Reactions of organotin compounds. VIII. The reactions of tin hydrides with perfluorovinyl silicon compounds

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The reactions of trimethyltin hydride and dimethyltin dihydride with $(CH_3)_3SiCF=CF_2$ and $(CH_3)_2-Si(CF=CF_2)_2$ respectively have been investigated. Under thermal conditions, reaction led to organotin fluorides and fluorovinyl-silanes. However, under ultraviolet irradiation at 25°, addition products were isolated of which $(CH_3)_3SiCFHCF_2Sn(CH_3)_3$ and $(CH_3)_3SiCF[Sn(CH_3)_3]CF_2H$ were fully characterized. Evidence is presented which shows that these addition products are formed by a free radical process and that their decomposition to organotin fluorides and fluorovinyl-silanes proceeds *via* a β -fluorine elimination. Spectroscopic data are presented for a number of new organo-silanes.

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Introduction

In previous papers (1-4), we have described the behavior of organotin hydrides with unsaturated fluorocarbon derivatives of two types, firstly fluoro-olefins and secondly perfluorovinyl tin compounds. For the reactions with fluoroolefins convincing arguments were presented (1-3) that a free radical mechanism is involved in which the formation of radicals from the tin hydride is probably the rate-determining step. This is in agreement with other studies of tin hydride addition reactions (e.g. ref. 5), although it has been established (6, 7) that, under other circumstances, reactions of tin hydrides may occur via a polar mechanism. The process by which perfluorovinyltin compounds are converted by tin hydrides to derivatives containing --CF=CFH, --CH=CF₂, and --C₂H₂F groups (4) is even less fully understood. A free radical type behavior may well be involved either directly or alternatively though the addition of the hydride across the vinylic C = C bond, followed immediately by elimination of trimethyltin fluoride or dimethyltin difluoride. The present study was undertaken in order to obtain further information on this process. By using perfluorovinyl silanes 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, R₃Si and R₃Sn groups, but also because of variations in $d\pi$ -p π interactions in the M-C-C group (8, 9) when M is changed from Sn to Si.

Discussion

The conversion of perfluorovinyl to fluorovinyl groups with the accompanying formation of R_3SnF or R_2SnF_2 results from the reaction of organotin hydrides with perfluorovinyltin derivatives (4). There was no evidence that addition compounds were formed, even as transient intermediates, even though such addition has been observed (9) in the reaction of triphenyltin hydride and triphenylvinyltin to give 1,2-bis-(triphenyltin) ethane. Similarly, triphenyltin hydride adds across the C=C bond of vinylsilanes very readily (9).

 $(C_6H_5)_3SnH + CH_2 = CHSi(C_6H_5)_3$

 \rightarrow (C₆H₅)₃SnCH₂CH₂Si(C₆H₅)₃

However, no evidence was provided which would distinguish between the two possible isomers, that above and $(C_6H_5)_3$ SiCH[Sn $(C_6H_5)_3$]-CH₃. Addition reactions of perfluorovinylsilanes are also known, although frequently the elimination of a fluoride occurs readily. Thus triphenylsilyllithium adds to $(C_2H_5)_3$ SiCF= CF₂ and the resulting adduct loses lithium fluoride (10).

$$(C_2H_5)_3SiCF = CF_2 + (C_6H_5)_3SiLi$$

 \rightarrow (C₂H₅)₃SiCF=CFSi(C₆H₅)₃ + LiF

These are also the features of the reactions of organotin hydrides with perfluorovinyl-silanes.

Trimethyltin hydride did not react with $(CH_3)_3SiCF=CF_2$ at room temperature, even over a long period, but at 55° reaction occurs readily with the deposition of trimethyltin fluoride and formation of fluorovinyl-silanes, notably $(CH_3)_3SiCH=CF_2$, *cis*-CFH=CFSi- $(CH_3)_3$, *trans*-CFH=CFSi(CH_3)_3, and $(CH_3)_3$ -SiC_2H_2F, these being listed in the order of decreasing yield. This may be compared with the analogous reaction of the hydride with $(CH_3)_3$ -SnCF=CF₂ (4) where very little reaction

occurred after 18 h at 70°. When the hydride and the perfluorovinyl-silane were irradiated at room temperature, a high yield of the two possible addition products, (CH₃)₃SiCFHCF₂Sn(CH₃)₃ and (CH₃)₃SiCF[Sn(CH₃)₃]CF₂H, in the ratio 3:2 was obtained, with virtually no formation of trimethyltin fluoride. Although this mixture is stable at room temperature for a short period, trimethyltin fluoride is rapidly deposited to leave (CH₃)₃SiCH=CF₂ and cis-CFH=CFSi(CH₃)₃ in a 2:1 ratio. This latter ratio, together with the above ratio of the addition products, clearly indicates that (CH₃)₃SiCH=CF₂ has been formed from the adduct (CH₃)₃SiCFHCF₂Sn-(CH₃)₃, and *cis*-CFH=CFSi(CH₃)₃ from the other adduct (CH₃)₃SiCF[Sn(CH₃)₃]CF₂H, 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 $Sn-F_{6}$ distance is the smaller. This evidence for β -elimination is particularly significant with respect to the addition of fluoro-olefins across metal-metal bonds. We have previously shown, for example, that trifluoroethylene (11) reacts with $(CH_3)_3$ - $SnMn(CO)_5$ to give trimethyltin fluoride and cis- and trans-CFH=CFMn(CO)₅. The similarity of the hypothetical addition product (CH₃)₃SnCFHCF₂Mn(CO)₅ to the present addition compounds, and the above evidence for β -elimination, strongly suggest that the same type of process is involved in all these reactions, as has been suggested by Booth (12). The alternative process would be an α -elimination followed by a fluoride ion migration (13), which seems much less likely from energetic grounds alone.

The isolation of these addition products under ultraviolet irradiation can be compared with the products formed in the irradiation of trimethyltin hydride with trimethyl (perfluorovinyl) tin (4). In the latter case, no addition compounds were isolated, only the fluoroalkyl derivatives, *cis*- and *trans*-CFH=CFSn(CH₃)₃, (CH₃)₃-SnCH=CF₂, and (CH₃)₃SnC₂H₂F, and trimethyltin fluoride, but it now seems very probable that these resulted from a β -fluorine elimination of trimethyltin fluoride from unstable addition products. Moreover, the fact that in this latter case the principal product was *cis*-CFH=CFSn(CH₃)₃, in contrast to $(CH_3)_3$ -SiCH=CF₂ for the silane reaction, is further support for the β -fluorine elimination process. The hypothetical products $(CH_3)_3$ SnCFHCF₂-Sn(CH₃)₃ and $[(CH_3)_3$ Sn]₂CFCF₂H can *both* give *cis*-CFH=CFSn(CH₃)₃ by such an elimination, while for the silane only β -fluorine elimination from $(CH_3)_3$ SiCF[Sn(CH₃)₃]CF₂H can give *cis*-CFH=CFSi(CH₃)₃.

There remains the question of the mechanism by which the tin hydride adds across the vinylic C==C bond. As mentioned above, there is good evidence that tin hydride additions to olefins proceed via a free radical mechanism (4, 5). One argument supporting this is the fact that free radical sources readily initiate these additions at room temperature (5). In the present case, therefore, the addition of trimethyltin luydride to $(CH_3)_3SiCF=CF_2$ in the presence of azobisisobutyronitrile as a free radical source (5) was studied. The same mixture of addition products was isolated, in approximately the same ratio, although for extensive reaction, a temperature of 50° was necessary so that reasonable yields of the fluorovinyl decomposition products were also obtained. It seems that azobisisobutyronitrile certainly initiates the addition process although less effectively than for other olefins (5). This is consistent with the generally lower reactivity of the perfluorovinylic C=C bond. A similar reaction in which the effect of hydroquinone on the formation of the addition product was studied likewise led to a high yield of the addition products. This supports earlier statements (14, 15) that hydroquinone does not inhibit addition reactions of tin hydrides. A more effective inhibitor was found to be "galvinoxyl" (16) which, even in the presence of azobisisobutyronitrile, completely quenched the addition reaction. This contrasts with other reactions of tin hydrides (7, 17) where "galvinoxyl" had no effect on the rate of the addition reaction, but leaves no doubt that these additions to C=C bonds are indeed free radical processes.

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. In view of the greater reactivity of dimethyltin dihydride compared with trimethyltin hydride, and also of their probable structures, it is not too surprising that the addition compounds were not isolated. A further obvious extension was to examine the reactions of dimethylbis(perfluorovinyl)silane with organotin hydrides, particularly since with dihydrides cyclic compounds might result similar to that obtained (18) from diphenyltin dihydride and phenylacetylene. Trimethyltin hydride and (CH₃)₂Si(CF=CF₂)₂ did not react at room temperature and only very slowly at 55°. Ultra-violet irradiation at 25° gave as the major product an involatile liquid identified spectroscopically as a mixture of the addition products 1, 2, and 3.



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The mixture was unstable at room temperature, slowly depositing trimethyltin fluoride; nor was it possible to separate individual compounds from the mixture chromatographically due to this instability.

In the presence of azobisisobutyronitrile, trimethyltin hydride and $(CH_3)_2Si(CF=CF_2)_2$ at 55° gave more of the above addition products although some trimethyltin fluoride and volatile silanes containing -CF=CFH (*cis* and *trans*), $-CH=CF_2$, and $-C_2H_2F$ groups were formed in low yield. Similarly, 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, $-CH=CF_2$, and $-C_2H_2F$ groups were formed. In neither case could any addition product be separated or detected.

As in our previous study (4), considerable use was made of spectroscopic methods in characterizing new products, since fluorovinyl compounds have very characteristic infrared and nuclear magnetic resonance (n.m.r.) features. The trimethyl- and dimethyl-fluorovinyl silanes are completely analogous to the fluorovinyltin compounds described previously (4) and it is only necessary to list the data in Tables I and II. The characterization of the addition products of trimethyltin hydride and (CH₃)₃SiCF=CF₂ is based on the n.m.r. spectra which are shown in Fig. 1 (proton spectrum) with the numerical data tabulated in Tables III and IV. The proton spectrum clearly shows the presence of two compounds, each of which gives a complex pattern of eight lines in addition to signals from the methyl-Si and methyl-Sn protons. 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 atom. Hence the proton spectrum for each proton is of the ABX pattern. The spectra of closely related compounds have been discussed in considerable detail (19, 20), and hence a full analysis of the proton and ¹⁹F spectra is not given here. Each set of eight lines in the proton spectrum could be attributed to the signal of the ethane proton, split successively three times into doublets by coupling with the three nonequivalent fluorine nuclei. For one molecule, the coupling constants, J_{H-F} , were 62, 56, and 10 c.p.s. respectively and for the other 37, 44, and 10 respectively. For the proton of a $-CF_2H$ group, where the two fluorines are not equivalent, coupling constants of 55-65 c.p.s. are normally observed (e.g. ref. 21) while the second set of values is consistent (19) with the group -CFHCF₂-. The proton spectrum is thus interpreted in terms of a mixture of (CH₃)₃- $SiCFHCF_2Sn(CH_3)_3$ and (CH₃)₃SiCF[Sn- $(CH_3)_3$]CF₂H in a ratio of 3:2. From closely coincident values of H-F coupling constants it 636

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TABLE I Proton n.m.r. assignments for perfluorovinyl and fluorovinyl silanes					
Si X ₁					
C==C					
X ₃ X ₂	δ_{CH_3}	δ _{vinyI}	J_{12}	J_{23}	J_{13}
(CH ₃) ₃ Si F					
C=C	-0.10	—	—		
F F					
(CH ₃) ₃ SI H	-0.18	-6 18	75		22
FF	0.10	quartet	10		
(cis)					
(CH ₃) ₃ Si F	0.22	C 00	70	10	
E H	-0.32	quartet	70	12	
(trans)					
(CH ₃) ₃ Si F				_	10
	-0.04	-3.18 quartet		7	40
H F (CH ₂) ₂ Si F					
C=C	Not	-6.2	82	6	96
H _b H _a	distinguished	quartet -5.4			
(CH ₃) ₂ Si / F		quartet			
	-0.45	_	—	_	
F $F/_2$					
$(CH_3)_2Si$					
	-0.14	-5.95 quartet	74	_	21
(cis)					
$(CH_3)_2Si/F$					
	-0.21	-6.14 quartet	74	15	—
VF H/ ₂ (trans)					
$(CH_3)_2Si/F$					
	-0.05	-3.39 quartet	—	7	30
H $F/_2$		-			
$(C_{13})_{2}$	Not	-6.2	76	5	95
$\left \left H_{b} \right ^{2} \right $	distinguished	quartet -5.81	.0	5	,,,
~0 1		quartet			

Chemical shifts (p.p.m.) are with respect to external TMS for trimethyl derivatives and to external CHCl₃ for dimethyl derivatives. Coupling constants are in c.p.s.

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TABLE II

Characteristic	C = C	stretching	and	C—F	frequencies	observed	in	trimethyl	and
dimethyl	perfluo	rovinyl and	l fluo	rovinyl	silanes [gas	phase - K	Br	windows	

Compound	$C = C region (\pm 2 cm^{-1})$	C—F region $(\pm 2 \text{ cm}^{-1})$
Me ₃ SiCF=CF ₂	1725 s	1290 vs, 1265 vs, 1135 vs, 1045 vs
$Me_3SiCF = CFH$ (cis)	1695 s	1290 s, 1255 vs, 1135 s, 1075 s, 920 s
Me ₃ SiCF=CFH (trans)	1665 s	1258 w, 1125 s, 1010 w
Me ₃ SiCH=CF ₂	1720 s	1295 s, 1260 vs, 1065 s
Me ₃ SiC ₂ H ₂ F	1625 s	1070 m, 1000 w, 950 s,b
$Me_2Si(CF=CF_2)_2$	1730 s	1305 vs, 1265 vs, 1150 s, 1110 m,
- 、		1055 m
Me ₂ Si(CF=CFH) ₂ (<i>cis</i>)	1700 s	1295 s, 1270 s, 1145 m, 900 s
Me ₂ Si(CF=CFH) ₂ (trans)	1665 s	1130 vs, 1000 vw
Me ₂ Si(CH=CF ₂) ₂	1722 s	1300 vs, 1262 s, 1175 m, 1050 s
$Me_2Si(C_2H_2F)_2$	1625 s	1140 s,b 905 m

was then possible to match the proton and ¹⁹F spectra (Fig. 2), thus showing the latter to consist of two sets of 24 lines each, the ratio of the species producing the sets being 3:2 respectively. The normal first-order analysis then gave the values shown in Table III.

The involatile liquid obtained from the ultraviolet irradiation of trimethyltin hydride and $(CH_3)_2Si(CF=CF_2)_2$ was quickly shown from spectroscopic evidence to be a mixture containing both — SiCFHCF_2Sn(CH_3)_3 and — SiCF- $[Sn(CH_3)_3]CF_2H$ groups, but it was not possible to distinguish between the three possible molecular species 1, 2, and 3. The proton n.m.r. spectrum, however, although complex, was completely consistent with the data for other addition products above and assignments to the above two types of ethane protons could be made on the same basis. The data are given in Table V.

Experimental

All reactions were carried out using standard high vacuum techniques. Reactions under thermal conditions were performed in pyrex Carius tubes, whereas those

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	F₁ (CH₃)₃Si—C- ∫ Sr	$ \begin{array}{c} F_{2} \\ F_{3} \\ \hline \hline$	$(CH_3)_3Si \stackrel{F_1}{\underset{H}{\overset{ }{\longrightarrow}}}$	$- \overset{F_2}{\underset{J}{\overset{J}{\overset{J}{\overset{J}{\overset{J}{\overset{J}{\overset{J}{J$
	¹ H spectrum	¹⁹ F spectrum	¹ H spectrum	¹⁹ F spectrum
$ \begin{array}{c} \delta_{S_{1}-CH_{3}} \\ \delta_{H} \\ \delta_{Sn-CH_{3}} \\ J^{119}_{Sn-CH_{3}} \\ J^{117}_{Sn-CH_{3}} \\ \delta_{F_{1}} \\ \delta_{F_{2}} \\ \delta_{F_{3}} \\ J_{H-F_{1}} \end{array} $	$ \begin{array}{r} -0.08 \\ -6.5 \\ -0.15 \\ 57 \\ 55 \\ 10 \\ (2) \end{array} $	220.9 205.9 192.7 10.9	$ \begin{array}{r} -0.08 \\ -4.72 \\ -0.15 \\ 57 \\ 55 \\ 44 \\ 47 \\ 44 \\ 37 \\ 44 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37 \\ 37$	233.3 216.6 203.7 43.1
$ \begin{array}{c} J_{H-F_2} \\ J_{H-F_3} \\ J_{F_1-F_2} \\ J_{F_1-F_3} \\ J_{F_2-F_3} \end{array} $	62 56	58.5 57.6 20 27 290	37 10	36 9.6 8.4 9.6 312

TABLE III N.m.r. data* for the addition products of $(CH_3)_3SnH$ with $(CH_3)_3SiCF=CF_2$

*Chemical shifts are in p.p.m. and coupling constants in c.p.s. Neat liquid samples were used with external CCl_3F and external $CHCl_3$ as references.

TABLE IV				
Infrared spectra of the addition products as liquid	films			

$(CH_3)_3SnH + (CH_3)_3SiCF=CF_2$	$\begin{array}{c} (CH_3)_3SnH + \\ (CH_3)_2Si(CF=CF_2)_2 \end{array}$		Assignment
510 (s) 535 (vs)	505 (s) 525 (vs)	}	Sn—C stretch
620 (w) 700 (m) 770 (s,b) 845 (vs)	675 (sh,m) 715 (s) 770 (vs,b) 830 (s,b)	}	CH₃—Sn and CH₃—Si rock
860 (sh,s) 875 (sh,m) 950 (vs) 985 (s)	860 (sh,m) 945 (vs) 982 (vs)	,	
1030 (s) 1040 (s) 1065 (m) 1110 (sh,m)	1030 (vs) 1060 (s,sh) 1110 (sh,s)		C-F stretch
1130 (s) 1190 (w) 1225 (m) 1255 (vs)	1125 (vs) 1190 (w) 1225 (m) 1250 (vs)	J	CH₃ deform. C—F stretch CH₃—Si
1300 (w) 1335 (m) 1360 (w) 1415 (w) 2360 (w)	1300 (m) 1330 (m) 1360 (m) 1405 (m) 2360 (w)		
2810 (w) 2920 (s) 2970 (s)	2795 (w) 2910 (s) 2995 (s)	}	C—H stretch

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=



TABLE V Proton n.m.r. data for the product of $(CH_3)_3SnH$ and $(CH_3)_2Si(CF=CF_2)_2$ in cyclohexane

	$\begin{array}{c c} Sn(CH_3)_3 H \\ \hline \\ Si - \begin{matrix} - \\ - \end{matrix} \\ Si - \begin{matrix} - \\ - \end{matrix} \\ F_1 \end{matrix} \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	$ \begin{array}{c} F_1 & F_2 \\ F_1 & F_2 \\ F_2 & F_2 $
$ \begin{array}{c} \delta_{S_{1}-CH_{3}} \\ \delta_{H} \\ \delta_{S_{n}-CH_{3}} \\ J_{119} \\ S_{n-CH_{3}} \\ J_{117} \\ S_{n-CH_{3}} \\ J_{H-F_{1}} \\ J_{H-F_{2}} \\ J_{H-F_{2}} \\ J_{H-F_{3}} \end{array} $	$ \begin{array}{r} -0.18 \\ -6.06 \\ -0.15 \\ 56 \\ 55 \\ 10 \\ 61 \\ 55 \\ \end{array} $	$ \begin{array}{r} -0.18 \\ -4.46 \\ -0.15 \\ 56 \\ 55 \\ 44 \\ 38 \\ 8 \\ \end{array} $

Chemical shifts (p.p.m.) are relative to internal cyclohexane. Coupling constants in c.p.s.

involving ultraviolet irradiation were conducted in silica tubes. Infrared spectra were recorded with a Beckman IR 10 double beam spectrophotometer using a 10 cm ccll for vapor samples, and liquid films for the spectra of liquids. Proton n.m.r. spectra were obtained with a Varian A60 spectrometer, and ¹⁹F spectra with a Varian DP-60 spectrometer operating at 56.4 Mc s⁻¹. Molecular weight measurements were performed on a Hewlett-Packard vapor pressure osmometer. Gas chromatographic separations were carried out on an Aerograph model A-700 Autoprep instrument with helium as carrier gas.

Trimethyltin hydride and dimethyltin dihydride were prepared by the procedure of Finholt et al. (22), using *n*-butyl ether as solvent. Trimethyl(perfluorovinyl)silane and dimethylbis(perfluorovinyl)silane were prepared by the method of Tarrant and Oliver (23) in 50 and 44% yields respectively.

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.

Reactions of Trimethyl(perfluorovinyl)silane with Organotin Hydrides

(a) Trimethyltin hydride (0.24 g, 1.4 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.204 g, 1.3 mmoles) were allowed to react at 25° for 24 h. 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 2 weeks. A trace of white solid was deposited but recovery of the reactants was essentially quantitative.

(b) Trimethyltin hydride (0.40 g, 2.4 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.40 g, 2.4 mmoles) were heated at 55° for 60 h. A white solid was deposited, which was identified spectroscopically as trimethyltin fluoride (0.228 g, ca. 50% yield). 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 silicone QF-1 column at 170° gave pure products which were identified by their characteristic infrared and proton n.m.r. spectra (Tables I and II). 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%).

(c) Trimethyltin hydride (0.54 g, 3.3 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.51 g, 3.3 mmoles) were exposed to ultraviolet irradiation at 25° for 10 h. 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 III and IV) 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 h, after which white crystals are slowly deposited. After 1 week, all liquid had disappeared and only a white solid remained. At this stage, the volatile products were removed and identified spectroscopically (Tables I and II) as $(CH_3)_3SiCH=CF_2$ and *cis*- $(CH_3)_3$ -SiCF=CFH, formed in the ratio 2:1. 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; molecular weight, 319. Found: C, 31.21; H, 6.50; molecular weight (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 (24).

(d) Trimethyltin hydride (0.24 g, 1.4 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.204 g, 1.3 mmoles) were sealed with 80 mg of azobisisobutyronitrile and allowed to react at

35° for 10 h. Examination of the reaction mixture then showed only the starting materials, which were accordingly resealed with a further sample (80 mg) of azobisisobutyronitrile and kept at 50° for a further 10 h. Vacuum fractionation gave a trace of noncondensable gas, presumably a mixture of hydrogen nitrogen, but the bulk of the material (0.221 g, 54% yield) condensed at -23° . It was spectroscopically identified (Tables III and IV) as a mixture of the two addition products, (CH₃)₃SiCFHCF₂-Sn(CH₃)₃ and (CH₃)₃SiCF[Sn(CH₃)₃]CF₂H, in a 3:2 ratio.

The fractions which condensed at -78 and -196° were shown spectroscopically to be mixtures of $(CH_3)_3$ -SiCH=CF₂, *cis*- and *trans*- $(CH_3)_3$ SiCF=CFH, and $(CH_3)_3$ SiC₂H₂F, 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 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.23 g, 1.5 mmoles) were sealed with hydroquinone (0.157 g) and irradiated for 10 h 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 with the mixture of addition products obtained previously, and corresponded to a 62% yield. The infrared spectra of the -78 and -196° fraction showed (CH₃)₃SiCF=CF₂ and its reduced products such as (CH₃)₃SiC₂F₂H to be present, but the yields were insufficient for full characterization. Trimethyltin fluoride, some metallic tin, and hydroquinone remained in the reaction tube.

(f) Galvinoxyl (421 mg) prepared by the method of Bartlett and Funahashi (16) and azobisisobutyronitrile (82 mg) with 2 ml of dry benzene were taken in a pyrex Carius tube, and trimethyltin hydride (0.265 g, 1.6 mmoles) and (CH₃)₃SiCF=CF₂ (0.247 g, 1.6 mmoles) were then added under vacuum. The reaction mixture was heated at 50° for 10 h. On opening the tube, a small amount of noncondensable gas was first pumped off and all volatile materials were removed to leave a dark-red solid as described by Bartlett and Funahashi (16). Vacuum fractionation of the volatiles gave (CH₃)₃SiCF=CF₂ (0.192 g) and trimethyltin hydride (0.260 g). No other compound was present.

(g) Dimethyltin dihydride (0.225 g, 1.5 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.462 g, 3.0 mmoles) were allowed to react at 60° for 24 h. The infrared spectrum (gas phase) of the volatile products showed a band at 1695 cm⁻¹ (C=C stretch) characteristic of *cis*-CFH=CFSi(CH₃)₃, with a shoulder at 1720 cm⁻¹ characteristic of $(CH_3)_2SiCF=CF_2$, 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 diffuoride (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 mmoles) and $(CH_3)_3SiCF=CF_2$ (0.462 g, 3.0 mmoles) were irradiated at 25° for 16 h, 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

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volatiles showed the presence of cis- and trans-CFH =CFSi(CH₃)₃, (CH₃)₃SiCH=CF₂, and (CH₃)₃SiC₂H₂F, based on the observed C=C stretching frequencies. Confirmation was obtained from the proton n.m.r. spectrum, which on integration showed the percentage composition to be cis-CFH=CFSi(CH₃)₃ 29%, trans-CFH=CFSi(CH₃)₃ 5.5%, (CH₃)₃SiCH=CF₂ 49%, and (CH₃)₃SiC₂H₂F 16.5%. From the reaction tube, dimethyltin diffuoride (0.223 g) was recovered, corresponding to 80% complete reaction.

Reactions of Dimethylbis(perfluorovinyl)silane with Organotin Hydrides

(a) Trimethyltin hydride (0.72 g, 4.5 mmoles) and (CH₃)₂Si(CF==CF₂)₂ (0.48 g, 2.18 mmoles) were allowed to react at 25° for 1 week. There was no visible reaction, and no noncondensable 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 h. A small amount of solid was deposited and a trace of a noncondensable 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 (CH₃)₂Si(CH=CF₂)₂, cis- and trans-(CFH =CF)₂Si(CH₃)₂, and (CH₃)₂Si(C₂H₂F)₂ with characteristic infrared C=C stretching frequencies at 1700, 1665, 1722, and 1625 cm⁻¹ respectively, in addition to the starting materials. 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 (0.012 g) recovered from the reaction tube showed that the reaction was only 1.5% complete.

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(c) Trimethyltin hydride (0.72 g, 4.5 mmoles) and (CH₃)₂Si(CF=CF₂)₂ (0.48 g, 2.18 nimoles) were irradiated for 4 h at 25°, at the end of which time a small amount of white solid had been deposited. Other than some noncondensable gas, the volatile products were identified as trimethyltin hydride (0.02 g) and (CH₃)₂Si(CF=CF₂)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 IV and V) showed the material to be a mixture of the addition products of (CH₃)₃SnH and (CH₃)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 mmoles) and $(CH_3)_2Si(CF=CF_2)_2$ (0.24 g, 1.1 mmoles) with azobis-isobutyronitrile (50 mg) were heated at 55° for 45 h. 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=CF₂ groups in addition to considerable amounts of the starting material. 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 mmoles) and $(CH_3)_2Si(CF=CF_2)_2$ (0.235 g, 1.07 mmoles) were allowed to react at 55° for 8 h. White to yellow solid was deposited and a small amount of noncondensable gas was pumped off. Spectroscopic examination (infrared and proton n.m.r.) showed the presence of cis- and trans-HCF=CF-, $-CH=CF_2$, and $-C_2H_2F$ groups, with *cis*-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 mmoles) and (CH₃)₂Si(CF=CF₂)₂ (0.475 g, 2.16 mmoles) were irradiated for 30 min at 25°. Treatment of the reaction mixture as in the last experiment showed the volatiles to consist of

(CH₃)₂Si derivatives containing cis- and trans-

CFH=CF-, --CH==CF2, and --C2H2F groups, with those containing cis-CFH=CF- and --CH=-CF2 being the major products. Some of the original reactants were also present. From the residue in the tube, dimethyltin difluoride (0.165 g, 41 % yield) was extracted.

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