Journal of Organometallic Chemistry, 55 (1973) C11–C14
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

^{13}C Fourier transform studies of organotin compounds
I. ^{119}Sn–^{13}C spin–spin coupling constants

HENRY G. KUIVILA, JOHN L. CONSIDINE, RICHARD J. MYNOTT and RAMASWAMY H. SARMA
Department of Chemistry, State University of New York at Albany, Albany, New York 12222 (U.S.A.)

(Received March 14th, 1973)

SUMMARY

^{119}Sn–^{13}C coupling constants have been measured for fourteen organotin compounds including aliphatic, unsaturated and cyclic derivatives yielding results which indicate that these parameters have great potential for revealing information concerning structures and conformations of organotin compounds and of other compounds into which organotin groups can be conveniently introduced.

Many reports on coupling constants between ^{13}C and other nuclei have appeared in the recent literature. These include data on transition metal complexes and σ-bonded organometallic compounds[1–5]. However, the data reported on coupling to ^{119}Sn has been limited mainly to simply aliphatic[2–4] and phenyl derivatives[5]. We wish to report some preliminary results of a systematic investigation of aliphatic, unsaturated and cyclic organotins in which couplings involving one to four bonds have been examined and the roles of carbon orbital hybridization and dihedral angle (three-bond couplings) have been investigated. The results point the way toward using these parameters in studies on the structures and conformations of organotin compounds. Of broader significance, since the R_3Sn group can be introduced into organic structures with relative ease, these data should be of considerable value in probing structures and conformations in a wide variety of compounds.

The spectra were recorded at 25.15 MHz both with and without broadband proton decoupling. Spectral assignments were based upon (i) relative intensities in the ^{13}C–{^{1}H} spectra, (ii) multiplicities in the ^{13}C spectra recorded without ^{1}H decoupling, (iii) for ^{13}C atoms directly attached to ^{119}Sn, the magnitude of $^1J(^{119}\text{Sn}–^{13}\text{C})$, and (iv) comparisons of the chemical shifts with other compounds. The coupling constants are given in Table 1. Data for I [2], II [3] and X [4] have been reported previously by others. For III, $|^2J(^{119}\text{Sn}–^{13}\text{C})|$ is 20.1 Hz, while $|^3J(^{119}\text{Sn}–^{13}\text{C})|$ is 51.4 Hz; the assignments were con-

TABLE 1

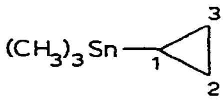
COUPLING CONSTANTS[a]

Compound		$^1J(Sn-^{13}C)$	$^2J(Sn-^{13}C)$	$^3J(Sn-^{13}C)$	$^4J(Sn-^{13}C)$	$^1J(Sn-^{13}C_{Me})$
I	$Sn(CH_3)_4$	337.8^{b,c}				337.8^{b,c}
II	$Sn(CH_2CH_3)_4$	320.3^{b,c}	23.4^{c}			
III	$Sn(CH_2CH_2CH_3)_4$	313.4^{b,c}	20.1^{c}	51.4^{b,c}		
IV	$Sn(CH_2CH_2CH_2CH_3)_4$	313.7^{b,c}	19.6^{d}	52.0^{b,c}	0	
V		502.8^{b,d}	18.8^{d}			341.6^{b,d}
VI		389.7^{b,e}	23.3^{d}	57.6^{b,d}		313.5^{b,d}
VII		405.6^{b,f}	<6	51.2^{b,e}		311.8^{b,d}
VIII		407.4^{b,e}	14.4^{e}	57.5^{e}	6.0^{f}	303.9^{b,e}
IX	$Sn(CH{=}CH_2)_4$	519.3^{b,d}	<6			
X	$Sn(CH_2CH{=}CH_2)_4$	264.9^{b,d}	48.3^{b,d}	51.3^{b,d}		
XI		431.4^{b,d}	J_1 24.1^{e} J_3 n.d.	51.5^{d}	28.2^{d}	342.5^{b,d}
XII		459.0^{b,d}	$J_{2,6}$ 17.3^{c} J_7 13.0^{c}	$J_{3,5}$ 51.9^{b,c} J_4 65.8^{f}		313.8^{b,c}
XIII		405.6^{b,d}	n.d.	J_{trans} 67.5^{b,c} J_{gauche} 11.9^{c}		314.2^{b,c}
XIV		373.6^{b,e}	n.d.	$J_{2,3}$ 67.9^{e} $J_{5,6}$ 5.6^{e}		314.1^{b,e}

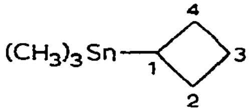
[a] Coupling constants in Hz. Unless otherwise stated, the value quoted is obtained from the centers of the unresolved ^{119}Sn and ^{117}Sn satellites. [b] The satellites due to ^{119}Sn and ^{117}Sn were resolved separately; the quoted coupling constant is for ^{119}Sn, and is the average of the value for ^{119}Sn, and of that of ^{117}Sn multiplied by the factor $\gamma_{119}/\gamma_{117}$ (1.0 462). [c] ±0.25 Hz. [d] ±0.6 Hz. [e] ±1.0 Hz. [f] ±2.0 Hz. n.d. = not detected. $J_{x,y}$ = coupling constant between Sn and carbon atoms labelled x, y.

firmed by a spectrum recorded with carbon—proton coupling present. The relative magnitudes of these coupling constants were used to assign the spectrum of IV, in which the β and γ carbons both give rise to triplets when coupling to ^{1}H. In the cycloalkyl derivatives of tin, $|^1J(^{119}Sn-^{13}C)|$ is generally larger (502.8—389.7 Hz) than for acyclic compounds (320.3—313.7 Hz), as was also found in the norbornyl compounds XII—XIV (459.0—405.6 Hz). For V, the direct coupling is expectionally large, but for VI it is smaller than might have been anticipated by comparison with the remainder of the series. In this group of compounds, V—VIII, the value of $|^1J(^{119}Sn-^{13}C_{Me})|$ also progressively decreases.

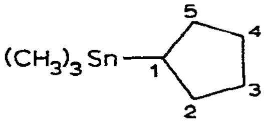
The most interesting results are those for the norbornyl and norbornenyl derivatives. For XIII, an unambiguous assignment of C_2, C_3 on the one hand and C_5, C_6 on the other is not possible on the basis of chemical shifts alone and the ^{13}C spectra with protons coupled are both triplets. However, in the 7-norbornenyl compound, both the chemical shift and ^{13}C (^{1}H not decoupled) spectra for the vinyl carbons C_2, C_3 are different from those of C_5, C_6, allowing a conclusive assignment. In the latter compound, $|^3J(^{119}Sn-^{13}C_{2,3})|$ (*trans*) is 67.9 Hz, while $|^3J(^{119}Sn-^{13}C_{5,6})|$ (*gauche*) is 5.6 Hz. Since the magnitude of the *gauche* coupling constant should not be very different in the spectrum of the 7-norbornyl compound, XIII, the peak with satellites of 11.9 Hz is assigned to C_5, C_6 (*gauche*), and that with satellites of 67.5 Hz is assigned to C_2, C_3 (*trans*).



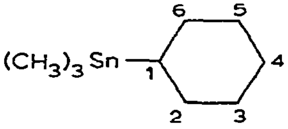
(V)



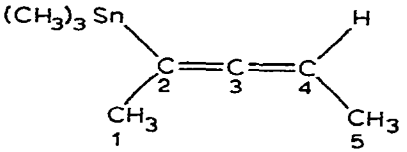
(VI)



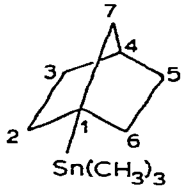
(VII)



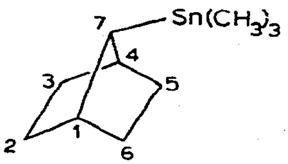
(VIII)



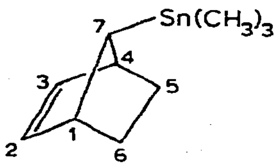
(XI)



(XII)



(XIII)



(XIV)

Surprisingly the *trans* coupling constants to the sp^2 and sp^3 carbons are nearly equal. These findings indicate a very strong dependence of the vicinal coupling constant upon dihedral angle and open up the prospect of using ^3J(Sn—C—C—C) as a highly useful probe in the study of conformation and structure.

In VI, VII and VIII, the coupling constants $|^3J(^{119}\text{Sn}-^{13}\text{C})|$ are for an essentially *trans* arrangement, and each is greater than 50 Hz. In III and IV, the large values of $|^3J(^{119}\text{Sn}-^{13}\text{C})|$ suggest that the alkyl chains have a predominantly *trans* conformation about the C_α—C_β bond, a conclusion compatible with the greater restriction to rotation for *gauche* conformations shown by space filling models.

In Table 1, there are coupling data for compounds of similar length of carbon chain, but which differ in their extent of unsaturation, *i.e.*, II and IX, or III and X, or IV and XI. The large long-range coupling constant $|^4J(^{119}\text{Sn}-^{13}\text{C})|$ in XI is greater than most two-bond coupling constants reported here, with the exception of that in X, which is itself much greater than in the corresponding saturated compound, III. Differences in the direct coupling in II and IX can undoubtedly be attributed to the change in hybridization of the directly attached atom. In the series V—VII, where modest changes in hybridization occur at the carbon atom bound to tin, the value of J does not change in the same order as the degree of *s* character. Thus it follows that such changes in coupling to carbon should not be attributed to changes in hybridization alone[6]. Indeed, even the Fermi contact term alone may be inadequate in such instances[7]. A future detailed report will contain chemical shifts and coupling constant data on a wider range of organotin compounds.

ACKNOWLEDGEMENT

This research was supported by the National Science Foundation under Grants GP 28061, GB 28015 and GP 29165X and by the National Cancer Institute of the National Institutes of Health under Grant CA 12462—012. We thank M & T Chemicals, Inc., for gifts of organotins.

REFERENCES

1 For a review of literature through 1969 see: J.B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, 1971
2 (a) W. McFarlane, *J. Chem. Soc., A*, (1967) 528.
(b) H. Dreeskamp and G. Stegmeier, *Z. Naturforschg. A*, 22 (1967) 1458.
(c) F.J. Weigert, M. Winokur and J.D. Roberts, *J. Amer. Chem. Soc.*, 90 (1968) 1566.
3 F.J. Weigert and J.D. Roberts, *J. Amer. Chem. Soc.*, 91 (1969) 4940.
4 Yu.K. Grishin, N.M. Sergeyev and Yu.A. Ustynyuk, *Org. Magn. Res.*, 4 (1972) 337.
5 C.D. Schaeffer, Jr., and J.J. Zuckerman, *J. Organometal. Chem.*, 47 (1973) C1.
6 G.E. Maciel, J.M. McIver, N.S. Ostlund and J.A. Pople, *J. Amer. Chem. Soc.*, 92 (1970) 1, 11.
7 A.C. Blizzard and D.P. Santry, *Chem. Commun.*, (1970) 1085.