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CARBON-13 FOURIER TRANSFORM NMR STUDIES OF ORGANOTIN COMPOUNDS

III *. CARBON-13 CHEMICAL SHIFTS AND TIN-119—CARBON-13 SPIN—SPIN COUPLING CONSTANTS IN ACYCLIC, MONOCYCLIC AND BICYCLIC ORGANOSTANNANES

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Summary

Carbon-13 NMR parameters for 33 organotin compounds with a variety of structural features were investigated in order to obtain information about the relationship between their structure and ^{13}C NMR parameters. It was found that the substitution of a proton by a trialkyltin group generally produces an upfield shift for the directly bonded carbon. The γ-nuclei usually resonate at lower fields except where there is appreciable steric strain while the β-carbons undergo relatively constant shifts of approximately 3.5 to 4.5 ppm to lower fields. The magnitude of direct bond coupling $|^1J(^{119}\text{Sn}—^{13}\text{C})|$ is influenced by the hybridization of the tin and the directly attached carbon atoms. In rigid organitins, the *vicinal* coupling constants show a Karplus type variation. In aliphatic organotins, the values of the *vicinal* ^{119}Sn—^{13}C coupling indicates a flexible molecular framework with a clear cut preference for certain conformations.

Introduction

There has been a plethora of NMR studies of organotin compounds in the ^{1}H, ^{13}C and ^{119}Sn modes [1—24]. ^{13}C NMR investigations are particularly suited to the determination of the structure, conformation and state of tin hybridization in organotins because signals of interest can easily be resolved and no second order analysis is necessary. In preliminary communications [1,2] we have shown

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* For parts I and II see refs. 1 and 2.

that ${}^3J({}^{119}Sn-{}^{13}C)$ is highly angular dependent and follows the equation $J = 30.4 - 7.6 \cos\theta + 25.2 \cos 2\theta$ where θ is the dihedral angle. In the present paper we report on the ${}^{13}C$ NMR parameters of a variety of saturated and unsaturated; acyclic and cyclic; and flexible and rigid organotins vis-a-vis their molecular geometry. From the data we seek possible general relationships between conformation and structure of organotins and their ${}^{13}C$ NMR parameters.

Results and discussion

Chemical shifts

The chemical shift data for 33 organotins investigated in this report are summarized in Table 1. In order to determine the effect on the direction and magnitude of the ${}^{13}C$ chemical shifts of the hydrocarbon moiety upon substitution by a trialkyltin group, we define the substituent shielding effect as:

$$\Delta\delta_i = \delta_i \text{ (trialkyltin derivative)} - \delta_i \text{ (parent hydrocarbon)} = \delta_i(R_3Sn{-}R') - \delta_i(H{-}R')$$

i.e., downfield shifts on substitution are positive.

Inspection of the results, and comparison of the chemical shifts with those of the parent hydrocarbons reveals the following trends for saturated compounds:
(i) The α-carbon resonances are shifted upfield, with the exceptions XIX—XXII and XXIV (Table 1).
(ii) The β-carbon resonances are shifted downfield in every case but one: C_3 of XXXII. This shift is fairly uniform and with few exceptions these resonances fall between 3.2 and 4.7 ppm from the parent hydrocarbon.
(iii) The γ-carbon resonances are mostly shifted downfield. The exceptions are certain resonances in the norbornyl, nortricyclyl * and adamantyl derivatives. These exceptions constitute examples of "steric compression", which shifts resonances to higher field than those observed for similar nuclei in "normal" environment [25]. In the 2-adamantyl derivative, for example, the γ_{syn} resonances (C_4, C_9) are 4.4 ppm to higher field than the γ_{anti} resonances (C_8, C_{10}) and lie 1.4 ppm to higher field than the corresponding signal in adamantane. Thus the γ-shift is usually positive except in those cases where the steric perturbation is relatively large.
(iv) There is insufficient data to make any comments upon the δ-shifts.

For the trimethyltin derivatives with saturated α-carbons examined here, the average values of the α-, β-, and γ-shielding effects are: α −1.7 ppm; β 4.1 ppm, γ 0.0 ppm.

Downfield shifts at the α-position are found for all common substituents and in several organometallics, such as Grignard compounds [26] $Zn(CH_3)_2$ and $Pb(CH_3)_4$ [17]. The upfield shift observed in these compounds probably reflects an increase in electron density at the α-nucleus, although changes in the paramagnetic term [27] are not easily estimated and the correlation of electronegativity with ${}^{13}C$ chemical shift (for example in the metal methyls) is very

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* Nortricyclyl = tricyclo[2.2.1.0^{2,6}]heptane.

poor indeed. Calculations of chemical shifts by Sichel and Whitehead [28] have included the series $(CH_3)_4X$ (X = C, Si, Ge, Sn) and have shown a good correlation of chemical shift with the charge on carbon calculated by the extended Hückel method, but the calculated electron distributions are probably unrealistically polar. Mason [29] has recently suggested the inclusion of adjacent nuclei in the calculations of the diamagnetic term. In the tin compounds this would mean a significant contribution to the overall shielding from the diamagnetic term. This hypothesis has been strongly criticised by Lippmaa et al. [30].

It is perhaps at first surprising to note that the shifts at the α-carbons of the 7-norbornyl, 7-*anti*- and 7-*syn*-norbornenyl, and 2-adamantyl derivatives are to a lower field. Closer examination of the α-carbon chemical shifts shows that they do not have a constant difference from the hydrocarbon shifts, but are best described by the equation:

$$\delta_\alpha[(CH_3)_3Sn{-}R] = 1.13\delta_\alpha[H{-}R] - 5.0 \qquad (1)$$

where δ_α is the chemical shift of the α-carbon in the appropriate compound. This is shown in Fig. 1. According to this equation, there should be no change in chemical shift on replacing a proton with a trimethyltin group in a hydrocarbon where the α-carbon has a chemical shift of 38.5 ppm. Where the α-carbon has a chemical shift to lower field of 38.5 ppm (i.e., greater than 38.5), the shift on substitution should be paramagnetic. The chemical shifts in the parent

(continued on p. 184)

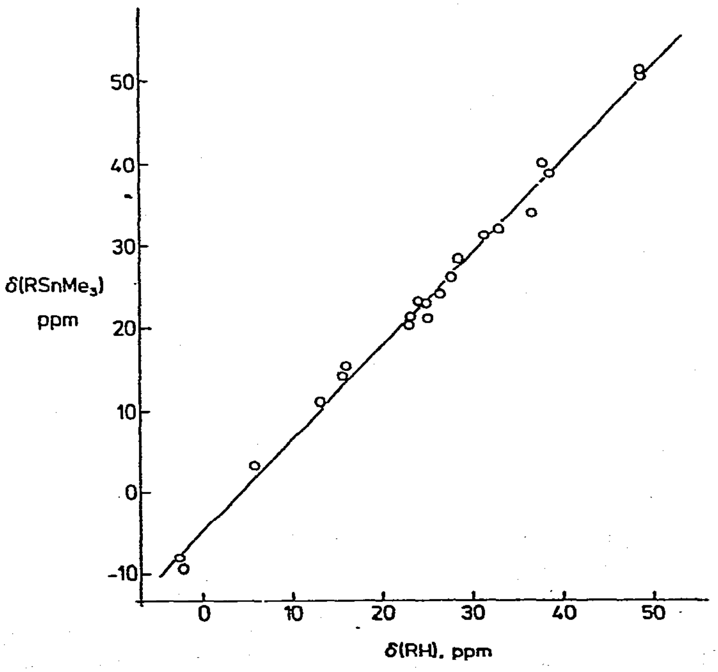


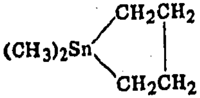
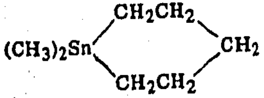
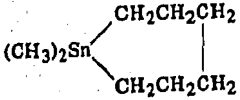
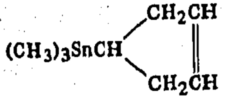
Fig. 1. Graph of chemical shifts of carbon nuclei α to trimethyltin in the saturated compounds plotted against the carbon chemical shift in the corresponding hydrocarbon. $\delta_\alpha[(CH_3)_3SnR] = 1.36\delta_\alpha[H{-}R] - 5.0$.

TABLE 1

CHEMICAL SHIFTS (±0.1 ppm)

The chemical shifts are given in ppm relative to TMS, downfield being positive. The numbers in parentheses indicate the changes in chemical shifts of similar atoms in the related hydrocarbons that have occurred upon substitution of a proton by the SnR_3 group. Data for the parent hydrocarbons were obtained from the compilation by Stothers [24].

Compound number	Compound	α	β	γ	δ	CH_3
I	$Sn(CH_3)_4$	—9.5 (—7.4)				—9.5
II	$Sn(CH_2CH_3)_4$	—0.1 (—6.0)	11.2 (4.3)			
III	$Sn(CH_2CH_2CH_3)_4$	12.1 (—3.5)	20.8 (4.7)	19.1 (3.5)		
IV	$Sn(CH_2CH_2CH_2CH_3)_4$	9.0 (—4.2)	29.6 (4.6)	27.7 (2.7)	13.8 (0.6)	
V	$(CH_3)_3SnH$					—11.8
VI	$(CH_3)_3SnCH_2CH_3$	2.8 (—3.1)	10.6 (4.7)			—11.2
VII	$(CH_3)_3SnCH_2CH_2CH_3$	13.9 (—1.7)	20.3 (4.2)	18.6 (3.0)		—10.4
VIII	$(CH_3)_3SnCH_2CH_2CH_2CH_3$	10.9 (—2.3)	29.2 (4.2)	27.2 (2.2)	13.7 (0.5)	—10.5
IX	$(CH_3)_3SnCH(CH_3)_2$	15.2 (—0.9)	21.1 (5.5)			—12.1
X	$(CH_3)_3SnCH(CH_3)CH_2CH_3$	22.9 (—2.1)	C_1 18.2 (6.0) C_3 29.3 (4.3)	14.4 (1.2)		—11.2
XI	$(CH_3)_3SnC(CH_3)_3$	21.0 (—4.2)	29.9 (5.6)			—12.2
XII	$(CH_3)_3SnCH_2CH(CH_3)_2$	23.2 (—1.1)	27.2 (2.0)	26.6 (2.3)		—9.6
XIII	$(CH_3)_3SnCH_2C(CH_3)_3$	31.5 (—0.4)	30.8 (2.9)	33.3 (1.8)		—8.4
XIV	$(CH_3)_3$Sn-*cyclo*-$[CH(CH_2)_2]$	—7.3 (—4.7)	1.3 (3.9)			—11.3
XV	$(CH_3)_3$Sn-*cyclo*-$[CH(CH_2)_3]$	21.2 (—2.1)	27.8 (4.5)	25.0 (1.7)		—11.5
XVI	$(CH_3)_3$Sn-*cyclo*-$[CH(CH_2)_4]$	24.0 (—2.5)	30.8 (4.3)	26.4 (—0.1)		—11.4
XVII	$(CH_3)_3$Sn-*cyclo*-$[CH(CH_2)_5]$	25.9 (—1.9)	31.4 (3.6)	29.0 (1.2)	27.3 (—0.5)	—11.8
XVIII	$(CH_3)_3$Sn-1-norbornyl	33.8 (—3.0)	$C_{2,6}$ 34.5 (4.4) C_7 42.5 (3.8)	$C_{3,5}$ 30.8 (0.7) C_4 36.5 (—0.3)		—11.8
XIX	$(CH_3)_3$Sn-7-norbornyl	38.8 (+0.1)	$C_{1,4}$ 40.3 (3.5)	$C_{2,3}$ 30.1 (0.0) $C_{5,6}$ 31.4 (1.3)		—9.8
XX	$(CH_3)_3$Sn-7-*anti*-norbornenyl	51.2 (+2.4)	$C_{1,4}$ 45.4 (3.2)	$C_{2,3}$ 137.8 (2.3) $C_{5,6}$ 24.9 (—0.6)		—10.3

XXI	$(CH_3)_3$Sn-7-*syn*-norbornenyl	50.4 (+1.6)	$C_{1,4}$ 46.1 (3.9)	$C_{2,3}$ 136.0 (0.5) $C_{5,6}$ 26.3 (0.8)		−9.1
XXII	$(CH_3)_3$Sn-3-nortricyclyl	31.8 (−1.4)	C_2 13.9 (4.0) C_4 33.2 (3.5)	C_1 10.0 (0.1) C_5 32.9 (−0.3) C_6 9.9 (0.0) C_7 35.0 (1.8)		−10.4
XXIII	$(CH_3)_3$Sn-1-adamantyl ^{a}	28.3 (−0.3)	42.2 (4.2)	29.5 (0.9)	38.0 (0.0)	−13.0
XXIV	$(CH_3)_3$Sn-2-adamantyl ^{a,b}	40.0 (+2.0)	32.4 (3.8)	$C_{8,10}$ 41.0 (3.0) $C_{9,4}$ 36.6 (−1.4)	C_5 28.7 (0.1) C_7 29.1 (0.5)	−9.5
XXV		10.7	29.8			−10.7
XXVI		10.8	28.6	32.8		−11.4
XXVII		11.3	31.4	25.7		−10.3
XXVIII	$Sn(CH{=}CH_2)_4$	135.3 (+12.5)	135.8 (13.0)			
XXIX	$Sn(CH_2CH{=}CH_2)_4$	16.2 (−2.5)	136.3 (3.2)	111.2 (−3.8)		
XXX	$(CH_3)_3SnCH{=}CHCH_3$ (*cis*)	129.7 (+14.7)	143.4 (10.3)	23.2 (4.5)		−9.9
XXXI	$(CH_3)_3SnC{\equiv}CCH_2CH_2CH_2CH_3$ ^{c}	81.9 (+13.3)	110.0 (26.0)	19.8 (1.2)	31.3 (0.2)	−8.1
XXXII	$(CH_3)_3SnC(CH_3)CCHCH_3$	87.5 (+3.0)	C_1 14.3 C_3 204.3 (−1.9)	76.1 (−8.4)	18.1	−9.8
XXXIII		20.2 (−2.9)	37.0 (4.4)	131.2 (0.6)		−11.2

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[a] Data for adamantane taken from Pehk et al. [32]. [b] Chemical shift for ϵ-carbon = 38.3 (0.3). [c] Chemical shift for ϵ-carbon = 21.9 (−0.5); for ζ-carbon = 13.7 (−0.4).

hydrocarbons of the compounds mentioned above are either close to 38.5 ppm or greater. Leibfritz et al. [26] have shown that a similar equation is valid for the chemical shifts of Grignard compounds compared with those of the related hydrocarbons.

There are generally few data on γ-shielding effects in metal alkyls. Reports in the literature include Grignard compounds [26] and some neopentylmercury compounds [31] where the γ-shifts are also downfield (in the mercury compounds, however, the shifts of the α-carbons are positive). Lippmaa et al. [30,32] have recently given extensive discussion of γ-shifts, and have pointed out that where there is no "steric" contribution the shifts of nuclei γ to a substituent often lie to lower field of the corresponding resonance in the hydrocarbon, as in the 1-adamantyl derivatives of a wide range of substituents. They also showed that there is not a good correlation between the γ-shifts and the polar substituent constants (σ^*). The positive γ-shifts of the compounds examined here may reflect at least in part, the low apparent steric bulk of the trimethyltin group [33] (discussed in the section on *vicinal* coupling constants, below) and the positive γ-shifts in the mercury compounds may indicate the same of the HgCl group [34].

The chemical shifts of the tin-methyl groups cover a range of nearly 5 ppm (—9.1 to —13.0 ppm) (Table 1). The chemical shifts of these groups in compounds I, V—XIII, XVI, XXX, and $(CH_3)_3SnC_5H_5$ [21] show no correlation with the polar substituent constants (σ^*) [35] of the R group. Within the series $(CH_3)_3SnR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$ there is a steady shift to higher field (δ_C = —9.5, —11.2, —12.1, —12.2).

A full discussion cannot be presented at present of the variation of the chemical shifts in the compounds where the α-carbon is unsaturated because of the limited range of such compounds investigated here. In these compounds there is a downfield shift of the resonance relative to the parent hydrocarbon (i.e., XXVIII, XXX—XXXII). The ^{13}C NMR spectra of 1-hexyne derivatives have been investigated elsewhere [36].

Spin—spin coupling constants

The derived coupling constant data are summarized in Table 2. Among the several types of coupling encountered viz., direct, *geminal*, *vicinal* and long range, the magnitudes of direct and *vicinal* ^{119}Sn—^{13}C couplings provide some fundamental information about tin hybridization and molecular conformation of organotin compounds.

Direct ^{119}Sn—^{13}C spin—spin coupling

The observed range for $|^1J(^{119}\text{Sn}—^{13}\text{C})|$ extends from 264.9 Hz (XXIX) to 519.3 Hz (XXVIII). Two factors determine the magnitude of this coupling constant.

(a) Hybridization at the α-carbon. Those coupling constants to saturated carbon atoms are generally less than those to unsaturated carbon atoms, undoubtedly reflecting the greater *s* character in the carbon hybrid orbitals directed towards the tin nucleus in the unsaturated cases. However, no simple relation appears to exist between carbon hybridization and $|^1J(^{119}\text{Sn}—^{13}\text{C})|$. For example, the direct coupling constants in the cyclopropyl and 1-hexynyl deri-

TABLE 2

COUPLING CONSTANTS (Hz)

Compound number	^1J(Sn—C)	^2J(Sn—C)	^3J(Sn—C)	^1J(Sn—C_{Me})	Σ
I	337.8			337.8	1351.2
II	320.3	23.4			1281.2
III	313.4	20.1	51.4		1253.6
IV	313.7	19.6	52.0		1254.8
V				351.8	
VI	374.2	23.6		320.8	1336.6
VII	368.9	20.8	53.0	320.0	1328.9
VIII	368.4	20.6	55.2	320.1	1328.7
IX	410.2	13.4		306.7	1330.3
X	408.1	C_1 13.2 C_3 13.4	35.6	304.5	1321.6
XI	436.9	0.0		295.7	1324.0
XII	368.1	19.8	42.1	319.7	1327.2
XIII	369.0	20.7	35.5	318.6	1324.8
XIV	502.8	18.8		341.6	1524.6
XV	389.7	23.3	57.6	313.5	1330.2
XVI	405.6	<6	51.2	311.8	1341.0
XVII	407.4	14.4	57.5	303.9	1319.1
XVIII	459.0	$C_{2,6}$ 17.3 C_7 13.0	$C_{3,5}$ 51.9 C_4 65.8	313.8	1400.4
XIX	405.6	n.d.	$C_{2,3}$ 11.9 $C_{5,6}$ 67.5	314.2	1348.2
XX	373.6	n.d	$C_{2,3}$ 67.9 $C_{5,6}$ 5.6	314.1	1315.9
XXI		5.2			
XXII	411.8	C_2 6.0 C_4 12.4	C_1 53.6 C_5 9.7 C_6 8.0 C_7 57.8	313.9	1353.5
XXIII	451.7	12.2	51.1	290.4	1322.9
XXIV	406.6	12.3	$C_{4,9}$ 8.5 $C_{8,10}$ 60.0	295.8	1294.0
XXV	334.8	17.0		300.6	1270.8
XXVI	322.1	29.6	46.4	306.9	1258.0
XXVII	339.7	11.9	23.0	300.4	1280.2
XXVIII	519.3	<6			
XXIX	264.9	48.3	51.3		
XXXI	513.4			404.2	1726.0
XXXII	431.4	C_1 24.1 C_3 n.d.	50.9	342.5	1458.9
XXXIII	400.0	6.8	n.d.	315.2	1345.3

vatives (XIV and XXXI, respectively) are nearly equal (502.8 and 513.4 Hz, respectively). The coupling constant in $Sn(CH{=}CH_2)_4$ is slightly larger still (XXVIII, J 519.3 Hz) but cannot be compared directly with the previous compounds because they are trimethyltin derivatives. That this is important can be seen by comparing the direct coupling constant in $Sn(CH_2CH{=}CH_2)_4$ (XXIX, J 264.9 Hz) with that in $(CH_3)_3SnCH_2CH{=}CH_2$ (J 298 Hz [22]). A comparison of some $|^1J(^{119}Sn—^{13}C)|$ coupling constants with those of the corresponding $^1J(^{13}C—^1H)$ coupling constants in the related hydrocarbons is given in Table 3.

(b) Hybridization changes at the tin. In the series $(CH_3)_3SnCH_{3-x}(CH_3)_x$ (x =

TABLE 3

COMPARISON OF ^{119}Sn—^{13}C SPIN—SPIN COUPLING CONSTANTS IN THE COMPOUNDS $(CH_3)_3SnR$ WITH THE CORRESPONDING ^{13}C—^{1}H SPIN—SPIN COUPLING CONSTANTS IN THE HYDROCARBONS RH

R	$\lvert{}^1J(^{119}Sn—^{13}C)\rvert$ (Hz)	$^1J(^{13}C—^1H)$ (Hz) [a]
Methyl	337.8	125
1-Norbornyl	459.0	142
Cyclopropyl	502.8	160.5
Allenyl	382 [b]	168
Phenyl	474.4 [c]	159
Vinyl [d]	519.3	156.2
1-Hexynyl	513.4	247.6 [d,e]

[a] Data in this column from collection by Stothers [24]. See references therein. [b] From ref. 22. [c] From ref. 21. [d] In $Sn(CH{=}CH_2)_4$. [e] In $CH_3C{\equiv}CH$.

0—3) there is a nearly linear relationship between the increase in $\lvert{}^1J(^{119}Sn—^{13}C_R)\rvert$ and the decrease in $\lvert{}^1J(^{119}Sn—^{13}C_{Me})\rvert$ (Fig. 2). In view of the similarity of these compounds, the three factors which can influence the coupling constants are (*i*) electron densities at the tin nuclei, *(ii)* hybridization at the α-carbon atom and *(iii)* hybridization at tin itself. Since the sum of the direct tin—carbon coupling constants (Σ, Table 2) remain relatively constant, one may assume very little changes in the electron densities at the tin nuclei and in the hybridization at the α-carbons. However, the observed range of the individual coupling constants is large compared with the variation in Σ, suggesting that hybridization changes

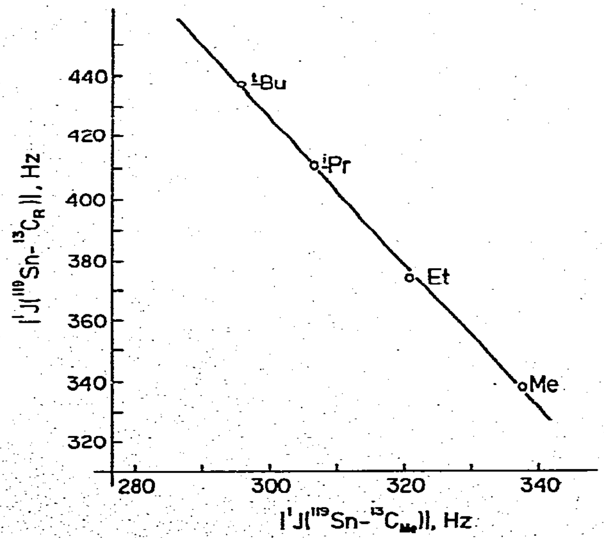


Fig. 2. Graph of $\lvert{}^1J(^{119}Sn—^{13}C_R)\rvert$ plotted against $\lvert{}^1J(^{119}Sn—^{13}C_{Me})\rvert$ for the molecules $(CH_3)_3SnCH_{3-x}(CH_3)_x$.

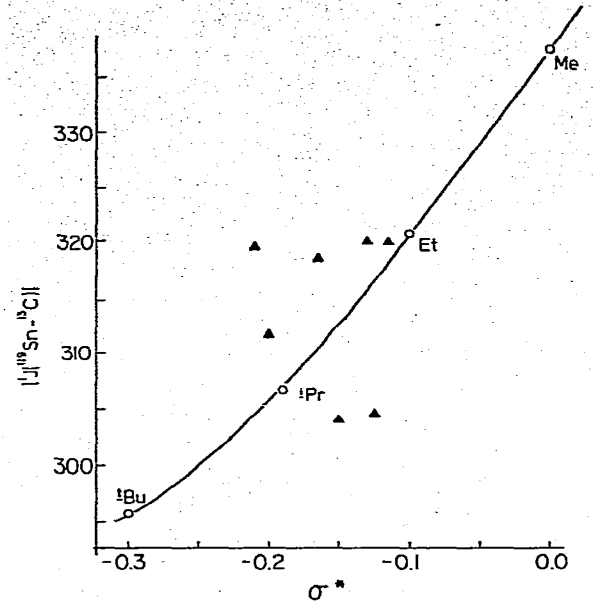


Fig. 3. Graph of $|^{1}J(^{119}Sn—^{13}C_{Me})|$ for molecules $(CH_3)_3SnCH_{3-x}(CH_3)_x$ plotted against σ^*. Also plotted are points for molecules of the type $(CH_3)_3SnR$ [R = n-Pr, i-Bu, n-Bu, cyclohexyl, neopentyl, cyclopentyl, s-Bu]. These are the same molecules as those listed in Table 4.

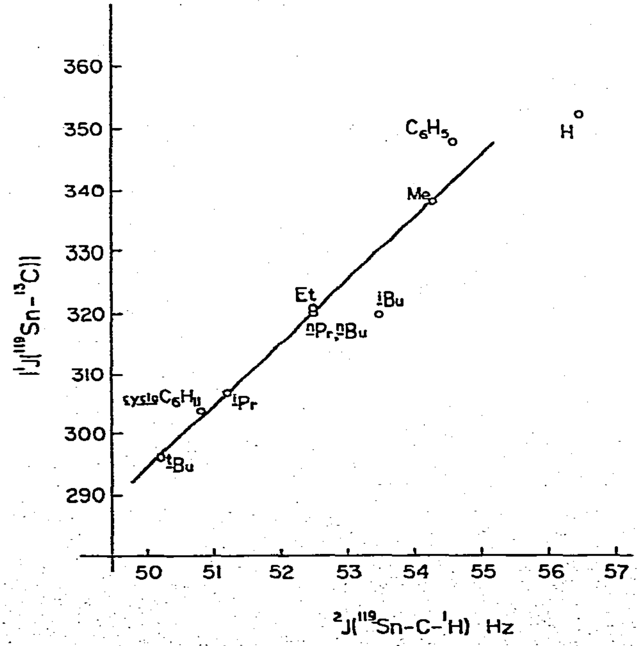


Fig. 4. Graph of $|^{1}J(^{119}Sn—^{13}C_{Me})|$ plotted against $^{2}J(^{119}Sn—C—^{1}H)$ for molecules $(CH_3)_3SnR$. Tin—proton coupling constants are taken from data compiled by Gielen et al. [8]. Note that for R = H, Ph, i-Bu, the points do not fall on the line.

at the tin atom are responsible for the differences between the coupling constants. In this connection it may be noted that the direction of the changes in $|^1J(^{119}Sn{-}^{13}C_{Me})|$ in the compounds examined is consistent with bond angle changes expected according to Bent's model of isovalent hybridization [37]. Data in Table 2 further show that as the bulk of R increases, the coupling constant $|^1J(^{119}Sn{-}^{13}C_{Me})|$ decreases, probably indicating steric rehybridization at tin. Although the steric and inductive effects could contribute to the observed trends, we believe that the steric factor is more important for the following two reasons: *(i)* In molecules of the general type $(CH_3)_3SnR$ (where Σ is also approximately 1330 Hz) there is only poor correlation of $|^1J(^{119}Sn{-}^{13}C_{Me})|$ with σ^* for the R group (Fig. 3). *(ii)* The observed coupling constants are more characteristic of the number of alkyl groups bonded to the α-carbon of the R group than they are of σ^* (Table 4).

A plot of $|^1J(^{119}Sn{-}^{13}C_{Me})|$ against $^2J(^{119}Sn{-}^1H_{Me})$ (Fig. 4) yields a linear correlation, but the line does not pass through the origin. A similar relationship between the tin—carbon and tin—proton coupling constants for methyltin halides has already been found by McFarlane [10]. His data extrapolated to $|^1J(^{119}Sn{-}^{13}C)| = 0$ indicate that $^2J(^{119}Sn{-}C{-}^1H)$ would then be 23.4 Hz, while for the compounds examined here $^2J(^{119}Sn{-}C{-}^1H)$ would be 20.9 Hz when the tin—carbon coupling constant is zero. The results indicate the dangers of using tin—proton coupling constants as measures of tin hybridization as has already been discussed by McFarlane [10].

The data in Table 2 show that large differences exist in the magnitude of $|^1J(^{119}Sn{-}^{13}C)|$ between R_4Sn and $(CH_3)_3SnR$ type of compounds. In $(CH_3)_3SnR$, (R = Me, Et, n-Pr, n-Bu) the coupling constants are 337.8, 374.2, 368.9, 368.4 Hz respectively and in R_4Sn they are 337.8, 320.3, 313.4 and 313.7 Hz respectively. One possible explanation for these changes involves variation in the hybridization of the α-carbons in the $(CH_3)_3SnR$ series. Opening up the Sn—C—C bond angles may relieve strain in the molecules. This angle change might be

TABLE 4

VARIATION OF $|^1J(^{119}Sn{-}^{13}C_{Me})|$ WITH σ^* AND WITH THE NUMBER OF ALKYL GROUPS ON THE α-CARBON OF R IN COMPOUNDS $(CH_3)_3SnR$

R	Number of alkyl groups on α-carbon of R	σ^*(R)	$|^1J(^{119}Sn{-}^{13}C_{Me})|$ (Hz)
Me	0	0.00	337.8
Et	1	−0.10	320.8
n-Pr	1	−0.115	320.0
n-Bu	1	−0.130	320.1
neo-Pe	1	−0.190	318.6
sec-Bu	1	−0.210	319.7
i-Bu	2	−0.125	304.5
cyclo-C_6H_{11}	2	−0.150	303.9
i-Pr	2	−0.190	306.7
cyclo-C_5H_9	2	−0.200	311.8
t-Bu	3	−0.300	295.7

expected to be greater for R = n-Pr than for Et, with little further change for longer chains. An alternate interpretation involving reduction of electron density at the tin nuclei cannot be excluded.

Within the series $(CH_3)_3Sn$-*cyclo*-(C_nH_{2n-1}) (n = 3—6), the magnitude of $|^1J(^{119}Sn—^{13}C_\alpha)|$ does not change uniformly with n (J = 502.8, 389.7, 405.6, 407.4 Hz for n = 3—6, respectively); however, the respective values for Σ are similar, except for n = 3; 1524.6, 1330.2, 1341.0, 1319.1 Hz, for n = 3—6 respectively. This is consistent with two superimposed effects: *(i)* a large change in *s* character of the C_α carbon is going from n = 3 to 4, and a small change thereafter, as indicated by the changes in Σ, and *(ii)* gradually increasing steric bulk of the cycloalkyl group, producing a decrease in $|^1J(^{119}Sn—^{13}C_{Me})|$ and increase in $|^1J(^{119}Sn—^{13}C_\alpha)|$ (see Table 2).

Vicinal ^{119}*Sn—*^{13}*C spin—spin coupling constants*

Measurements on a series of compounds incorporating a range of SnCCC dihedral angles θ, show that the variation of the coupling constants $|^3J(^{119}Sn—CC—^{13}C_\gamma)|$ is consistent with the form of the Karplus equation (see Table 5 and also Fig. 1 in ref. 2). This assumes that the sign of J is the same for all θ.

In assigning the resonances, it was determined unequivocally that $|J_{trans}|$ is much greater than $|J_{gauche}|$ in several rigid molecules in which assignments were made on the basis of multiplicities in the ^{1}H-coupled spectra. In 1-adamantyltrimethyltin (XXIII), the *trans* coupling is 51.1 Hz, while in 7-*anti*-norbornenyltrimethyltin (XX), the *gauche* coupling is 5.6 Hz. In several other compounds, where structurally similar carbon nuclei lie such that one type is *trans* to the tin atom while the other is *gauche*, the coupling constants are large (50—70 Hz) to one type of nucleus and small to the other (5—15 Hz). On the basis of the results for XX and XXIII, these have been assigned to *trans* and *gauche* respectively. In each case, these assignments are completely consistent with the differences in chemical shifts between the γ-carbons arising from steric

TABLE 5

MAGNITUDES OF *vicinal* $^{119}SnCC^{13}C$ SPIN—SPIN COUPLING CONSTANTS AND ASSOCIATED DIHEDRAL ANGLES

θ = dihedral angle $Sn—C_\alpha—C_\beta—C_\gamma$ about $C_\alpha—C_\beta$ bond.

Compound	C	J (Hz)	θ°	Compound	C	J (Hz)	θ°
XVIII [a]	3, 5	51.9	165	XXIV	4, 9	8.5	70
	4	65.8	180		8, 10	11.9	5
XIX [a]	2, 3	67.5	175	A [b]	4	23	120
	5, 6	11.9	5		6	69	170
XXII	1	53.6	154		7	≃0	85
	5	9.7	67	B [c]	4	22	120
	6	8.0	83		6	36 ± 2	35
	7	57.8	174		7	59	160
XXIII	3, 5, 7	51.1	180				

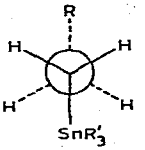
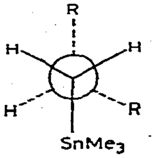
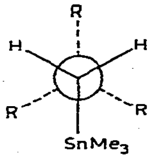
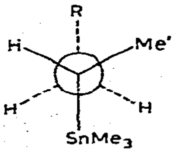
[a] Data previously reported in ref. 1. [b] A = *exo*-2-norbornyltrimethyltin: data reported in ref. 2. [c] B = *endo*-2-norbornyltrimethyltin: data reported in ref. 2.

interactions. It should be noted that the magnitudes of the *vicinal* ^{119}Sn—^{13}C coupling constants for most compounds reported here are larger than those of the *geminal* ^{119}Sn—^{13}C coupling constants, as found in many other organometallic systems for metal—proton and for metal—carbon [31,38] coupling constants.

In several molecules with aliphatic chains, the magnitudes of $|^3J(^{119}\text{Sn—}^{13}\text{C})|$ show variations attributable to variations of rotamer population about the C_α—C_β bonds. The classical rotamers of the compounds $(CH_3)_3SnCH_2CH_xR_{3-x}$ ($x = 0$—2), $(CH_3)_3SnCH(CH_3)CH_2CH_3$, and R'_4Sn (R' = n-Pr, n-Bu), are shown in Table 6. The observed coupling constants are weighted averages of the various contributing forms. For case A, the large coupling constants (all over 50 Hz) are consistent with the methyl group mainly *trans* to the $Sn(CH_3)_3$ group. For case B, the average coupling constant is large enough to suggest that the $g^\star g$

TABLE 6

TABLE OF *vicinal* ^{119}Sn—^{13}C SPIN—SPIN COUPLING CONSTANTS, SHOWING VARIATIONS ATTRIBUTABLE TO CHANGES IN ROTAMER POPULATION ABOUT THE C_α—C_β BONDS

Case	Compound	Possible types of rotamer [a]	R	R′	$\|^3J(^{119}\text{Sn—}^{13}\text{C})\|$ (Hz)
A			Me	Me	53.0
		$t^\star$(*trans*)	Et	Me	55.2
		$g^\star$(*gauche*)	Me	n-Pr	51.4
		(two *g* rotamers)	Et	n-Bu	52.0
B		$g^\star g$ $g^\star t$ $t^\star g$	Me		42.1
C		$g^\star gt$ $g^\star tg$ $t^\star gg$	Me		35.5
D		$g^\star g'$ $g^\star t'$ $t^\star g'$	Me		35.6

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[a] The letters *t* and *g* indicate the positions of the R groups relative to SnMe$_3$. The asterisk against one of them indicates that the γ-carbon atom in that group is ^{13}C. Thus for case B, the two R groups can both lie *gauche* to the SnMe$_3$ group ($g^\star g$), or such that a given R group will be *trans* in one and *gauche* in the other ($t^\star g$ and $g^\star t$). In case C, there are three similar rotamers, in which the ^{13}C containing methyl group lies *gauche* in two and *trans* in one. In case D, the prime refers to the position of R relative to the Me′ group.

rotamer ($Sn(CH_3)_3$ *gauche* to both γ-methyl groups) provides only a minor contribution, and that the observed coupling constant is an average from the equally populated g^*t and t^*g rotamers (where $Sn(CH_3)_3$ is *gauche* to the ^{13}C-containing γ-methyl group in the former rotamer and *trans* in the latter). In case C, the observed coupling constant is a 2 : 1 weighted average of the *gauche* and *trans* coupling constants, respectively. One might use the Karplus relationship [2] developed in this laboratory to quantitatively compute the rotamer population, but we feel that more points in Fig. 5 will be necessary before one can arrive at accurate quantative values.

In case D (Table 6) the γ-methyl group can interact with both the $Sn(CH_3)_3$ group and with Me'. If one assumes that the rotamer in which the γ-methyl group is *gauche* to both these groups (g^*g') is a minor contributor, then the relatively small coupling constant (only the same magnitude as in Case C) indicates that the population of t^*g' is smaller than that of g^*t'. This shows that the methyl—methyl interaction is greater than the methyl—trimethyltin interaction, which is consistent with recent suggestions that the trimethyltin group has a relatively low steric bulk. Davis et al. [21] found in some reactions of *syn*-7-norbornenes, an order of effective steric hindrance of t-Bu > Me > Br > $Sn(CH_3)_3$ > Cl > H.

Experimental

(a) NMR spectra

The ^{13}C NMR spectra were recorded at 25.15 MHz on a Varian HA-100D NMR spectrometer interfaced to a Digilab FTS-3 pulse and data system. The spectra were 8 K or 16 K Fourier transformed spectra recorded at bandwidths of 2000 Hz (except in the case of unsaturated compounds where greater bandwidths were necessary). These conditions were selected to give good resolution and accurate coupling constants. Samples were examined as neat liquids in 8 mm tubes, with TMS (ca. 10%) added as internal standard. Spectra were recorded with broadband ^1H decoupling by a Digilab 50-80 decoupler; the probe and samples were cooled with nitrogen during decoupling. For details of instrumentation, see ref. 39.

Spectral assignments were based upon *(i)* multiplicities in the NMR spectra recorded with off resonance decoupling or without ^1H decoupling, *(ii)* the magnitude of $^1J(^{119}Sn—^{13}C)$, which indicates which ^{13}C nuclei are directly attached to Sn, *(iii)* comparisons of chemical shifts with those of other compounds, and *(iv)* the magnitudes of $^3J(^{119}Sn—^{13}C)$, which were used to distinguish between carbon nuclei *trans* or *gauche* relative to ^{119}Sn.

The utility of ^{13}C NMR spectra in the study of organotin compounds and the application of the stereochemical dependence of *vicinal* $^{119}Sn—^{13}C$ coupling to spectral assignment is illustrated by the ^{13}C NMR spectrum of 3-nortricyclyltrimethyltin (XXII). There are (except for the three tin methyl carbon atoms, which are not illustrated in the spectrum) no symmetrically equivalent carbon atoms; all their separate resonances are resolved. An unambiguous assignment was made, based upon the following: *(i)* off-resonance decoupling. *(ii)* The chemical shifts of C_1, C_2, and C_6 are to considerably higher field than the other carbons. *(iii)* C_2 is β to the trimethyltin group. The resonance assigned to this atom is less shielded (β-shift 4.0 ppm) than in the parent hydrocarbon, while C_1 and C_6 show much smaller shifts relative to nortricyclene (γ-shifts of 0.1 and 0.1 ppm, respectively). These shifts are consistent with those outlined earlier in this paper. *(iv)* The magnitude of $^1J(^{119}Sn—^{13}C)$ identifies C_3. *(v)* C_5 is nearly *gauche* to the tin atom, while C_7 is nearly *trans* (dihedral angles 67° and 174°, respectively, estimated from the structure of 4-chloronortricyclene) [46]. The corresponding $^{119}Sn—^{13}C$ spin—spin coupling constants are 9.7 Hz (to C_5) and 57.8 Hz (to C_7). *(vi)* C_1 is nearly *trans* to the tin atom, while C_6 is nearly *gauche* (dihedral angles 154° and 83°, respectively). The corresponding $^{119}Sn—^{13}C$ spin—spin coupling constants are 53.6 and 8.0 Hz.

(b) Synthesis of organotins

The simple alkyltins used in this work were commercially available samples or are well known and were prepared by the reaction of the appropriate Grignard reagent with trimethyltin chloride. Some of the others were prepared by an alternate method and others have not been previously reported. Their preparations are described below. All manipulations involving alkali metal or Grignard derivatives were conducted under argon.

Cyclobutyltrimethyltin. Trimethylstannyllithium was prepared in 80 ml of tetrahydrofuran by stirring together 8.0 g (0.040 mol) of trimethyltin chloride and 7.1 g (0.10 mmol) of lithium ribbon.

A solution of 5.0 g (0.037 mol) of bromocyclobutane in 15 ml of tetrahydrofuran was added dropwise to a stirred trimethylstannyllithium solution. The reaction mixture was stirred overnight and then treated with saturated aqueous ammonium chloride solution. The organic layer was separated from the aqueous layer, dried ($MgSO_4$) and filtered. Excess tetrahydrofuran was removed by distillation: Purification by preparative GLPC (160 in. × 0.75 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W) yielded 2.1 (26%) of cyclobutyltrimethyltin.

Cyclopropyltrimethyltin was prepared by the same procedure as above providing product with the same physical properties as described for that prepared from the cyclopropyl Grignard reagent and trimethyltin chloride [40].

i-Propyltrimethyltin. A solution of 0.040 mol (8.0 g) of trimethyltin chloride in 30 ml of diethyl ether was added dropwise to a stirred solution of 0.044 mol (35 ml of a 1.25 *M* solution) of i-propylmagnesium chloride in diethyl ether. After the addition was complete the reaction mixture was stirred and heated under reflux for 2 h. Saturated aqueous ammonium chloride solution was then added dropwise to the stirred reaction mixture until magnesium salts precipitated. The organic solution and the washings were combined, dried (Na_2SO_4) and filtered. Fractional distillation yielded 4.7 g (57%) of i-propyltrimethyltin: b.p. 121°C (lit. [41] b.p. 123°C).

t-Butyltrimethyltin. A solution of 0.050 mol (10.0 g) of trimethyltin chloride in 50 ml of pentane was added dropwise to a stirred solution of 0.055 mol (50 ml of a 1.1 *M* solution) of t-butyllithium in pentane. After the addition was complete the reaction mixture was heated under reflux for 2 h and then treated with water. The organic layer was separated from the aqueous layer, dried (Na_2SO_4) and filtered. Excess pentane was removed by fractional distillation. t-Butyltrimethyltin, 4.9 g (45%), was obtained from the concentrate by sublimation; m.p. 20—29°C (lit. [42] m.p. 32°C).

1,1-Dimethylstannacyclopentane. The di-Grignard of 1,4-dibromobutane was prepared in 150 ml of tetrahydrofuran from 32.4 g (0.15 mol) of 1,4-dibromobutane and 8.0 g (0.33 g-at.) of magnesium.

A solution of 29.0 g (0.132 mol) of dimethyltin dichloride in 200 ml of tetrahydrofuran was then added rapidly to the stirred Grignard reagent. After the addition was complete the reaction mixture was stirred and heated under reflux for 4 h. Saturated aqueous ammonium chloride solution was then added dropwise to the stirred reaction mixture until magnesium salts precipitated. The organic solution was decanted from the precipitated salts, dried (Na_2SO_4) and filtered. Excess tetrahydrofuran was removed by distillation. Distillation of the concentrate under reduced pressure yielded 10.9 g (36%) of 1,1-dimethylstannacyclopentane; b.p. 35—37°C/10 Torr; 60 MHz $^1H'$ NMR δ 0.17 (s, 6) and 0.58—2.41 ppm (m, 8). Anal. Found: C, 35.29; H, 6.96. $C_6H_{14}Sn$ calcd.: C, 35.16; H, 6.88%.

1,1-Dimethylstannacycloheptane. This compound was prepared by substantially the same procedure, in 34% yield; b.p. 75°C/13 Torr (lit. [43] 68°C/4 Torr).

1-Hexynyltrimethyltin. A solution of 0.051 mol (30 ml of 1.7 *M* solution) of methyllithium in diethyl ether was added to a stirred solution of 0.050 mol (4.1 g) of 1-hexyne in 10 ml of diethyl ether. The rate of addition was regulated so that the reaction mixture was kept under gentle reflux. After the reaction had subsided, a solution of 10 g (0.05 mol) of trimethyltin chloride in 20 ml of diethyl ether was added dropwise. The stirred reaction mixture was then heated under reflux for 2 h. The reaction mixture was treated with water; the organic layer was separated from the aqueous layer, dried (Na_2SO_4), filtered, and concentrated. Distillation yielded 5.8 g (47%) of 1-hexynyltrimethyltin: b.p. 79—80°C/11 Torr (lit. [44] b.p. 82°C/12 Torr).

Syn and anti-7-norbornenyltrimethyltin. Sodium naphthalene was prepared by stirring 2.0 g (0.087 g-at.) of sodium and 5.6 g (0.043 mol) of naphthalene for 2 h in 85 ml of tetrahydrofuran. The green sodium naphthalene solution was then decanted from unreacted sodium into a graduated addition funnel and added dropwise to a stirred solution of 2.0 g (0.01 mol) of trimethyltin chloride in 20 ml of tetrahydrofuran cooled with an ice bath. The temperature was kept below 5°C during the course of the addition. The green color of sodium naphthalene was discharged rapidly upon addition and sodium chloride precipitated from solution. The reaction mixture remained colorless until 20 ml of sodium naphthalene solution had been added. At this point the reaction mixture turned pale yellow, indicating that all of the trimethyltin chloride had been converted into hexamethylditin and formation of trimethylstannylsodium had begun. Another 20 ml of sodium naphthalene solution was then added to convert the hexamethylditin to trimethylstannylsodium [45].

This solution was cooled to —20°C, and 1.74 g (0.01 mol) of *syn*-7-bromonorbornene [46] in 18 ml of tetrahydrofuran was then added dropwise with stirring at —15°C.

The reaction mixture was allowed to come to ambient temperature and stirred overnight. Examination by GLPC indicated that *syn*- and *anti*-7-norbornenyltrimethyltin had been formed in a ratio of 90 : 10 respectively. The reaction mixture was treated with water and extracted with hexane. The extracts were dried ($MgSO_4$), filtered and concentrated. The products were separated from naphthalene by column chromatography on acid washed alumina activated by heating at 200°C overnight with hexane as eluant. The 7-norbornenyltrimethyltins were eluted first and *syn*-7-norbornenyltrimethyltin [47] was purified by preparative GLPC (160 in. × 0.75 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W).

When *syn*-7-bromonorbornene was allowed to react with trimethylstannylsodium as described above using 1,2-dimethoxyethane as solvent in place of tetrahydrofuran, *syn*- and *anti*-7-norbornenyltrimethyltin were formed in a ratio of 19 : 81 respectively. *Anti*-7-Norbornenyltrimethyltin [47,48] was purified as described above.

3-Nortricyclyltrimethyltin. A solution of trimethylstannylsodium (0.01 mol in 20 ml of THF) was cooled to —20°C and a solution of 1.75 g (0.01 mol) of 3-bromonortricyclene in 18 ml of tetrahydrofuran was added dropwise. The cooling bath was removed and stirring continued for 1 h. GLPC (6 ft. × 0.25 in. column of 10% Apiezon L on 60-80 Mesh chromosorb W and 15 ft. × 0.25 in. column of 1,2,3-tris-2-cyanoethoxypropane on 60-80 mesh diatoport P) indicated that the reaction was complete and that 3-nortricyclyltrimethyltin and *exo*-5-norbornenyltrimethyltin had been formed in a ratio of 64 : 36. The products of the reaction were identified by comparison of their NMR spectra and GLPC retention times with those of authentic samples [49]. The reaction mixture was then treated with water and extracted with hexane. The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated. The two products were then separated from naphthalene on acid washed alumina using hexane as the eluent. The alumina used was activated by heating at 200°C for at least 18 h before use. The two tin compounds were eluted before naphthalene and pure 3-nortricyclyltrimethyltin was obtained by preparative GLPC (160 in. × 0.75 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W). Anal. Found: C, 46.92; H, 7.00. $C_{10}H_{18}Sn$ calcd.: C, 46.74; H, 7.06%.

7-Norbornyltrimethyltin. Trimethylstannyllithium was prepared under argon in 75 ml of tetrahydrofuran by stirring together 0.45 g (0.065 mol) of lithium and 6.5 g (0.033 mol) of trimethyltin chloride. A solution of 5.25 g (0.0300 mol) of 7-bromonorbornane in 10 ml of tetrahydrofuran was added dropwise to the stirred solution. The addition was accompanied by slight exotherm. The reaction mixture was heated under reflux for 2 h after the addition of the halide was complete. The reaction mixture was diluted with 50 ml of hexane and treated with saturated aqueous ammonium chloride solution. The aqueous layer was separated from the organic layer and extracted with hexane. The extract and the organic layer were combined, dried ($MgSO_4$), filtered and concentrated. Purification by preparative GLPC (160 in. × 0.75 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W) yielded 2.8 g (37%) of 7-norbornyltrimethyltin [48].

1-Norbornyltrimethyltin. A solution of 6.5 g (0.05 mol) of 1-chloronorbornane [50] in 20 ml of hexane under argon was added dropwise to a stirred dispersion (20° C) of 5 g (0.7 mol) of lithium in 10 ml of hexane. Heating was required to initiate the reaction and the rate of addition of the chloride solution was regulated to maintain gentle reflux. After the addition was complete the reaction mixture was heated under reflux for 1 h. Unreacted lithium was removed by filtration through a medium frit sintered glass disc.

Then 9.0 g (0.045 mol) of trimethyltin chloride in 40 ml of hexane was added rapidly to the stirred 1-norbornyllithium solution. The reaction mixture was then heated under reflux for 2 h and treated with water. The organic layer was separated and concentrated under reduced pressure. Preparative GLPC (160 in. × 0.75 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W) of the concentrate yielded 1.6 g (14%) of 1-norbornyltrimethyltin: 60 MHz H′ NMR δ 0.03 (s, 9), 0.92—1.88 (m, 10) and 2.03 ppm (s, 1).

2-Adamantyltrimethyltin. To 2.0 g (0.01 mol) of trimethylstannyllithium in 60 ml of 1,2-dimethoxyethane at —20°C was added 2.15 g (0.01 mol) of 2-bromoadamantane in 18 ml of the same solvent. The cold bath was removed and the reaction mixture was stirred overnight. Examination of the reaction mixture by GLPC (6 ft. × 0.25 in. column of 10% Apiezon L on 60-80 mesh Chromosorb W) indicated that the reaction was complete and a single product had been formed. The reaction mixture was then concentrated under reduced pressure and treated with water and the aqueous layer was separated from the organic layer and extracted with hexane. The organic layers were combined, dried ($MgSO_4$), filtered and concentrated. The product was separated from naphthalene by column chromatography with hexane on acid washed alumina activated by heating at 200°C for 18 h. Colorless crystals of 2-adamantyltrimethyltin were obtained upon evaporation of solvent from chromatography fractions: m.p. 37—38°C. Anal. Found: C, 52.46; H, 8.32. $C_{13}H_{24}Sn$ calcd.: C, 52.21; H, 8.09%.

1-Adamantyltrimethyltin. When 1-bromoadamantane was allowed to react with trimethylstannyllithium in 1,2-dimethoxyethane under the conditions described above, 1-adamantyltrimethyltin was formed after 2.5 days. 1-Adamantyltrimethyltin was isolated as described above, m.p. 56—57°C; 60 MHz H′. NMR (CS_2) δ —0.05 (s, 9) and 1.72—2.22 ppm (m, 15). Anal. Found: C, 52.48; H, 8.10. $C_{13}H_{24}Sn$ calcd.: C, 52.21; H, 8.09%.

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