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Synthesis and NMR Study of Ethyl- and Perfluoroethyltin Vinyl and Hydride Derivatives

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The syntheses of four perfluoroethyltin compounds, $(C_2H_5)_2Sn(C_2F_5)_2$, $(C_2H_5)_2Sn(I)C_2F_5$, $(CH_2{=}CH)_2Sn(C_2F_5)_2$ and $(CH_2{=}CH)_3SnC_2F_5$, are reported for the first time via a Barbier reaction from the corresponding ethyl- and vinyltin bromides. The synthetic reactions resulted in the iodide transhalogenation product in the ethyltin case and the vinyl group redistribution product in the vinyltin case as well as the expected products. The new compounds were characterized by infrared and mass spectral data, and studied by proton and fluorine-19 nmr. Analyses of these data yielded the ν_A, ν_B, ν_E and $|J_{AB}|$, $|J_{AC}|$, $|J_{BC}|$ parameters. The four ethylstannane compounds, $(C_2H_5)_nSnH_{4-n}$, were synthesized and utilized in comparison nmr studies.

Introduction

Among the tetraorganotin compounds, several are known with perfluoroalkyl groups [2–4]. Their synthesis by cleavage of the tin–tin bond in hexamethylditin was discovered independently by two groups of workers in 1960: [5–8]

$$(CH_3)_3SnSn(CH_3)_3 + CF_3I \xrightarrow[\text{heat}]{h\nu} (CH_3)_3SnCF_3 + (CH_3)_3SnI \qquad (1)$$

Perfluoroethyl iodide and hexaphenylditin also react [5]. Tetrafluoroethylene inserts into the tin–tin bond of hexamethylditin: [9]

$$(CH_3)_3SnSn(CH_3) + C_2F_4 \xrightarrow{h\nu} (CH_3)_3SnC_2F_4Sn(CH_3)_3 \qquad (2)$$

and dimethylbis(perfluoropropyl)tin has been prepared by treating the dichloride with perfluoro-n-propyllithium: [10]

$$(CH_3)_2SnCl_2 + 2n\text{-}C_3F_7Li \longrightarrow (CH_3)_2Sn(C_3F_7\text{-}n)_2 \qquad (3)$$

A Barbier reaction has been used to prepare methyl- and n-butyltin perfluoroethyltin compounds using perfluoroethyl iodide in THF: [11]

$$R_2SnX_2 + 2C_2F_5I + 2Mg \longrightarrow R_2Sn(C_2F_5)_2 + 2MgXI \qquad (4)$$

The perfluoroalkyltin derivatives lend themselves readily to study by fluorine-19 nmr techniques, and first-order spectra with large separations in the CF_2 and CF_3 resonances in these A_3B_2X systems have been observed [12]. The fluorine–fluorine couplings in perfluoroethyltin compounds are small compared with those found in perfluoroethyl iodide.

The study of the proton nmr spectra of vinyltin compounds has received considerable attention [13–18], including those tin derivatives with perfluoroalkyl groups attached [19].

We report in this paper the synthesis of four perfluoroethyltin compounds not previously reported, and their study by nmr techniques. The four ethyltin compounds, $(C_2H_5)_nSnH_{4-n}$, were synthesized for comparison nmr studies.

Experimental

All materials were reagent grade and used without further purification. Operations were carried out in an inert atmosphere. Infrared spectra were recorded on a Beckman IR-10 using NaCl liquid cells. Mass spectra were obtained on an A.E.I. MS-902 spectrometer. Sample purification was carried out on an F + M Model 5750 Research Gas Chromatograph using an SE-30 packed 0.5 in diameter, 30 ft, preparative column. Routine nmr spectra were run on Varian A-60A and HA-100D spectrometers. The stannanes were examined as *ca.* 20% solutions in benzene with TMS (*ca.* 20%) as the reference. Runs on the HA-100D were made in frequency sweep with a benzene lock. The chemical shifts were measured by counting the difference between the manual oscillator and the sweep oscillator with a Hewlett-Packard Model 521C electronic counter. The nmr parameters

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TABLE I. Infrared Absorptions for the Perfluoroethyltin Compounds.[a,b]

$(C_2H_5)_2Sn(C_2F_5)_2$	$(C_2H_5)_2Sn(I)C_2F_5$	$(CH_2{=}CH)_2Sn(C_2F_5)_2$	$(CH_2{=}CH)_3SnC_2F_5$	Assign.
2960 s	2965 s	–	2985 m	ν(C–H)
–	2940 m	–	2943 m	ν(C–H)
2880 s	2880 s	–	–	ν(C–H)
–	–	–	1915 w	ν(C=C)
1520 w	–	–	–	–
1460 m	1462 m	–	–	–
–	1423 w	–	–	–
1385 w	1388 m	1398 vw	1398 m	–
1315 vs	1318 vs	1318 vs	1318 vs	ν(C–F)
1270 vs	1292 s	1292 w	1290 w	–
1195 vs	1188 vs	1203 vs	1195 vs	ν(C–F)
1098 vs	1100 vs	1103 vs	1095 s	ν(C–F)
1060 vs	1068 vs	1072 m	1052 s	ν(C–F)
1017 m	1023 m	–	1002 s	–
–	958 m	965 w	960 s	–
927 s	930 s	942 s	930 s	ν(C–C)

[a] ±1 cm^{-1}. [b] 10% solutions in CH_2Cl_2.

were calculated on a Univac 1108 computer. The fluorine-19 spectra were recorded with the spectrometer operating in the frequency sweep mode at 94.1 MHz using a fluorotrichloromethane lock material. The perfluoroethyltin samples were run as *ca.* 20% solutions in methylene chloride. The larger range of the ^{19}F chemical shifts necessitated substituting an external audio oscillator for the manual oscillator of the HA-100D spectrometer.

Syntheses

Triethyltin hydride was prepared from triethyltin bromide which in turn was made from tin(IV) bromide and tetraethyltin (Alpha Inorganics, Inc.) in a 1:3 molar ratio [20]. The triethyltin bromide was then reduced with lithium aluminum hydride [21] and identified by its infrared spectrum which shows a strong ν(SnH) mode at 1820 cm^{-1} [22].

Diethyltin dihydride was prepared from diethyltin dibromide which in turn was made from tetraethyltin and tin(IV) bromide in a 1:1 mixture [20]. The dibromide was reduced by lithium aluminum hydride and the product identified by its infrared spectrum [22].

Ethyltin tribromide was prepared by adding bromine slowly to an equimolar amount of molten diethyltin dichloride or dibromide according to:

$$(C_2H_5)_2SnX_2 + Br_2 \rightarrow C_2H_5SnX_2Br + C_2H_5Br \quad (5)$$

The mixture was allowed to reflux until the bromine color was dissipated. The resulting ethyl bromide was removed by distillation. The ethyltin trihalide was reduced to the trihydride by lithium aluminum hydride [23].

Diethylbis(perfluoroethyl)tin and Diethylperfluoroethyltin Iodide

Diethyltin dibromide (15.9 g, 0.05 mol) and magnesium metal (2.4 g, 0.10 gm-at) were placed in THF (200 ml). A solution of perfluoroethyl iodide (24.6 g, 0.10 mol) in THF (50 ml) precooled to 0 °C was added dropwise over 2 hrs and the reaction mixture stirred for 24 hr. The precipitated magnesium salts were filtered, the volatiles stripped *in vacuo*, and three major products were isolated and purified by glc.: $(C_2H_5)_2Sn(C_2F_5)_2$ in 10% yield. *Anal.*: Calcd. for $C_8H_{10}F_{10}Sn$: C, 23.15; H, 2.43; F, 48.50%. Found: C, 23.37; H, 2.37; F, 48.32%; $(C_2H_5)_2Sn(I)C_2F_5$ in 8% yield. *Anal.*: Calcd. for $C_6H_{10}F_5ISn$: C, 17.05; H, 2.38; F, 22.47%. Found: C, 17.27; H, 2.38; F, 22.41%; and $(C_2H_5)_2SnBr_2$. The compounds were identified by infrared (as *ca.* 10% solutions in methylene chloride), mass spectral and ^1H, ^{19}F and ^{119}Sn nmr techniques.

Divinylbis(perfluoroethyl)tin and Trivinylperfluoroethyltin

Divinyltin dibromide (16.6 g, 0.05 mol) and magnesium metal (2.4 g, 0.10 gm-at) were placed in THF (200 ml). A solution of perfluoroethyl iodide (24.6 g, 0.10 mol) in the THF (50 ml) precooled to 0 °C was added dropwise over 2 hr and the reaction mixture stirred for 24 hr. The precipitated magnesium salts were filtered, the volatiles stripped *in vacuo*, and two major products were isolated and purified by glc.: $(C_2H_3)_2Sn(C_2F_5)_2$ in 10% yield. *Anal.*: Calcd. for $C_8H_6F_{10}Sn$: C, 23.39; H, 1.47; F, 46.25% Found: C, 23.44; H, 1.16; F, 45.96%; and $(C_2H_3)_3SnC_2F_5$ in 5% yield. *Anal.*: Calcd. for $C_8H_9F_5Sn$: C, 30.14, H, 2.84; F, 29.80%. Found: C,

TABLE II. Mass Spectral Fragments for Perfluoroethyltin Compounds.[a]

$(C_2H_5)_2Sn(C_2F_5)_2$			$(C_2H_5)_2Sn(I)C_2F_5$		
M/e[b]	Ion	Abund.	M/e	Ion	Abund.
297	$(C_2H_5)_2SnC_2F_5$	0.33	305	$(C_2H_5)_2SnI$	0.21
287	$C_2H_5Sn(F)C_2F_5$	0.01	295	$C_2H_5Sn(I)F$	0.10
196	$(C_2H_5)_2SnF$	1	247	$(C_2H_5)_2SnCF_3$ or SnI	0.16
186	$C_2H_5SnF_2$	0.27	213	$C_2H_5(C_2H_2F)SnF$	1
149	C_2H_5Sn	0.36	155	CH_2FSnF	1
139	SnF	0.48	149	C_2H_5Sn	0.63
100	C_2F_4	0.007	139	SnF	0.37
$(CH_2{=}CH)_2Sn(C_2F_5)_2$			101	C_2F_4H	0.21
			100	C_2F_4	0.21
293	$(C_2H_3)_2SnC_2F_5$	0.20	$(CH_2{=}CH)_2Sn(C_2F_5)_2$		
285	$(C_2H_3)(C_2F_5)SnF$	0.02			
209		0.01	201	$(C_2H_3)_3Sn$	1
193	$(C_2H_3)_2SnF$	1	193	$(C_2H_3)_2SnF$	0.33
185	$(C_2H_3)SnF_2$	0.25	175		0.25
147	$(C_2H_3)Sn$	0.37	147	$(C_2H_3)Sn$	0.45
139	SnF	0.42	139	SnF	0.20
108		0.06			
100	C_2F_4	0.05			

[a] Recorded at an ionization voltage of 20 eV. [b] Based on tin-120.

30.73; H, 2.81; F, 28.37%. The compounds were identified by infrared (as *ca.* 10% solutions in methylene chloride), mass spectral, and ^1H, ^{19}F and ^{119}Sn nmr techniques.

Results and Discussion

The Barbier reaction was used to synthesize the perfluoroethyltin derivatives. Using diethyltin dibromide with perfluoroethyl iodide in THF, a new organotin iodide derivative resulted:

$$(C_2H_5)_2SnBr_2 + 2C_2F_5I + Mg \longrightarrow (C_2H_5)_2Sn(C_2F_5)_2 + (C_2H_5)_2Sn(I)C_2F_5 + MgBr_2 \qquad (6)$$

With divinyltin dibromide a new trivinyltin derivative resulted:

$$(C_2H_3)_2SnBr_2 + C_2F_5I + Mg \longrightarrow (C_2H_3)_2Sn(C_2F_5)_2 + (C_2H_5)_2Sn(I)C_2F_5MgBr_2 \qquad (7)$$

In the first reaction (Eq. 6) the transhalogenation reaction product is unexpected; in the second (Eq. 7) the redistribution reaction of the vinyl groups is unexpected.

The infrared data for these products are given in Table I. The perfluoroethyltin compounds show four sets of strong bands associated with the ν(C–F) stretching modes in the 1325–1050 cm^{-1} region [5]. In addition, all the C_2F_5 derivatives have a single band at 927 ± 1 cm^{-1} arising from a carbon–carbon skeletal mode. The vinylic carbon–carbon stretching mode at 1915 cm^{-1} in $(C_2H_3)_3SnC_2F_5$ compares with the similar band at 1908 cm^{-1} in tetravinyltin [24], but no absorption in this region was observed in $(C_2H_3)_2Sn(C_2F_5)_2$. The normal ν(C–H) stretching modes at 3000 - 2800 cm^{-1} were also seen in all compounds studied except for $(C_2H_3)_2Sn(C_2F_5)_2$, perhaps because of low concentration of the dilute solution used.

Table II lists the major tin-bearing fragments observed in the mass spectrometer. In all cases the highest mass fragment observed is the (parent – $C_2F_5^+$) ion. That this is true as well for $(C_2H_5)_2Sn(I)C_2F_5$ implies that C_2F_5 may be a more stable fragment than the iodine atom in the low density gas phase conditions in the mass spectrometer. Decomposition schemes are outlined in Eq. 8 below by analogy with proposals for other ethyltin compounds [25]:

$$\begin{tikzcd}
 & (C_2H_5)_2Sn(C_2F_5)_2^+ \arrow[r] & (C_2H_5)_2SnC_2F_5^+ + C_2F_5 \arrow[dl] \arrow[dr] & \\
 & C_2H_5 + C_2F_3 + C_2H_5SnF_2^+ \arrow[dl] \arrow[dr] & & (C_2H_5)_2SnF^+ + C_2F_4 \\
2F + C_2H_5Sn^+ & & SnF^+ + C_2H_5 + F &
\end{tikzcd} \qquad (8)$$

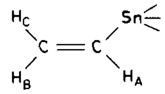
TABLE III. ^{19}F Nmr Assignments for Perfluoroethyltin Compounds.[a,b]

	$(C_2H_5)_2Sn(C_2F_5)_2$	$(C_2H_5)_2Sn(I)C_2F_5$	$(CH_2{=}CH)_2Sn(C_2F_5)_2$
ν_A[c]	7888.5	7764.3	7832.5
ν_B[d]	10958.5	11094.6	10910.6
J_{AB}[e]	not obs.	2.0	not obs.
$\lvert ^2J(^{117/119}Sn\text{–}A)\rvert$	<10	<10	3.7 (?)
$\lvert ^3J(^{119}Sn\text{–}B)$[f]$\rvert$	228.2	241.5	272.8
$J^{119/117}$[g]	1.045	1.045	1.043

[a] 10% solutions in CH_2Cl_2. [b] $A_3B_2Sn = CF_3CF_2Sn$. [c] Chemical shifts in Hz relative to $CFCl_3$. [d] ±0.5 Hz. [e] b0.1 Hz. [f] ±0.5 Hz. [g] Theoretical ratio = 1.046.

TABLE IV. ^1H Nmr Assignments for the Perfluoroethyltin Compounds.[a]

	$(C_2H_5)_2Sn(C_2F_5)_2$[b,c]	$(C_2H_5)_2Sn(I)C_2F_5$[b,d]	$(C_2H_3)_2Sn(C_2F_5)_2$[e,f]	$(C_2H_3)_3SnC_2F_5$[e,f]	$(C_2H_3)_4Sn$[e,f,g]
ν_A[h]	392.6	398.3	633.1	634.6	631.8
ν_B[h]	372.5	362.8	640.1	629.0	614.1
ν_C[h]	–	–	600.5	585.6	568.6
$\lvert ^3J_{AB}\rvert$[i]	8.0	7.8	13.3	13.2	13.8
$\lvert ^3J_{AC}\rvert$	–	–	20.1	19.9	20.7
$\lvert ^2J_{BC}\rvert$	–	–	2.8	3.2	3.1
$\lvert ^2J(^{119}Sn\text{–}H_A)\rvert$[j]	102.6	117.8	129.8	112.0	–
$\lvert ^3J(^{119}Sn\text{–}H_B)\rvert$	59.4	48.2	246.7	210.8	–
$\lvert ^3J(^{119}Sn\text{–}H_C)\rvert$	–	–	116.3	105.5	–

[a] In Hz relative to TMS. [b] The values relative to the CH_2Cl_2 internal standard were converted to TMS using 532 Hz; lettering refers to A_3B_2Sn. [c] The tin-119 chemical shift is 65 p.p.m. upfield of tetramethyltin [39]. [d] The tin-119 chemical shift is 17 p.p.m. upfield of tetramethyltin [39]. [e] Relative to TMS. [f] Lettering refers to 

. [g] Ref. 16. [h] ±0.2 Hz. [i] ±0.1 Hz. [j] ±0.2 Hz.

The same generalized decomposition pathways seem to hold for the vinyl compounds studied, as seen in Table II.

Table III lists the fluorine-19 nmr data for the perfluoroethyltin compounds studied. The spectra of ethyl- or perfluoroethyltin compounds is the result of the superposition of three subspectra: 85% A_3B_2, 8.68% A_3B_2 ^{119}Sn and 7.67% $A_3B_2{}^{117}Sn$, which in the proton nmr, are rarely first-order. The spectral analyses of the A_3B_2 portions were performed by the exact solution of the secular equation method [26]. The observation of one set of $^{117,119}Sn$–A and $^{117,119}Sn$–B satellites permits evaluation of the two J values. Transition frequencies and intensities for the A_3B_2 system are obtained from experimental parameters [27]. The proton nmr assignments listed in Table IV were derived from this treatment.

The vinyltin system is of the three-spin ABC type so far as the nonmagnetic tin isotopes are concerned, and large second-order effects are present. Solutions for the six independent parameters in the secular equations, ν_A, ν_B, ν_C, and $|J_{AB}|$, $|J_{AC}|$, $|J_{BC}|$, were obtained using a modification [28] of Part I of the LAOCOON II Fortran Program [29]. Most of the tin satellites are observable, and these allow the chemical shifts and coupling constants to be estimated. Since the relative signs of the coupling constants can also alter the calculated spectrum, trials with various signs for the three J values were run. Convergence was achieved for the ABC centerbands only. The ABCX and ABCY systems are first-order because of the large chemical shifts of the tin isotopes.

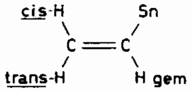
The proton nmr spectra of the diethyltin perfluoroethyl derivatives closely resemble those of the diethyltin dihalides. An increase in δ_{AB} on going to $(C_2H_5)_2Sn(I)C_2F_5$ reflects the smaller electronegativity of iodine relative to the C_2F_5 group [30]. The values of $|J(Sn\text{–}A)|$ and $|J(Sn\text{–}B)|$ also fall into the range of couplings observed for the diethyltin dihalides.

In the vinyltin compounds it is observed that the *trans*-proton resonance moves progressively downfield when perfluoroethyl groups replace vinyl groups in tetravinyltin [14–16], and this is accompanied by a downfield shift of the *cis*-proton resonance while the *gem*-proton resonance remains almost unchanged.
]

TABLE V. ^1H Nmr Assignments for the Ethylstannanes.

	$(C_2H_5)_4Sn$	$(C_2H_5)_3SnH$	$(C_2H_5)_2SnH_2$	$C_2H_5SnH_3$
ν_A[a,b]	120.0[c]	120.3	125.8[d]	125.7
ν_B[b]	81.5[e]	85.9	101.1[f]	–
ν_C[b]	–	503.5[g]	464.8[h]	431.0[i]
ν_{Sn}[j,k,l]	–1	–40	–231	–280
$\lvert {}^3J({}^{119}Sn–A) \rvert$[m]	69.2[n]	75.8	82.8[o]	89.7
$\lvert {}^2J({}^{119}Sn–B) \rvert$[m]	49.7[p,q]	55.2[q]	60.2[q]	65.6[q]
$\lvert {}^1J({}^{119}Sn–C) \rvert$[r]	–	1613.2[q,s]	1689.6[q,t]	1790.4[q,u]
J_{AB}[h,n]	8.2	8.2	8.0	7.8

[a] All chemical shifts are in Hz and are relative to TMS at 100 MHz; $CH_3CH_2SnH = A_3B_2SnC$. [b] ±0.3 Hz. [c] ν_A for $(C_2H_5)_4Sn$ has been listed as –1.08 [30], –1.18 (CCl_4/TMS) [40], –1.21 ($CDCl_3$/TMS) [18], –1.20 p.p.m. (DMSO/TMS) [18], –70.6 (TMS) [41], –71.0 (CCl_4/TMS) [42], 6.6 Hz (*vs.* cyclohexane at 25 MHz) [43], and $\tau = 9.22$ [44]. [d] ν_A for $(C_2H_5)_2SnH_2$ has been listed as $\tau = 8.80$ [45]. [e] ν_B for $(C_2H_5)_4Sn$ has been listed as –0.69 (CCl_4/TMS) [30], –0.74 (CCl_4/TMS) [40], –0.76 [46], –0.83 ($CDCl_3$/TMS) [18], –0.79 p.p.m. (DMSO/TMS) [18], –47.0 (CCl_4/TMS) [42], 15.9 Hz (*vs.* cyclohexane at 25 MHz) [43] and $\tau = 8.84$ [44]. [f] ν_B for $(C_2H_5)_2SnH_2$ has been listed as $\tau = 9.17$ [45]. [g] ν_C for $(C_2H_5)_3SnH$ has been listed as $\tau = 5.24$ (CS_2) [47], 5.17 [38], 5.00 (cyclopentane) [48] and $\delta = -293.5$ Hz [49]. [h] ν_C for $(C_2H_5)_2SnH_2$ has been listed as $\tau = 5.25$ (cyclopentane) [47], 5.38 (10% in TMS) [45], 5.52 (cyclopentane) [38, 48, 50] and $\delta = -4.59$ p.p.m. [51]. [i] ν_C for $C_2H_5SnH_3$ has been listed as $\tau = 5.66$ (cyclopentane) [38, 47, 48]. [j] A negative sign indicates a shift upfield of tetramethyltin. [k] Ref. 39. [l] The tin-119 chemical shift for $(C_2H_5)_4Sn$ has been listed as –1.4 (CCl_4) [52, 53], 5.97 [54], 6.0 [55] and 6.7 p.p.m. [56] *vs.* $(CH_3)_4Sn$. [m] ±0.2 Hz. [n] $\lvert {}^3J({}^{119}Sn–C–C–{}^1H) \rvert$ for $(C_2H_5)_4Sn$ has been listed as 65.7 [41], 66.8 [43], 69.2 [42], 71.2 [30, 44, 57, 58], 68.5 ($CDCl_3$) [18] and 67.9 Hz (DMSO) [18]. [o] $\lvert {}^3J({}^{119}Sn–C–C–{}^1H) \rvert$ for $(C_2H_5)_2SnH_2$ has been listed as –83.7 Hz [45]. [p] $\lvert {}^2J({}^{119}Sn–C–{}^1H) \rvert$ for $(C_2H_5)_4Sn$ has been listed as 32.2 [30, 44, 57–59]. [q] Ref. 60. [r] ±0.2 Hz. [s] $\lvert {}^1J({}^{119}Sn–{}^1H) \rvert$ for $(C_2H_5)_3SnH$ has been listed as 1574 [38], 1611.3 [48] and 1612.4 [49] Hz. [t] $\lvert {}^1J({}^{119}Sn–{}^1H) \rvert$ for $(C_2H_5)_2SnH_2$ has been listed as –1688.4 [45] and 1691.1 [38, 48, 50] Hz. [u] $\lvert {}^1J({}^{119}Sn–{}^1H) \rvert$ for $(C_2H_5)_3SnH$ has been listed as 1790.1 [38, 48] Hz.



In $(C_2H_3)_2Sn(C_2F_5)_2$ $\nu_{trans\text{-}} < \nu_{gem\text{-}}$, but the order $\nu_{trans\text{-}} > \nu_{cis\text{-}} > \nu_{gem\text{-}}$ has been observed in several hundred vinyl compounds [31]. Anomalous orders have also been found for acrylonitrile [32–33] and vinyl ethers [34–36]. In vinyl ethers the high shifts are thought to arise from delocalization effects, while strong diamagnetic anisotropies associated with the triple bond are thought to cause the anomalous order of shifts in the nitrile. It has been suggested that anisotropies arising from the Sn–C bond act to deshield the vinyl protons in tetravinyltin in the order *gem-* > *trans-* > *cis-* [15]. Since the order in the vinyltin compounds studied here is trans $\nu_{trans\text{-}} \cong \nu_{cis\text{-}} \gg \nu_{gem\text{-}}$, the bond anisotropies do not predominate.

The effect of substituting strongly electronegative groups at tin should be to deshield the *gem*-proton most, contrary to what is observed. Canonical forms such as $^+CH_2–CH=Sn^-$ involving (p → d)–π interactions and charge separation [16] could rationalize the deshielding of the β-protons and the small effect on the α-proton as well, but this is not a suggestion that we favor. Steric effects would be expected to give rise to temperature-dependent spectra, but no change in the fluorine-19 spectrum of $(C_2H_3)_2Sn(C_2F_5)_2$ was observed to –120 °C.

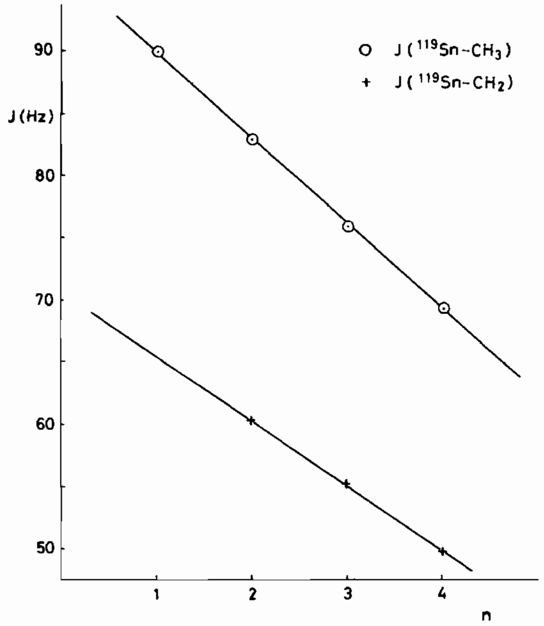


Fig. 1. J values *vs.* number of ethyl groups in ethylstannanes.

Unlike the ethyltin case, the vinyltin-nmr data are much closer to those of tetravinyltin [14–16] than to the vinyltin halides [37].

The related ethyltin hydrides are of interest. The proton nmr assignments are listed in Table V. One set of $SnCH_2CH_3$ satellites and both the tin-117 and tin-119 Sn-H satellites are observable, as is ν_A. The slight discrepancy between the calculated and observed B resonances probably arises as a result of the hydridic proton coupling with the methylene group.

The $|^2J(^{119}Sn–C–^1H)|$ and $|^3J(^{119}Sn–C–C–^1H)|$ both decrease linearly with the number of ethyl groups at tin as shown in Figure 1. The value of $|^2J(^{119}Sn–C–^1H)|$ could not be discerned from the spectrum of ethyltin trihydride directly, but its value was estimated from the line in Figure 1, and found in this way. The magnitude of the $|^1J(^{119}Sn–^1H)|$ values have also been found to correlate with the number of alkyl groups at tin [38].

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