^nJ(SnD) Coupling Constants: a Powerful Tool for Structural Analysis of Organotin Compounds by ^{119}Sn Fourier Transform N.M.R. Spectroscopy

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Summary ^nJ(SnD) coupling constants, very easily deduced from the triplets observed by ^{119}Sn Fourier transform n.m.r. spectroscopy with proton decoupling, may be used for the direct identification of isomeric or diastereoisomeric organotin compounds.

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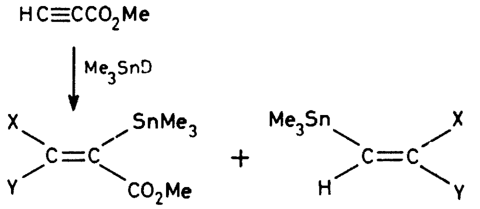
^nJ(SnH) COUPLING constants could be very important for determining structures of organotin compounds. However one faces the difficulties that ^{117}Sn and ^{119}Sn satellites are weak and often difficult to distinguish in ^{1}H n.m.r. spectra, and that the signals in ^{119}Sn Fourier transform (FT) n.m.r. spectra are usually very complex because of the couplings by the many alkyl hydrogen atoms. If it were possible to introduce convenient selective deuterium labels, then ^{119}Sn n.m.r. spectroscopy with broad-band proton decoupling would give straightforward signals as 1 : 1 : 1 triplets for ^nJ(SnD). We now report some preliminary results we have obtained by this approach.†

Methyl propiolate and trimethyltin deuteride were caused to react as described previously,[1] equation (1), and the mixture was directly analysed by ^{119}Sn n.m.r. spectroscopy at 33·54 MHz using gated decoupling techniques. The spectrum gave four triplets for organotin acrylates, quantitatively determined by integration, and identified by their chemical shifts and their coupling constants (Table 1) The results were similar to those reported by Leusink but the long analysis by ^{1}H n.m.r. spectroscopy was replaced by a fast and convenient determination showing directly the regio- and stereo-chemistry of the addition.



(1)

(1) X = H, Y = D, 60%
(2) X = D, Y = H, 11%
(3) X = CO$_2$Me, Y = D, 25%
(4) X = D, Y = CO$_2$Me, 4%

TABLE 1.

Compound	δ ^{119}Sn/p.p.m.	^3J(SnD)/Hz	^3J(SnH) calc.[a]/Hz	^3J(SnH) lit.[b]/Hz
(1)	−27·8	19·5	127·0	127·5
(2)	−27·8	9·2	59·9	63
(3)	−51·2	19·5	127·0	127·5
(4)	−32·5	9·9	64·5	64

[a] ^3J(SnD) measured × 6·5144(γ_H/γ_D). [b] Ref. 1.

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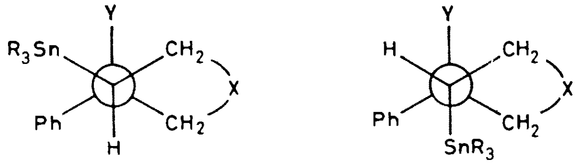
† All the spectra were run in C_6D_6 as solvent, with Me_4Sn as external standard. Negative signs indicate shifts with frequencies lower than that of the Me_4Sn resonance.

The reaction of a mixture of *cis* (12%) and *trans* (88%) styryltrimethyltin with 2,3-dimethylbutadiene at 180 °C gave two isomeric adducts: (**5**) (88%) and (**6**) (12%).[2] The configuration of (**5**) (*trans*-isomer) was first determined by ^{13}C n.m.r. spectroscopy at 15·08 MHz by consideration of ^{3}J(Sn-allylic C) assuming a half-chair conformation[3] and the fact that Me$_3$Sn has a lower preference for the equatorial position than has an alkyl or aryl group.[4] The observed value (54 Hz) was compatible only with a dihedral angle close to 180°.[5]



(**5**) R = Me, X = CMe=CMe, Y = H (**6**) R = Me, X = CMe=CMe, Y = H

(**7**) R = Me, X = CMe=CMe, Y = D (**8**) R = Me, X = CMe=CMe, Y = D

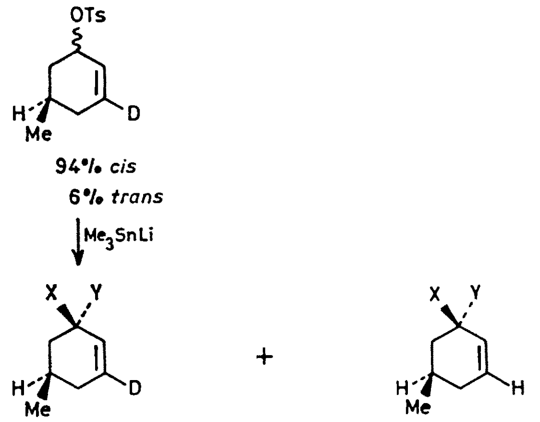
(**9**) R = Bu^n, X = CH$_2$CH$_2$, Y = D

Another and more convenient approach is to start from a mixture of (*Z*) (25%) and (*E*) (75%) deuteriated organotin (easily prepared by deuteriostannation of phenylacetylene).[6] The ^{119}Sn n.m.r. spectrum of the reaction mixture showed two triplets at δ −3·39 p.p.m. [^{3}J(SnD) 2·15 Hz] for (**7**) (80%) and at −5·18 p.p.m. [^{3}J(SnD) 18·4 Hz] for (**8**) (20%). Such ^{3}J(SnD) values were ascribed to the most highly populated conformations which show dihedral angles of 60° [(*E*)-isomer] and 180° [(*Z*)-isomer] in agreement with ^{13}C n.m.r. analysis.

The advantage of this method is that each isomer gives only a triplet in the ^{119}Sn n.m.r. spectrum while ^{13}C n.m.r spectroscopy requires first the attribution of certain specific carbons and then the search for $^{117-119}$ Sn satellites.

To investigate the stereochemistry of alkene deuteriostannation, tributyltin deuteride was allowed to react with phenylcyclohexene either under azobis-isobutyronitrile initiation (5—10% yield) or under 10 kbar pressure (*ca.* 95% yield).[2] The ^{119}Sn n.m.r. spectra of the adduct (**9**) obtained in both cases showed a triplet at δ −21·3 p.p.m. with ^{3}J(SnD) 20·5 Hz. This value is consistent with a dihedral angle close to 180°, as in compound (**8**). The configuration of (**9**) was also confirmed by mass spectroscopy.[7] The addition therefore occured in an *anti* sense across the double bond.

To determine the regio- and stereo-chemistry of the stannylation of allyl tosylates, trimethylstannyl-lithium was allowed to react with a specifically deuteriated allyl toluene-*p*-sulphonate.[8] ^{119}Sn N.m.r. spectroscopy allowed the characterisation and the quantitative analysis of the reaction mixture which contained four isomers (**10**)—(**13**) (Table 2).



(10) X = Me$_3$Sn, Y = H, *ca.*13%

(11) X = H, Y = Me$_3$Sn, *ca.*36%

(12) X = Me$_3$Sn, Y = D, *ca.*17%

(13) X = D, Y = Me$_3$Sn, *ca* 34%

Ts = *p*-MeC$_6$H$_4$SO$_2$

Table 2.

Compound	δ ^{119}Sn/p.p.m.	^{n}J(SnD)/Hz
(**10**)	−0·29	2·6
(**11**)	−2·72	3·5
(**12**)	−0·37	12·7
(**13**)	−2·82	12·9

The *cis* and *trans* configurations had been previously identified using ^{3}J(^{119}Sn^{13}C) coupling constants in non-deuteriated compounds.[9] The choice between rearranged and non-rearranged derivatives was made on the basis that ^{2}J(SnD) is larger than ^{4}J(SnD).[10] Although this metallation appears to be neither stereospecific nor regiospecific, results can be achieved close to stereo- and regio-specificity using tributylstannyl-lithium under similar conditions.[11]

We conclude that ^{n}J(SnD) is a valuable tool for structural determinations using ^{119}Sn FT n.m.r. spectroscopy because of its direct accessibility. The angular dependence of ^{3}J(SnD) seems to be most promising for configuration identification, but further model molecules have to be designed and built in order to establish the exact relationship which, at first sight, appears to be Karplus-like.

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