STERIC EFFECTS IN NEOPHYLTIN(IV) CHEMISTRY

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Summary

The stability and self-association in solution of $(neophyl_3Sn)_2O$, $neophyl_3SnOH$, and $(neophyl_3Sn)_2CO_3$ $(neophyl = C_6H_5(CH_3)_2CCH_2)$ have been examined by ^{119}Sn NMR. The presence of Sn,Sn spin coupling through oxygen ($^2J(^{119}Sn,^{117}Sn)$) has been used to distinguish between the distannoxane and stannol. Facile dehydration prevents the isolation of $neophyl_3SnOH$ from solution at room temperature and the equilibrium constant for $H_2O + (neophyl_3Sn)_2O \rightleftharpoons 2neophyl_3SnOH$ is 0.3 at 304 K. These observations are in sharp contrast with a previous report that the sterically bulky neophyl ligands render $neophyl_3SnOH$ stable toward dehydration. $|^1J(^{119}Sn,^{13}C)|$ observed for $neophyl_3SnOH$ and $(neophyl_3Sn)_2CO_3$ indicates that these compounds, unlike their n-alkyl-substituted homologues, are unassociated in solution, a result attributed to the steric bulk of the neophyl ligand.

Introduction

The potent but selective biocidal properties of certain organotin compounds have led to their wide use in agriculture and commerce [1–3]. Among these are several hexaorganodistannoxanes, $(R_3Sn)_2O$, and triorganostannols, R_3SnOH, which are interconverted according to eq. 1.

$$(neophyl_3Sn)_2O + H_2O \overset{K_{eq}}{\rightleftharpoons} 2 \, neophyl_3SnOH \tag{1}$$
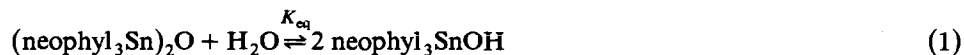
We have recently observed [4] that the presence of Sn,Sn spin coupling ($^2J(^{119}Sn,^{117}Sn)$) through oxygen in the ^{119}Sn solution NMR of hexaorganodistannoxanes is a useful diagnostic for the presence of the Sn–O–Sn linkage; the magnitude of the spin coupling is extremely sensitive to substituent and solvent effects and appears to be directly related to the size of the Sn–O–Sn bond angle [4].

We were particularly interested in examining the ^{119}Sn NMR of hexaneophyldistannoxane, $(neophyl_3Sn)_2O$ $(neophyl = C_6H_5(CH_3)_2CCH_2)$, an organotin used in agriculture [2], in order to determine the influence of the bulky neophyl ligand on the Sn,Sn spin coupling. In the course of our investigation we have found several marked inconsistencies between its properties and behavior in our hands and those which have been reported in the literature [5–8]. The ^{119}Sn NMR studies reported here provide insight into this problem and the general influence of the neophyl ligand on the properties of $(neophyl_3Sn)_2O$, trineophylstannol $(neophyl_3SnOH)$, and bis(trineophyltin) carbonate $((neophyl_3Sn)_2CO_3)$.

Results

^{119}Sn NMR data for $(neophyl_3Sn)_2O$, $neophyl_3SnOH$, and $(neophyl_3Sn)_2CO_3$ are collected in Table 1; ^{119}Sn NMR spectra obtained in a $(neophyl_3Sn)_2O$ hydrolysis experiment are shown in Fig. 1. Figure 2 shows ^{119}Sn spin coupling to ^{117}Sn and ^{13}C present in the ^{119}Sn NMR of $(neophyl_3Sn)_2CO_3$.

Pure $(neophyl_3Sn)_2O$ was obtained by recrystallization from dry hydrocarbon solvent (heptane). ^{119}Sn NMR data for $neophyl_3SnOH$ were obtained with hydrolyzed solutions of the distannoxane. Although reported to be stable with regard to loss of H_2O [5–7], attempts to isolate $neophyl_3SnOH$ by concentration of $CDCl_3$, benzene, or aqueous acetone solutions of the stannol (under vacuum or N_2 sweep at room temperature) yielded only $(neophyl_3Sn)_2O$, as determined by m.p. and ^{119}Sn NMR.

The instability of $neophyl_3SnOH$ toward dehydration prevented its isolation and full characterization. Instead, the identification of $neophyl_3SnOH$ rests on the following observations: (1) The stannol was interconverted with the distannoxane several times using the same sample. (2) Narrow distannoxane and stannol resonances were observed simultaneously in the ^{119}Sn NMR of partially hydrolyzed $CDCl_3$ and benzene solutions of $(neophyl_3Sn)_2O$ (Fig. 1). (3) No Sn,Sn spin coupling was observed in the hydrolysis product, under conditions where $^{1}J(^{119}Sn,^{13}C)$ was visible. (4) The magnitude of $^{1}J(^{119}Sn,^{13}C)$ of the hydrolysis

TABLE 1

^{119}Sn SOLUTION NMR DATA FOR NEOPHYLTIN COMPOUNDS [a]

Compound [b]	Solvent	δ (ppm)	$\omega_{1/2}$ [c] (Hz)	$\|^{2}J(^{119}Sn,^{117}Sn)\|$ (Hz)	$\|^{1}J(^{119}Sn,^{13}C)\|$ (Hz)
$(neophyl_3Sn)_2O$	$CDCl_3$	54.8	4	531	363
	C_6H_6	57.7	≦ 6	533	363
$neophyl_3SnOH$	$CDCl_3$	75.9	4	–	368
	C_6H_6(0.05 M)	67.5	5	–	–
	(ca. 0.2 M)	69.1	65 [d]	–	–
	$(CD_3)_2CO$	69.2	6–11 [e]	–	361 ± 6
$(neophyl_3Sn)_2CO_3$	$CDCl_3$	81.5	4	44 [f]	357
	toluene	74.4	≦ 8 [e]	–	367 ± 11

[a] All solutions at 304 K. Digital resolution ≦ 2.5 Hz/pt., conc. < 0.2 M or as noted. Me$_4$Sn internal standard (0 ppm). [b] Neophyl = $C_6H_5(CH_3)_2CCH_2$. [c] $\omega_{1/2}$ = width at half-height. [d] Broad resonance may be due either to presence of excess H_2O in solution or to self-association at ca. 0.2 M. [e] Digital resolution 5.5 Hz/pt. [f] $\|^{4}J(^{119}Sn,^{117}Sn)\|$.
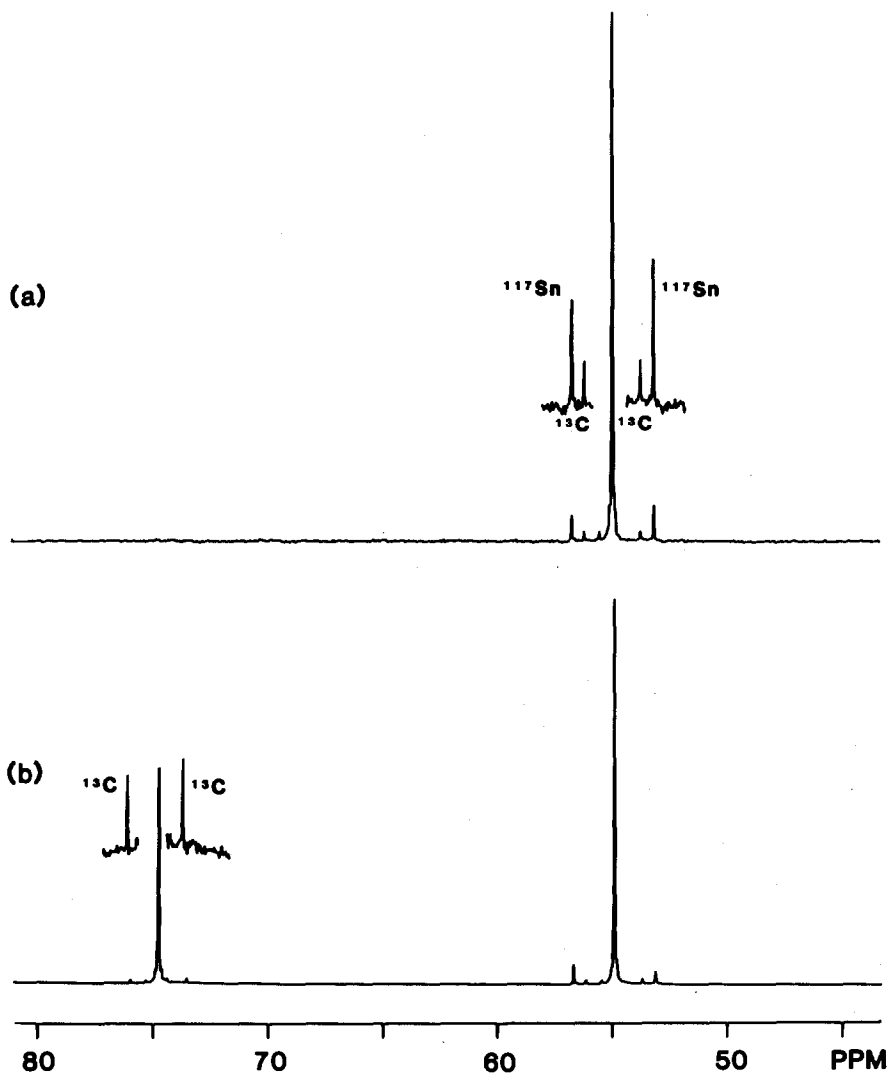
Fig. 1. ^{119}Sn NMR of the hydrolysis of (neophyl$_3$Sn)$_2$O in CDCl$_3$ solution at 304 K. (a) Pure (99%) (neophyl$_3$Sn)$_2$O before hydrolysis; ^{13}C and ^{117}Sn satellites ($^{1}J(^{119}$Sn,^{13}C), $^{2}J(^{119}$Sn,^{117}Sn)) are labelled. (b) Both neophyl$_3$SnOH and (neophyl$_3$Sn)$_2$O are present after addition of H$_2$O to the NMR solution; ^{13}C satellites ($^{1}J(^{119}$Sn,^{13}C)) in the hydrolysis product are labelled.

product, 368 Hz in CDCl$_3$, indicates that it is an unassociated species with tetracoordinated tin [9,10]. This rules out the possibility that a distannoxane-H$_2$O complex might account for the new resonance. (5) The ^{119}Sn chemical shift of the hydrolysis product moved 8.4 ppm to lower field on going from dilute benzene to CDCl$_3$ solution, consistent with deshielding of Sn owing to hydrogen bonding of the stannol with the CDCl$_3$ solvent.

The equilibrium constant, K_{eq}, for hydrolysis of (neophyl$_3$Sn)$_2$O in CDCl$_3$ solution (eq. 1) is 0.3 at 304 K and was determined by combining a known

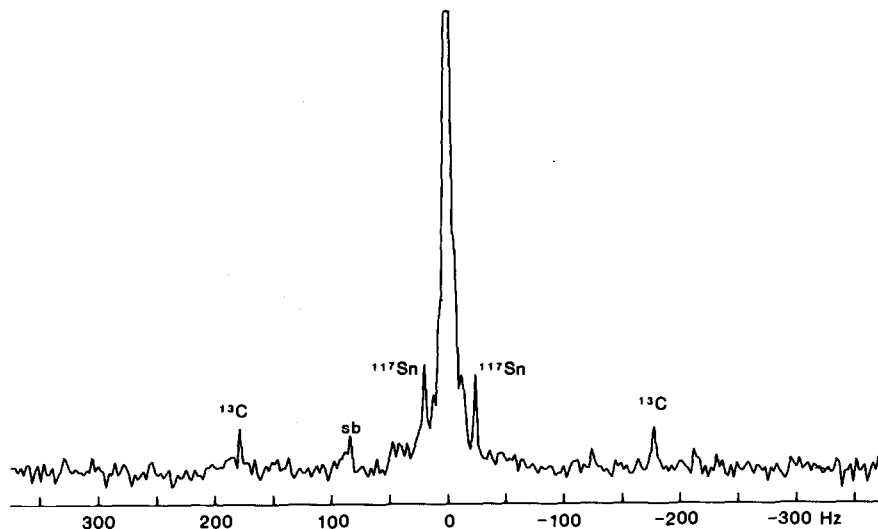Fig. 2. ^{119}Sn NMR of (neophyl$_3$Sn)$_2$CO$_3$ in CDCl$_3$ solution at 304 K. ^{13}C and ^{117}Sn satellites ($^1J(^{119}$Sn,^{13}C), $^4J(^{119}$Sn,^{117}Sn)) are labelled. Spinning side band (sb) indicated.

concentration of the distannoxane with a known amount of H$_2$O. Care was taken that the concentration of H$_2$O employed was lower than its solubility limit [11].

(Neophyl$_3$Sn)$_2$CO$_3$ was obtained by the exposure of toluene or CDCl$_3$ solutions of the distannoxane or stannol to CO$_2$ gas for several days. This compound was very sensitive to heat, rapidly decarboxylating in solution at 50°C under a stream of N$_2$. During routine m.p. analyses the white microcrystalline carbonate turned opaque at 50–55°C, presumably owing to loss of CO$_2$. The opaque solid melted at about 140°C, very near the melting point of (neophyl$_3$Sn)$_2$O. Infrared spectroscopy was particularly diagnostic for the presence of the carbonate linkage [12].

Discussion

Neophyl-substituted tin compounds were first prepared in 1966 by Reichle [5], who used IR, NMR, and Mössbauer spectroscopy to examine the influence of the sterically bulky neophyl group on the chemistry of its triorganotin(IV) derivatives. Among the derivatives he examined was neophyl$_3$SnOH, prepared by the reaction of neophyl$_3$SnCl with sodium hydroxide in aqueous ethanol. The stannol structure was assigned on the basis of a hydroxyl stretching mode in the IR of the melt and on elemental analysis data. Unsuccessful attempts to dehydrate this compound on heating up to 350°C led the author to conclude that the steric bulk of the neophyl ligand confers extraordinary stability on neophyl$_3$SnOH, a conclusion which has been cited elsewhere in the organotin literature [6,7].

Ironically, shortly after the synthesis of neophyl$_3$SnOH was reported, Zimmer, Homberg, and Jawayant reported [13] the isolation of (neophyl$_3$Sn)$_2$O by a similar route. The product had the same melting point as the purported stannol (143–144°C vs. 145–146°C) [5], but no hydroxyl function, by IR, and gave a good elemental analysis for the distannoxane. The authors pointed out the apparent similarity of the

two products and suggested the possibility of an error in the earlier assignment of neophyl$_3$SnOH. The similar elemental compositions of the compounds (which differ only by one H$_2$O per two neophyl$_3$Sn groups) makes elemental analysis marginally useful for distinguishing between them.

The large ^{119}Sn,^{117}Sn coupling constants observed in the ^{119}Sn NMR of hexaorganodistannoxanes [4] provide a convenient means for distinguishing between neophyl$_3$SnOH and (neophyl$_3$Sn)$_2$O in solution. Using ^{119}Sn NMR we have found that the equilibrium constant for formation of the stannol in CDCl$_3$ is 0.3 at 304 K, which indicates that the distannoxane is the thermodynamically preferred product. Further, efforts to isolate neophyl$_3$SnOH at room temperature from solutions in which it was known to be present in quantitative yields were unsuccessful. In combination, these observations indicate a facile interconversion of (neophyl$_3$Sn)$_2$O and neophyl$_3$SnOH in solution at room temperature and demonstrate the reported [5] synthesis of the stannol to be in error. The misidentification of (neophyl$_3$Sn)$_2$O provides a simple explanation for the reported [5] resistance of the stannol to dehydration, even at high temperature.

Our investigation of the hydrolysis chemistry of (neophyl$_3$Sn)$_2$O led us to another disagreement with the neophyltin literature. In 1972 McFarlane and Wood [14] reported the ^{119}Sn chemical shift of neophyl$_3$SnOH (161 ppm, apparently in CDCl$_3$ solution [14b]) which was determined by a double resonance technique. The authors noted the "anomalous", large positive value of the chemical shift of the stannol relative to the other trineophyltin compounds they examined. The reported chemical shift is in sharp disagreement with that of the product we identify as neophyl$_3$SnOH (75.9 ppm in CDCl$_3$). Based on our experimental observations, and our use of a direct measurement technique, we believe the higher value to be in error.

An effort was made to determine the source of the discrepancy between these two chemical shifts for neophyl$_3$SnOH. First, neophyl$_3$SnCl was prepared from the distannoxane used in this study. The agreement of the ^{119}Sn chemical shift of this compound (117.7 ppm in dilute CDCl$_3$ solution) with that reported by McFarlane and Wood (118 ppm) [14] eliminates the possibility that we were examining different organofunctional tin compounds. The general tendency of distannoxanes to react rapidly with CO$_2$ in the air [7,15] raised the possibility that the earlier NMR study of neophyl$_3$SnOH may have inadvertently been carried out on (neophyl$_3$Sn)$_2$CO$_3$. Our synthesis of the carbonate, however, shows this to be an unlikely possibility, given its instability and ^{119}Sn chemical shift (75–80 ppm, see Table 1).

Examination of the ^{119}Sn NMR spectra of neophyl$_3$SnOH, (neophyl$_3$Sn)$_2$CO$_3$, and (neophyl$_3$Sn)$_2$O reveals clear examples of the steric influence of the neophyl group on their behavior in solution. Thus, whereas IR studies [16] indicated that trimethylstannol is associated (dimeric) in solution (A), neophyl$_3$SnOH is unassoci-

$$\begin{array}{c} H \\ | \\ O \\ R_3Sn \diagup \diagdown SnR_3 \\ \diagdown O \diagup \\ | \\ H \end{array}$$
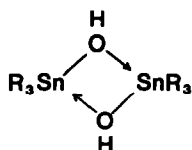
(A)

ated in CDCl$_3$ and acetone solution ($|^1J(^{119}Sn,^{13}C)|$ 368, 361 Hz, respectively; see

Table 1). This difference in behavior presumably reflects steric interference of the neophyl ligands upon close approach of two molecules of neophyl$_3$SnOH.

The ^{119}Sn NMR spectra of bis(trimethyltin)- and bis(tributyltin)-carbonates have recently been reported [17]. The presence of two broad resonances (+82, −66.7 ppm, line width > 10 ppm) in the ^{119}Sn NMR of the n-butyl compound was interpreted in terms of the formation of an oligomeric or polymeric species (B) [17].

(B)
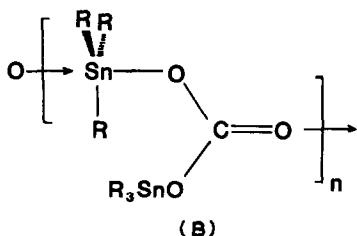
In sharp contrast, the ^{119}Sn NMR of (neophyl$_3$Sn)$_2$CO$_3$ shows a single, narrow resonance with resolved spin coupling to ^{13}C (Fig. 2). The magnitude of $^1J(^{119}$Sn,^{13}C) 357 Hz, indicates that this carbonate is monomeric in CDCl$_3$ solution [9,10]. Sn,Sn spin coupling through four bonds, $^4J(^{119}$Sn,^{117}Sn), is also visible in the well-resolved ^{119}Sn NMR spectrum. Few other examples of such long distance coupling of tin nuclei have been reported [18].

The neophyl ligand also has a pronounced influence on the stability of (neophyl$_3$Sn)$_2$CO$_3$ relative to other triorganotin carbonates: the neophyltin carbonate loses CO$_2$ rapidly at 50–55°C, whereas n-alkyl-substituted tin carbonates decompose above 100°C [12,19].

Comparison of (neophyl$_3$Sn)$_2$O with other distannoxanes indicates that the neophyl group significantly reduces the influence of solvent on the ^{119}Sn NMR parameters: $^2J(^{119}$Sn,^{117}Sn) decreases about 75 Hz and ^{119}Sn is deshielded about 7 ppm for n-alkyl-substituted distannoxanes in going from benzene to CDCl$_3$ solvent [4]; much smaller changes (2 Hz, 3 ppm) are observed for (neophyl$_3$Sn)$_2$O. Since the solvent is believed to affect these parameters through interaction with the polar Sn–O–Sn function (i.e., through hydrogen bonding of CDCl$_3$ to the distannoxane oxygen [4]), this comparison indicates that the neophyl ligand significantly shields the (neophyl$_3$Sn)$_2$O oxygen atom from solvent.

Conclusions

The presence of Sn,Sn spin coupling through oxygen, $^2J(^{119}$Sn,^{117}Sn), has been used to discriminate between (neophyl$_3$Sn)$_2$O and neophyl$_3$SnOH. The steric influence of the neophyl ligand eliminates the self-association of neophyl$_3$SnOH and (neophyl$_3$Sn)$_2$CO$_3$ in solution; in fact, these compounds appear to be the only well-established members of their respective classes which are monomeric in solution. The observation that neophyl$_3$SnOH is stable only in the presence of added water, however, requires a correction of the report that the bulky ligand renders neophyl$_3$SnOH extraordinarily resistant to dehydration.

Experimental

Materials. The (neophyl$_3$Sn)$_2$O used in this study was generously provided by P.J. Smith of the International Tin Research Institute, Great Britain. The solvents

employed in the synthetic work were of high commercial quality, and were dried over freshly activated 4A molecular sieves. The IR spectrum of $(neophyl_3Sn)_2CO_3$ was obtained with a Perkin–Elmer Model 337 grating infrared spectrometer.

NMR Spectroscopy. Solution NMR experiments were carried out with a Bruker WM 400 spectrometer. The ^{119}Sn NMR spectra were collected with a 90° pulse and 4 s relaxation delay at 149.212 MHz and 304 K. Proton decoupling at 400 MHz was gated on only during data acquisition in order to minimize the negative nuclear Overhauser effect (NOE). Solutions of the neophyltins were examined in 10 mm tubes; with benzene solutions a 5 mm concentric tube insert containing a deuterated lock solvent was used. A small amount of Me_4Sn ($< 1\%$ v/v) was added as reference (0 ppm). Repeated runs indicated that the uncertainty in the chemical shifts is < 0.1 ppm and in the spin coupling values was approximately equal to the digital resolution. The assignment of ^{117}Sn and ^{13}C satellites (natural abundances 1.1, 7.6%, respectively) was based on their intensity relative to the uncoupled central resonance. Varying the relaxation delay from 4 to 8 s produced $< 10\%$ change in relative areas of the $neophyl_3SnOH$ and $(neophyl_3Sn)_2O$ ^{119}Sn resonances.

Bis(trineophyltin) carbonate. Following literature procedures [12,17,19], CO_2 gas was bubbled through a toluene solution (10 ml) of $(neophyl_3Sn)_2O$ (0.3 mmol) at 23°C with occasional monitoring of the reaction by ^{119}Sn NMR. After 5 days conversion to the carbonate reached 90%. The product was isolated by slowly concentrating the solution at or below room temperature under a stream of CO_2. The product oil crystallized to a white solid on prolonged standing at room temperature under an atmosphere of CO_2. During routine melting point analysis the clear crystalline solid turned opaque at 50–55°C, evidently owing to the loss of CO_2. ^{119}Sn NMR showed the presence of $(neophyl_3Sn)_2O$ alone after a solution of the carbonate had been evaporated to a white solid under a stream of N_2 at 55°C.

Analysis: IR (thin film of product oil) showed the presence of carbonate frequencies similar in intensity and position to those reported for simple bis(tri-n-alkyltin) carbonates [12]: 1600, 1350, 1078, 830, 760, 700 cm^{-1}. ^{119}Sn NMR: spectrum shown in Fig. 2, data in the Table 1; the spectrum was scanned from $+200$ to -130 ppm but no evidence was found for a second ^{119}Sn resonance (vide supra) [17]. ^{13}C NMR (CDCl$_3$): 151.2 (C=O); 128.3, 125.7, 125.4 (aromatic ^{13}C); 37.8 (Sn–^{13}C); 37.6 (tert. ^{13}C); 32.9 ppm (^{13}CH$_3$); $^1J(^{119}$Sn,^{13}C) 356 Hz. ^{1}H NMR (CDCl$_3$): 6.8–7.1 (m, 5H); 0.96, 0.99 ppm (8H).

Trineophyltin chloride. The method of Reichle [5] for preparing $neophyl_3SnBr$ was used with minor changes: 2 ml aqueous HCl (37%) were added to a saturated solution of $(neophyl_3Sn)_2O$ (ca. 0.5 g) in 10 ml EtOH. After stirring overnight, the solution was heated to 56–60°C for a few hours. The white microcrystalline product was isolated by suction filtration. M.p. of crude product, 113–117°C (lit. [5], 117.5–118.5°C). ^{119}Sn NMR showed a single resonance at 117.7 ppm (lit. [14], 118 ppm).

Hydrolysis reactions of $(neophyl_3Sn)_2O$. The hydrolysis of $(neophyl_3Sn)_2O$ was carried out in CDCl$_3$, benzene, and acetone solutions (ca. 0.4 M) by adding several equivalents of H_2O. ^{119}Sn NMR indicated complete conversion to a single new product (NMR data given in Table 1), but attempts to isolate the product from these solutions were unsuccessful. For example, concentrating the hydrolysis solution under a vacuum at 25–35°C or under a stream of N_2 yielded a white microcrystalline solid. The m.p. of the solid ranged between 140–146°C (the m.p. of

(neophyl$_3$Sn)$_2$O [13]) depending on the presence of residual solvent. Attempted recrystallization of the product from a concentrated aqueous acetone solution (ca. 1/1 v/v) again gave the distannoxane. The ^{119}Sn NMR spectra of the hydrolysis solutions were recorded up to $+220$ ppm but the low-field resonance reported [14] was not observed.

The K_{eq} determination was carried out with a solution of 0.23 g (0.22 mmol) (neophyl$_3$Sn)$_2$O in 2.5 ml CDCl$_3$. After recording the preliminary spectrum, 1.3 μl (0.072 mmol) H$_2$O was added by syringe. The ratio of the areas of the distannoxane and stannol resonances were determined several times over 24 h and stabilized at a distannoxane/stannol ratio of 3/1. Correcting for the relative number of Sn atoms per molecule of stannol and distannoxane, and setting the moles of H$_2$O reacted equal to the amount of distannoxane converted gave $K_{eq} = 0.27$. In view of the small amount of materials involved and the nature of the measurement, the value $K_{eq} = 0.3$ is preferred.

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