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CARBON MAGNETIC RESONANCE OF ORGANOMETALLIC COMPOUNDS: PHENYL AND BENZYL TRIMETHYL STANNANES AND RELATED COMPOUNDS

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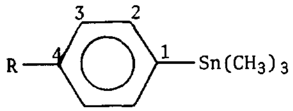
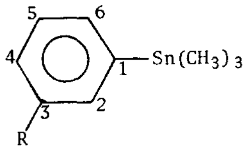
As part of our studies of the ^{13}C nmr spectra of certain classes of organometallic compounds, we wish to report the chief features of the proton-decoupled, natural abundance spectra of series of *meta* and *para*-substituted phenyl and benzyltrimethyl stannanes, and the related allenyl (1,2-propadienyl) and allyl (3-propenyl) compounds.

Phenyltrimethylstannanes: The chemical shift and ^{13}C-^{119}Sn, ^{117}Sn coupling constants are listed in Table 1. Assignments were made on the basis of signal intensities, chemical shifts and the relative magnitudes of ^{119}Sn-^{13}C coupling constants. In appropriate cases, values of $J_{^{19}F-^{13}C}$ have also been employed.

TABLE 1

COMPOUND	R	C_1	C_2	C_3	C_4	C_5	C_6	CH_3-Sn
	H	51.2	57.2	64.8	64.8	-	-	203.2
		(473.0)	(35.4)	(45.4)	(10.0)			(351.4)
	Cl	55.9	59.0	67.7	61.3	-	-	203.1
		(452.0)	(38.0)	(47.0)	(11.5)			(348.0)
	CF_3	45.2	56.9	68.5	61.8	-	-	203.5
		†	(37.0)	(38.6)	(<10)			†
	OCH_3	61.2	56.2	78.7	32.4	-	-	204.4
		(488)	(42.0)	(52.0)	(<10)			(347)
	CH_3	55.4	57.10	63.8	55.2	-	-	202.7
		(488)	(42.0)	(52.0)	(<10)			(350)
	Cl	48.2	57.4	58.3	64.5	63.6	59.3	202.6
		(442.0)	(38.7)	(61.0)	(<10)	(47.0)	(34.6)	(356.8)
	CF_3	48.7	60.5	62.2	67.9	64.7	53.4	203.2
		†	†	†	†	(46.0)	(35.0)	†
	OCH_3	49.3	71.3	33.4	70.5	63.6	64.7	202.6
		(474)	(40.0)	(52.0)	(<10)	(51.0)	(37.0)	(346.0)
	CH_3	51.6	56.6	56.1	64.0	65.0	60.2	202.9
		(482)	(36.0)	(47.0)	(<10)	(48.0)	(37)	(344)

Chemical shifts in p.p.m. from CS_2. Values in parentheses are coupling constants in Hz and only the ^{119}Sn-^{13}C constants are tabulated. For coupling constants <100 Hz, the ^{119}Sn and ^{117}Sn values are unresolved.

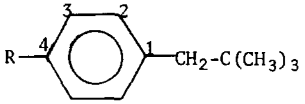
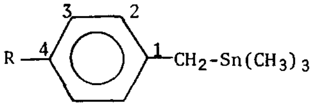
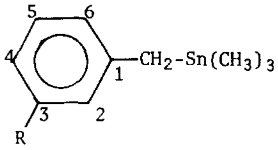
† ≡ not determined.

In general, the chemical shifts of aryl carbons in the above compounds respond to the nature of R in the expected way[1], and the chemical shift of C_1 in para $-R-C_6H_4-Sn(CH_3)_3$ was correlated satisfactorily with the shift of C_4 in C_6H_5-R (by a line through the origin and the point for R=H) suggesting that π-electron withdrawal by $Sn(CH_3)_3$ was unimportant or somehow balanced by other substituent-induced effects. The C_1-^{119}Sn coupling constants respond to substituents and range from ca 488 Hz for p-CH_3 and p-OCH_3 to 452 Hz for p-Cl, and 442 Hz for m-Cl. For substituents with larger σ-constants, the coupling constants decline. The opposite trend occurs in the ^{119}Sn-CH_3 coupling constants although the range is much less eg. for m-Cl, J=356.8 Hz while for p-OCH_3, J=347 Hz. These responses are accommodated by the hypothesis[2] that as the electron donating ability of R increases those hybrid orbitals directed from Sn to C_1 will have exalted 5s character and hence an increased coupling constant if the (Fermi) contact mechanism is dominant. This does seem indicated by the relative magnitudes of $J_{C_1\text{-}^{119}Sn}$ (473 Hz) and $J_{CH_3\text{-}^{119}Sn}$ (351 Hz) which reflect the s-coefficient ratio for sp^2 and sp^3 hybridised carbons in the crude V.B. approach.

It is noteworthy that the order of coupling to ring carbons is $J_{C_1\text{-}Sn} > J_{C_3\text{-}Sn} > J_{C_2\text{-}Sn} > J_{C_4\text{-}Sn}$, which order is also obeyed for C_6H_5-X where X=H, $B^{\ominus}$,C,$P^{\oplus}$,Hg,Pb.[3,4,5]

The data is condensed in Table 2.

TABLE 2

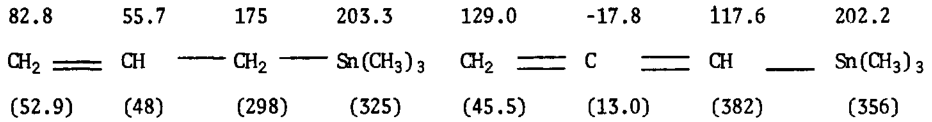
COMPOUND	R	C_1	C_2	C_3	C_4	C_5	C_6	CH_2-Sn	$(CH_3)_3Sn$
	H	53.3	62.5	65.0	67.1	-	-	-	-
	H‡	50.0	66.0	64.4	69.5	-	-	172.3	202.9
		(36.6)*	(22.6)*	(12.0)*	(14.8)*	-	-	(285.4)	(322)
	Cl	51.2	64.9	64.6	64.3	-	-	173.3	203.0
	CF_3	43.4	65.2	66.8	66.9	-	-	171.7	203.0
	CH_3	53.4	66.0	63.8	60.7	-	-	173.4	203.0
	Cl	47.2	67.8	58.7	69.4	63.2	66.1	172.7	203.1
		(38.0)*	(22.5)*	(15)*	(15)*	(12.2)*	(22.5)*	(280)	(327)
	CF_3	47.2	72.6	61.5	69.0	63.4	62.1	171.9	203.0
	CH_3	50.3	65.4	55.5	68.8	64.7	69.0	173	203.3
		(38.5)*	(23.0)*	(13.6)*	(15.4)*	(13.2)*	(22.2)*	†	†

† ≡ Not determined. *≡^{119}Sn,^{117}Sn couplings not resolved.

‡ Assignments confirmed by examination of O-deuterated compound.

Regarding chemical shifts, the most noteworthy feature is the increased shielding of C_4 in benzyltrimethylstannane compared with the carbon analogue, neopentylbenzene. (Δ=2.4 p.p.m.). This is in line with the pronounced hyperconjugative electron-releasing ability of the $CH_2Sn(CH_3)_3$ substituent[3,6]. Note also the variation in coupling from ^{119}Sn to aryl carbons where in the benzyl case, $J_{C_1-Sn} > J_{C_2-Sn} > J_{C_4-Sn} > J_{C_3-Sn}$ (cf. phenyl case where $J_{C_3-Sn} > J_{C_4-Sn}$). The larger coupling to C_4 compared with C_3, may also be due to a C-Sn σ-π resonance interaction with the ring, promoting the π-type coupling mechanism to C_4[3].

Other systems capable of sustaining appreciable σ-π interactions are the allyl[7] and allenyl trimethylstannanes, and here $J_{C_3-Sn} > J_{C_2-Sn}$ also.



$$\underset{(52.9)}{\overset{82.8}{CH_2}} = \underset{(48)}{\overset{55.7}{CH}} - \underset{(298)}{\overset{175}{CH_2}} - \underset{(325)}{\overset{203.3}{Sn(CH_3)_3}} \qquad \underset{(45.5)}{\overset{129.0}{CH_2}} = \underset{(13.0)}{\overset{-17.8}{C}} = \underset{(382)}{\overset{117.6}{CH}} - \underset{(356)}{\overset{202.2}{Sn(CH_3)_3}}$$

Notice the variation in $J_{^{119}Sn-C_1}$ in both systems due to the differing s-content in the C_1 hybrid orbital directed to Sn.

The ^{13}C n.m.r. data on phenyl, benzyl and related compounds[8] provides a basis for assignments in organo-tin systems and has facilitated assignments in larger ring systems[9].

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