which showed only the presence of the β phase. The pattern was indexed and indicated the material had a distorted cubic symmetry with $a = 3.44$ Å. Komjathy[10] reported $NbH_{0.82}$ to have a distorted bcc structure with $a = 3.409$ Å. The degree of distortion is small and Wainwright, *et al.*,[11] calculated a c/a ratio of 1.005 for $NbH_{0.85}$.

As with vanadium it is possible to construct a phase diagram of the niobium–hydrogen system from data abstracted from the pressure–composition isotherms. In Figure 5 such a diagram is shown in which our results have been combined with those of Walter and Chandler,[12] who have constructed a phase diagram for the Nb–H system up to $NbH_{0.86}$. It is somewhat difficult to place exactly the $\beta/(\beta + \gamma)$ phase boundary as determined by the isotherm shape; however, its placement at $NbH_{1.1}$ is consistent with recent results obtained by Aronson, *et al.*,[13] in magnetic susceptibility studies. The $(\beta + \gamma)/\gamma$ boundary can be more readily defined and is approximately at $NbH_{1.95}$ at 40° but is displaced toward the left as the temperature is increased.

Acknowledgments.—The authors wish to thank Mr. Jonathan Hughes and Mr. Albert Holtz for their expert assistance in the laboratory.

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Preparation and Properties of Some Fluorocarbon Derivatives of Tin

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The Mössbauer spectra of the compounds $(CH_3)_3SnR_f$ show a quadrupole splitting which is believed to be due to an electronegativity difference between the methyl groups and the R_f group. The magnitude of the splitting indicates that the electronegativity of the R_f group increases in the order: $CH_2F < CHF_2 < CF{=}CF_2 < CF_3 \approx CH(CF_3)_2 < CF_2CF_3 < C{\equiv}CCF_3 < CF(CF_3)_2$. The compound $(CH_3)_3SnCF_2H$ wasp repared by treating $(CH_3)_3SnH$ with $(CH_3)_3SnCF_3$. Apart from $(CH_3)_3SnCF_3$ none of the compounds appears to be a useful carbene source.

Introduction

Trimethyltrifluoromethyltin, $(CH_3)_3SnCF_3$, was first prepared by the reaction of trifluoroiodomethane with hexamethylditin[1-3] (eq 1, $R_f = CF_3$). Clark and

$$(CH_3)_3Sn\text{-}Sn(CH_3)_3 + R_fI \xrightarrow[h\nu]{} (CH_3)_3SnR_f + ISn(CH_3)_3 \qquad (1)$$

Willis[1] found that it was a good source of difluorocarbene (eq 2) on pyrolysis at 150°. The carbene produced in this way has been added to C=C bonds to

$$(CH_3)_3SnCF_3 \xrightarrow{150^\circ} (CH_3)_3SnF + CF_2 \qquad (2)$$

yield cyclopropanes[1,4,5] and to C≡C bonds to yield cyclopropenes.[4-6] The addition to *cis*- and *trans*-butene occurs stereospecifically indicating that the carbene is produced in the singlet state.[7] This is the usual state of difluorocarbene from other sources.[8]

Seyferth and his coworkers[9] have recently used the same tin compound as a source of difluorocarbene at lower temperatures in DME solution by the method indicated in eq 3. Here also the carbene adds to olefins

$$\begin{aligned}(CH_3)_3SnCF_3 + I^- &\longrightarrow (CH_3)_3SnI + CF_3^- \\ CF_3^- &\longrightarrow F^- + CF_2\end{aligned} \qquad (3)$$

to give cyclopropanes.[9] Very little is known about the abilities of other fluorocarbon derivatives of tin to act as sources of carbenes so it was decided to synthesize a few to investigate their thermal decomposition.

Recently there have appeared some reports that the Mössbauer spectra of compounds of the type R_3SnR' show splittings which appear to be caused, at least in the main, by differences in σ bonding, that is, electronegativity differences between R and R′.[10-12] Parish and Platt[11] reported a quadrupole splitting for $(CH_3)_3SnCF_3$ ($\Delta = 1.38$ mm/sec) and slightly smaller but well-resolved splittings for R_3SnR' ($R = CH_3$ or C_6H_5; $R' = C_6F_5$ or C_6Cl_5). The splitting in the $R_3SnC_6F_5$ compounds is probably due to electronegativity differences since nmr studies indicate little π donation from the C_6F_5 group to $(CH_3)_3Sn$.[13] Thus the investigation of the Mössbauer absorption spectra of the fluoroalkyl-

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trimethyltin derivatives prepared during the course of this investigation was undertaken to explore further the causes of quadrupole splitting in R_3SnR' compounds, particularly electronegativity-induced splittings.

Experimental Section

Manipulations of volatile reagents and products were carried out in a vacuum system. Molecular weights were determined using Regnault's method. Nmr spectra were obtained from neat liquids using Varian A-60 (^1H spectra relative to external TMS) and HA-100 (^{19}F spectra relative to internal $CFCl_3$) spectrometers: positive values of chemical shifts in ppm are to higher field. Infrared spectra were run on a Perkin-Elmer Model 457 instrument. The Mössbauer spectrometer and the associated data-processing techniques have been described previously.[14]

Microanalyses were made by Mr. Peter Borda of this department.

Reaction of Trimethyltrifluoromethyltin with Trimethyltin Hydride.—Trimethyltin hydride (2.194 g, 13.3 mmol) and trimethyltrifluoromethyltin (1.093 g, 4.7 mmol) were heated at 150° for 24 hr. After heating, the tube walls were coated with trimethyltin fluoride crystals. Vpc separation (20% Kel-F grease at 95°) of the −78° fraction yielded tetramethyltin (0.336 g), identified by its known infrared and ^1H nmr spectra and molecular weight of 178 (calcd for $C_4H_{12}Sn$: 179), and difluoromethyltrimethyltin (0.635 g, 63% yield), bp (micro) 111.5° (760 mm). *Anal.* Calcd for $C_4H_{10}F_2Sn$: C, 22.38; H, 4.66; F, 17.71; mol wt 215. Found: C, 22.48; H, 4.77; F, 17.51; mol wt 210. Infrared spectrum (vapor): 3043 (w), 2993 (w), 2910 (m), 1282 (m), 1200 (w), 1120 (w), 1085 (w), 1052 (s), 1009 (s), 775 cm^{-1} (s). The ^1H nmr spectrum showed a singlet at −0.18 ppm (–CH_3) with tin satellite peaks ($J_{^{117}Sn-CH_3}$ = 53.54 cps; $J_{^{119}Sn-CH_3}$ = 57.5 cps) and a triplet centered at −6.25 ppm (J_{F-H} = 45.5 cps). The ^{19}F nmr spectrum showed a doublet centered at 127 ppm (J_{F-H} = 45.0 cps) with tin satellite peaks ($J_{^{117}Sn-F}$ = 254.5 cps; $J_{^{119}Sn-F}$ = 265.5 cps).

Preparation and Reactions of Trimethylpentafluoroethyltin.—Following the published procedure[2] hexamethylditin (27.00 g, 82.5 mmol) and pentafluoroethyl iodide (30.41 g, 124 mmol) were irradiated for 24 hr (450-W uv source). Pentafluoroethane (6.94 g) which was not condensed in a trap at −95° was isolated and identified by its known infrared spectrum and molecular weight of 122 (calcd for C_2F_5H: 121). Distillation under nitrogen of the remaining volatile material gave two fractions: bp 99–109° (1 atm) and 93–150° (70 mm). The first fraction was separated by vpc (20% Kel-F at 85°) into tetramethyltin (1.206 g), identified by its known infrared and ^1H nmr spectra and molecular weight of 178 (calcd for $C_4H_{12}Sn$: 179), and trimethylpentafluoroethyltin (3.908 g, 17% yield), bp (micro) 106.5° (1 atm) (lit.[2] bp 107° (760 mm)). *Anal.* Calcd for $C_5H_9F_5Sn$: C, 21.45; H, 3.18; F, 33.61. Found: C, 21.00; H, 3.09; F, 33.3. Infrared spectrum (vapor): 3002 (w), 2918 (w), 1329 (s), 1300 (m), 1202 (s), 1105 (s), 1070 (s), 941 (s), 788 cm^{-1} (s). The ^1H nmr spectrum showed a singlet at −0.23 ppm with tin satellite peaks ($J_{^{117}Sn-CH_3}$ = 55.6 cps, $J_{^{119}Sn-CH_3}$ = 58.2 cps). The ^{19}F nmr spectrum showed two resonances, a quartet centered at 113.2 ppm with J_{Sn-F} satellite peaks (–CF_2–) (J_{F-F} = 1.4 cps, $J_{^{117}Sn-F}$ = 208.0 cps, $J_{^{119}Sn-F}$ = 217.8 cps) and a very broad singlet at 84.90 ppm (–CF_3) (width at base of peak 8 cps).

The higher boiling fraction was identified as $(CH_3)_3SnI$ (26.66 g) by its known infrared and ^1H nmr spectra.

(a) **Pyrolysis.**—Trimethylpentafluoroethyltin (0.846 g, 3.0 mmol) was heated at 200° for 72 hr. A small amount of white precipitate formed. There was a minimum of charring. Starting material (0.766 g, 91% recovery) was recovered as well as a small amount of pentafluoroethane (0.026 g).

(b) **Reaction with Cyclohexene.**—Cyclohexene (1.451 g, 1.78 mmol) and the tin compound (1.044 g, 3.7 mmol) were combined and heated at 200° for 72 hr. The fraction which passed through a −78° bath was identified as pentafluoroethane (0.030 g). The ^1H nmr spectrum of the −78° fraction showed peaks due to cyclohexene and the pentafluoroethyltin compound only.

Preparation and Reactions of Heptafluoroisopropyltrimethyltin.—A mixture of hexamethylditin (15.05 g, 46.0 mmol) and heptafluoroisopropyl iodide (20.45 g, 69.1 mmol) was irradiated for 24 hr (100-W uv source). The reaction mixture was yellow and contained a yellow precipitate after irradiation. Distillation under nitrogen gave the following fractions: bp 102–104° (457 mm), bp 117° (156 mm), and bp 103° (93 mm). The first fraction was identified as heptafluoroisopropyltrimethyltin (6.65 g, 42% yield). An analytical sample was obtained by vpc (20% silicone GE-SS-96 at 100°). *Anal.* Calcd for $C_6H_9F_7Sn$: C, 21.64; H, 2.71; F, 39.97. Found: C, 21.48: H, 2.86; F, 39.67. Infrared spectrum (vapor): 2990 (w), 2938 (w), 1302 (s), 1282 (s), 1221 (s), 1211 (s, sh), 1150 (m), 1071 (m), 950 (m), 915 (w), 784 (m), 745 (w), 701 cm^{-1} (s). The ^1H nmr spectrum showed a singlet at −0.33 ppm with tin satellites ($J_{^{117}Sn-CH_3}$ = 56.8 cps; $J_{^{119}Sn-CH_3}$ = 57.8 cps). The ^{19}F nmr spectrum showed two absorptions: one was a doublet of septets at 71.1 ppm (–CF_3) (J_{F-F} = 12.4 cps; J_{H-F} = 0.1 cps) and the other, a well-defined septet at 211.4 ppm ($\equiv$CF) with tin satellite peaks ($J_{^{117}Sn-F}$ = 160.5 cps; $J_{^{119}Sn-F}$ = 167.5 cps).

The higher boiling fractions were identified as trimethyltin iodide, by its known ^1H nmr spectrum.

(a) **Pyrolysis.**—The tin compound (0.858 g, 2.58 mmol) was heated at 150° for 24 hr. There was little evidence of decomposition and the tube was heated for a further 40 hr at 150°. Starting material (0.46 g, 54% recovery) was recovered in a −78° bath after two passes. Perfluoropropene (0.097 g, 56% based on the starting material consumed) was also recovered. The white crystals which formed on the side of the tube were identified as trimethyltin fluoride. *Anal.* Calcd for C_3H_9FSn: C, 19.71; H, 4.93. Found: C, 19.94; H, 5.09.

(b) **Reaction with Cyclohexene.**—Cyclohexene (0.800 g, 9.75 mmol) and the tin compound (0.744 g, 2.24 mmol) were heated at 250° for 123 hr. Some white crystals had formed. Perfluoropropene (0.233 g) was recovered. The ^1H nmr spectrum of the remaining volatiles showed peaks due to cyclohexene and a small peak at 0.2 ppm with tin satellites which may have been due either to the remaining starting material or tetramethyltin. The peak at 0.2 ppm integrated as less than 10% of the total number of protons.

(c) **Reaction with Trimethyl-3,3,3-trifluoropropynylgermane.**—A mixture of the propynylgermane[5] (0.779 g, 3.69 mmol) and the tin compound (1.107 g, 3.32 mmol) was heated at 150° for 64 hr. Vpc analysis (20% silicone GE-SS-96 at 95°) of the −78° fraction yielded the starting propynylgermane (0.640 g, 82% recovery) and the tin compound (0.24 g). Perfluoropropene was isolated in the −196° bath.

Preparation of Trifluorovinyltrimethyltin.—A mixture of hexamethylditin (20.53 g, 62.7 mmol) and trifluorovinyl iodide (17.77 g, 85.5 mmol) was irradiated for 24 hr (100-W uv source). All volatiles with a vapor pressure greater than 1 cm were taken into the vacuum system. The less volatile fraction which condensed at −95° was identified as slightly impure trifluorovinyl iodide (1.37 g). The more volatile material was identified as trifluoroethylene (<0.5 g) by its known infrared spectrum. Distillation under nitrogen of the least volatile material gave two fractions. The first, bp 120–135° (1 atm), was separated by vpc (20% silicone GE-SS-96 at 100°) into tetramethyltin (0.58 g) and trifluorovinyltrimethyltin (3.70 g, 23.3% yield). *Anal.* Calcd for $C_5H_9F_3Sn$: C, 24.52; H, 3.68; F, 23.25. Found: C, 24.53; H, 3.57; F, 23.41. The ^1H nmr spectrum showed a singlet at −0.20 ppm with tin satellite peaks ($J_{^{117}Sn-CH_3}$ = 56.8 cps; $J_{^{119}Sn-CH_3}$ = 59.2 cps) (lit.[15] singlet at 0.33 ppm (internal TMS), $J_{^{117}Sn-CH_3}$ = 58.0; $J_{^{119}Sn-CH_3}$ = 60.5 cps). The second

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fraction, bp 74–77° (14 mm), was identified as trimethyltin iodide by its known ^1H nmr spectrum.

Pyrolysis.—The tin compound (0.711 g, 2.91 mmol) was heated at 200° for 147 hr. A ^1H nmr spectrum of the volatiles showed peaks at -0.2 and -0.12 ppm which were assigned to starting material and tetramethyltin (area ratio 5.3:1). On this basis 73% of the vinyltin compound was recovered. In another reaction the tin compound was heated at 300° for 168 hr. There was extensive charring. Small quantities of SiF_4 (0.071 g) and tetramethyltin (0.038 g) were recovered.

Results and Discussion

The ultraviolet-induced reactions of heptafluoroisopropyl iodide and trifluorovinyl iodide with hexamethylditin give a 42% yield of heptafluoroisopropyltrimethyltin and a 23% yield of trifluorovinyltrimethyltin, respectively (eq 1, $R_f = CF(CF_3)_2$ or $CF{=}CF_2$). Trimethyltin iodide is also isolated from both reaction mixtures as well as small amounts of $(CH_3)_4Sn$ and $CF_2{=}CFH$ from the reaction involving $CF_2{=}CFI$. Similar preparations of $(CH_3)_3SnR_f$ ($R_f = CF_3$, CF_2CF_3, and $CF{=}CF_2$) *via* CF_3I, CF_3CF_2I, and $CF_2{=}CFBr$ have been previously reported.[1-3,16] The reaction involving C_2F_5I to give $(CH_3)_3SnC_2F_5$ was found, during the course of this investigation, to produce a large amount of C_2F_5H.

All the ultraviolet-induced reactions described by eq 1 involving hexamethylditin and a fluoroorgano iodide that have been reported,[1-3] as well as those performed during this investigation, were carried out in Pyrex tubes. These tubes are transparent only to light of $\lambda > 2850$ Å. The ultraviolet absorption maximum of hexamethylditin occurs at ≤ 2100 Å;[16] those of CF_3I and C_2F_5I occur at 2680 Å[17] and that of $CF{=}CFI$ is at 2580 Å.[18] The longer wavelength absorption limits of CF_3I and C_2F_5I are at *ca.* 3170 Å, respectively,[17] and the ultraviolet absorption spectrum of $(CF_3)_2CFI$ is expected to be similar. On the basis of the ultraviolet absorption maxima of $(CH_3)_3SnSn(CH_3)_3$ and the fluoroorgano iodides, and, further, on the basis that all four of the iodides are known to undergo radical reactions under the influence of light of wavelength $\lambda > 2850$ Å,[19] a mechanism involving initial homolytic cleavage of the C–I bond of the fluoroorgano iodides seems more reasonable than the initial cleavage of the tin–tin bond previously proposed for eq 1.[3]

The reaction of trimethyltrifluoromethyltin with trimethyltin hydride in the gas phase at 150° gives difluoromethyltrimethyltin as the major product (eq 4).

$$(CH_3)_3SnH + (CH_3)_3SnCF_3 \longrightarrow (CH_3)_3SnCF_2H + (CH_3)_3SnF \quad (4)$$

A small amount of tetramethyltin is also isolated. The new product which may have been formed either by reduction of one of the fluorine atoms by the tin hydride or more likely by insertion of a molecule of CF_2 into the Sn–H bond has the expected infrared and nmr spectra (see Experimental Section and Table I). Similar reactions of tin hydrides with dihalocarbene precursors have been described; however, only Ts'eng and coworkers[20] have previously actually isolated a product resulting from apparent carbene insertion into the Sn—H bond (eq 5). Although Seyferth and coworkers have inserted

$$R_3Sn\text{–}H + CCl_3CO_2Na \xrightarrow{\Delta} R_3SnCCl_2H \quad (R = C_2H_5,\ n\text{-}C_4H_9) \quad (5)$$

CX_2 (X = Cl, Br) into Si–H bonds using as carbene sources CCl_3CO_2Na[21] and $C_6H_5HgCX_2Br$ (X = Cl, Br)[22] and CCl_2 into Ge–H bonds using $C_6H_5HgCCl_2Br$ as the source,[22] the reaction between R_3SnH ($R = n\text{-}C_4H_9$, C_6H_5) and $C_6H_5HgCX_3$ ($X_3 = Cl_2Br$, $ClBr_2$, Br_3) gives only products arising from the reduction of the mercurial by the tin hydride (eq 6).[22]

$$R_3SnH + C_6H_5HgCX_3 \longrightarrow C_6H_5HgCX_2H + R_3SnBr \quad (6)$$

Table I lists the nmr parameters of the saturated $(CH_3)_3SnR_f$ derivatives prepared for this investigation. The compound $(CH_3)_3SnCH(CF_3)_2$ was obtained by treating $(CH_3)_3SnH$ with $(CF_3)_2CN_2$.[23] The chemical shifts and coupling constants from the ^{19}F nmr spectra of the new compounds are similar to those of other derivatives containing an R_f group bonded to a main group metal or metalloid.[24,25] It is notable that in the fluoroalkyltrimethyltin compounds coupling takes place between the methyl hydrogens and a fluorine atom on the carbon that is β to the tin but no coupling takes place between the hydrogens and the fluorines attached to the carbon atom that is α to the tin atom. This long-range coupling has been noted before[26] and similar even more remote couplings are found in $(CH_3)_3SiR_f$ compounds.[27]

Table I

Nmr Parameters of Some $(CH_3)_3SnR_f$ Derivatives[a]

	^1H	^{19}F		J_{F-F} or	
	δ_{CH_3}	$\delta_{F\alpha}$	δ_{F^β}	J_{F-H}	J_{CH_3-F}
$(CH_3)_3SnCF_2H$	−0.18	127.0		45	
$(CH_3)_3SnCF_3$[b]	−0.30	103.3			
$(CH_3)_3SnCF_2CF_3$	−0.23	113.2	84.90[c]	1.4	0.1
$(CH_3)_3SnCH(CF_3)_2$	−0.3		56.1	11.5	0.5
$(CH_3)_3SnCF(CF_3)_2$	−0.33	211.4	71.1	12.4	0.1

[a] *J* in cps. [b] $\delta_F = 29.1$ with respect to CF_3COOH.[1] [c] Broad singlet—width at base ~8 cps.

Pyrolysis of $(CH_3)_3SnC_2F_5$ at 200° for 72 hr either by itself or with cyclohexene fails to give any products resulting from reaction of the predicted carbene intermediate CF_3CF. The tin compound is 91% recovered

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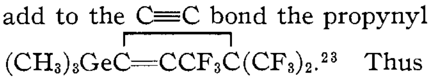
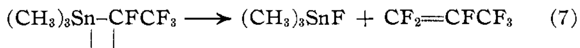
when heated alone and its observed stability contrasts with an earlier report that it is extensively decomposed at temperatures >180°.[2] The small amounts of C_2F_5H detected in both reactions suggest that the tin compound is thermally decomposed by homolytic fission of the Sn–C bond rather than by either α- or β-fluorine elimination.

Heptafluoroisopropyltrimethyltin decomposes at 150° (64 hr) to give trimethyltin fluoride and hexafluoropropene. The propene may arise from rearrangement of the carbene $C(CF_3)_2$; however, thermally induced decompositions of the tin compound in the presence of trimethyl-3,3,3-trifluoropropynylgermane (150°, 64 hr) or cyclohexene (250°, 123 hr) fail to give either the expected cyclopropene or cyclopropane. Products which could have been produced by a carbene insertion reaction were also not detected. In related studies it has been found that the carbene, $C(CF_3)_2$, produced by the pyrolysis of bis(trifluoromethyl)diazomethane *does* add to the $C{\equiv}C$ bond the propynyl germane, yielding  $(CH_3)_3GeC{=}CCF_3C(CF_3)_2$.[23] Thus the decomposition of the tin compound probably takes place *via* a β elimination to give hexafluoropropene directly (eq 7). Both



$$(CH_3)_3Sn\text{–}CFCF_3(F\text{–}CF_2) \longrightarrow (CH_3)_3SnF + CF_2{=}CFCF_3 \qquad (7)$$

α and β elimination have often been suggested to account for the products of the thermal decomposition of fluoroalkyl compounds of tin and silicon[1,28,29] but it is rather difficult to establish any pattern.

Trifluorovinyltrimethyltin is partly decomposed at 200° after 147 hr (73% recovery) and completely decomposed at 300° after 168 hr. Small amounts of tetramethyltin are detected in each reaction as well as some SiF_4 in the product mixture of the reaction at 300°. No other volatile fluorine-containing products are isolated after heating at 300°.

Mössbauer Studies.—The results are listed in Table II together with those obtained from some related compounds. Figure 1 shows a typical spectrum consisting of one symmetric doublet. The isomer shifts of the saturated $(CH_3)_3SnR_f$ compounds studied are identical, within the experimental limits of the spectrometer (±0.03 mm/sec), and it can be concluded that the electron densities at the tin atoms of the compounds studied are constant.

The quadrupole splitting of the saturated $(CH_3)_3SnR_f$ derivatives listed in Table II increases with increasing fluorine substitution and increasing size and chain branching of the R_f group.[30,31] It seems reasonable to assume that these compounds are axially symmetric and that the quadrupole splitting is given by $^1/_2eQV_{zz}$ (V_{zz} is the electric field gradient in the z direction and eQ is a constant). Parish and Platt[11] have concluded that in this type of compound quadrupole splittings are caused predominantly by the polarity of the σ bonds between tin and the groups bound to it and found no indication that π bonding plays a large part in determining the magnitude of the splittings in spite of earlier suggestions to this effect.[31-33] The magnitude of the quadrupole splitting of the $(CH_3)_3SnR_f$ compounds, therefore, may indicate the electronegativity of the R_f

TABLE II

MÖSSBAUER PARAMETERS OF SOME $(CH_3)_3SnR_f$ AND RELATED COMPOUNDS[a]

	δ	Δ	Γ_1	Γ_2	Ref
$(CH_3)_4Sn$	1.29	0.00	0.80	. . .	11, *f*
$(CH_3)_3SnCH_2F$	1.38	0.00	. . .	. . .	*e*,*g*
$(CH_3)_3SnCHF_2$	1.28	0.94	0.81	0.67	*c*
$(CH_3)_3SnCF_3$	1.31	1.38	0.98	0.92	11, *f*
	1.31	1.57	0.71	0.71	*c*
$(CH_3)_3SnCF_2CF_3$	1.30	1.63	0.85	0.77	*c*
$(CH_3)_3SnCF(CH_3)_2$	1.32	1.89	0.89	0.87	*c*
$(CH_3)_3SnCH(CHF_3)_2$	1.30	1.57	0.78	0.77	*c*
$(CH_3)_3SnCH{=}CH_2$	1.30	1.00	. . .	. . .	*d*, *g*
$(CH_3)_3SnCF{=}CF_2$	1.30	1.41	. . .	. . .	*c*
$(CH_3)_3SnC{\equiv}CC_6H_5$	1.23	1.17	0.92	0.78	11, *f*
$(CH_3)_3SnC{\equiv}CCF_3$	1.25	1.77	1.25	1.39	*b*, *c*
$(CH_3)_2Sn(C{\equiv}CCF_3)_2$	1.19	1.95	1.17	1.12	*b*, *c*

[a] Unless otherwise indicated δ is the isomer shift relative to SnO_2 at 77°K and Δ is the quadrupole splitting in the units mm/sec. For this work both δ and Δ are accurate to within ±0.03 mm/sec. Γ_1 and Γ_2 at the widths at half-height of the absorptions at lower and higher velocities, respectively, and are accurate to within ±0.05 mm/sec. [b] Spectrum obtained using Pd(Sn) source; therefore, Γ's are not really comparable. [c] This work. [d] A. Yu. Aleksandrov, O. Yu. Okhlobystin, L. S. Polak, and V. S. Shipnel, *Dokl. Akad. Nauk SSSR*, **157**, 934 (1964). [e] V. V. Khrapov, V. I. Gol'danskii, A. K. Prokof'ev and R. G. Kostyanovskii, *Zh. Obshch. Khim.*, **37**, 3 (1967). [f] Source: Pd(Sn) at room temperature. Isomer shift is relative to SnO_2 at room temperature. [g] Source: SnO_2 at room temperature. Isomer shift is relative to SnO_2 at room temperature.

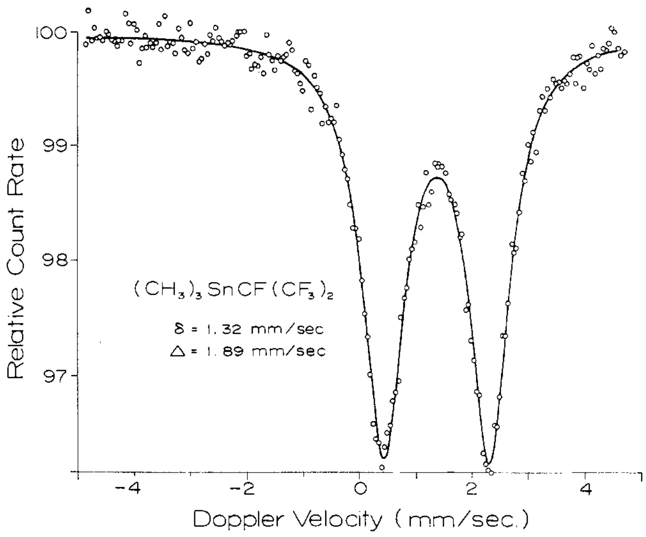


Figure 1.—The Mössbauer spectrum of $(CH_3)_3SnCF(CF_3)_2$.

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(28) For tin compounds see, for example: ref 24; W. R. Cullen and G. E. Styan, *J. Organometal. Chem.*, **6**, 533 (1966).

(29) For silicon compounds see, for example: J. Lee, C. Parkinson, P. J. Robinson, and J. G. Speight, *J. Chem. Soc., B*, 1125 (1969); and G. Fishwick, R. N. Haszeldine, C. Parkinson, P. J. Robinson, and R. F. Simmons, *Chem. Commun.*, 382 (1965).

(30) The spectrum of $(CH_3)_3SnCH_2F$ was obtained using ^{119m}Sn-enriched SnO_2 as the source. SnO_2 has a very large γ-ray line width (1.5 ± 0.2 mm/sec)[31] and thus a small quadrupole splitting may not have been resolved.

(31) R. H. Herber and G. I. Parisi, *Inorg. Chem.*, **5**, 769 (1968).

(32) *E.g.*, T. C. Gibb and N. N. Greenwood, *J. Chem. Soc., A*, 43 (1966); N. N. Greenwood and J. N. R. Ruddick, *ibid.*, 1677 (1967).

(33) J. C. Hill, R. S. Drago, and R. H. Herber, *J. Amer. Chem. Soc.*, **91**, 1644 (1969), have recently interpreted the quadrupole splitting of $(CH_3)_3SnCl$ on the basis of a σ-only effect.

groups, that is: $CH_2F < CHF_2 < CF_3 \approx CH(CF_3)_2 < C_2F_5 < CF(CF_3)_2$. The order $CF_3 < C_2F_5 < CF(CF_3)_2$ is in agreement with an order of effective electronegativities based on the chemical shifts of the H atoms in the nmr spectra of the compounds $HC{\equiv}CR_f$ and $\overline{HC{=}CR_fCF_2}$, assuming that the shifts are due to an increased deshielding of the hydrogen atom caused by an increase in electronegativity of the R_f substituent. In all cases a shift to lower field occurs as the size of the R_f group increases.[6] The apparent equivalence of the electronegativities of CF_3 and $CH(CF_3)_2$ is surprising and it appears that there may be another affect causing an electric field gradient in $(CH_3)_3SnCH(CF_3)_2$. Powell and Lagowski[34] have attempted to estimate the electronegativities of various saturated R_f groups but their results are not definitive.

The constant isomer shift ($\Delta = 1.25 \pm 0.06$ mm/sec) of the vinyltin derivatives implies a constant electron density at the tin nuclei. The quadrupole splitting observed in the spectrum of $(CH_3)_3SnCF{=}CF_2$ ($\Delta = 1.41$ mm/sec) is probably due to the electronegativity effect of the fluorocarbon group rather than π-bonding interactions since no quadrupole splitting is observed in the Mössbauer spectra of the vinyl compounds R_3Sn-$CH{=}CH_2$.[11] The quadrupole splitting observed in the spectrum of $(CH_3)_3SnC{\equiv}CCF_3$ is larger than that observed in $(CH_3)_3SnC{\equiv}CC_6H_5$. This increase might be explained by the larger inductive effect of CF_3 relative to the C_6H_5 ring. The still larger splitting observed for $(CH_3)_2Sn(C{\equiv}CCF_3)_2$ ($\Delta = 1.95$ mm/sec) may be due to both the increased total electronegativity effect on the electric field gradient caused by the addition of a second propynyl group and the fact that the asymmetry parameter is now nonvanishing. It cannot be stated, at this time, which mechanism has the greater influence.

If it is assumed that the unsaturated fluorocarbon groups do not π bond to the tin and that the quadrupole splittings are due only to σ-bonding effects, then the results indicate that the electronegativity of the groups increases in the order $CH_2F < CHF_2 < CF{=}CF_2 < CF_3 \approx CH(CF_3)_2 < CF_2CF_3 < C{\equiv}CCF_3 < CF(CF_3)_2$. However, it does not seem possible to extract group electronegativities from these data since although the electronegativities of CF_3 and Cl are believed to be similar[34] the quadrupole splittings observed for $(CH_3)_3$-$SnCl$ and $(CH_3)_3SnCF_3$ are very different.[33]

Several authors have found correlations between the Mössbauer and nmr data of tin compounds.[12,35,36] In the present work no good correlation between Δ and $J_{^{119}Sn-CH_3}$ or between Δ and the chemical shift of the tin methyl group has been found.

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(35) V. V. Khrapov, V. I. Gol'danskii, A. K. Prokof'ev, and R. G. Kostyanovskii, *Zh. Obshch. Khim.*, **37**, 3 (1967).

(36) B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, **7**, 1120 (1968).

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Mössbauer Spectroscopy of Organometallic Compounds. Organotin Azides

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Infrared, Mössbauer, and related physicochemical data are presented for a series of trialkyltin azides and dialkyltin diazides and interpreted in terms of the structure and bonding in such molecules. From the isomer shift and quadrupole splitting data for $(CH_3)_3SnN_3$ and the temperature dependence of the Mössbauer–Lamb fraction it is concluded that this molecule contains five-coordinate tin atoms with bridging azide groups linking the $(CH_3)_3Sn$ moieties. The higher alkyl homologs of this molecule are probably nonpolymeric at room temperature, as suggested by their liquid nature, but polymeric solids with (weakly) bridging N_3 groups at liquid nitrogen temperature. No evidence is observed for octahedral coordination for $(CH_3)_2Sn(N_3)_2$ or the related higher alkyl homologs at liquid nitrogen temperature. From Mössbauer isomer shift systematics for octahedral halogen complexes of the type SnX_6^{2-} and for trimethyltin halides, a group electronegativity (Mulliken) of 8.54 ± 0.10 has been derived for the nonbridging covalent N_3 group in $[(CH_3)_4N]_2Sn(N_3)_6$ and of 7.66 ± 0.06 for the bridging covalent N_3 group in $(CH_3)_3SnN_3$.

I. Introduction

Extensive study in recent years by a wide variety of physicochemical techniques has shown that the structure and bonding in organotin compounds is sensitively dependent on the nature of the ligands bonded to the metal atom and that four-, five-, and six-coordinations are all observed in closely related molecules. As part of a continuing series of investigations, Mössbauer spectroscopy has been used—in conjunction with other spectroscopic techniques—to elucidate the nature of organotin halides and pseudohalides, and the present study was undertaken to clarify the ligand character of the azide group (N_3) in such compounds.

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