mixed solvent (0.5 mL of dry THF and 2.1 mL of dry ether) under N_2 was added 1.6 mL of a 0.35 M solution of 1 in THF at 0 °C. After a certain time period, with stirring, the reaction mixture was quenched with water and analyzed by GLC. Both uncyclized and cyclized substitution products were confirmed by GC–MS and NMR spectrometry.

Reaction of Me_3SnNa (1) with *endo*-5-(2-Bromoethyl)-2-norbornene (8) in the Presence of DCPH–Solvent (THF–Pentane (1:1)). To a solution of the bromide (0.05 mmol) and DCPH (0.05 mmol) in 0.71 mL of mixed solvent (0.21 mL of dry THF and 0.50 mL of dry pentane) under N_2 was added 0.29 mL of a 0.35 M solution of 1 in THF at 0 °C. After 15 min, with stirring, the reaction mixture was quenched with water and analyzed by GLC. All products were confirmed by GC–MS and NMR spectroscopies. *endo*-5-(2-(Trimethylstannyl)ethyl)-2-norbornene: ^1H NMR δ 0.05 (9 H, s, J(SnCH) = 48 Hz), 0.44–1.50 (7 H, m), 1.66–2.04 (2 H, m), 2.64–2.89 (2 H, m), 5.8–6.2 (2 H, m). Anal. Calcd: C, 50.56; H, 7.79. Found: C, 50.68; H, 7.80. *endo*-5-Ethyl-2-norbornene (10): ^1H NMR δ 0.5–0.6 (1 H, m), 0.8–0.9 (3 H, d, J = 4 Hz), 1.0–1.4 (4 H, m), 1.65–1.9 (2 H, m), 2.6–2.8 (2 H, m), 5.8–6.2 (2 H, m). Tricyclo[4.2.1.0^{3,7}]nonane (11): ^1H NMR δ 0.70 (1 H, m), 0.87 (1 H, m), 1.15–1.9 (12 H, m); mp 99–100 °C (lit.[17] mp 98–99 °C).

Control Experiments: Reaction of TBA and DCPH with Halides. In a typical experiment, 1.5 mmol of an additive under N_2 was added to 0.15 mmol of halide in 0.5 mL of dry THF at 0 °C. After 1 h the solution was analyzed by GLC.

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Registry No. 1, 16643-09-7; 4, 109-65-9; 6, 18908-66-2; 7, 2695-47-8; 8, 94417-50-2; 9, 94417-49-9; 10, 32166-37-3; 11, 1521-75-1; 18, 97232-56-9; 19, 85807-80-3; 5-hexen-1-ol, 821-41-0; *endo*-5-(2-trimethylstannylethyl)-2-norbornene, 97150-43-1.

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^{119}Sn NMR Spectroscopic Study on Tetraorganodistannoxanes

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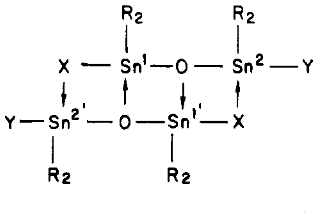
^{119}Sn NMR spectra of various tetraorganodistannoxanes were investigated. The two tin atoms in these compounds were successfully differentiated as expected from the dimeric formulation. The most probable assignments for these signals were provided. Tin–tin coupling was detected for the first time, and there was observed a marked difference between halogen- and oxygen-bridged distannoxanes. Observation of one kind of coupling in the former compounds can be interpreted in terms of an anionic chloride bridge, while a covalently bonded oxygen bridge is suggested on the basis of the appearance of additional coupling in the latter compounds.

Introduction

In contrast to corresponding organosilicon analogues, a unique feature of diorganotin dihalides is the stability of partial hydrolysis products, 1,3-dihalotetraorganodistannoxanes, that can be converted, on further partial hydrolysis, to 3-halo-1-hydroxytetraorganodistannoxanes (eq 1). Due to their structural and chemical characteristics, these compounds have been studied extensively for a long time[1] and are still receiving attention.[2] It is now apparent that their facile formation and stability may be ascribed to the ladder structure

$$R_2SnCl_2 \xrightarrow{OH^-} {}^1/_2ClR_2SnOSnR_2Cl \xrightarrow{OH^-} {}^1/_2ClR_2SnOSnR_2OH \quad (1)$$



that was proposed first by Okawara et al.[3] and confirmed later by various X-ray analyses.[2,4] Contrary to these solid-state studies, solution work has been rather limited. Obviously, the structural elucidation in solution is of importance for an understanding of the chemical properties of distannoxanes such as their unusual catalytic activity for urethane formation.[5] Molecular weight measurements indicate that the dimeric formulation also is retained in solution for most distannoxanes[6] and IR spectra of isothiocyanate derivatives (X, Y = NCS) in solution show the existence of a bridging isothiocyanate group.[7] However, none of these studies can afford satisfactory information on structural properties in solution. Presumably, ^{119}Sn NMR spectroscopy is the most promising approach to this end. Indeed, two tin resonances have been detected for

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(1) Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137.

(2) For the most recent study on this subject: Vollano, J. F.; Day, R. O.; Holmes, R. R. *Organometallics* **1984**, *3*, 745.

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Table I. ^{119}Sn NMR Parameters of Distannoxanes in $CDCl_3$ (30 wt/vol %).

distannoxane				Sn(1)			Sn(2)		
	R	X	Y	δ	J, Hz	$W_{1/2}$,[a] Hz	δ	J, Hz	$W_{1/2}$,[a] Hz
1a	Bu	Cl	Cl	−139.8	73.2		−92.0	73.2	
1b		OH	Cl	−175.0	195.3 78.1		−158.6	195.3 78.2	
1c		PhO	Cl	−170.9	163.6 70.8		−138.4	168.4 70.8	
2a		Br	Br	−131.3	78.1		−82.8	78.1	
2b		OH	Br	−175.5	195.3		−162.0	195.3	
2c		PhO	Br	−171.3	180.6 61.1		−139.4	185.5 61.0	
3a		NCS	NCS	−147.2		116.7	−168.2		321.0
3b		OH	NCS	−162.2	239.3		−211.8		291.8
3c		PhO	NCS	−156.4	205.1 68.3		−202.9		310.6
4		OAc	OAc	−202.2[b,c]	112.3		−218.4[b,c]	112.3	68.6
5	Et	Cl	Cl	−140.6	73.3		−91.8		53.3
6		NCS	NCS	−148.2		149.0	−169.2		290.0
7	Me	Cl	Cl	−117.4	58.5		−62.6		46.8
8		OAc	OAc	−174.4[b]	102.5		−190.0[b]	102.5	28.5

[a] The $W_{1/2}$ value is less than 20 Hz unless noted. [b] Tentative assignment: see text. [c] Additioinal signal at −149.0 ppm appears: see text.

1,3-dihalotetrabutyldistannoxanes, consistent with the dimeric formulation,[8] though Davies et al.[8b] have observed only broad singlets for other tetrabutyldistannoxanes by means of the heteronuclear double magnetic resonance technique. These unsatisfactory results may be largely attributable to instrumental limitations. Our continuing studies on ^{119}Sn NMR spectra[9] led us to expect that improvements should be attainable by means of FT NMR spectroscopy. In the hope of obtaining more improved resolution and hence a better understanding of the properties of distannoxanes in solution, we have undertaken thorough FT NMR spectroscopic investigations.[10]

Results and Discussion

As expected, ^{119}Sn FT NMR spectra differentiated successfully the two tin atoms Sn(1) and Sn(2) in tetraorganodistannoxanes. The results are summarized in Table I. A pair of signals always was observed for various types of distannoxanes in the region reasonable for five-coordinate tin in support of the ladder structure. Most of signals are quite sharp so that satellites due to the tin–tin coupling were detectable, while in some cases, there was observed broadening of signals whose peak widths at half-height are given as $W_{1/2}$ in Table I. It should be noted that in the spectrum of 1,3-diacetoxytetrabutyldistannoxane (**4**), there appears a weak signal at −149.0 ppm in addition to the main two singlets (−202.2 and −218.4 ppm). It has been reported[11] that **4** readily dissociates partially into its parent monomer even at relatively high concentration in chloroform (~0.03 g/G). Dilution of the concentration of **4** from 40 wt/vol % (0.27 g/G) to 2 wt/vol % resulted in an increase of the ratio of the weaker signal from 1.4% to 14%. Accordingly, this signal may be attributable to a monomeric species.

Chemical Shift. We have already reported the probable assignment of $\delta(^{119}Sn)$ in butyl compounds **1–3**.[10] The assignment is based on the following: (i) substitution of oxygen by halogen at tin induces a low-field shift and (ii) attachment of the isothiocyanate group causes characteristic broadening of signals. Ethyl and methyl analogues give rise to quite similar results. However, the assignment for 1,3-diacetates **4** and **8** is not possible with the above criteria. It should be noted, therefore, that the assignment for these compounds is made only tentatively in Table I.

Tin–Tin Coupling. In most of the compounds investigated in this study, distinct satellites due to tin–tin coupling appeared.[12] Typical examples are illustrated in Figure 1. First, it seems of interest to compare the results obtained for 1,3-dihalo and 3-halo-1-hydroxy or 3-halo-1-phenoxy derivatives. The former compounds, in general, give rise to a pair of satellites, J_1 (60–80 Hz), whereas an additional pair of satellites with a larger coupling constant, J_2 (160–195 Hz), was observed in the latter. Two kinds of tin–tin coupling can be possible on the basis of the dimeric formulation: one between Sn(1) and Sn(2), $J_{Sn(1)Sn(2)}$, and the other between Sn(1) and Sn(2′), $J_{Sn(1)Sn(2')}$. Recent X-ray analyses revealed that the bridging chlorine in **5** and **7** is a chloride anion.[4e] Accordingly, the bond between the tin atoms and the bridging chlorine possesses highly ionic character in the 1,3-dihalo compounds. On the other hand, covalently bonded oxygen-bridged structures have been found for $[Cl(i\text{-}Pr)_2SnOSn(i\text{-}Pr)_2OH]_2$,[4g] $[Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2OH]_2$,[4g] and $[ClPh_2SnOSnPh_2OH]_2{\cdot}2(CH_3)_2CO$.[2] It seems reasonable to assume analogous structures for the present 3-halo-1-hydroxy compounds (X = OH, Y = halogen) since these compounds exhibit a sharp ν(OH) band at 3500 cm^{-1} characteristic of a bridging OH group.[11,13] The oxygen-bridged structures may be reasonably proposed for the phenoxy derivatives as well. These structures are consistent with those of the isothiocyanate analogues **3b** and **3c**, whose IR spectra exhibit no band attributable to the bridging NCS group. On the basis of these structural features, enhanced coupling between Sn(1) and Sn(2′) is expected for the covalently bonded Sn(1)OSn(2′)O ring in the 3-halo-1-hydroxy or 3-halo-1-phenoxy compounds compared with the ionic Sn(1)OSn(2′)Cl ring in the 1,3-dihalo compounds. As a result, appearance of J_2 exclusively in the former compounds leads us to ascribe this coupling to $J_{Sn(1)Sn(2')}$. J_1 is thus attributable to $J_{Sn(1)Sn(2)}$.

As described already,[10] characteristic broadening of signals is observed for tin bonded to the NCS group. However, Sn(1) in **3b** and **3c** gives rise to sharp signals

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[8] (a) Considine, W. J.; Baum, G. A. *J. Organomet. Chem.* **1965**, *3*, 308. (b) Davies, A. G.; Smith, L.; Smith, P. J. *Ibid.* **1971**, *29*, 245. (c) Mitchell, T. N. *Org. Magn. Resnon.* **1976**, *8*, 34.

[9] For the previous study of this series: Otera, J.; Yano, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 387.

[10] A part of this study has appeared in a preliminary form: Otera, J.; Yano, T.; Nakashima, K.; Okawara, R. *Chem. Lett.* **1984**, *2109*.

[11] Maeda, Y.; Okawara, R. *J. Organomet. Chem.* **1967**, *10*, 247.

[12] $J(^{119}Sn-^{119}Sn)$ and $J(^{119}Sn-^{117}Sn)$ could not be resolved.

[13] Okawara, R.; Yasuda, K. *J. Organomet. Chem.* **1964**, *1*, 356.

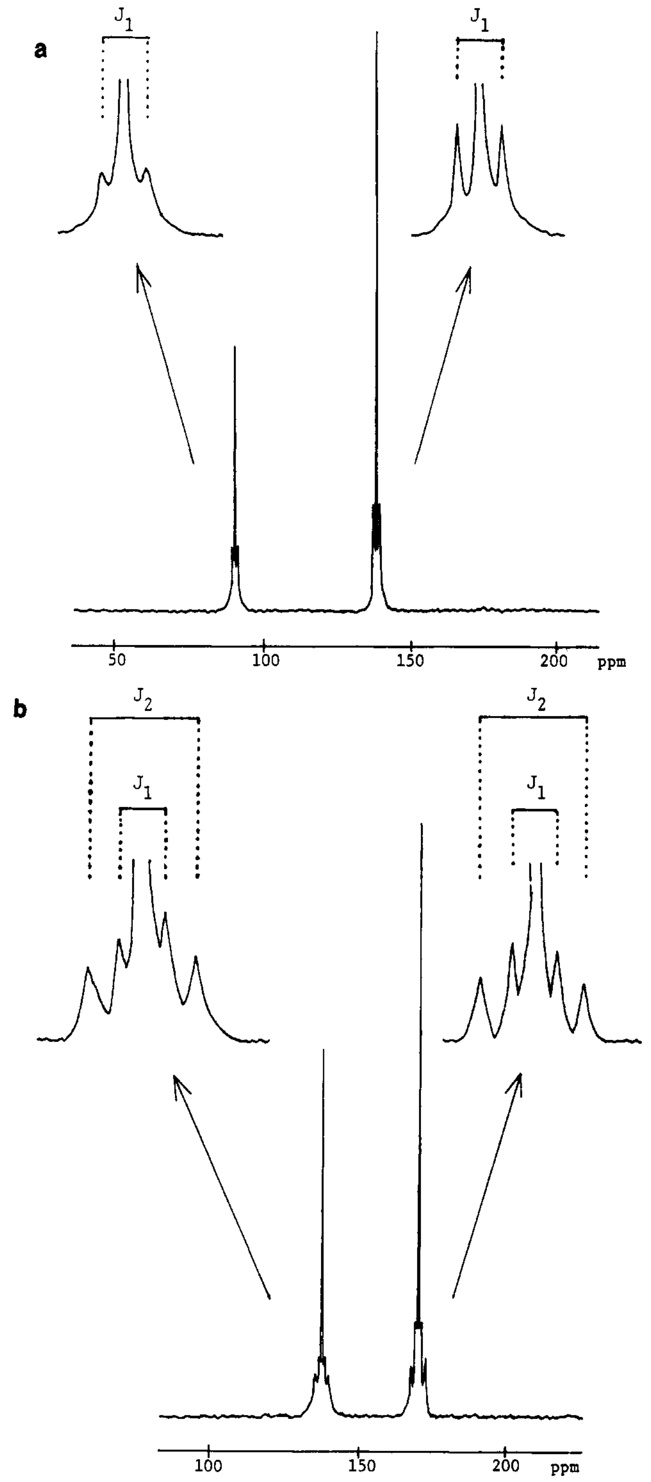
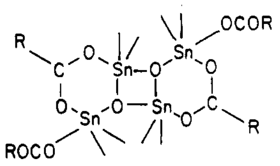


Figure 1. ^{119}Sn NMR spectra of (a) **1a** and (b) **1c**.

which enable us to detect tin–tin couplings. Contrary to J_1 in **3c**, that is comparable with those in halo derivatives, larger J_2 values were observed in **3b** and **3c**, a result which suggests a more rigid association in the isothiocyanate compounds than in the halo analogues.

1,3-Diacetoxy compounds **4** and **8** give rise to only a single coupling whose magnitude is intermediate between those of J_1 and J_2 described above. One might suppose that J_1 is too small to be detected. Although no crystallographic data are available for these compounds, the acetoxy-bridged structure



is plausible by analogy with $[(CH_2{=}CH)_2SnOCOCF_3]_2O$[4c] and $[Bu_2SnOCOCCl_3]_2O$.[4d] No significant difference in Sn–O–Sn bond lengths between the 1,3-diacetoxy compounds and other distannoxanes has been observed so there seems to be no reason why J_1 should be small in the 1,3-diacetoxy derivatives exclusively. Alternatively, we prefer to assume that J_1 and J_2 are nearly coincidental.

In summary, it has been found that the two tin atoms in distannoxanes can be successfully discriminated by means of ^{119}Sn NMR chemical shifts. Moreover, tin–tin coupling constants provide useful information of the coordination behavior. These fundamental observations provide a powerful method for elucidating reactions of distannoxanes. The results of these applications will be published in due course.

Experimental Section

^{119}Sn FT NMR spectra with complete proton noise decoupling were obtained by using a JEOL FX-100 spectrometer operating at 37.08 MHz. Field-frequency control was made with a deuterium-labeled solvent ($CDCl_3$) lock. The chemical shifts were determined relative to internal Me_4Sn, negative signs indicating high-field shifts from the reference. IR spectra were measured in Nujol mull or in $CHCl_3$ solution with a JASCO IRA-I spectrometer.

Distannoxanes were prepared according to literature methods[3,11,14] except for the phenoxy derivatives. The new compounds **1c**, **2c**, and **3c** were obtained by treating the corresponding hydroxy compounds with phenol in refluxing benzene while water was removed azeotropically. Recrystallization from hexane at −78 °C for **1c** and **2c** or from hot hexane for **3c** gave pure compounds. Anal. Calcd for $C_{22}H_{41}O_2ClSn_2$ (**1a**): C, 43.29; H, 6.77. Found: C, 43.00; H, 6.83. Anal. Calcd for $C_{22}H_{41}O_2BrSn_2$ (**1b**): C, 40.35; H, 6.31. Found: C, 40.34; H, 6.37. Anal. Calcd for $C_{23}H_{41}NO_2SSn_2$ (**1c**): C, 43.63; H, 6.53. Found: C, 43.66; H, 6.59.

Registry No. **1a**, 33194-92-2; **1b**, 95970-99-3; **1c**, 95971-00-9; **2a**, 33335-94-3; **2b**, 95971-01-0; **2c**, 95971-02-1; **3a**, 97170-99-5; **3b**, 95971-04-3; **3c**, 95971-05-4; **4**, 97171-00-1; monomeric **4**, 5967-09-9; **5**, 97171-01-2; **6**, 97171-02-3; **7**, 85990-37-0; **8**, 97171-03-4; PhOH, 108-95-2.

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(14) Wada, M.; Nishino, M.; Okawara, R. *J. Organomet. Chem.* **1965**, *3*, 70.