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SYNTHESIS AND CHARACTERIZATION OF ORGANOSTANNATRANES*

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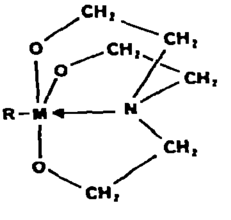
Summary

Organostannatranes, $RSn(OC_2H_4)_3N$, which are pentacoordinated complexes of tin containing an intramolecular dative bond between nitrogen and tin, are prepared by transesterification of $RSn(OC_2H_5)_3$ and triethanolamine. The compounds are white solids which are monomers in the vapor state and in solution. Pentavalency is confirmed by proton NMR and relative rates of quaternization with methyl iodide. IR and mass spectral data are presented. Evidence for an equilibrium between the pentacoordinated and uncoordinated structure in solution is discussed.

Introduction

There is considerable interest in the class of compound commonly called "metallatrane" owing to the observation that certain of these compounds (e.g., organosilatranes) are known to possess surprising neurophysiological properties not present in the parent organometallic triesters [1]. A particularly interesting feature of the metallatrane structure which has been linked to the biological



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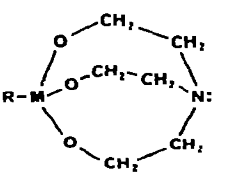

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activity is the presence of an unusual intramolecular transannular dative bond between the lone pair of electrons on nitrogen and a low lying vacant *p* or *d* orbital on M (A).

Although a number of compounds have been reported to have the "atrane" structure, confirmative evidence for the existence of the dative interaction is scant except where M is boron [2, 3] and silicon [1, 4]. In a recent article, Davies et al. [5] described the synthesis of organotin compounds prepared from organostannonic acids and triethanolamine and characterized the insoluble substances as organostannatranes soley on the basis of elemental analysis and Mössbauer spectral parameters. On the other hand, soluble products identified as pentacoordinate tin compounds by molecular weight and ^{1}H NMR studies were prepared by Tzschach et al., using similar reactants [6, 7]. We now wish to report an alternative synthetic route (eqn. 1) for the preparation of soluble organotin compounds with identical formulation to those species mentioned above [8]. An evaluation of the properties of these compounds (IR, mass spectra, ^{1}H NMR, rates of reaction with methyl iodide) unequivocally supports a pentacoordinated structural assignment. Some evidence indicating conformational and dative bond dynamics will be presented.

$$RSn(OC_2H_5)_3 + N(CH_2CH_2OH)_3 \rightarrow RSn(OCH_2CH_3)_3 + 3C_2H_5OH \qquad (1)$$

$$(I, R = C_2H_5;\ II, R = CH_3;$$
$$III, R = C_4H_9;\ IV, R = C_6H_5)$$

Experimental

Owing to the moisture sensitivity of compounds containing Sn—O and Sn—N bonds, all manipulations were carried out in a dry, inert gas environment. All solvents were stored under suitable drying agents and freshly distilled prior to use. Triethanolamine (Fisher), TEA, was distilled thrice (b.p. 203° / 12 Torr) and stored under dry nitrogen until used. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, New York 11377. Infrared spectra, taken as KBr pellets and in solution, were recorded on a Perkin—Elmer 521 grating spectrometer. Proton resonance spectra were taken on a Varian A60 spectrometer. All chemical shift data are reported relative to TMS as an internal reference. The mass spectra were taken at 80 eV on a Perkin—Elmer—Hitachi RMU-6 spectrometer by direct injection into the ionization chamber. Molecular weights were determined with a Coleman Molecular Weight Apparatus, Model 115 (thermistor osmometer) at a minimum of four concentrations. The reported data are extrapolations of molecular weight to infinite dilution.

Synthesis of 1-ethyl-2,8,9-trioxa-5-aza-stannatricyclo[3.3.3.0]undecane (ethylstannatrane, I)

$C_2H_5Sn(OC_2H_5)_3$ is prepared from $C_2H_5Sn[N(C_2H_5)_2]_3$ by the method described by Lörberth and Kula [9]. The triester is a clear, colorless oil on purification by vacuum distillation (b.p. 130° /0.1 Torr; lit. 127-130°/0.1 Torr). To a 500 ml round bottom flask containing a magnetic stirring bar and fitted with a condensing head and collection flask is added 5.90 g (0.021 mol) $C_2H_5Sn(OC_2H_5)_3$ and 250 ml dry benzene. 3.09 g (0.021 mol) triethanolamine is added. The reaction mixture is refluxed with vigorous stirring. When evolution of ethanol has ceased, as indicated by GLC or a negative iodoform test, the reaction mixture is cooled to room temperature and filtered. As the solvent is removed under vaccum, 6.2 g (100%) of crude product precipitates. The solids are isolated by filtration and washed with several small portions of cold, anhydrous benzene. Purification of I may be effected by sublimation at 75°/10^{-4} Torr, or by recrystallization from hot xylene. The pure product (85%) is a white crystalline solid, which melts at 179.5-181° without decomposition. I is soluble in polar organic solvents such as $CHCl_3$ and slightly soluble in aromatic solvents and alkanes at room temperature.

Other organostannatranes (R = methyl, butyl and phenyl) are prepared similarly and their properties are summarized in Table 1. The infrared, mass and proton resonance spectra are summarized in Tables 4, 5, and 6 respectively. Other metallatranes (M = B, Si) were prepared by known methods [1a, 2].

Rates of reaction of I-IV with methyl iodide

Equimolar solutions of the organotin compounds (I-IV) or triethanolamine and methyl iodide in acetonitrile were prepared. 5.00 ml of each solution were syringed into each of six flat bottom reaction ampoules of approximately 25 ml capacity. The ampoules were sealed with a septum and the reactants were stirred with a magnetic stirring bar at constant temperature (25.00 ± 0.02°). At prescribed intervals, the ampoules were opened and dilute sulfuric acid (~ 10 ml) was added to quench the reaction. Free iodide was determined by titration with a standard solution of $AgNO_3$. Rate constants were calculated from the integrated form of the second order rate expression, $k = x/ta(a'-x)$, where x and a' denote the quantity of reacted material and initial reactants, respectively, expressed in ml of $AgNO_3$ solution, and a is the initial concentration of reactants in molarity units. Typical rate data for the reaction of methyl iodide with triethanolamine and I are given in Table 2. Rate constants at 25° for compounds I-IV, TEA and boratrane are summarized in Table 3.

Results and discussion

Although a number of synthetic routes have been used to prepare metallatranes, only transesterification of organotin triesters with triethanolamine, TEA (eqn. 1) was found to be applicable to the high yield synthesis organotin compounds I-IV (Table 1), which exhibit molecular weights both in solution and in the vapor phase indicative of monomeric substances. That only monomeric compounds are produced by this reaction regardless of refluxing temperature and concentration of reactants suggests that a concerted bimolecular reaction mechanism occurs initially which, for steric reasons, favors an intramolecular rather than an intermolecular transesterification. When analogous organostannonic acids, prepared by the hydrolysis of the corresponding organotin trichloride, were used as precusors, high molecular weight solids

TABLE 1

PROPERTIES OF COMPOUNDS PREPARED FROM $RSn(OC_2H_5)_3$ AND $N(CH_2CH_2OH)_3$

R	Yield (%)	Molecular weight		M.p. (°C)	Analysis (found (calcd.) (%))			
		Solution (CH_2Cl_2) [a]	Mass spectra (*m/e*) [b]		C	H	N	Sn
C_2H_5 (I)	85	295 (293.9)	295	181-183 [c]	32.68 (32.68)	5.86 (5.78)	4.70 (4.76)	40.28 (40.41)
CH_3 (II)	90	288 (280.0)	281	279-280	30.71 (30.03)	5.61 (5.40)	4.96 (5.00)	42.28 (42.40)
C_4H_9 (III)	95	324 (322.0)	323	170-171 [c]	36.92 (37.30)	6.56 (6.52)	4.36 (4.35)	37.17 (36.89)
C_6H_5 (IV)	90	340 (342.0)	343	> 300 (dec.) [c]	41.88 (42.15)	5.05 (5.01)	4.62 (4.10)	34.64 (34.71)

[a] In each case a minimum of four determinations were made in the concentration range from 10^{-2}-10^{-4} *M* and the reported values are obtained by extrapolation to infinite dilution. [b] The molecular ion consists of a cluster of seven masses with relative ratios identical to natural abundance of $^{116, 117, 118, 119, 120, 122, 124}Sn$. The reported values of *m/e* correspond to ^{120}Sn. [c] Melting points reported by Davies et al. for the ethyl, butyl and phenyl compounds are 172-178° (dec.), 158-159° and 220° (dec.) respectively (see ref. 5).

TABLE 2

RATES OF REACTION OF TRIETHANOLAMINE AND I WITH METHYL IODIDE AT 25°

Compound	Time (sec) X 10^{-4}	$AgNO_3$ (ml)	k (l/mole sec) X 10^4
$(HOCH_2CH_2)_3N$	0.5	0.70	1.69
(a = 0.0563*M*	1.0	1.29	1.63
	1.5	1.88	1.65
	2.0	2.32	1.58
	2.5	2.88	1.64
	3.5	3.68	1.60
		a' = 15.35	Av. 1.63 ± 0.06
$C_2H_5Sn(OC_2H_5)_3N$	2.0	0.23	0.135
(a = 0.0563*M*)	5.0	0.61	0.147
	9.0	1.09	0.151
	12.0	1.38	0.146
	15.5	1.68	0.141
	17.5	2.02	0.154
		a' = 15.35	Av. 0.146 ± 0.010

(*m/e* > 900) which had properties similar to the substances reported by Davies et al. [5] (i.e. large melting point ranges and insolubility in polar and non-polar organic solvents) were obtained.

Brown and Fletcher [2] have shown that evidence for a metallatrane structure may be obtained from the relative reactivity of the lone pair of electrons on nitrogen toward quaternization with an alkyl halide. A more rapid reaction is expected where the electron pair on nitrogen is free from association as in TEA or B than where it is coordinated to the metal as in A. Moreover, a cage structure without the transannular bond (B) should be sterically more susceptible to attack by the alkyl halide and should react more rapidly than TEA*. Specific rate constants for the reaction of CH_3I with TEA, boratrane and I-IV in acetonitrile at 25°, are summarized in Table 3. The slow reaction observed for boratrane (k_{TEA}/k_{II} = 2-3 X 10^3) is indicative of a datively bonded structure [2]. Similarly rate constants for the tin compounds are smaller than TEA and, thus,

TABLE 3

RATE CONSTANTS FOR REACTION OF TRIETHANOLAMINE AND I-IV WITH METHYL IODIDE AT 25°

Compound	k (l/mole sec)	k_{TEA}/k_M
$(HOCH_2CH_2)_3N$ [a]	1.63 X 10^{-4}	
$B(OCH_2CH_2)_3N$ [a]	7.35 X 10^{-8}	2.22 X 10^3
I	1.46 X 10^{-5}	11.2
II	1.52 X 10^{-5}	10.7
III	1.39 X 10^{-6}	11.7
IV	1.30 X 10^{-5}	12.5

[a] The value of k_{TEA}/k_M from Brown and Fletcher is 1.76 X 10^3 (see ref. 2).

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* The rate of reaction of CH_3I with quinuclidine, $N(CH_2CH_2)_3CH$, a cage compound with a localized electron pair on nitrogen is 57 times faster than with TEA [2].

TABLE 4

INFRARED SPECTRA OF ORGANOSTANNATRANES

Compound	Frequency (cm^{-1})
$CH_3Sn(OC_2H_4)_3N$	2975 vs, 2925 vs, 2860 vs, 2700 w, 1465 s, 1375 m, 1360 m, 1335 w, 1300 w, 1265 w, 1160 m, 1110 vs, 1063 s, 1050 s, 1025 s, 928 s, 893 vs, 753 m, 680 m, 640 m, 620 m, 580 m, 578 m, 550 m, 525 (sh), 490 s, 450 m, 370 w
$C_2H_5Sn(OC_2H_4)_3N$	2950 s, 2920 s, 2860 vs, 2700 w, 1460 m, 1375 (sh), 1368 w, 1340 w, 1300 w, 1260 w, 1158 w, 1105-1040 vs (br), 1018 s, 920 m, 888 s, 749 w, 688 (sh), 665 m, 635 m, 615 w, 583 (sh), 572 m, 543 w, 515 (sh), 484 s, 448 m, 365 w
$C_4H_9Sn(OC_2H_4)_3N$	2970 vs, 2925 vs, 2860 vs, 2700 w, 1462 m, 1425 w, 1365 w, 1335 w, 1300 w, 1265 w, 1160 w, 1105-1045 vs (br), 1020 s, 925 m, 905 m, 890 s, 750 w, 665 m, 630 m, 588 m, 570 m, 545 w, 488 s, 445 m, 365 w
$C_6H_5Sn(OC_2H_4)_3N$	2970 s, 2920 s, 2880 vs, 2690 w, 1475 m, 1460 m, 1425 m, 1380 w, 1355 m, 1300 w, 1260 w, 1155 w, 1105 vs, 1075 vs, 1040 (sh), 1020 s, 995 w, 915 m, 888 s, 860 (sh), 738 m, 695 m, 680 (sh), 650 w, 585 m, 570 (sh), 545 w, 525 m, 495 s, 450 s, 380 w, 355 w, 345 w.

are consistent with a metallatrane structure. The magnitude of the decrease is smaller than that of boratrane and suggests either a relaxed steric effect owing to the relatively larger tin atom or, more likely, a weaker Sn ← N interaction which, aided by the polar solvent, gives rise to an equilibrium mixture of A and B, where the latter species reacts more rapidly with CH_3I than with TEA.

The infrared spectra of compounds I-IV from 4000-300 cm^{-1} are reported in Table 4. With minor exceptions the spectra of all the organostannatranes are composites of the spectra of the reactants. Of great interest in the spectra of organosilatranes is the medium intensity band in the region 568-590 cm^{-1} which has been assigned by Voronkov to the stretching frequency of the Si ← N coordinate bond [1a]. Comparable absorptions in I-IV would be expected at lower frequencies owing to the heavier metal and presumably weaker Sn ← N interaction*. A common band of relatively high intensity in the spectra of I-IV, but not present in TEA or $RSn(OC_2H_5)_3$, is observed between 484-495 cm^{-1} (Table 4) and has been tentatively assigned to $\nu(Sn \leftarrow N)$. It is noteworthy that the relative intensity of this band decreases when the spectra are taken in polar solvents such as methylene chloride, and may be a result of a solvent interaction giving rise to an equilibrium between A and B.

The mass spectra of the organostannatranes are summarized in Table 5. The tabulation reports the masses corresponding to the ^{120}Sn peak of the major ion clusters for which the relative abundances are equivalent to the calculated distribution for the principle tin isotopes. A formulation for each of the fragment ions is postulated based upon repeated patterns within the series, which changes only in the organic substituent, and reasonable assumptions of the cleavage units. In all cases the molecular ion carries only a relatively small portion of the ion current. For all the organostannatranes, fragmentation

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* The spectra of pyridine complexes of $(CH_3)_2SnX_2$ (X = Cl, Br, I) and $C_2H_5SnCl_3$ have been reported by Tanaka [10]. The band near 200 cm^{-1} was assigned to the Sn←N bond. Little other work on this subject has been published.

TABLE 5

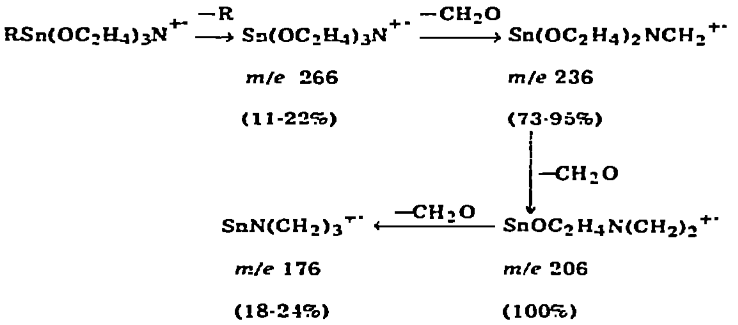
^{120}Sn PEAKS FOR THE PRINCIPLE FRAGMENT ION CLUSTERS IN THE MASS SPECTRA OF $RSn(OC_2H_4)_3N$ AT 80 eV AND 100°

R = CH_3			C_2H_5			n-C_4H_9			C_6H_5		
m/e	Ion	%	*m/e*	Ion	%	*m/e*	Ion	%	*m/e*	Ion	%
281	$CH_3Sn(OC_2H_4)_3N^+$	4	295	$C_2H_5Sn(OC_2H_4)_3N^+$	5	323	n-$C_4H_9Sn(OC_2H_4)_3N^+$	4	343	$C_6H_5Sn(OC_2H_4)_3N^+$	12
						293	n-$C_4H_9Sn(OC_2H_4)_3NCH_2{}^+$	8	313	$C_6H_5Sn(OC_2H_4)_2NCH_2{}^+$	62
									266	$Sn(OC_2H_4)_3N^+$	11
206	$Sn(OC_2H_4)_3N^+$	12	266	$Sn(OC_2H_4)_3N^+$	16	266	$Sn(OC_2H_4)_3N^+$	22			
251	$CH_3Sn(OC_2H_4)_2NCH_2{}^+$	34	265	$C_2H_5Sn(OC_2H_4)_2NCH_2{}^+$	12	264	$(CH_2)_2Sn(OC_2H_4)_2NCH_2{}^+$	17			
236	$Sn(OC_2H_4)_2NCH_2{}^+$	78	236	$Sn(OC_2H_4)_2NCH_2{}^+$	86	236	$Sn(OC_2H_4)_2NCH_2{}^+$	95 [a]	236	$Sn(OC_2H_4)_2NCH_2{}^+$	73
206	$Sn\ OC_2H_4N(CH_2)_2{}^+$	100	206	$SnOC_2H_4N(CH_2)_2{}^+$	100	206	$SnOC_2H_4N(CH_2)_2{}^+$	96 [a]	206	$SnOC_2H_4N(CH_2)_2{}^+$	100
176	$SnH(CH_2)_3{}^+$	24	176	$SnN(CH_2)_3{}^+$	24	176	$SnN(CH_2)_3{}^+$	18 [a]	176	$SnN(CH_2)_3{}^+$	22
121	SnH^+	13	121	SnH^+	16	121	SnH^+	15	121	SnH^+	~10 [a]
120	Sn^+	10	120	Sn^+	11	120	Sn^+	7	120	Sn^+	~10 [a]

[a] Corrected for overlapping tin clusters.

involves primarily cage rupture with the elimination of one, two and three CH_2O units consecutively (Scheme 1)* . It is noteworthy that ions corresponding to the cleavage of the organic substituent, R, from the cage (*m/e* 266) are observed

SCHEME 1



(2)

only in comparatively small quantities in I-IV, although this is the principle fragmentation mode for all organogermatranes [11] and organosilatranes [11, 12] (Fig. 1). In both the silicon and germanium compounds the intact cage ions occur as base peaks at *m/e* 174 and 220 (^{74}Ge), respectively. The prevalence of the intact cage ions for the lighter metallatranes is assumed to be a reflection of the relative strengths of the Si—O and Ge—O bonds.

The cluster of peaks in I-IV at *m/e* 176 has been attributed to the ion $SnN(CH_2)_3^+$, which is consistent with the stannatrane structure. Analogous ions are observed for germatranes at *m/e* 130 and for silatranes at low intensity at *m/e* 84.

The proton NMR spectra of the organotin compounds I-IV in $CHCl_3$ at 60 MHz are summarized in Table 6. Data for TEA, boratrane and several silatranes are included for comparison purposes. It has been proposed by Voronkov that the transannular dative bond, which has been confirmed for boratrane and organosilitranes by X-ray diffraction [3, 4] and dipole moment studies [1, 13] should exert an inductive influence on the chemical shifts of the ring methylene** and R group protons. Thus, it was observed that the OCH_2 and NCH_2 protons in silatranes were deshielded relative to equivalent protons in TEA presumably owing to a decrease in electron density at the nitrogen atom; and, the R group protons were shielded relative to like protons in the corresponding organosilicon triesters owing to an increase in electron density on silicon [1].

The NMR data for the boron and tin compounds in this report are consistent with a metallatrane structure. Boratrane exhibits the largest downfield ring methylene proton shifts from TEA (0.43 and 0.60 ppm) which is attributed to the inherently high acidity of the boron atom and high polarity (8.8 D) of the $B \leftarrow N$ dative bond [13]. In organostannatranes the ring protons are shifted approximately 0.3-0.4 ppm downfield from TEA whereas the R protons, like organosilatranes, are upfield approximately 0.1 ppm from parallel protons in the parent triester.

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[*] Presumably stabilized as formaldehyde.

[**] Analogously, deshielding of the protons in the γ-ethoxy group of $Cl_3SnCH(COOC_2H_5)CH_2COOC_2H_5$ has been attributed to the presence of a $Sn \leftarrow O$ coordinate bond [14].

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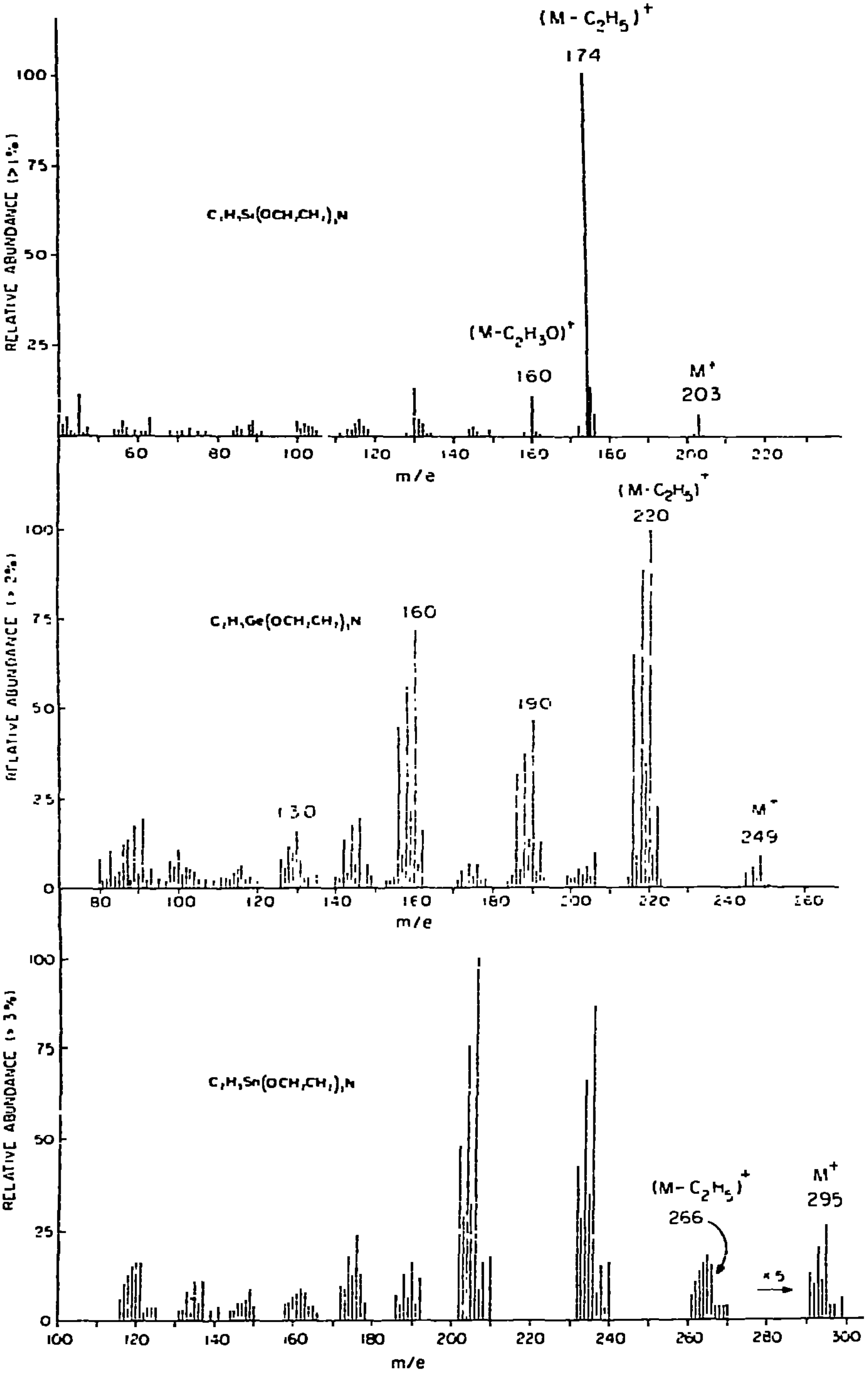

Fig. 1. Mass spectra of ethylsilatrane, ethylgermatrane and ethylstannatrane at 80 eV and 100°.

TABLE 6

PROTON NMR CHEMICAL SHIFTS FOR SOME METALLATRANES AND TEA IN $CHCl_3$ AT 60 MHz

Compound		Chemical shift (ppm)		
		$\delta(OCH_2)$	$\delta(NCH_2)$	$\delta(R)$
$(HOCH_2CH_2)_3N$		3.55(t)^{b}	2.51(t)	
$B(OCH_2CH_2)_3N$		3.98(t)	3.11(t)	
$HSi(OCH_2CH_2)_3N$		3.81(t)	2.85(t)	3.87(s)^{d}
		(3.80)^{c}	(2.88)	(3.94)
$CH_3Si(OCH_2CH_2)_3N$		3.78(t)	2.88(t)	−0.12
		(3.78)	(2.89)	(−0.12)
$C_2H_5Si(OCH_2CH_2)_3N$		3.76(t)	2.70(t)	0.34(CH_2,q)
		(3.76)	(2.89)	(0.30)
$C_2H_5Sn(OCH_2CH_2)_3N$ (I)	(−18°)	3.82(m, br)	2.83(m, br)	1.33(s), 1.20(s)
	(69°)	3.80(t)	2.79(t)	1.22(s)
		(3.88)	(2.86)	
$CH_3Sn(OCH_2CH_2)_3N$ (II)	(−20°)	3.68(s, br)	2.77(s, br)	0.69(s), 0.56(s), 0.43(s)
	(29°)	3.71(u, br)	2.85(u, br)	0.69(s), 0.52(s)^{e}
	(70°)	3.88(t)	2.96(m, br)	0.56(s)
		(3.93)	(2.88)	(0.80, 0.72, 0.54, 0.42)
$C_4H_9Sn(OCH_2CH_2)_3N$ (III)		3.93(t, br)	2.92(t, br)	0.50(t), 0.45(p), 0.38(h), 0.24(t)^{f}
		(3.91)	(2.89)	
$C_6H_5Sn(OCH_2CH_2)_3N$ (IV)		3.78(t)	2.80(t)	~ 7.4(m)
		(3.98)	(2.95)	
$(CH_3)_2CHOSn(OCH_2CH_2)_3N$ (V)		3.92(t)	2.83(t)	0.03(CH_3, d)

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[a] Chemical shifts are reported relative to TMS at 35° and 60 MHz except where noted. [b] s, singlet; d, doublet; t, triplet; q, quartet; p, quintet; h, sextet; br, broad; m, multiplet; u, unresolved. [c] Shifts in parentheses are taken from ref. 1a for organosilatranes and from refs. 6 and 7 for organostannatranes. [d] For $RSi(OC_2H_5)_3$: δ(H) 4.26; $\delta(CH_3)$ 0.04; $\delta(CH_3CH_2)$ 0.70; for $RSn(OC_2H_5)_3$: $\delta(CH_3)$ 0.63(s); $\delta(CH_3CH_2)$ 1.38(s). [e] $J(^{117}Sn-H)$ = 101 Hz; $J(^{119}Sn-H)$ = 115 Hz. [f] Shifts determined at 40° at 220 MHz and multiplied by 0.273 to reflect conversion to 60 MHz.

The proton spectra of boratrane and silatranes are temperature independent and exhibit sharp lines with characteristic spin—spin coupling patterns for the ring methylene (AA'BB') and R group protons. The spectra of organostannatranes at room temperature appear as broad lines (singlets or unresolved multiplets) and are temperature dependent. For example, the ring protons in the methyl derivative II (Fig. 2), are broad, unresolved multiplets at 29° ; below room temperature the lines broaden and coalesce; at 69° the multiplets sharpen and resolve into characteristic triplets. Similar effects are seen for the other organostannatranes.

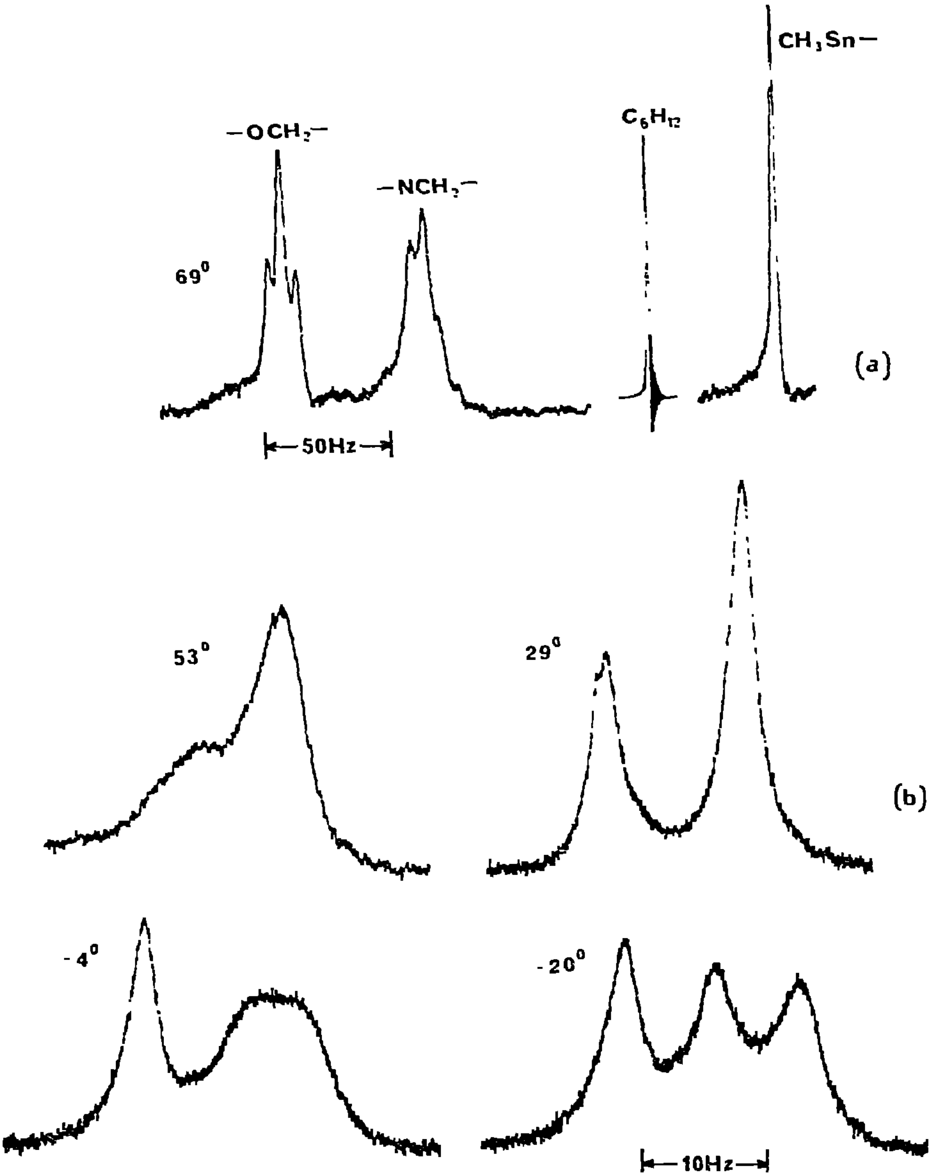

Fig. 2. Proton NMR spectra of methylstannatrane. (a) Full spectrum at 69° (top). (b) CH_3Sn region from −20 to 53° (bottom).

Thermal effects are observed for the R group protons of I and II. At room temperature the methyl group of II consists of two lines of unequal intensity at 0.52 and 0.69 ppm. Above 60° the lines coalesce into a relatively sharp singlet. Below room temperature the signal at 0.69 ppm remains essentially unchanged while the signal at higher field broadens and splits into two lines of nearly equal intensity. Similarly in I the ethyl group protons, which fortuitously are magnetically equivalent and adsorb as a singlet (δ = 1.24 ppm, $w_{1/2}$ = 2Hz)* at room temperature, sharpen at 69° ($w_{1/2}$ = 1 Hz). At −18° the singlet splits into two broad lines ($w_{1/2}$ = 5-6 Hz) of unequal intensity**. Difficulty was encountered in detecting an appreciable effect of temperature on the R group protons of III-V.

The temperature dependent NMR spectrum of II has been reported by Tzschach et al. [6, 7]. They interpreted the thermal effects in terms of a slow equilibrium between several conformations of the metallatrane cage; i.e. pseudorotation about Sn where N occupies the axial (A-1) or the equatorial (A-2) position at room temperature; and, ring inversion between chair-chair (*cc*) and boat-chair (*bc*) conformations for each pseudorotary form at low temperature. Unfortunately, the suggested mechanism is inconsistent with chemical shift and area ratio data. Regarding chemical shift data, Tzschach reportes four lines between 0.4 and 0.8 ppm (100 MHz) at −30° for II***. Based on Voronkov's observations for organosilatranes, it is unlikely that a structure containing a Sn ← N dative bond, whether in the A-1 or A-2 form, would deshield the methyl protons relative to comparable protons in the model triester, $CH_3Sn(OC_2H_5)_3$ [$\delta(CH_3)$ = 0.63 ppm]. Additionally, it is difficult to explain why an equal population of inversion forms would be observed for A-I and not for A-2 at low temperatures since molecular stereomodels indicate a relatively small steric inhibition for inversion of the latter, if such form exists†. Furthermore, it is questionable, for steric and statistical reasons, whether equal populations of A-1 and A-2 should exist at ambient temperatures.

An alternative explanation, which is consistent with the data for II presumes a slow equilibrium between the bonded (A-1) and the dissociated (B) compounds at room temperature††. The high field peak, which appears

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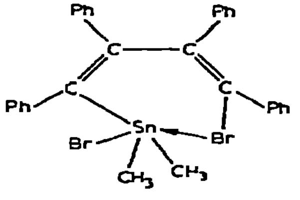
* $w_{1/2}$ for cyclohexane as an internal reference is 0.6 Hz.

** No ^{119,117}Sn—C—H satellites are observed for I from −18 to 69°. Additionally, the protons in the C_2H_5 group of $C_2H_5SnX_3$ (X = OCH_3, OC_2H_5, Cl) are magnetically equivalent at 60 MHz (Table 6, footnote *d*) and temperature independent.

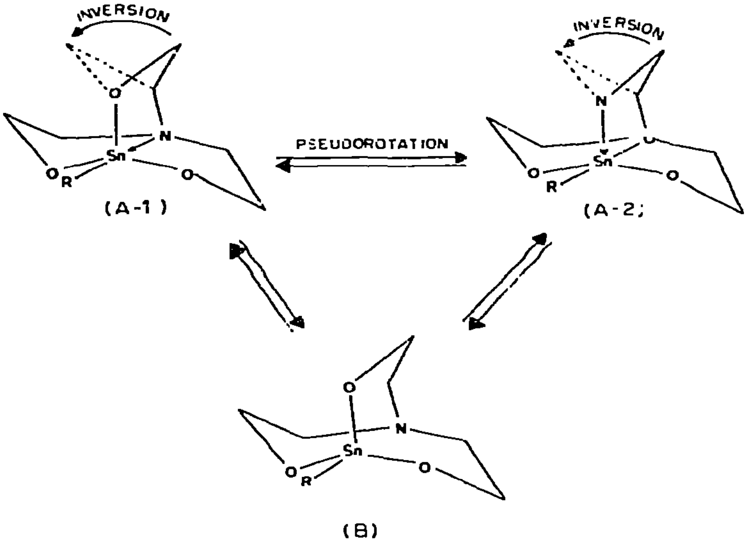
*** Two lines (δ 0.54 and 0.42 ppm: area ratio, 1) were assigned by Tzschach et al. to the *cc* and *bc* forms of A-1 and two lines (δ 0.80 and 0.72; area ratio, 10) were assigned to the *cc* and *bc* forms of A-2. At 30° the area ratio A-1/A-2 is approximately unity.

† Dreiding stereomodels of the stannatrane structure were constructed using dsp^2 or sp^3 hybridized Sn and sp^3 hybridized N. Comparisons were made by substituting Si, Ge and B (sp^2) for Sn.

†† A dative bond dynamic effect has been proposed to explain the magnetic nonequivalence of methyl resonances in stannole dihalides in CCl_4 solution. For example, the dibromide, which has a dissymmetrical nonplanar *cis* conformation in the solid state owing to a Sn ← Br interaction (see below) exhibits two methyl group proton lines at 36° (δ 0.48, 0.98 ppm) which coalesce to a broad singlet at 87° [15].



0.11 ppm upfield from $CH_3Sn(OC_2H_5)_3$, has been assigned to the methyl group in A-1. At elevated temperatures the interconversion rate between A-1 and B increases such that only the time-average spectrum, a singlet (δ 0.56 ppm), is observed. At low temperature, however, both interconversion (A-1 $\rightleftharpoons$ B) and inversion [A-1 (*cc*) $\rightleftharpoons$ A-1 (*bc*)] rates are slow, the latter giving rise to the splitting of the upfield line (Fig. 2). It is proposed that slow inversion occurs only in A-1 whereas only the *cc* form prevails in B. This theory is supported by examination of stereomodels which clearly indicate that the *bc* form of B is unstable owing to gross steric interference between the NCH_2 and OCH_2 protons on adjacent bridges. Interestingly, the models reveal that the Sn ← N bond distance in the *bc* form of A-1 is approximately 0.2 Å longer, and therefore presumably both weaker and less polar, than in the *cc* form. For this reason the lower field signal (0.56 ppm) at −20° is assigned to the methyl group in A-1 (*bc*).



The temperature dependent spectrum of I may be rationalized in terms of either inversion or dissociation mechanisms. Further studies are currently underway and will be reported later.

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