluoroethylene (20 g, 0.124 mole) was bubbled through the above mixture under a nitrogen atmosphere. After five minutes a vigorous reaction started with the formation of a dark colour. The reaction mixture was stirred at 40-45° for eight hours after the complete addition of bromotrifluoroethylene. The volatiles were transferred to another flask at -78° under vacuum. Most of the tetrahydrofuran was removed from this mixture by distillation. The remaining liquid products were separated by gas chromatography on a silicone QF-1 column at 150°. Thus, pure $(CH_3)_3GeCF = CF_2$ (8 g, 36% yield), was obtained along with some unreacted $(CH_3)_3GeBr$ (6 g). The spectroscopic data are given in Tables 22 and 24.

TABLE 21

Infrared Spectra of $(CH_3)_3SiCF = CF_2$ and $(CH_3)_2Si(CF = CF_2)_2$.

(Gas phase)

$(CH_3)_3SiCF = CF_2$	$(CH_3)_2Si(CF = CF_2)_2$	Assignment (76, 77, 82).
625 m		
660 m	605 w	
705 m	690 s	CH_3(-Si) rock
765 s		
850 vs,b	805 s	
	820 s	
	840 s	
1050 s	1055 s	C-F stretch
1070 s	1070 s	
1140 vs	1150 s	
1255 vs	1258 vs	CH_3(-Si) sym. defn.
1300 vs	1302 vs	C-F stretch
1420 w	1415 w	CH_3(-Si) asym. defn.
1725 s	1730 s	C = C stretch
2400 vw		
2580 vw		
2922 m	2920 w	CH_3 sym. stretch
2990 s	2990 s	CH_3 asym. stretch

TABLE 22

Infrared Spectra of $(CH_3)_3GeCF = CF_2$ and $(CH_3)_2Ge(CF = CF_2)_2$.

(Gas phase)

$(CH_3)_3GeCF = CF_2$	$(CH_3)_2Ge(CF = CF_2)_2$	Assignment (81, 82).
570 w	580 w	Ge–C sym. stretch
615 s	620 m	Ge–C asym. stretch
	648 w	
765 m	762 m	CH_3(–Ge) rock
	820 s	
840 vs	850 vs	
1030 vs	1030 vs	C–F stretch
1135 s	1145 vs	
1254 m	1254 m	CH_3(–Ge) sym. defn.
1290 vs	1291 vs	C–F stretch
1410 w	1410 w	CH_3(–Ge) asym. defn.
1730 vs	1730 vs	C = C stretch
	1780 vw	
2060 vw	2050 vs	
	2400 vw	
2595 vw	2600 vw	
2800 vw	2780 vw	
2915 w	2915 w	CH_3 sym. stretch
3000 m	3000 m	CH_3 asym. stretch

(d) Dimethylbis(perfluorovinyl)germane, $(CH_3)_2Ge(CF = CF_2)_2$

In a similar experiment as (c) above $(CH_3)_2Ge(CF = CF_2)_2$ was prepared in 33 % yield, starting from $(CH_3)_2GeCl_2$ (17.5 g, 0.1 mole), magnesium chips (4.8 g, 0.2 mole) and bromotrifluoroethylene (35 g, 0.2 mole). In this experiment unreacted dimethyldichlorogermane (4.5 g) was recovered. The spectroscopic data are given in Tables 22 and 24.

(e) Preparation of Trimethylperfluorovinyltin, $(CH_3)_3SnCF = CF_2$.

Trimethyltin chloride (50 g, 0.25 mole), magnesium chips (6.1 g, 0.254 mole) and 500 ml. of tetrahydrofuran were placed in a three necked quick-fit flask fitted with a condenser and a Teflon stirrer. Bromotrifluoroethylene (41 g, 0.254 mole) was bubbled through the above mixture under a nitrogen atmosphere. A vigorous reaction started upon the addition of bromotrifluoroethylene with the formation of a dark colour. The reaction mixture was stirred at 40-45° for 12 hours after the complete addition of bromotrifluoethylene. The volatiles were transferred to another flask at -78° under vacuum. Tetrahydrofuran was removed from this mixture by distillation and $(CH_3)_3SnCF = CF_2$ (32.5 g, 53 %) was collected, distilling at 110.5°. Final purification was achieved by vacuum fractionation. The spectroscopic data are given in Tables 23 and 24.

TABLE 23

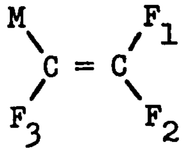
Infrared Spectrum of $(CH_3)_3SnCF = CF_2$

(Gas phase)

Frequency (cm^{-1})	Assignment (81, 82)
510 vs	Sn–C sym. stretch
520 vs	Sn–C asym. stretch
755 vs	CH_3(–Sn) rock
832 s	
990 s	C–F stretch
1120 b,s	
1210 m	CH_3(–Sn) sym. defn.
1275 b,s	C–F stretch
1380 w	CH_3(–Sn) asym. defn.
1711 vs	C = C stretch
2840 m	
2900 m	
2960 vs	CH_3 sym. stretch
3025 m	CH_3 asym. stretch

TABLE 24

^{1}H and ^{19}F N.M.R. Data for Perfluorovinyl Compounds of Silcon, Germanium and Tin.*

	δ_{CH_3}	δ_{F_1}	δ_{F_2}	δ_{F_3}	J_{12}	J_{23}	J_{13}
$(CH_3)_3SiCF = CF_2$	−0.10	88.6	118	119	69	30	117
$(CH_3)_2Si(CF = CF_2)_2$	−0.45	83	113	198	62	22	120
$(CH_3)_3GeCF = CF_2$	−0.52	86.4	117	203	67	25	118
$(CH_3)_2Ge(CF = CF_2)_2$	−0.45	87.5	120.5	199.4	63.7	29	118
$(CH_3)_3SnCF = CF_2$	−0.33	103.6	130	207.3	79	30	118

* The assignment of fluorine atoms was made according to Stone *et al.* (124). Chemical shifts (accurate to ± 0.5 p.p.m.) are relative to internal TMS and CCl_3F. Coupling constants are accurate to ± 4 Hz.

4. The Reactions of Organotin Hydrides with Perfluorovinyl Silicon Compounds.

In all of the reactions described below, the reaction mixture was worked up as follows. The reaction tube was opened to the vacuum system and all volatile components were separated by conventional trap-to-trap fractionation. Further purification was achieved by gas chromatography and each fraction was identified from its infrared spectrum, and for pure compounds ultimately by their n.m.r. spectra. Any involatile material remaining in the reaction tube was examined spectroscopically.

(i) Reactions of Trimethylperfluorovinylsilane with Organotin Hydrides.

(a) Trimethyltin hydride (0.24 g, 1.4 mmole) and $(CH_3)_3SiCF = CF_2$ (0.204 g, 1.3 mmole) were allowed to react at 25° for 24 hours. There was no visible reaction and vacuum fractionation gave the starting materials quantitatively. In a similar experiment using identical quantities, the reaction mixture was allowed to stand at 25° for two weeks. A trace of white solid was deposited but recovery of the reactants was essentially quantitative.

(b) Trimethyltin hydride (0.40 g, 2.4 mmole) and $(CH_3)_3SiCF = CF_2$ (0.40 g, 2.4 mmole) were heated at 55° for 60 hours. A white solid was deposited, which was identified spectroscopically as trimethyltin fluoride (0.228 g, <u>ca</u>. 50 % yield) (96). Vacuum fractionation gave incomplete separation, but an examination of the infrared spectrum of the gas phase mixture showed the presence of both reactants and at least four reaction products. Gas chromatography on a silicon QF-1 columnat 170°

gave pure products which were identified by their characteristic infrared and proton n.m.r. spectra (Tables 2 and 9). From the peak areas of the latter spectra the percentage of each component in the total reaction mixture could be determined. The products were cis-$CFH = CFSi(CH_3)_3$ (36 %), trans-$CFH = CFSi(CH_3)_3$ (5 %), $CF_2 = CHSi(CH_3)_3$ (41 %), and $(CH_3)_3SiC_2H_2F$ (18 %).

Trimethyltin hydride (0.54 g, 3.3 mmole) and $(CH_3)_3SiCF = CF_2$ (0.51 g, 3.3 mmole) were heated in 1 ml. of butyronitrile at 55° for 40 hours. A white solid was deposited, which was identified spectroscopically as trimethyltin fluoride (0.24 g, ca 40 % yield). Examination of the infrared spectrum of the gas phase mixture confirmed the presence of the same products as obtained by heating the neat reactants. The proton n.m.r. spectrum (Table 9) of this mixture was recorded and from its integration the following percentage of each component in the total reaction mixture was obtained:- cis-$CFH = CFSi(CH_3)_3$ (40 %), trans $CFH = CFSi(CH_3)_3$ (6 %), $(CH_3)_3SiCH = CF_2$ (38 %) and $(CH_3)_3SiC_2H_2F$ (16 %).

(c) Trimethyltin hydride (0.54 g, 3.3 mmole) and $(CH_3)_3SiCF = CF_2$ (0.51 g, 3.3 mmole) were exposed to ultraviolet irradiation at 25° for ten hours. A trace of trimethyltin fluoride, identified spectroscopically was deposited, as well as a small amount of metallic tin. Vacuum fractionation gave, at -78°, a negligible amount of the two reactants, and a high yield (0.773 g) of a very involatile liquid at -23°. This was identified unambiguously, from infrared and n.m.r. studies (Tables 6 and 14) as a mixture of the two addition compounds, $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$, and $(CH_3)_3SiCF(Sn(CH_3)_3)CF_2H$ in the ratio 3:2. The total yield of addition products was 77 %.

The addition products are stable under vacuum at 25° for about 4 hours, after which white crystals are slowly deposited. After one week, all liquid had disappeared and only a white solid remained. At this stage, the volatile products were removed and identified spectroscopically (Tables 2 and 9) as $(CH_3)_3SiCH = CF_2$ and cis-$(CH_3)_3SiCF = CFH$ formed in the ratio 2:1 respectively. The remaining white solid was shown to be pure trimethyltin fluoride. The addition products are stable at 80° for only a few minutes, while at 100° decomposition is very rapid to give trimethyltin fluoride and a complex mixture of volatile products. Because of the instability of the addition products, completely satisfactory analytical data could not be obtained. Anal. Calcd. for $C_8H_{19}F_3SiSn$: C, 30.12 %; H, 5.95 %; M.W., 319. Found: C, 31.21 %; H, 6.50 %; M.W. (in benzene osmometrically), 368. Further characterization was obtained by alkaline hydrolysis of the products. A sample (0.110 g, 0.344 mmole) was hydrolyzed with 20% sodium hydroxide solution at 25°. The only volatile product was trifluoroethylene (0.028 g, 0.34 mmole) characterized spectroscopically (125).

(d) Trimethyltin hydride (0.24 g, 1.4 mmole) and $(CH_3)_3SiCF = CF_2$ (0.204 g, 1.3 mmole) were sealed with 80 mg of azobisisobutyronitrile and allowed to react at 35° for 10 hours. Examination of the reaction mixture then showed only the starting materials, which were accordingly re-sealed with a further sample (80 mg) of azobisisobutyronitrile and kept at 50° for a further 10 hours. Vacuum fractionation gave a trace of non-condensible gas, presumably a mixture of hydrogen and nitrogen but the bulk of the material (0.221 g, 54 % yield), condensed at -23°. It was spectroscopically identified (Tables 6 and 14) as a mixture of the two addition products, $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$ and $(CH_3)_3SiCF(Sn(CH_3)_3)$-CF_2H, in a 3:2 ratio respectively.

The fractions which condensed at -78° and -196° were shown spectroscopically to be mixtures of $(CH_3)_3SiCH = CF_2$, cis- and trans-$(CH_3)_3SiCF = CFH$, and $(CH_3)_3SiC_2H_2F$, with the first two compounds being the major components. A mixture of metallic tin, trimethyltin fluoride and azobisisobutyronitrile remained in the reaction tube.

(e) Trimethyltin hydride (0.247 g, 1.5 mmole) and $(CH_3)_3SiCF = CF_2$ (0.23 g, 1.5 mmole) were sealed with hydroquinone (0.157 g) and irradiated for 10 hours at 25-50°. A small amount of hydrogen was obtained, but the bulk of material condensed in the -23° trap, with very small amounts in the -78° and -196° traps. The -23° fraction (0.287 g) was spectroscopically identical to the mixture of addition products obtained previously, and corresponded to a 62 % yield. The infrared spectra of the -78° and -196° fraction showed $(CH_3)_3SiCF = CF_2$ and its reduced products such as $(CH_3)_3SiC_2F_2H$ to be present, but they were insufficient for full characterization. Trimethyltin fluoride, some metallic tin, and hydroquinone remained in the reaction tube.

(f) Phenoxyl (421 mg.) prepared by the method of Bartlett and Funahashi (26) and azobisisobutyronitrile (82 mg.) with a 2 ml. of dry benzene were taken in a pyrex Carius tube, and trimethyltin hydride (0.265 g, 1.6 mmole) and $(CH_3)_3SiCF = CF_2$ (0.247 g, 1.6 mmole) were then added under vacuum. The reaction mixture was heated at 50° for 10 hours. On opening the tube, a small amount of non-condensible gas was first pumped off and all volatile materials were removed to leave a darkred solid as described by Bartlett and Funahashi (26). Vacuum fractionation of the volatiles gave $(CH_3)_3SiCF = CF_2$ (0.192 g) and trimethyltin hydride (0.260 g). No other compound was present.

(g) Dimethyltin dihydride (0.225 g, 1.5 mmole) and $(CH_3)_3SiCF = CF_2$ (0.462 g, 3.0 mmole) were allowed to react at 60° for 24 hours. The infrared spectrum (gas phase) of the volatile products showed a band at 1695 cm^{-1} (C = C stretch) characteristic of cis-$CFH = CFSi(CH_3)_3$, with a shoulder at 1665 cm^{-1} characteristic of $(CH_3)_3SiCH = CF_2$, but the amounts were so small that the proton n.m.r. spectrum showed only $(CH_3)_2SnH_2$ and $(CH_3)_3SiCF = CF_2$. From the reaction tube, a trace of dimethyltin difluoride (0.002 g) was recovered, from which it could be calculated that the reaction was only about 1 % complete.

(h) Dimethyltin dihydride (0.225 g, 1.5 mmole) and $(CH_3)_3SiCF = CF_2$ (0.462 g, 3.0 mmole) were irradiated at 25° for 16 hours, leading to the extensive formation of a white solid. A mixture of methane and hydrogen (total pressure 4 mm) was present in the tube on opening, and was pumped off. The infrared spectrum (gas phase) of the volatiles showed the presence of cis- and trans-$CFH = CFSi(CH_3)_3$, $(CH_3)_3SiCH = CF_2$, and $(CH_3)_3SiC_2H_2F$, based on the observed C = C stretching frequencies (Table 2). Confirmation was obtained from the proton n.m.r. spectrum, which on integration showed the percentage composition to be cis-$CFH = CHSi(CH_3)_3$ 29 %, trans-$CFH = CFSi(CH_3)_3$ 5.5 %, $(CH_3)_3SiCH = CF_2$ 49%, and $(CH_3)_3SiC_2H_2F$ 16.5 %. From the reaction tube, dimethyltin difluoride (0.223 g) was recovered, corresponding to 80 % complete reaction.

(ii) Reactions of Dimethylbis(perfluorovinyl)silane with Organotin Hydrides.

(a) Trimethyltin hydride (0.72 g, 4.5 mmole) and $(CH_3)_2Si(CF = CF_2)_2$ (0.48 g, 2.18 mmole) were allowed to react at 25° for one week. There was no visible reaction, and no non-condensible gas was formed. Vacuum fractionation lead to complete recovery of the reactants.

(b) In a similar reaction, the mixture was heated at 55° for 45 hours. A small amount of solid was deposited and a trace of a non-condensible gas was pumped off. Satisfactory separation by vacuum fractionation could not be achieved although infrared spectra and proton n.m.r. spectra showed the presence in small and decreasing amounts of $(CH_3)_2Si(CH = CF_2)_2$, cis- and trans-$(CFH = CF)_2Si(CH_3)_2$, and $(CH_3)_2Si(C_2H_2F)_2$ with characteristic infrared C = C stretching frequencies at 1665, 1700, 1722, and 1625 cm^{-1} respectively, in addition to the starting materials (Table 3). However, the amounts of these products were too small to determine quantitatively even by integration of the n.m.r. spectrum, and the quantity of trimethyltin fluoride recovered from the reaction tube showed that the reaction was only 15 % complete.

(c) Trimethyltin hydride (0.72 g, 4.5 mmole) and $(CH_3)_2Si(CF = CF_2)_2$ (0.48 g, 2.18 mmole) were irradiated for 4 hours at 25°, at the end of which time a small amount of white solid had been deposited. Other than some non-condensible gas, the volatile products were identified as trimethyltin hydride (0.02 g) and $(CH_3)_2Si(CF = CF_2)_2$ (0.082 g). There remained in the reaction tube an involatile liquid which was washed out with cyclohexane, and examined spectroscopically after removal of the solvent. The infrared and proton n.m.r. spectra (Tables 6 and 17) showed the material to be a mixture of the addition products of $(CH_3)_3SnH$ and $(CH_3)_2Si(CF = CF_2)_2$, which could not be separated chromatographically because of instability. On standing at 25°, decomposition occurred slowly with the deposition of trimethyltin fluoride. The yield (0.417 g) was 34.7 %.

(d) Trimethyltin hydride (0.36 g, 2.25 mmole) and $(CH_3)_2Si(CF = CF_2)$ (0.24 g, 1.1 mmole) with azobisisobutyronitrile (50 mg.) were heated at 55° for 10 hours. The infrared spectrum (gas phase) of the volatile products showed, from the C = C stretching frequencies, the presence of $-CF = CFH$, $-C_2H_2F$ and $-CH = CF_2$ groups, but separation of this complex mixture was not attempted. The reaction tube contained some trimethyltin fluoride and azobisisobutyronitrile, but none of the involatile liquid addition products.

(e) Dimethyltin dihydride (0.127 g, 0.85 mmole) and $(CH_3)_2Si(CF = CF_2)_2$ (0.186 g, 0.85 mmole) were allowed to react at room temperature. After 2 days, a white solid had appeared and this became grey in color after another 15 days. The infrared spectrum (gas phase) of the volatile reaction products showed the presence of $-CF = CFH$ and $-CH = CF_2$ groups in addition to considerable amounts of the starting materials. The grey solid (0.026 g) was washed out of the tube, examined, and found to be mainly metallic tin with a little dimethyltin difluoride.

(f) Dimethyltin dihydride (0.161 g, 1.07 mmole) and $(CH_3)_2Si(CF = CF_2)_2$ (0.235 g, 1.07 mmole) were allowed to react at 55° for 8 hours. White to yellow solid was deposited and a small amount of non-condensible gas was pumped off. Spectroscopic examination (infrared and proton n.m.r., Tables 3 and 9) showed the presence of <u>cis</u>- and <u>trans</u>-HCF = CF-, $-CH = CF_2$, and $-C_2H_2F$ groups, with <u>cis</u>-HCF = CF- and $-CH = CF_2$ being the most abundant. Only traces of the original reactants were still present. From the residue in the reaction tube, dimethyltin difluoride (0.158 g) was extracted, corresponding to a 79 % yield.

(g) Dimethyltin dihydride (0.323 g, 2.17 mmole) and $(CH_3)_2Si(CF = CF_2)_2$ (0.475 g, 216 mmole) were irradiated for 30 minutes at 25°. Treatment of the reaction mixture as in the last experiment showed the volatiles to consist of $(CH_3)_2Si-$ derivatives containing <u>cis</u>- and <u>trans</u>-CFH = CF-, $-CH = CF_2$, and $-C_2H_2F$ groups, with those containing <u>cis</u>-CFH = CF- and $-CH = CF_2$ being the major products. Some of the original reactants were also present.. From the residue in the tube, dimethyltin difluoride (0.165 g) was extracted, being a 41 % yield.

5. The Reactions of Organotin Hydrides with Perfluorovinyl Germanium and Tin Compounds.

In all of the reactions described below, the reaction mixture was worked up as described in the preceeding section for silicon compounds.

(i) Reactions of Trimethylperfluorovinylgermane with Organotin Hydrides

(a) Trimethyltin hydride (0.225 g, 1.36 mmole) and $(CH_3)_3GeCF = CF_2$ (0.27 g, 1.36 mmole) were allowed to react at 25° for 10 days. There was no visible reaction and vacuum fractionation gave the starting materials quantitatively.

(b) Trimethyltin hydride (0.33 g, 2 mmole) and $(CH_3)_3GeCF = CF_2$ (0.395 g, 2 mmole) were heated at 55° for 30 hours. A white solid was deposited, which was identified spectroscopically as trimethyltin fluoride (0.145 g, <u>ca</u>. 40 % yield). Examination of the infrared spectrum of the gas phase mixture showed the presence of both reactants and at least four reaction products. The proton n.m.r. spectrum (Table 10) of this mixture was recorded and from its integration the following percentage of each component in the total reaction mixture was obtained:- <u>cis</u>-$CFH = CFGe(CH_3)_3$ (45 %, <u>trans</u>-$CFH = CFGe(CH_3)_3$ (6 %), $CF_2 = CHGe(CH_3)_3$ (40 %) and $(CH_3)_3GeC_2H_2F$ (9 %). Gas chromatography on a silicone QF-I column at 150° gave pure products which were identified by their characteristic infrared spectra (Table 4).

(c) Trimethyltin hydride (0.45 g, 2.7 mmole) and $(CH_3)_3GeCF = CF_2$ (0.54 g, 2.7 mmole) were exposed to ultraviolet irradiation at 25° for eight hours. A trace of trimethyltin fluoride, identified spectroscopically was deposited, as well as a small amount of metallic tin. Vacuum fractionation gave, at -78° a small amount of cis-CFH = CFGe$(CH_3)_3$ and trimethyltin hydride and a high yield (0.72 g, 73 %) of a slightly volatile liquid at -23°. This was identified unambiguously, from infrared and n.m.r. studies (Tables 7 and 15) as a mixture of two addition products $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ and $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ in the ratio 2:5.

This mixture of addition products is unstable at room temperature. A small amount was sealed into a 5 mm. pyrex tube with 1 ml. of cyclohexane, and left at room temperature for 24 hours. Then its proton n.m.r. spectrum was recorded in the same glass tube. This showed a very small amount of $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ still to be present along with a considerable amount of cis-CFH = CFGe$(CH_3)_3$ and some $(CH_3)_3SnF$. The original amount of $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ remained unchanged. A similar sample of the addition products was left at 55° for two hours. Its proton n.m.r. spectrum showed the complete disappearance of $(CH_3)_3GeCF(Sn(CH_3)_3)$-CF_2H with the formation of cis-CFH = CFGe$(CH_3)_3$ and elimination of $(CH_3)_3SnF$. But this time a small amount of $(CH_3)_3GeCH = CF_2$ also appeared with a decrease in the amount of $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$. Another sample of the addition products $(CH_3)_3GeCF(Sn(CH_3)_3)CF_2H$ and $(CH_3)_3GeCFHCF_2Sn(CH_3)_3$ in the ratio 2:5 was sealed into a glass tube with 1.5 ml. of cyclohexane and left at 55° for 24 hours. A considerable amount of $(CH_3)_3SnF$ was deposited in the tube. The volatiles were transferred to a 5 mm. glass tube under vacuum, and the proton n.m.r. spectrum showed cis-CFH = CFGe$(CH_3)_3$ and $(CH_3)_3GeCH = CF_2$ in the ratio of 1:2. M.W. (in benzene osmometrically), 365, Calcd. M.W. 363.3. Further characterization was obtained by alkaline hydrolysis of the products. A sample (0.3063 g, 0.844 mmole) was hydrolyzed with 20 % potassium hydroxide alcoholic solution. The only volatile product was trifluoroethylene (0.068 g, 0.84 mmole) characterized spectroscopically (125).

(d) Trimethyltin hydride (0.45 g, 2.7 mmole) and $(CH_3)_3GeCF = CF_2$ (0.54 g, 2.7 mmole) were sealed with 50 mg. of azobisisobutyronitrile and allowed to react at 55° for eight hours. Examination of the reaction mixture gave a small amount of a non-condensible gas, presumably a mixture of hydrogen and nitrogen along with <u>cis</u>-$CFH = CFGe(CH_3)_3$ as the main product, and $(CH_3)_3GeCH = CF_2$ and $(CH_3)_3GeC_2H_2F$ in about equal amounts, these being identified by their characteristic C = C stretching frequencies at 1700, 1665 and 1625 cm^{-1} respectively. A mixture of trimethyltin fluoride, metallic tin and azobisisobutyronitrile remained in the reaction tube.

(e) Trimethyltin hydride (0.112 g, 0.68 mmole) and <u>cis</u>-$CFH = CFGe(CH_3)_3$ (0.123 g, 0.68 mmole) were allowed to react at 55° for 10 hours. Vacuum fractionation of the volatile products gave $(CH_3)_3GeC_2H_2F$ as the main reaction product with a characteristic C = C stretching frequency at 1625 cm^{-1}. Another band was observed at 1725 cm^{-1} (C = C stretch) characteristic of <u>trans</u>-$CFH = CFGe(CH_3)_3$. Trimethyltin fluoride remained in the reaction tube and was identified spectroscopically.

(f) Dimethyltin dihydride (0.204 g, 1.36 mmole) and $(CH_3)_3GeCF = CF_2$ (0.27 g, 1.36 mmole) were allowed to react at room temperature for 10 days. The infrared spectrum of the volatile products showed a strong band at

1625 cm^{-1} (C = C stretch) characteristic of $(CH_3)_3GeC_2H_2F$ and two other medium bands at 1700 and 1665 cm^{-1}, characteristic of (C = C stretch) cis-$CFH = CFGe(CH_3)_3$ and $(CH_3)_3GeCH = CF_2$ respectively. However, the amounts were so small that the proton n.m.r. spectrum showed only $(CH_3)_2SnH_2$ and $(CH_3)_3GeCF = CF_2$. From the reaction tube a small amount (0.008 g) of $(CH_3)_2SnF$ was recovered, from which it could be calculated that the reaction was about 3 % complete.

(g) Dimethyltin dihydride (0.204 g, 1.36 mmole) and $(CH_3)_3GeCF = CF_2$ (0.27 g, 1.36 mmole) were irradiated at 25° for 6 hours, leading to the extensive formation of a white solid. A mixture of methane and hydrogen present in the reaction tube was pumped off. The infrared spectrum (gas phase) of the volatiles showed the presence of cis-$CFH = CFGe(CH_3)_3$, $(CH_3)_3GeCH = CF_2$, $(CH_3)_3)GeC_2H_2F$ and trans-$CFH = CFGe(CH_3)_3$, based on the observed C = C stretching frequencies (Table 4) and listed in the order of decreasing concentration. From the reaction tube, dimethyltin difluoride (0.125 g) was recovered, corresponding to 50 % complete reaction.

(ii) Reactions of Dimethylbis(perfluorovinyl)germane with Organotin Hydrides.

(a) Trimethyltin hydride (0.33 g, 2 mmole) and $(CH_3)_2Ge(CF = CF_2)_2$ (0.264 g, 1 mmole) were allowed to react at 25° for 10 days. There was no visible reaction and vacuum fractionation led to complete recovery of the reactants.

(b) Trimethyltin hydride (1.29 g, 7.8 mmole) and $(CH_3)_2Ge(CF = CF_2)_2$ (0.875 g, 3.3 mmole) were allowed to react at 55° for 20 hours. A considerable amount of white solid was deposited and a trace of a non-condensible gas was pumped off. Infrared and ^1H n.m.r. spectra of the volatiles showed the presence of $-CF = CFH$ (cis), $-CH = CF_2$, $-C_2H_2F$ and $-CF = CFH$ (trans) groups, with characteristic infrared C = C stretching frequencies at 1700, 1665, 1628 and 1722 cm^{-1} respectively, these groups being listed in the order of decreasing amounts. Complete spectroscopic data are listed in Tables 5 and 10. From the residue in the reaction tube 0.9023 g of $(CH_3)_3SnF$ was extracted, corresponding to 63 % reaction.

(c) Trimethyltin hydride (0.898 g, 5.4 mmole) and $(CH_3)_2Ge(CF = CF_2)_2$ (0.719 g, 2.72 mmole) were irradiated at 25° for 5 hours, at the end of which time a very small amount of metallic tin and a white solid had deposited. Other than a small amount of a non-condensible gas, the only volatile product was a negligible amount of trimethyltin hydride. There remained in the reaction tube an involatile liquid which was washed out with cyclohexane, and examined spectroscopically after removal of the solvent. The infrared and proton spectra (Tables 7 and 18) showed the material to be a mixture of three addition products of $(CH_3)_3SnH$ and $(CH_3)_3GeCF = CF_2$, listed in Table 18, which could not be separated chromatographically due to instability. On standing at 25° decomposition occurred slowly with the deposition of $(CH_3)_3SnF$ and formation of $-CF = CFH$ (cis) and $-CH = CF_2$ groups with characteristic C = C stretching frequencies at 1700 and 1665 cm^{-1} respectively.

(d) Dimethyltin dihydride (0.29 g, 2 mmole) and $(CH_3)_2Ge(CF = CF_2)_2$ (0.53 g, 2 mmole) were allowed to react at room temperature for 10 days. A white to yellow solid appeared in the reaction tube. The infrared spectrum (gas phase) of the volatile reaction products showed the presence of $-CF = CFH$, $-CH = CF_2$ and $-C_2H_2F$ groups, in addition to considerable amounts of the starting materials. The residue (0.003 g) in the reaction tube was washed out, examined, and found to be mainly dimethyltin difluoride with a little metallic tin.

(e) Dimethyltin dihydride (0.76 g, 5 mmole) and $(CH_3)_2Ge(CF = CF_2)_2$ (1.32 g, 5 mmole) were allowed to react at 55° for 8 hours. A considerable amount of white to black solid was deposited. Non-condensible gas, a mixture of hydrogen and methane was pumped off. The ^1H n.m.r. spectrum of the volatile products (Table 10) confirmed the presence of four reaction products, in addition to some unidentified peaks, these being listed with the percentage of each component in the total reaction mixture, as determined by integration of the ^1H n.m.r. spectrum. The products were <u>cis-</u>$(CFH = CF)_2Ge(CH_3)_2$ (33.3 %), $(CH_3)_2Ge(CH = CF_2)_2$ (41.7 %), <u>trans-</u>$(CFH = CF)_2Ge(CH_3)_2$ (13.8 %) and $(CH_3)_2Ge(C_2H_2F)_2$ (11.1 %). Gas chromatography on a silicone QF-1 column at 150° gave pure products, in addition to unreacted $(CH_3)_3SnH_2$ and $(CH_3)_2Ge(CF = CF_2)_2$, which were identified by their characteristic infrared and proton n.m.r. spectra (Tables 5 and 10). From the reaction tube 0.552 g of $(CH_3)_2SnF_2$ with some metallic tin was recovered.

(f) Dimethyltin dihydride (0.29 g, 2 mmole) and $(CH_3)_2Ge(CF = CF_2)_2$ (0.53 g, 2 mmole) were irradiated at 25° for 1 hour. A white solid was deposited and the non-condensible gas was pumped off. The infrared spectrum (gas phase) of the volatile products confirmed the presence of

$(CH_3)_2Ge$- derivatives containing $-CF = CFH$, $-CH = CF_2$ and $-C_2H_2F$ groups, based on their C = C stretching frequencies, (Table 5), but the amounts were so small that the proton n.m.r. spectrum showed only $(CH_3)_2SnH_2$ and $(CH_3)_2Ge(CF = CF_2)$. From the reaction tube 0.061 g of dimethyltin difluoride containing a trace of metallic tin was recovered.

(iii) Reactions of Trimethylperfluorovinyltin with Trimethyltin Hydride

(a) Trimethyltin hydride (0.45 g, 2.8 mmole) and $(CH_3)_3SnCF = CF_2$ (0.682 g, 2.8 mmole) were irradiated at 25° for 1 hour. A considerable amount of white solid was deposited. A negligible amount of non-condensible gas was pumped off. The infrared spectrum of the volatile reaction products confirmed (42) the presence of cis-$CFH = CFSn(CH_3)_3$ and trans-$CFH = CFSn(CH_3)_3$, in addition to some unreacted $(CH_3)_3SnCF = CF_2$. This mixture was sealed in a 5 mm. glass tube and its ^1H n.m.r. spectrum was recorded. This again confirmed the presence of cis-$CFH = CFSn(CH_3)_3$ and trans-$CFH = CFGe(CH_3)_3$, from the available spectroscopic data (42). The amounts of the reaction products in the total reaction mixture were determined by integration of the ^1H n.m.r. spectrum, which gave cis-$CFH = CFSn(CH_3)_3$ (78 %) and trans-$CFH = CFSn(CH_3)_3$ (18 %). Trimethyltin fluoride (0.406 g) was recovered from the reaction tube, corresponding to 80% complete reaction.

(b) Trimethyltin hydride (0.22 g, 1.4 mmole) and $(CH_3)_3SnCF = CF_2$ (0.682 g, 2.8 mmole) and 1 ml. of cyclohexane were irradiated at 25° into a 5 mm. pyrex glass tube. After one hour, a considerable amount of white solid ($(CH_3)_3SnF$) was visible in the reaction tube. Immediately the ^1H n.m.r. spectrum of the reaction mixture was recorded in the same 5 mm.

reaction tube, and this confirmed the presence of the addition products $((CH_3)_3Sn)_2CFCF_2H$ and $(CH_3)_3SnCFHCF_2Sn(CH_3)_3$, spectroscopic data being given in Table 16. From the integration of the proton n.m.r. spectrum the ratio of $((CH_3)_3Sn)_2CFCF_2H$ to $(CH_3)_3SnCFHCF_2Sn(CH_3)_3$ was 1:1. The tube containing the reaction mixture was left at room temperature for 6 hours, after which time extensive elimination of $(CH_3)_3SnF$ had taken place, and the proton n.m.r. spectrum of the reaction products in the same reaction tube confirmed the presence of only one reaction product i.e. cis-$CFH = CFSn(CH_3)_3$.

6. The Reactions of Organotin Hydrides with Pentacarbonyl-perfluorovinylrhenium and Pentacarbonyl-perfluoropropenylrhenium.

Pentacarbonyl-perfluorovinylrhenium was prepared (52 % yield) by bubbling C_2F_4 through a solution of $(CO)_5ReNa$ in THF at -78°, by the method described by Stone et al. (59a). Similarly, pentacarbonyl-perfluoropropenylrhenium was prepared (57 % yield) by passing $CF_2 = CFCF_3$ through a solution of $(CO)_5ReNa$ in THF.

(a) Trimethyltin hydride (0.1 g, 0.6 mmoles) and $(CO)_5ReCF = CF_2$ (0.234 g, 0.57 mmoles) were allowed to react in 3 ml. of benzene at 25° for one week. There was no visible reaction and the vacuum fractionation lead complete recovery of the reactants.

(b) Trimethyltin hydride (0.215 g, 1.3 mmoles) and $(CO)_5ReCF = CF_2$ (0.54 g, 1.3 mmoles) were sealed with 50 mg. of azobisisobutyronitrile and 4 ml. of benzene and allowed to react at 50° for 20 hours. The reaction tube was connected to the vacuum line and opened at -196°C. A small amount of a non-condensable gas, presumably a mixture of hydrogen, nitrogen and methane was present in the tube and was pumped off. The volatiles were removed from the reaction tube at 0° and 5 mm. pressure, while a yellowish residue remained in the tube. Vacuum fractionation of the volatiles gave only benzene and a small amount of unreacted trimethyltin hydride.

The reaction tube was disconnected from the vacuum line and the solids washed out with tetrahydrofuran under a nitrogen atmosphere, and filtered through a sintered glass funnel. Thus a white residue (0.155 g, ca. 70 % yield) was obtained, and identified spectroscopically to be trimethyltin fluoride. THF was removed from the filtrate, by maintaining it at 0° and 2 mm. pressure, and a yellow solid was obtained after complete removal of the solvent. The infrared spectrum of this material (nujol mull) showed three new C = C stretching absorptions (cm^{-1}) at 1675 s, 1625 m and 1615 m in addition to the ν(C = C) for unreacted $(CO)_5ReCF = CF_2$ at 1705 cm^{-1}. This solid mixture was dissolved in acetonitrile and its ^1H n.m.r. spectrum was recorded, (Table 19), which confirmed the presence of trans-$CFH = CFRe(CO)_5$ (60 %), cis-$CFH = CFRe(CO)_5$ (13 %), and $(CO)_5ReCH = CF_2$ (27 %). After recording the proton spectrum, acetonitrile was removed from this mixture at 0°, under vacuum. The remaining solids were then sublimed under reduced pressure at room temperature, over a -78° cold probe. During the first 10 minutes, $(CO)_5ReCF = CF_2$ and cis-$CFH = CFRe(CO)_5$ were collected. The presence of cis-$CFH = CFRe(CO)_5$ was confirmed by its proton spectrum and the corresponding C = C stretching absorption at 1625 cm^{-1}. After the removal of cis-$CFH = CFRe(CO)_5$ from the mixture, trans-$CFH = CFRe(CO)_5$ and $(CO)_5ReCF = CF_2$ were collected on the cold probe for the next 20 minutes. The proton spectrum of this fraction corresponded to trans-CFH = CFRe(CO)$_5$ and the C = C stretching absorption at 1675 cm^{-1} present in this fraction was thus assigned to trans-CFH = CFRe(CO)$_5$. The infrared spectrum of the remaining solid material at the bottom of the sublimation flask showed weak absorptions at 1705 and 1675 cm^{-1} and a strong absorption at 1615 cm^{-1}. The proton spectrum of this material (Table 19) showed the presence of only (CO)$_5$ReCH = CF$_2$, this indicating that trans-CFH = CFRe(CO)$_5$ whose presence in this mixture was indicated by the infrared spectrum is still there but in a very small amount which cannot be detected by n.m.r. spectrum. Hence the C = C stretching absorption at 1615 cm^{-1} was assigned to (CO)$_5$ReCH = CF$_2$.

The products trans-CFH = CFRe(CO)$_5$, cis-CFH = CFRe(CO)$_5$ and (CO)$_5$ReCH = CF$_2$ could not be separated from (CO)$_5$ReCF = CF$_2$. Hence, due to the overlapping of absorptions in the CO and C - F stretching region, individual assignments could not be made for the new reaction products.

In the following experiments (c - h) the reaction mixture was worked up as (b) above, and the products were identified by their infrared and proton n.m.r. spectra.

(c) Trimethyltin hydride (0.1 g, 0.6 mmoles) and (CO)$_5$ReCF = CF$_2$ (0.237 g, 0.58 mmoles) were sealed into a silica tube with 2 ml. of benzene and exposed to ultraviolet irradiation at 35°. After 36 hours, a considerable amount of solid had appeared in the tube, the walls of which were covered with a yellow material. Examination of the reaction mixture gave a small amount of a non-condensible gas, presumably a mixture of hydrogen and methane, along with unreacted trimethyltin hydride. Some unreacted (CO)$_5$ReCF = CF$_2$ was still present in the reaction mixture (C = C stretching absorption at 1705 cm^{-1}), along with trans-CFH = CFRe(CO)$_5$

as the main product, and <u>cis</u>-CFH = CFRe(CO)$_5$ and (CO)$_5$ReCH = CF$_2$ in about equal amounts, these being identified by their characteristic C = C stretching frequencies at 1675, 1625 and 1615 cm^{-1} respectively. From the reaction tube, trimethyltin fluoride (0.0485 g) was recovered, corresponding to 47.6 % complete reaction.

A sample (0.15 g), containing (CO)$_5$ReCF = CF$_2$ and <u>cis</u>-CFH = CFRe(CO)$_5$ in approximately equal amounts, was dissolved in 2 ml. of benzene and exposed to ultraviolet irradiation at 35° for 8 hours. The infrared spectrum of this mixture showed a strong band at 1675 cm^{-1} (C = C stretch) characteristic of <u>trans</u>-CFH = CFRe(CO)$_5$, along with the bands at 1705 and 1625 cm^{-1}, corresponding to the starting materials (CO)$_5$ReCF = CF$_2$ and <u>cis</u>-CFH = CFRe(CO)$_5$ respectively. The band at 1625 cm^{-1} (C = C stretch) characteristic of <u>cis</u>-CFH = CFRe(CO)$_5$ had grown weak and was about 25 % of its original intensity.

(d) Trimethyltin hydride (0.1 g, 0.6 mmoles) and (CO)$_5$ReCF = CF$_2$ (0.234 g, 0.57 mmoles) were sealed with 3 ml. of butyronitrile and allowed to react at 45°. After 48 hours a small amount of a white solid had been deposited. Unreacted trimethyltin hydride and solvent were removed from the reaction mixture. The infrared spectrum of this mixture showed a strong band at 1705 cm^{-1} (C = C stretch) characteristic of (CO)$_5$ReCF = CF$_2$, and two weak bands of almost equal intensity at 1625 and 1615 cm^{-1} corresponding to the C = C stretching frequencies of <u>cis</u>-CFH = CFRe(CO)$_5$ and (CO)$_5$ReCH = CF$_2$ respectively. From the reaction mixture, trimethyltin fluoride (0.018 g) was recovered, corresponding to 17 % complete reaction.

(e) Dimethyltin dihydride (0.2 g, 0.13 mmoles) and $(CO)_5ReCF = CF_2$ (0.54 g, 1.3 mmoles) were allowed to react in 4 ml. of benzene at 25° for 48 hours. There was no visible reaction and the vacuum fractionation gave the starting materials quantitatively. In a similar experiment using identical quantities, the reaction mixture was exposed to ultraviolet irradiation at 25° for 6 hours. A mixture of methane and hydrogen (total pressure 5 cm.) was present in the tube on opening, and was pumped off. The infrared spectrum of the gas phase mixture showed the presence of unreacted $(CH_3)_2SnH_2$. A white solid insoluble in benzene and THF, was separated from the other reaction products and identified spectroscopically as dimethyltin difluoride (0.0348 g, <u>ca</u>. 14 % yield).

The infrared spectrum (nujol mull) of the involatile products, (which weresoluble in THF and benzene), showed a band at 1705 s characteristic of (C = C stretching) $(CO)_5ReCF = CF_2$, and three other bands at 1675 s, 1625 m and 1615 m characteristic of (C = C stretching) <u>trans</u>-$CFH = CFRe(CO)_5$, <u>cis</u>-$CFH = CFRe(CO)_5$ and $(CO)_5ReCH = CF_2$ respectively. However, the amounts of these products were too small to be determined quantitatively even by integration of the n.m.r. spectrum.

(f) Trimethyltin hydride (0.29 g, 1.75 mmoles) and $(CO)_5ReCF = CFCF_3$ (0.8 g, 1.75 mmoles) were allowed to react at 45° in butyronitrile for one week. Examination of the infrared spectrum of the gas phase mixture showed the presence of a non-condensible gas, presumably a mixture of hydrogen and methane, and some unreacted trimethyltin hydride. The infrared spectrum of the involatiles in the reaction tube, confirmed the presence of unreacted $(CO)_5ReCF = CFCF_3$ and hexamethylditin (59 a, 95). The proton n.m.r. spectrum of this mixture did not show the presence of any vinylic proton. From the reaction tube, a gray solid (0.024 g) was recovered, which consisted of metallic tin and a trace of trimethyltin fluoride.

(g) Trimethyltin hydride (0.22 g, 1.33 mmoles) and $(CO)_5ReCF = CFCF_3$ (0.554 g, 1.23 moles) were sealed with 50 mg. of azobisisobutyronitrile and 4 ml. of benzene and allowed to react at 45° for one week. Examination of the gas phase mixture showed the presence of a non-condensible gas, presumably a mixture of hydrogen, nitrogen and methane. The infrared spectrum of the mixture in the reaction tube confirmed the presence of hexamethylditin and unreacted $(CO)_5ReCF = CFCF_3$ (95,59a).

(h) Trimethyltin hydride (0.25 g, 1.5 mmoles) and $(CO)_5ReCF = CFCF_3$ (0.685 g, 1.5 mmoles) were exposed to ultraviolet irradiation in benzene at 40°. After 50 hours, there was considerable decomposition and the reaction tube became black. Infrared examination of the gas phase mixture showed the presence of a non-condensible gas, presumably a mixture of hydrogen, methane and carbon monoxide, and unreacted trimethyltin hydride. Infrared spectrum of the involatile component showed the presence of unreacted $(CO)_5ReCF = CFCF_3$; the proton spectrum of this solid did not indicate any vinylic proton. From the reaction tube a small amount (0.0112 g) of trimethyltin fluoride was recovered.

7. The Reactions of Organotin Hydrides with Phosphonitrilic Halides.

$N_3P_3Cl_6$ (95 % trimer) obtained from Borden Chemical Co. Philadelphia, Penn., U.S.A. was used without further purification. $N_3P_3F_6$ was prepared by refluxing $N_3P_3Cl_6$ with NaF in nitrobenzene and was freed from the solvent by fractional distillation (126). The product thus obtained was passed several times over a column packed with AgF at 100° under vacuum (126). Thus pure $N_3P_3F_6$ was obtained (50 % yield). Anal. Calcd. for $N_3P_3F_6$: F, 45.78 %; N, 16.9 %; P, 37.33 %. Found: F, 45.83 %; N, 17.25 %; P, 36.07 %.

In the reactions described below, the components of the reaction mixture were separated by trap-to-trap fractionation, and each fraction was identified from its infrared and n.m.r. spectra. Any involatile material remaining in the reaction tube was examined spectroscopically.

(a) Trimethyltin hydride (0.33 g, 2 mmoles) and $N_3P_3F_6$ (0.50 g, 2 mmoles) were allowed to react at 50° in a 250 c.c. glass bulb. After 48 hours a yellow solid had deposited, which was identified spectroscopically as trimethyltin fluoride (0.013 g) containing a small amount of a rubber-like polymer. Vacuum fractionation gave trimethyltin hydride and $N_3P_3F_6$.

In a similar experiment dimethyltin dihydride (0.3 g, 2 mmoles) and $N_3P_3F_6$ (0.50 g, 2 mmoles) were allowed to react at 50° for 24 hours. A mixture of methane and hydrogen (total pressure 1.5 cm) was present in the glass bulb on opening, and was pumped off. The infrared and n.m.r. spectra of the volatiles showed the presence of dimethyltin dihydride and $N_3P_3F_6$. From the reaction bulb a yellow solid (0.102 g) was recovered, which was identified spectroscopically as a mixture of $(CH_3)_2SnF_2$ and $(CH_3)_2SnFH$ containing a small amount of a rubber-like material.

(b) Trimethyltin hydride (0.25 g, 1.5 mmoles) and $N_3P_3F_6$ (0.37 g, 1.5 mmoles) were allowed to react in benzene at 45° in a Carius tube. After 4 hours a white solid had deposited (0.025 g) which was identified as trimethyltin fluoride containing a small amount of a rubber-like material. A small amount of a non-condensible gas present in the tube was pumped off. The infrared and n.m.r. spectra of the volatiles showed the presence of only trimethyltin hydride and $N_3P_3F_6$. In two similar experiments using identical quantities, the reaction was repeated using butyronitrile and cyclohexane as the solvents, but again a small amount of a white solid was deposited and recovery of the reactants was essentially quantitative.

(c) Trimethyltin hydride (0.25 g, 1.5 mmoles) and $N_3P_3Cl_6$ (0.53 g, 1.5 mmoles) were allowed to react in benzene at 45° for 4 hours. Examination of the reaction mixture gave a small amount of a non-condensible gas, presumably a mixture of hydrogen and methane, along with unreacted trimethyltin hydride(0.212 g). A mixture of trimethyltin chloride and $N_3P_3Cl_6$ remained in the tube. In a similar experiment using identical quantities, the reaction was repeated using butyronitrile as the solvent, but again some trimethyltin chloride was formed and the recovery of the reactants was essentially quantitative.

(d) Trimethyltin hydride (0.99 g, 6 mmoles) and $N_3P_3F_6$ (0.25 g, 1.0 mmoles) were exposed to ultraviolet irradiation at 25° in benzene. After 3 hours a considerable amount of a white solid had deposited.

Other than some non-condensible gas, the volatile products were identified as trimethyltin hydride (0,65 g) and $N_3P_3F_6$ (0.20 g). From the reaction tube, a residue (0.45 g) consisting of trimethyltin fluoride and a rubber-like polymer was recovered. In a similar experiment using identical quantities, the reactants were heated to 40° with 80 mg. of azobisisobutyronitrile for 8 hours. Except for some trimethyltin fluoride and a polymeric material (0.48 g) only the starting materials were recovered.

(e) Trimethyltin hydride (0.25 g, 1.5 mmoles) and $N_3P_3Cl_6$ (0.53 g, 1.5 mmoles) were exposed to ultraviolet irradiation in benzene at 25°. After 8 hours a considerable amount of a white solid had deposited. Non-condensible gas, a mixture of hydrogen and methane, was pumped off. Infrared spectrum of the volatiles showed the presence of only trimethyltin hydride. From the reaction tube, a mixture of trimethyltin chloride, $N_3P_3Cl_6$ and a rubber-like material was extracted.

(f) Dimethyltin dihydride (0.3 g, 2 mmoles) and $N_3P_3F_6$ (0.50 g, 2 mmoles) were exposed to ultraviolet irradiation in benzene at 25°. After 4 hours a considerable amount of white solid had deposited. A non-condensible gas (total pressure 3 cm. in the tube), presumably a mixture of hydrogen and methane was pumped off. The infrared and n.m.r. spectra of the volatiles showed the presence of dimethyltin dihydride and $N_3P_3F_6$. From the reaction tube, a mixture (0.212 g) consisting of $(CH_3)_2SnF_2$, $(CH_3)_3SnFH$ and a rubber-like polymer was recovered.

(g) Dimethyltin dihydride (0.45 g, 3 mmoles) and $N_3P_3Cl_6$ (0.348 g, 1.0 mmole) were irradiated at 25° in benzene for 5 hours. Other than some non-condensible gas, the only volatile product was dimethyltin dihydride (0.21 g). From the reaction tube a white residue was recovered, which consisted of metallic tin, $(CH_3)_2SnCl_2$, $(CH_3)_2SnClH$, $N_2P_2Cl_6$ and a rubber-like polymer.

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