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^{1}H, ^{13}C, ^{15}N AND ^{119}Sn NMR INVESTIGATIONS ON STANNATRANES

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Summary

^{1}H, ^{13}C, ^{15}N and ^{119}Sn NMR data for alkyl- and phenyl-stannatranes are reported. A trimeric structure and an intramolecular dynamic process are proposed.

As in other "atranes" [1,2] the nitrogen atom should be close to the tin in stannatranes and thus interaction of the orbitals of the nitrogen and tin, with pentacoordination at the tin atom, should be possible [3,4]. In triorganotin halide-amine complexes an intramolecular coordination between the amine-nitrogen and the tin atom has been observed [5], and the tin atom exhibits a trigonal bipyramidal geometry [6]. In $Sn[(OC_2H_4)_2NC_2H_4OH]_2$, however, the tin atom is octahedrical being surrounded by four oxygen and two nitrogen atoms of both the triethanolamine molecules, with the OH-groups not participating in the coordination [7].

In order to obtain information about the structure and internal mobility of the stannatranes I—V we investigated the ^{1}H, ^{13}C, ^{15}N and ^{119}Sn NMR spectra of these compounds, which were synthesized from the appropriate organotin oxide [8] or monoorganostannoic acid [3] and triethanolamine. The NMR data are given in Tables 1—3.

TABLE 1

CHEMICAL SHIFTS OF METHYLSTANNATRANE (I)

The chemical shifts are given in ppm relative to TMS for ^{1}H and ^{13}C, relative to NO_3^- for ^{15}N and relative to $SnMe_4$ for ^{119}Sn, downfield being positive.

Nucleus	Signal a CH_3Sn	Signal b CH_3Sn		Signal c CH_3Sn	CH_2O	CH_2N	Temperature (°C)	Solvent
^{1}H	0.64	0.38		0.27	3.81	2.81	−20	CH_2Cl_2
	0.66		0.36		3.85	2.85	+30	CH_2Cl_2
	0.62	0.46		0.34	3.85	2.85	−20	$CDCl_3$
	0.64		0.42		3.85	2.85	+34	$CDCl_3$
		0.53			3.90	2.95	+80	$CDCl_3$
	C—Sn	C—Sn		C—Sn	—N—C···C—O			
^{13}C	10.9	−1.4		−2.6	50—60		−20	$CDCl_3$
	10.9		−2.0		50—60		+30	$CDCl_3$
^{15}N	−353.5		−360.1				−30	$CDCl_3$
	−353.5		−360.1				+20	$CDCl_3$
	−353.5		−360.1				+33	$CDCl_3$
^{119}Sn	−537	−350.2		−346.5			−40	$CHCl_3$
	−537.2	−351.6		−347.6			−10	$CHCl_3$
	−537.2	−352.3		−348.3			+10	$CHCl_3$
	−536.8	−351.5		−349.0			+27	$CHCl_3$
	−537.9		−351.5				+50	$CHCl_3$
	−532.9	−356.4		−352.3			−50	n-BuOH
	−533.7	−357.8		−354.3			+27	n-BuOH
	−535.4		−356.7				+100	n-BuOH
	−537.5		−354.4				+27	Pyridin

TABLE 2

^{119}Sn CHEMICAL SHIFTS OF COMPOUNDS II—V

The chemical shifts are given in ppm relative to $SnMe_4$, downfield being positive.

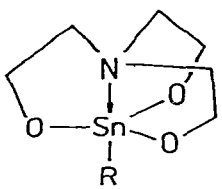
Compound	Signal a	Signal b		Signal c	Signal d	Temperature (°C)	Solvent
II	−556.7	−380.7		−375.4		−40	$CHCl_3$
	−558.1	−380.7		−377.2		−10	$CHCl_3$
	−558.8		−379.8			+10	$CHCl_3$
	−559.7		−380.7			+27	$CHCl_3$
	−561.8		−381.4			+50	$CHCl_3$
	−552.7	−386.3		−380.3	−357.3	−50	n-BuOH
	−555.8		−386.1		−316.3	+27	n-BuOH
III	−559.0	−382.9		−375.9		−40	$CHCl_3$
	−561.6		−380.8			+25	$CHCl_3$
	−558.7		−385.4			+50	$CHCl_3$
	−555.6	−388.7		−385.8	−360.6	−50	n-BuOH
	−557.9		−387.7		−316.4	+27	n-BuOH
IV	−620.5	−443.4		−433.2		−40	$CHCl_3$
	−621.0	−444.5		−434.4		−10	$CHCl_3$
	−620.8	−438.5		−432.8		+25	$CHCl_3$
	−621.7		−441.4			+50	$CHCl_3$
V		−245.5				+27	$CHCl_3$
		−246.4				−50	$CHCl_3$

TABLE 3

COUPLING CONSTANTS OF METHYLSTANNATRANE (I). J (Hz)

J	Signal a	Signal b		Signal c	Temperature (°C)	Solvent
$^2J(^1H—C—^{119}Sn)$	118	107		102	—20	CH_2Cl_2
	116		105		+30	$CDCl_3$
		103			+60	$CDCl_3$
$^2J(^1H—C—^{117}Sn)$	113	102		97	—20	CH_2Cl_2
	110		101		+30	$CDCl_3$
		98			+60	$CDCl_3$
$^1J(^{13}C—^{119}Sn)$	1275	1090		1090	—20	$CDCl_3$
	1273		1085		+30	$CDCl_3$
$^1J(^{13}C—^{117}Sn)$	1218	1039		1039	—20	$CDCl_3$
	1220		1034		+30	$CDCl_3$
$^1J(^{15}N—^{119}Sn)$	75.6		110.0		—30	$CDCl_3$
	75.6		110.0		+20	$CDCl_3$
	75.6		110.0		+33	$CDCl_3$
$^1J(^{15}N—^{117}Sn)$	72.4		104.6		—30	$CDCl_3$
	72.4		104.6		+20	$CDCl_3$
	72.4		104.6		+33	$CDCl_3$
$^2J(^{119}Sn—O—^{117/119}Sn)$ [a]	156	156		156	—40	$CHCl_3$
	156	156		156	—10	$CHCl_3$
	156		156		+50	$CHCl_3$

[a] For II J(SnSn) 220 Hz.



(I, R = methyl; II, R = ethyl; III, R = n-butyl; IV R = phenyl; V, R = t-butyl)

^1H NMR spectra

The NCH_2- and OCH_2-protons of compounds I—IV give rise to unresolved multiplets, which change to pseudo-triplets at temperatures above 80°C. Compound V shows relatively sharp pseudo-triplets at all temperatures.

At —20°C the methylstannatrane (I) in $CDCl_3$ or CH_2Cl_2 shows three CH_3 proton signals of equal intensity. The two highfield signals, b and c (see Table 1), coalesce at 6.7°C, and finally at 63.2°C all three signals coalesce, yielding a single signal for the CH_3—Sn groups [9]. The chemical shifts of the CH_3 proton signals of I are very similar to those in $CH_3Sn(OCH_3)_3$(δ($SnCH_3$) 0.63 ppm) [4]. The shifts and intensities of all three signals are constant in the concentration range of 0.5 to 0.001 mol/l in $CDCl_3$ solution.

The t-butyl-proton signal of V is a singlet at all temperatures.

^{13}C NMR spectra

The OCH_2 and NCH_2 carbons of compounds I—IV show broad, partially-resolved signals with temperature-dependent fine structures which must be connected with different conformations or different orientations of the

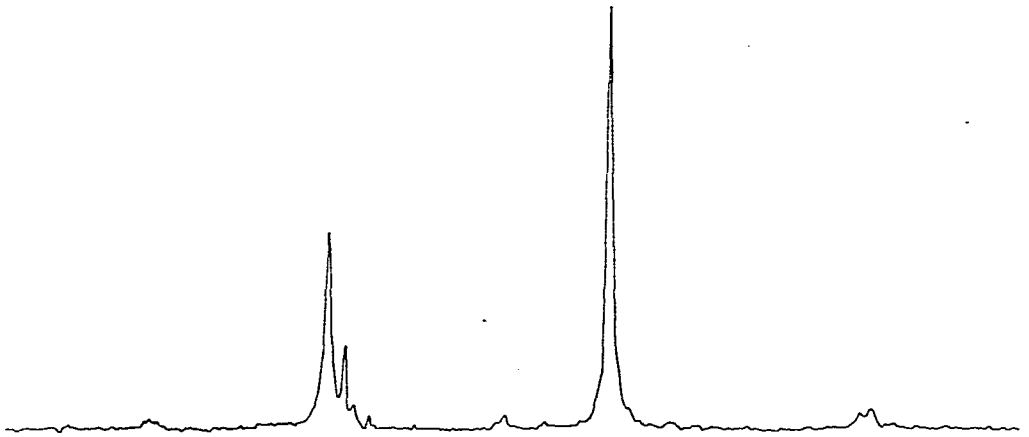


Fig. 1. ^{15}N NMR spectrum of methylstannatrane (I) in $CDCl_3$ solution. Temperature +30°C, scans, 5700; *SW*, 1.2 kHz; *RT*, 7.0 s; *PW*, 19 μs (45°); proton noise decoupling; $\nu_0(^{15}N)$ 9.1 MHz (I is 90% ^{15}N enriched).

OCH_2CH_2N fragment. Again three different signals of equal intensity appear for the CH_3 groups of I, and again the two highfield signals b and c coalesce first. The more complex spectra of II and III displays an analogous behaviour. In V the four sharp carbon signals are not changed by temperature variation.

^{15}N NMR spectra

In the ^{15}N NMR spectra of ^{15}N-enriched methylstannatrane (I) two signals with the intensity ratio 2/1 were observed (see Fig. 1). Both signals show satellites due to $^{15}N—^{117,119}Sn$ coupling. The spectra are not changed in the temperature range of −30 to +35°C (see Table 3). The singular ^{15}N signal of V is split by the $^{117/119}Sn$ coupling ($^1J(^{119/117}Sn—^{15}N)$ 69.9/66.6 Hz at −20°C in $CDCl_3$).

^{119}Sn NMR spectra

In agreement with the ^1H and ^{13}C spectra of the CH_3 group of I, the ^{119}Sn spectrum of this compound also shows three different signals of equal intensity at low temperatures (see Fig. 2). Here the two signals at lower field (b and c) with very close chemical shifts coalesce between 25 and 50°C. By using heteronuclear $^1H—^{119}Sn$-double-resonance (INDOR) it could be shown that the tin nucleas at highest field (signal a) is coupled with the methyl protons lying at lowest field. Consequently the assignment of the CH_3 groups to the different tin atoms is possible (see Table 1).

The most interesting feature of the ^{119}Sn spectra of I and II is the appearance of satellites due to tin—tin coupling for each of the three signals. The intensities of these satellites agree with the natural abundance of ^{119}Sn and ^{117}Sn isotopes and show that the ^{119}Sn nucleus at high field (signal a) is coupled with two tin nuclei. For the signals b and c the satellite intensities allow no similar conclusion because of the similar values of shift difference and coupling constant for these nuclei.

The main signals of the ^{119}Sn spectra of III and IV are very similar to those of I and II, but some weak additional signals appear close to both main signals and in the range of −470 to −490 ppm for III and −520 to −550 ppm for IV.

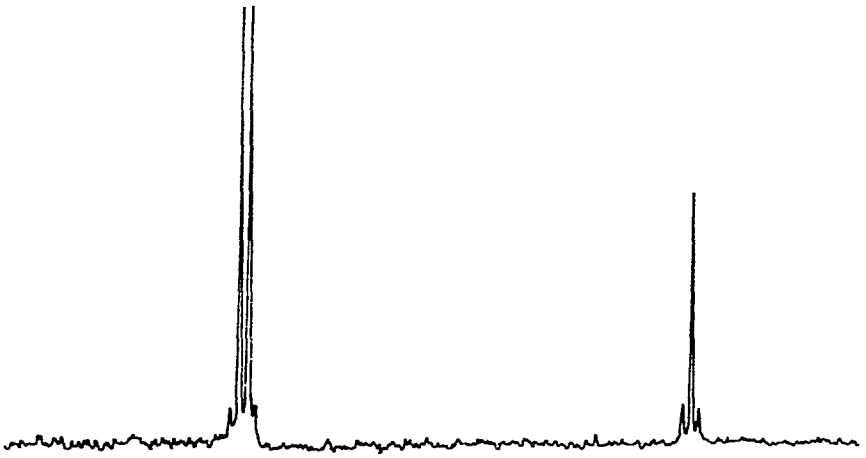


Fig. 2. ^{119}Sn NMR spectrum of methylstannatrane (I) in 1 *M* $CHCl_3$ solution. Temperature —40°C; scans, 1024; *SW* 8 kHz; *RT* 0.5 s; *PW* 60 μs (45°); gated, ^{1}H; $\nu_0(^{119}Sn)$ 22.37 MHz. In the spectrum the signal intensities are not correct, because of the short pulse width. It has been shown that the intensity ratio is 1/1/1.

The ^{119}Sn spectrum of V shows only one sharp signal at lower field, which is not changed in the temperature range +27 to —50°C.

Discussion

Butyl- and ethyl-tin trialkoxides show ^{119}Sn chemical shifts of ca. —440 ppm if they are strongly associated and the tin atom is six-coordinated [10—12]. The ^{119}Sn chemical shifts of the stannatranes I—IV agree roughly with a hexacoordination of the tin atoms in these compounds. The large differences between the signal a and the signal b or c however point to different coordination spheres around the tin atom. The introduction of electronegative substituents and the increase of the coordination number at tin cause high field shifts in the ^{119}Sn NMR spectrum, but these effects are not yet fully understood [12]. However, there are some useful empirical rules, which associate a specific coordination at the tin atom with a typical range of chemical shifts [12,13]. The ^{119}Sn chemical shifts of stannatranes cannot be assigned to these ranges without contradictions. The small temperature dependence of the ^{119}Sn chemical shifts and the appearance of the tin—tin couplings in the spectrum of I and II point to rather stable associates. Kennedy and his coauthors [10] assume that in liquid butyltin alkoxides the association does not lead to a polymeric structure but to trimeric and tetrameric species. However, the exchange of the associates is rapid for alkyltin trialkoxides in the NMR time-scale, so that only one time-averaged ^{119}Sn signal is observed.

Assuming association in the case of the stannatranes I—IV we have to postulate longer life-times for the associates. The higher coalescence temperature of the ^{119}Sn signals b and c (see Tables 1 and 2) of methylstannatrane (I) in comparison to those of ethylstannatrane (II) suggests a higher stability for the associates in the case of I. I shows the same ^{119}Sn NMR spectrum in $CDCl_3$ and n-butanol solution whereas for II an additional signal (signal d in Table 2) appears in the n-butanol solution, and we assign this to a complex between

ethylstannatrane and n-butanol. In a n-butanol solution of III this signal for the "hetero-associate" dominates (signal d). This behaviour suggest a decreasing stability of "auto-associates" in the sequence I, II, and III.

The main factor affecting the coupling constants of the tin nucleus to other nuclei is the *s*-character of the hybrid orbital used to form the bond to the coupling nucleus [14—16]. The increase of the coordination number of tin by addition of electronegative ligand atoms should increase the *s*-character of the Sn—C bond [17]. The extremely high absolute values of the coupling constants $^1J(^{13}C—^{119}Sn)$ and $^1J(^{13}C—^{117}Sn)$ (see Table 3) suggest clearly six-coordination for tin in I [18]. Likewise the coupling constants $^2J(^1H—^{119}Sn)$ and $^2J(^1H—^{117}Sn)$ are as large as usually found in six-coordinated tin compounds [12,19,20]. The $^{15}N—^{119}Sn$ coupling demonstrates the existence of the N—Sn bond in all these forms, and consequently shows that at least pentacoordination of its tin atoms takes place (see Fig. 1).

In accordance with Bent's rules [21] and the statements above, the signals with the largest $^{119}Sn—^{13}C$ and $^{119}Sn—C—^1H$ coupling constants (signal a) shows the smallest $^{119}Sn—^{15}N$ coupling. Finally the observed Sn—Sn couplings and the intensity relations of the satellites can only be understood by the assumption of a trimeric structure for the methylstannatrane. In accordance with this conclusion, the sixfold coordination at the tin atom discussed above, and the three different ^{119}Sn, ^{13}C and ^1H NMR signals of I we propose the structure shown in Fig. 3 for the trimeric associate.

In this molecule all three tin atoms are six-coordinate. The dynamic process which makes the two signals b and c in all the spectra equivalent at higher temperatures could be opening of the six-membered ring followed by exchange of bridging oxygens as demonstrated in Fig. 4.

We assign the signal a to the stannatrane unit β, and the signals b and c to the units α and γ (see Fig. 3). The proposed process converts the trimeric molecule into its enantiomer, and the units α and γ become equivalent.

The equal number of signals (and the satellites in the ^{119}Sn spectrum of II) suggest the same structure and the same dynamic process for the stannatranes II—IV. The decreasing stability of the associates in the order I to IV shown by the ^{119}Sn NMR spectra can be explained by increasing steric hindrance to association with increasing size of the substituent R. In agreement with this conclusion, in the t-butylstannatrane (V) the single signal is observed at considerably lower field. Thus V is not associated because of the steric hindrance by the t-butyl group, and so the tin atom in this compound is only five coordinate and exhi-

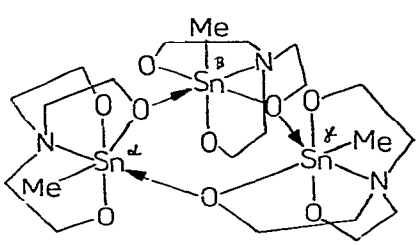


Fig. 3. Proposed structure of the trimeric methylstannatrane (I).

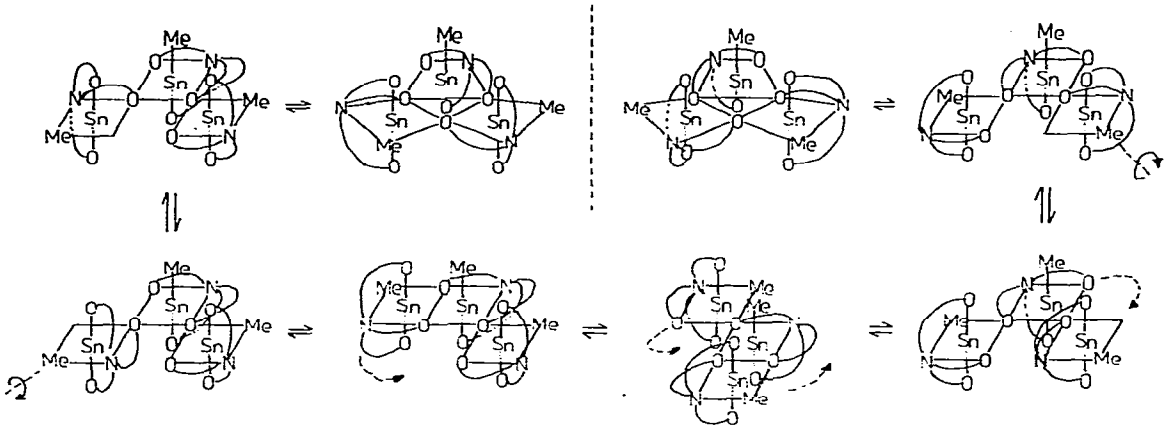


Fig. 4. Proposed mechanism of the intramolecular process of trimeric methylstannatrane (I).

bits the corresponding low field shift. It should be mentioned that this model does not satisfactorily explain the differences in the ^{119}Sn chemical shifts, and further studies of related compounds are in progress.

Experimental

All reactions were carried out under dry, oxygen-free argon. The solvents were purified by standard methods. Compounds I—IV were synthesized as described in earlier publications [1,2]. The 1-t-butylstannatrane (V) was prepared from t-butylphenyltin oxide, $(t\text{-BuPhSnO})_n$, and triethanolamine in xylene.

The ^{1}H NMR spectra were recorded on a Varian HA-100 D 15 spectrometer and the ^{13}C and ^{15}N NMR spectra on a Bruker HX-90 spectrometer at 22.63 and 9.1 MHz respectively. The ^{119}Sn NMR spectra were recorded on a modified JEOL instrument (^{1}H at 60.0 MHz) and the ^{1}H{^{119}Sn} INDOR spectra on a Tesla BS-487 C (80 MHz for H) spectrometer fitted with a universal device for heteronuclear double resonance.

1-t-Butylstannatrane (V)

t-Butylphenyltin oxide (10.7 g, 0.037 mol), triethanolamine (5.9 g, 0.037 mol) and a catalytical amount of potassium hydroxide in 300 ml xylene were heated with vigorous stirring, the xylene/water-azeotrope being distilled of continuously. The mixture was boiled under reflux for 24 h and the solvent removed in vacuo. The white precipitate was recrystallized from benzene/ether to give 10.5 g (88.2%) 1-t-butylstannatrane, m.p. 193°C. (Anal.: Found: C, 37.22; H, 6.50; N, 4.33; Sn, 36.70. $C_{10}H_{21}NO_3Sn$ calcd.: C, 37.30; H, 6.52; N, 4.35; Sn, 36.89).

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