Journal of Organometallic Chemistry, 104 (1976) 311—315

TIN-119 MAGNETIC SHIELDING IN NORBORNENYLTRIMETHYLTINS

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(Received July 28th, 1975)

Summary

The ^{119}Sn NMR chemical shifts of a series of isomeric norbornenyltrimethyltins have been measured in order to assess the effect of isolated double bonds on the magnetic shielding of the tin nucleus. It is concluded that changes in C—Sn—C inter-bond angles may have to be invoked to account for the observed changes in tin shielding.

Introduction

Over forty-five research papers and two review articles [1,2] have appeared in which ^{119}Sn chemical shift data for over 600 compounds have been reported. However, no quantitative explanations of variations in tin shielding have been advanced, although many empirical trends can be qualitatively rationalized. For example, the variation of tin shielding in organotin carboxylates as the inductive effect of the carboxylate moiety changes has been interpreted in terms of change in electron imbalance among the tin valence orbitals [3] which affects the paramagnetic term in general expressions [4,5] that describe the shielding. Similarly, the characteristic curve of a plot of the tin chemical shift $\delta(^{119}\text{Sn})$ against n in a series of compounds $R_{4-n}SnX_n$, where X is an electronegative element (e.g. for R, X = Me, O-tBu; Fig. 1), has also been rationalized on the basis of the paramagnetic contribution changing with changing electron imbalance [6]. Polarizable substituents (e.g. hydride) on tin apparently reduce this paramagnetic term, and a multiple bond α- to the tin atom also increases the shielding (Table 1 and Fig. 1) [7]. Shifts to high field associated with unsaturated substituents have usually been interpreted in terms of $p_\pi \rightarrow d_\pi$ bonding [1,2] but it is not easy to see how this can actually lead to the observed effect, and this certainly cannot account for the high-field shifts of organotin hydrides, or for increases in shield-

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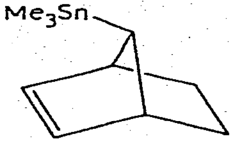
ing observed when the multiple bond system is more distant from the tin atom (Table 1 and Fig. 1).

In an attempt to determine the origin of this effect, we have measured the ^{119}Sn chemical shifts of a series of trimethylnorbornenyltin compounds (I-V) [8] in which the rigidity of the carbocyclic system accurately defines the relative positions of the tin atom and the multiple bond.



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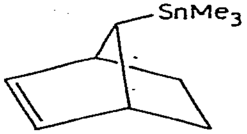

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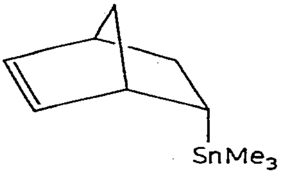

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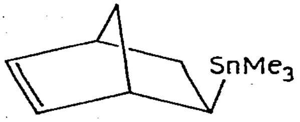

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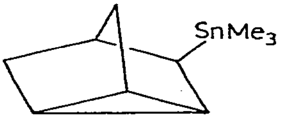

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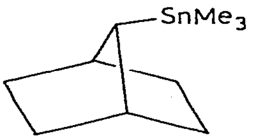

(VI)

Experimental

Norbornenyltrimethyltins (compounds I-IV) and nortricyclytrimethyltin (compound V) were prepared by published methods [8-10], and were examined in benzene solution using a JEOL C60-H 60 MHz NMR instrument modified [6] for $^1H-\{^{119}Sn\}$ double resonance, the ^{119}Sn frequency at 22.37 MHz being supplied by a Schlumberger FS-30 Frequency Synthesizer. The tin—proton coupling $^2J(^{119}Sn-^1H)$ (natural abundance of ^{119}Sn = 8.68%) was well defined

TABLE 1

TIN CHEMICAL SHIFTS [$\delta(^{119}Sn)$ (ppm)] OF ALKYLTIN HYDRIDES AND UNSATURATED ALKYLTIN COMPOUNDS $R_{4-n}SnX_n$

	R, X	*n*			
		1	2	3	4
A	Me, H	—104.5 [a]	—224.6 [b]	—347 [c]	
B	Et, $-C\equiv CH$	—52 [d]	—141 [d]		—279 [d]
C	Me, $-CH=CH_2$	—39	—79.4 [e]		—165.1 [e]
D	Me, Ph	—30.3 [e]	—59.8 [e]	—93 [f]	—137 [c]
E	Et, $-CH_2Ph$	—6 [d]	—13 [d]	—23 [d]	—36 [g]
F	n-Bu, $-CH_2CH=CH_2$			—34.3 [a]	—47.9 [a]
G	Me, —O-t-Bu	+89.5 [h]	—2 [h]	—177 [h]	

[a] Ref. 15. [b] Calculated from data given by H. Elser and H. Dreeskamp, ref. 16. [c] Ref. 2. [d] Ref. 7. [e] Ref. 17. [f] Ref. 6. [g] Ref. 18. [h] Ref. 19.

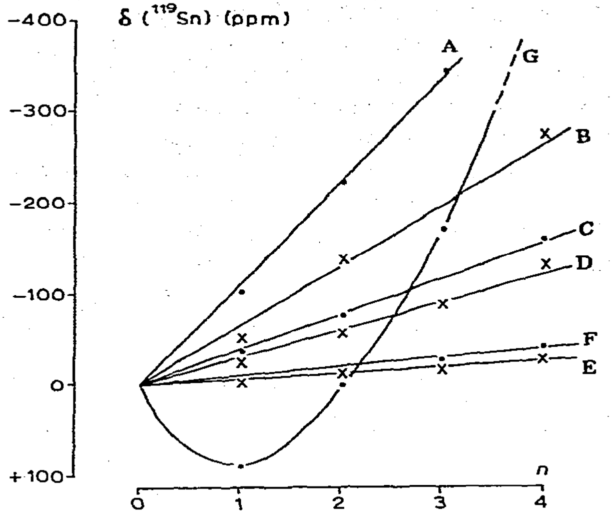

Fig. 1. Plot of $\delta(^{119}Sn)$ vs. *n* for series of compounds $R_{4-n}SnX_n$, where R, X = (A) Me, H; (B) Et, $-C{\equiv}CH$; (C) Me, $-CH{=}CH_2$; (D) Me, Ph; (E) Et, $-CH_2Ph$; (F) n-Bu, $-CH_2CH{=}CH_2$; (G) Me, —O-t-Bu. This shows the linear increase in shielding with *n* for unsaturated substituents on tin (A-F) in contrast to the markedly non-linear relationship when the substituent atoms are of widely differeing electronegativities (curve G).

for the *Sn*-methyl groups [8] and the double resonance experiments were straightforward. Results are presented in Table 2, in which tin chemical shifts are given relative to tetramethyltin (Ξ 37.290665 MHz) as zero; a shift to high field of this is given a negative sign.

Discussion

The anisotropy of induced electronic circulation in the π-system of the double bond of the norborn-2-enyl skeleton can produce variations in the applied magnetic field of up to ca. 0.0002% in other parts of the molecule, and these changes are significant in the interpretation of proton [11,12], and to some extent ^{13}C [13], chemical shifts in norbornenyl and related compounds. This is a magnetic effect, and is of the same order, i.e. ⩽ ca. 2 ppm, for other nuclei

TABLE 2

TIN CHEMICAL SHIFTS [$\delta(^{119}Sn)$ (ppm)] AND TIN TO METHYL—PROTON COUPLING CONSTANTS [$^2J(^{119}Sn-^1H)$ (Hz)] OF NORBORNENYLTRIMETHYLTINS AND RELATED COMPOUNDS

Compound	$^2J(Sn-H)$ [a]	$\delta(^{119}Sn)$ [b]
I, *syn*-7-trimethylstannylnorborn-2-ene	+51.1	—13.2 [c]
II, *anti*-7-trimethylstannylnorborn-2-ene	+50.25	—25.6 [d]
III, *endo*-5-trimethylstannylnorborn-2-ene	+50.2	—1.2
IV, *exo*-5-trimethylstannylnorborn-2-ene	+49.55	+7.8
V, 3-trimethylstannylnortricyclene	+50.65	—11.4
VI, 7-trimethylstannylnorbornane [d]		—9.2

[a] Neat liquids. [b] Solution in C_6H_6. [c] —11.3; 25% *v/v* in CH_2Cl_2; ref. 20. [d] 25% *v/v* in CH_2Cl_2; values taken from ref. 20.

bonded to the carbocyclic skeleton and will not be of great importance in the interpretation of the tin chemical shifts reported here which span a range of 37 ppm. Effects due to single bond anisotropies will be even less significant.

A dependance of the tin shielding on the polarizability of the double bond in compounds (I—IV) would be expected to decrease as the magnitude of the vector joining the mid-point of the C(2)-C(3) bond with the tin nucleus increases, and there may also be a dependence on the angle that this vector makes with the axes of the double bond. Interactions of this nature could in principle result in changes in tin shielding of either sign, but it is found empirically [1,2,7] that polarizable substituents near to the tin atom generally increase the shielding of the tin nucleus (Table 1). On this basis the order of tin shielding in compounds IV < III < I follows the expected sequence, but the high-field shift of compound II is anomalous, as are the shifts of the two compounds V and VI which do not have π-systems but nevertheless exhibit a degree of tin shielding comparable to that of compound I.

Expressions which describe the paramagnetic contribution to nuclear shielding contain terms which depend on the elements of the charge-density and bond-order matrix for the valence *p*- and *d*-orbitals [4,5]. These will be modified when the geometry at tin deviates from tetrahedral sp^3 and concomitant changes in the nuclear shielding will result. This relationship has not been quantified, but it has been found empirically that incorporation of a tin atom into five- and six-membered carbocyclic rings changes the tin chemical shift by +50 ppm and −40 ppm respectively [14]. These changes can be associated with decreases of the ring C—Sn—C bond angle from tetrahedral of ca. +5° and +35° respectively, estimated on the basis of normal bond lengths and tetrahedral stereochemistry at the carbon atoms. The relationship is therefore not simple, but it is evident that only small inter-bond angle modifications are required to produce significant changes of either sign in the tin shielding. This presumably accounts for the apparently haphazard variation [1,2] of tin chemical shift with n in tetraorganotin compounds $R_{4-n}SnR'_n$ where R and R′ are saturated organic groups with different spatial requirements. In the compounds examined here, significant steric interactions are believed to occur between trimethyltin groups and *syn* hydrogen atoms, especially in compounds II and IV [8,9]. These will result in different deviations from tetrahedral in the geometry of the trimethyltin-carbon groups among compounds I-VI and can therefore account to a large extent for the observed differences in tin shielding. It should be pointed out however that little is known about the influence that a constrained carbocyclic ring might have on the shielding of a tin atom bonded to it, for example in cycloalkyltrimethyltin compounds.

Acknowledgements

I thank the SRC for support and Dr. W. McFarlane for coorporation.

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