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ORGANOMETALLIC COMPOUNDS
XXXI*. PMR SPECTRA OF TETRAORGANOTINS

M. GIELEN AND M. DE CLERCQ

Université Libre de Bruxelles, Faculté des Sciences, Collectif de Chimie Organique Physique, Av. F. D. Roosevelt 50, B-1050 Bruxelles (Belgium)

B. DE POORTER

Vrije Universiteit Brussel, Fakulteit der Toegepaste Wetenschappen, Dienst: Algemene en Organische Scheikunde, Ad. Buyllaan 105, B-1050 Brussel (Belgium)

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SUMMARY

The NMR study of a large number of mixed tetraorganotins shows that the J *vs.* $\Sigma\sigma^*$ relationship is invalid, even in the mixed tetraalkyltin series. Malinovski's additivity rule may be used to predict tin–methyl, tin–benzyl and tin–tert-butyl coupling constants.

INTRODUCTION

The linear relationship between $J(Sn-CH_3)$ and the % s character is well known[2] and has been used to evaluate valence angles[3]. An identical relationship exists for the $J(Sn-CH_2C_6H_5)$ coupling[4], but seems to be less exact for $J(Sn-CH_2-CH_3)$[5], or even for $J(Sn-CH_3)$ in methyltin halides[6]. The coupling constant thus depends on all the factors which influence the hybridization of the atomic orbitals of the tin atom, and linear relationships between J and the sum of Taft's σ^* of the substituents bound to the tin atom[7] seem unsatisfactory. We have already shown that these linear relationships are not valid if one includes phenyl-[3] or benzyltin[4] compounds. There is other evidence against these relationships: in *meso*-dimethylbis(α-methylbenzyl)tin, the two methyl groups which are diastereoisomeric are characterized by two different coupling constants, which are different from the $J(Sn-CH_3)$ coupling constant of the analogous *dl*-mixture[8]. On the other hand, the $J(Sn-CH_3)$ coupling constant of dimethyldianisyltin is identical to that of dimethyldiphenyltin[9] and, similarly, $J(Sn-CH_3)$ is the same in trimethylbenzyltin and trimethyl-*p*-(fluorobenzyl)tin ($^{117}Sn-CH_3$ 50.8 Hz). Furthermore, the NMR spectrum of 1,1-dimethyl-1-stanna-4-tert-butylcyclohexane exhibits (in addition to the expected tert-butyl singlet) two methyl peaks, at 0.097 and 0.087 ppm, respectively, with $J(^{119}SnCH_3)$ equal to 52.1 and 53.9 Hz[20].

We will show that the J *vs.* $\Sigma\sigma^*$ relationship is not satisfactory even in the mixed tetraalkyltin series.

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* For Part XXX, see ref. 1.

TABLE 1

NMR SPECTRA OF THE METHYL PART OF MIXED TETRAORGANOTINS

Compound	$J(^{117}SnCH_3)$ (Hz)	J^{117}_{calc} (Hz)	$J(^{119}SnCH_3)$ (Hz)	δ (CH$_3$) (ppm)	$\Sigma\sigma^*$	Ref.
Me_4Sn	52.0	[51.9]	54.3	0.057	0.00	3
Me_3SnPh	52.3	[52.3]	54.7	0.267	0.60	3
Me_2SnPh_2	52.6	52.7	55.0	0.475	1.2	12
$MeSnPh_3$	53.4	53.1	55.7	0.676	1.8	3, 12, 21
Me_2Sn-cyclo-HexPh	48.8	49.0	51.1	0.215	0.45	
MeSn-cyclo-Hex_2Ph	45.3	45.7	47.3	0.153	0.30	
MeSn-cyclo-$HexPh_2$	49.2	49.4	51.4	0.420	1.05	
Me_3Sn-cyclo-Hex	48.6	[48.6]	50.8		−0.15	3
Me_2Sn-cyclo-Hex_2	45.4	45.3	47.5		−0.30	
MeSn-cyclo-Hex_3	42.0	42.0	43.9		−0.45	
Me_2-t-BuSnBenz	~46.3	46.3	48.5	0.041	−0.085	
Me-t-BuSn$Benz_2$	44.8	45.2	46.8	−0.176	+0.130	
Me-t-Bu_2SnBenz	41.9	41.8	43.8	0.163	−0.385	
Me_3Sn-t-Bu	47.5	[47.4]	49.7	0.000	−0.30	12, 22
Me_2Sn-t-Bu_2	42.9	42.9	44.9	−0.053	−0.60	
MeSn-t-Bu_3	38.4	38.4	40.2		−0.90	
Me_2-t-BuSn-cyclo-Hex	44.2	44.1	46.1	−0.080	−0.45	13
Me-t-BuSn-cyclo-Pent	44.8	44.6	46.7	−0.068	−0.50	13
Me_3Sn-cyclo-Pent	49.1	[49.1]	51.4		−0.20	
Me_2Sn-cyclo-$Pent_2$	46.4	46.3	48.4		−0.40	
MeSn-cyclo-$Pent_3$	43.7	43.5	45.7		−0.60	

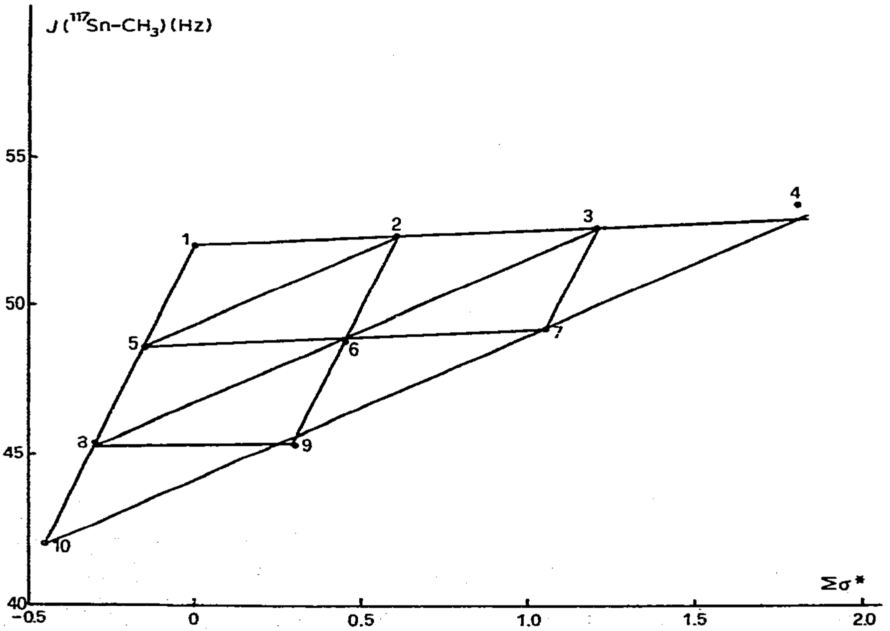

Fig. 1. $J(^{117}Sn{-}C^1H_3)$ coupling constants as a function of $\Sigma\sigma^*$ for mixed cyclohexylmethylphenyltin compounds. 1, Me_4Sn; 2, Me_3SnPh; 3, Me_2SnPh_2; 4, $MeSnPh_3$; 5, Me_3Sn-cyclo-hex; 6, Me_2Sn-cyclo-HexPh; 7, MeSn-cyclo-$HexPh_2$; 8, Me_2Sn-cyclo-Hex_2; 9, MeSn-cyclo-Hex_2Ph; 10, MeSn-cyclo-Hex_3.

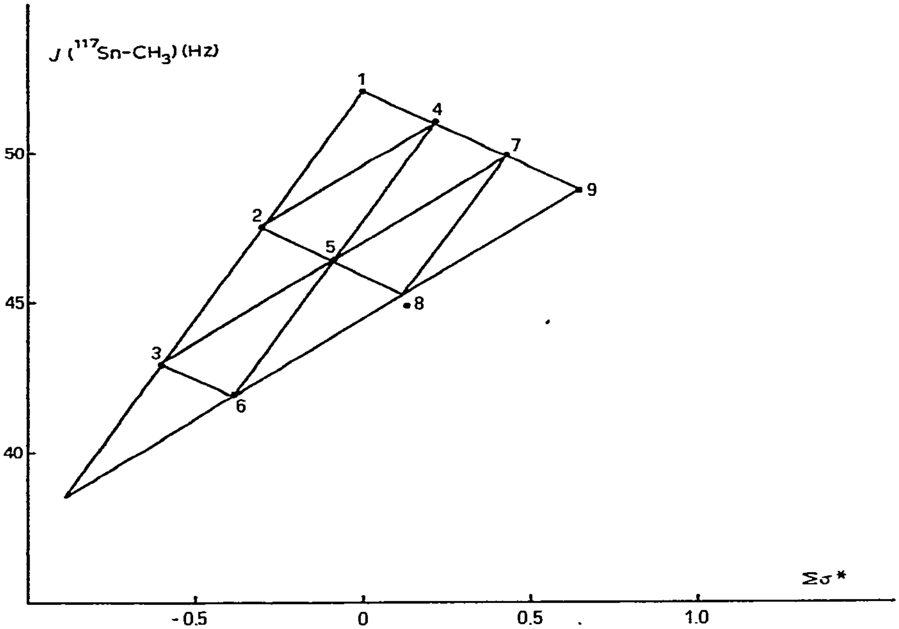

Fig. 2. $J(^{117}Sn{-}C^1H_3)$ coupling constants as a function of $\Sigma\sigma^*$ for mixed benzyl-tert-butylmethyltin compounds. 1, Me_4Sn; 2, Me_3Sn-t-Bu; 3, Me_2Sn-t-Bu_2; 4, $Me_3SnBenz$ (ref. 10); 5, Me_2-t-BuSnBenz; 6, Me-t-$Bu_2SnBenz$; 7, $Me_2SnBenz_2$ (ref. 10); 8, Me-t-$BuSnBenz_2$; 9, $MeSnBenz_3$ (ref. 10).

TABLE 2

$\chi(SnCH_3)$, $\kappa(SnCH_2Ph)$ AND $\zeta[SnC(CH_3)_3]$-VALUES FOR DIFFERENT GROUPS

Radical	χ-value	κ-value	ζ-value
Me	17.3	20.1	20.9
Benz	16.2	18.9	22.2
cyclo-Hex	14.0	16.8	17.5
cyclo-Pent	14.5		18.4
Ph	17.7	21.6	
t-Bu	12.8	15.7	17.0
Et	15.6	18.2	19.1
i-Pr	14.2	16.8	

RESULTS AND DISCUSSION

The $J(Sn{-}CH_3)$ coupling constant

Table 1 lists NMR data for the methyl entity in a series of mixed tetraorganotins. Figs. 1 and 2 show that the J *vs.* $\Sigma\sigma^*$ relationship is not linear, except for a series of closely related compounds such as $Me_{4-n}SnR_n$. [Sisido[10] has already expressed J as a function of the number n of phenyl groups for the series with R = Ph.] Fig. 3 shows clearly that a linear J *vs.* $\Sigma\sigma^*$ relationship is not valid even for mixed alkyl compounds.

These graphical representations are in fact illustrations of the additivity rule

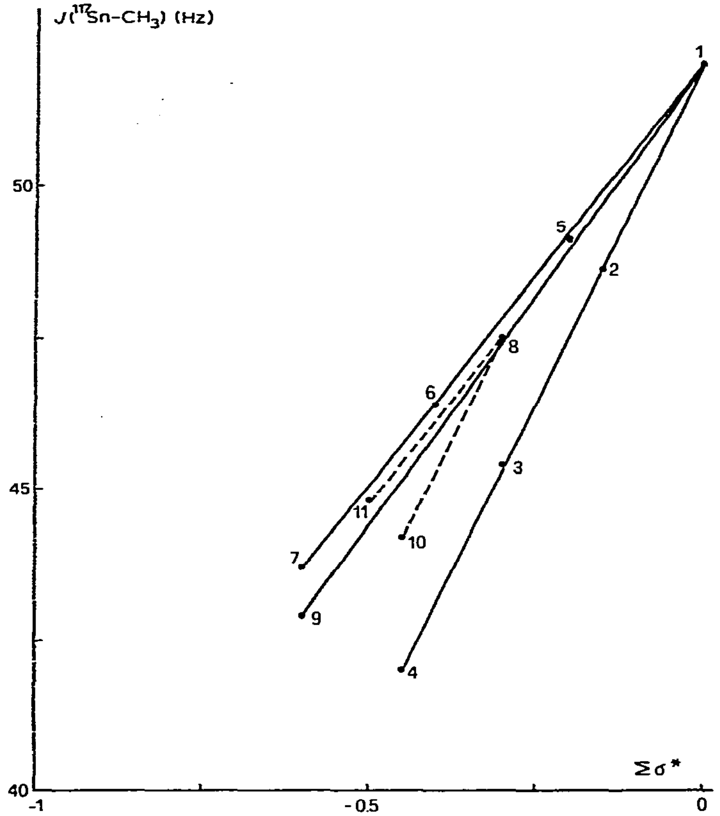

Fig. 3. $J(^{117}Sn-C^1H_3)$ coupling constants as a function of $\Sigma\sigma^*$ for mixed tetraalkyltin compounds. Vector sum determination of the $J(SnCH_3)$ coupling constant of cyclohexyl- and cyclopentyl-tert-butyldimethyltins. 1, Me_4Sn; 2, Me_3Sn-cyclo-Hex; 3, Me_2Sn-cyclo-Hex_2; 4, MeSn-cyclo-Hex_3; 5, Me_3Sn-cyclo-Pent; 6, Me_2Sn-cyclo-$Pent_2$; 7, MeSn-cyclo-$Pent_3$; 8, Me_3Sn-t-Bu; 9, Me_2Sn-t-Bu_2; 10, Me_2-t-BuSn-cyclo-Hex; 11, Me_2-t-BuSn-cyclo-Pent.

proposed by Malinovski[11]. This rule may be put in the algebraic form: $\chi_R = J(Sn-CH_3)[CH_3-SnRMe_2]-2\chi_{Me}$; so that

$$\chi_{Me} = \frac{J(Sn-CH_3)\,[CH_3SnMe_3]}{3}.$$

The χ-values derived in this way are given in Table 2.

Values of $J(^{117}SnCH_3)$ calculated from the χ-values (J^{117}_{calc}) are listed in Table 1.

The dynamic molecules

From the coupling constants given in Table 1, it is possible to calculate angles for molecules having C_{2v} or C_{3v} symmetry[3]: one finds that the MeSnR angle is 111° 13′ for trimethylcyclohexyltin, 111° 00′ for trimethylcyclopentyltin, 107° 38′ for tricyclohexylmethyltin, and 107° 57′ for tricyclopentylmethyltin; the MeSnMe angle is 106° 11′ for dimethyldicyclohexyltin and 106° 41′ for dimethyldicyclopentyltin; the RSnR angle is 113° 08′ for Me_2Sn-cyclo-Hex_2, and 112° 32′ for the analogous dicyclopentyl derivative.

Gutovsky[14] has pointed out that J-values calculated from the angles of static molecules (J_{stat}) can be different from the mean coupling constants $\langle J \rangle$ taking bending motions into account. If we apply Gutovsky's calculations to the organotin molecules, with a bending motion of C–Sn–C of about 5°, it is possible to compare the relationship between J_{stat} and θ, the C–Sn–C angle, with that between $\langle J \rangle$ and θ:

$$J_{\text{stat}}(\phi) = b - \frac{a}{\cos^2\phi}, \text{ (ref. 3) where } \theta = \phi + \frac{\pi}{2}, \; a = 138.5 \text{ and } b = 208$$

$$\langle J \rangle = \frac{\int_{\phi_1}^{\phi_2} J_{\text{stat}}(\phi)\, \mathrm{d}\phi}{\phi_2 - \phi_1} = b - \frac{a}{\phi_2 - \phi_1}(\operatorname{tg}\phi_2 - \operatorname{tg}\phi_1)$$

It will be seen that the difference $\langle J \rangle - J_{\text{stat}}$ is < 0.2 Hz for mean angles varying from 106° to 114° (ref. 15) which shows that Gutovsky's objection is not valid in this case.

The $J(Sn{-}CH_2C_6H_5)$ coupling constant

An analogous J *vs.* $\Sigma\sigma^*$ graph may be drawn up for the benzyltin coupling constants (see Fig. 4). The κ values (analogous to the χ values for the methyl groups),

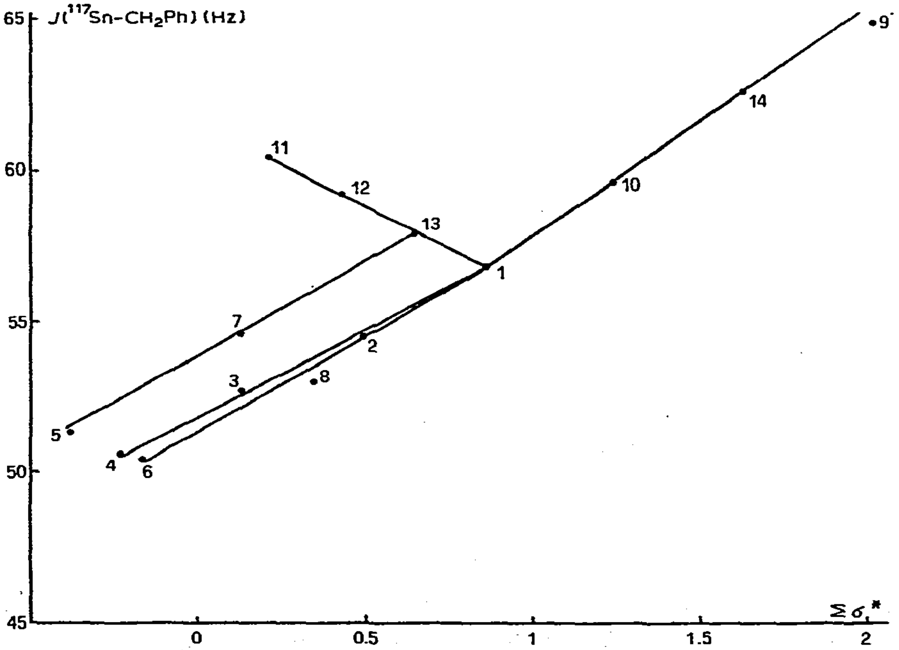

Fig. 4. $J(^{117}Sn{-}C^1H_2{-}C_6H_5)$ coupling constants as a function of $\Sigma\sigma^*$ for mixed tetraorganotins. 1, Benz$_4$Sn (ref. 10); 2, Benz$_3$Sn-cyclo-Hex; 3, Benz$_2$Sn-cyclo-Hex$_2$; 4, BenzSn-cyclo-Hex$_3$; 5, BenzSn-t-Bu$_2$Me; 6, Benz$_2$Sn-t-Bu$_2$; 7, Benz$_2$Sn-t-BuMe; 8, Benz$_3$Sn-t-Bu; 9, BenzSnPh$_3$; 10, Benz$_3$SnPh; 11, BenzSnMe$_3$ (ref. 10); 12, Benz$_2$SnMe$_2$ (ref. 10); 13, Benz$_3$SnMe (ref. 10); 14, Benz$_2$SnPh$_2$.

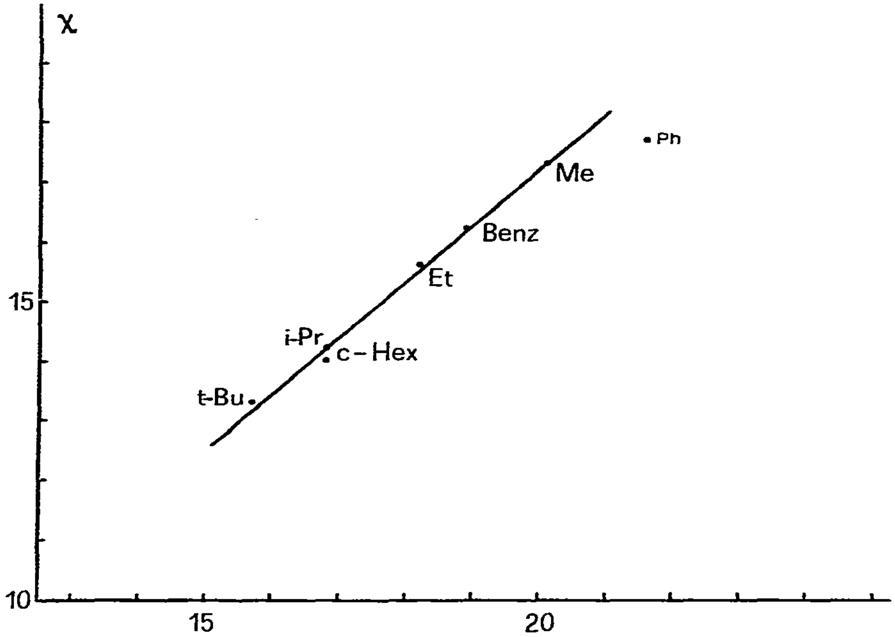

Fig. 5. Relationship between χ and κ.

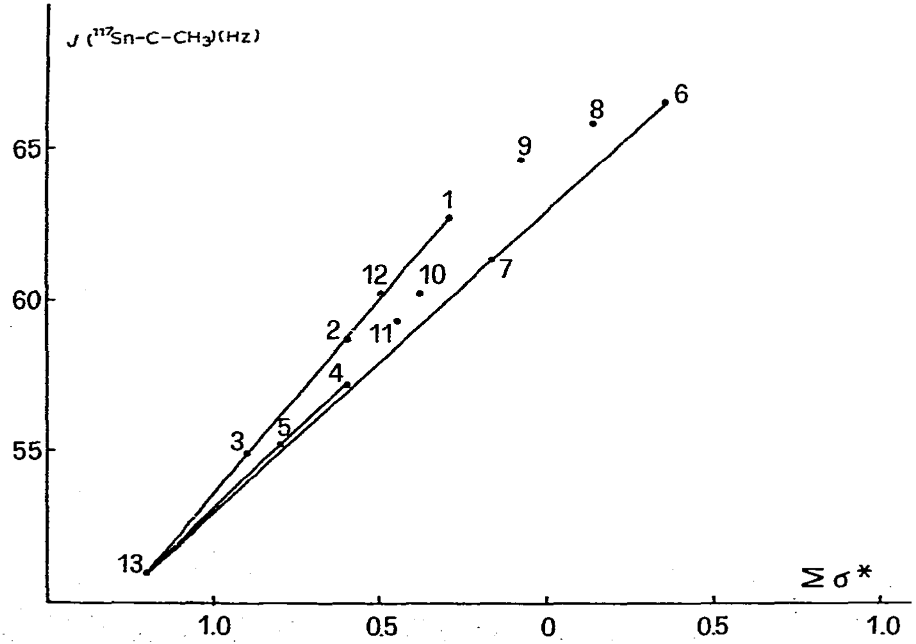

Fig. 6. $J[^{117}Sn{-}C(C^1H_3)_3]$ coupling constants as a function of $\Sigma\sigma^*$ for mixed tetraorganotins. 1, t-BuSnMe$_3$; 2, t-Bu$_2$SnMe$_2$; 3, t-Bu$_3$SnMe; 4, t-BuSnEt$_3$; 5, t-Bu$_2$SnEt$_2$; 6, t-BuSnBenz$_3$; 7, t-Bu$_2$SnBenz$_2$; 8, t-BuSnMeBenz$_2$; 9, t-BuSnMe$_2$Benz; 10, t-Bu$_2$SnMeBenz; 11, t-BuMe$_2$Sn-cyclo-Hex; 12, t-BuMe$_2$Sn-cyclo-Pent; 13, t-Bu$_4$Sn (calcd.)

TABLE 3

NMR SPECTRA OF THE BENZYL PART OF MIXED TETRAORGANOTINS

Compound	$J(^{117}SnCH_2\ Ph)$ (Hz)	J^{117}_{calc} (Hz)	J^{119} (Hz)	$\delta(CH_2\ Ph)$ (ppm)	$\Sigma\sigma^*$	Ref.
$Benz_3Sn$-cyclo-Hex	54.5	[54.6]	56.7	2.16	+0.495	
$Benz_2Sn$-cyclo-Hex_2	52.7	52.5	54.7	2.21	+0.13	
BenzSn-cyclo-Hex_3	50.6	50.4	53.3	2.27	−0.235	
BenzSn-t-$BuMe_2$	56.1	55.9		2.28	−0.085	
BenzSn-t-Bu_2Me	51.3	51.5	53.2	2.30	−0.385	
$Benz_2Sn$-t-Bu_2	50.4	[50.3]	52.5	2.30	−0.170	
$Benz_2Sn$-t-BuMe	54.7	54.7	56.7	2.27	+0.13	
$Benz_3Sn$-t-Bu	53.0	53.5	55.0	2.19	+0.345	4
$BenzSnPh_3$	64.8	[64.8]	67.0		2.015	
$Benz_2SnPh_2$	62.4	62.1	65.0	2.62	1.630	
$Benz_3SnPh$	59.6	59.4	62.30	2.34	1.245	

TABLE 4

NMR SPECTRA OF THE TERT-BUTYL PART OF MIXED TETRAORGANOTINS

Compound	$J(^{117}Sn{-}C{-}CH_3)$ (Hz)	J^{117}_{calc} (Hz)	J^{119} (Hz)	δ(t-Bu) (ppm)	$\Sigma\sigma^*$
t-$BuSnMe_3$	62.7	62.7	65.7	1.09	−0.30
t-$BuSnEt_3$	57.2	57.3	66.0	1.12	−0.60
t-Bu_2SnMe_2	58.7	58.8	61.4	1.20	−0.60
t-Bu_2SnEt_2	55.2	(55.2)	57.7	1.17	−0.80
t-Bu_3SnMe	54.9	(54.9)	57.3		−0.90
t-$BuSnBenz_3$	66.5	66.6	69.6	0.99	+0.345
t-$Bu_2SnBenz_2$	61.3	(61.4)	64.0	1.10	−0.170
t-$BuSnMeBenz_2$	65.8	65.3	68.8	1.07	+0.130
t-$BuSnMe_2Benz$	64.6	64.0	67.6	1.08	−0.085
t-$Bu_2SnMeBenz$	60.2	60.1	63.0		−0.385
t-$BuMe_2Sn$-cyclo-Hex	59.3	(59.3)	61.0	1.100	−0.45
t-$BuMe_2Sn$-cyclo-Pent	60.2	(60.2)	63.0	1.105	−0.50

derived from these results are given in Table 2. $J(SnCH_2\phi)[\phi CH_2SnRR'R''] = \kappa_R + \kappa_{R'} + \kappa_{R''}$.

Figure 5 shows the relationship between χ and κ. The relationship is satisfactorily linear except for the phenyl group.

The $J[Sn{-}C(CH_3)_3]$ coupling constant

A J *vs.* $\Sigma\sigma^*$ graph can also be drawn for the tert-butyl coupling constant (see Fig. 6). As for the methyl- and benzyl-derivatives, ζ-values can be calculated for different alkyl radicals, reflecting the influence of these radicals on the $J(SnC{-}CH_3)$ coupling constant (see Table 2). To use the relationship $\zeta_R = J(SnC{-}CH_3)\ [(CH_3)_3CSn\text{-t-}Bu_2R] - 2\zeta_{t\text{-}Bu}$ it is necessary to know the tert-butyltin coupling constant for tetra-tert-butyltin. It can be obtained by extrapolation, using the additivity rule ($3\ \zeta_{t\text{-}Bu}$) or by the procedure described in ref. 3, and is found to be 51.0 Hz. Attempts are being made in our laboratory to synthesize tetra-tert-butyltin by a method fundamentally very different from those previously used[16].

EXPERIMENTAL

All the compounds were made by standard procedures[17], involving the reactions of Grignard compounds on organotin halides[4,16,18]. The required organotin halides R_3SnX were generally made by bromodemetallation in a polar solvent such as methanol, to avoid dibromination and to increase the selectivity[18]. However, for tetracyclopentyl- and tetracyclohexyltins, which are quite insoluble in alcohols, chloroform was used. In addition to the expected triorganotin bromide, the dibromide is also formed even when only 80% of the stoichiometric amount of bromine is added. The following procedure is recommended for obtaining pure R_3SnX: 5 g of the mixture of R_4Sn, R_3SnX, and R_2SnX_2 are put on to a column ($\Phi = 4$ cm, $l = 60$ cm) packed with Al_2O_3 and eluted with petroleum ether (60–65°) to give unreacted R_4Sn. Further elution with ethanol or isopropanol affords an alcoholic solution of very pure ($>99\%$)R_3SnX, the R_2SnX_2 staying on the column. The alcohol is then evaporated and progressively replaced by benzene to avoid the disproportion reaction[19] $2R_3SnX \rightleftarrows R_2SnX_2 + R_4Sn$ which seems to occur with highly concentrated alcoholic solutions of R_3SnX. The benzene solution is then distilled.

The NMR spectra were recorded on a Varian A60 apparatus (with 5% solutions in CCl_4, and tetramethylsilane as internal standard).

All the new compounds were further characterized by mass spectrometry, and their purities have been checked by GLC.

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