UNRAVELLING THE HYDROLYSIS PATHWAY OF DIORGANOTIN DIHALIDES TOWARDS MOLECULAR DIORGANOTIN OXIDES

Jens Beckmann¹, Dainis Daktnerieks², Andrew Duthie²,
Klaus Jurkschat¹ *, and Markus Schürmann¹

¹ Lehrstuhl für Anorganische Chemie II der Universität Dortmund, 44221 Dortmund, Germany
² Centre for Chiral and Molecular Technologies, Deakin University, Geelong 3217, Australia

Abstract

The synthesis and controlled hydrolysis is reported of \((\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2\) (\(X = \text{Cl} \ (1), \text{Br} \ (2)\)), which provided the water adduct \((\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2\cdot\text{H}_2\text{O} \ (1a)\), and the symmetrically substituted dimeric tetraorganodistannoxanes \([\text{R}_2(\text{X})\text{SnOSnX}\text{R}_2]_2\) (\(X = \text{Cl} \ (3), \text{OH} \ (5), R = \text{CH}_3\text{SiMe}_3\)). The asymmetrically substituted dimeric tetraorganodistannoxanes \([\text{R}_2(\text{HO})\text{SnOSnCl}\text{R}_2]_2\) (\(4, R = \text{CH}_3\text{SiMe}_3\)) was prepared by a redistribution reaction of 3 and 5. Dehydration of 5 using activated molecular sieves afforded the trimeric diorganotin oxide, \([\text{Me}_3\text{SiCH}_2]_3\text{SnO}\) (6). Compounds 1a, 3, 5 and 6 were investigated by X-ray diffraction.

Introduction

Depending on the identity of the substituents R and X and the reaction conditions applied, the hydrolysis of diorganotin dihalides (\(R = \text{alkyl, aryl; } X = \text{Cl, Br}\)) gives rise to the formation of different molecular products, such as dimeric tetraorganodistannoxanes, \([\text{R}_2(\text{X})\text{SnOSnX}\text{R}_2]_2\), dimeric diorganotin hydroxide halides, \([\text{R}_2\text{Sn(OH)}\text{X}]_2\), or trimeric diorganotin oxides, \([\text{R}_2\text{SnOSnOSnCl}]_2\) (\(R = \text{alkyl, aryl; } X, Y = \text{Cl, Br, OH}\) [1-10]. However, so far no case is known, in which a full series of hydrolysis products containing the same organic substituents, has been described. Regarding this matter, we report here preliminary results on the hydrolysis of \((\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2\) (\(X = \text{Cl, Br}\)) including four fully characterized new compounds, \(\text{R}_2\text{SnCl}_2\cdot\text{H}_2\text{O}\), \(\text{R}_2(\text{Cl})\text{SnOSnCl}\text{R}_2\), \(\text{R}_2(\text{HO})\text{SnOSn(OH)}\text{R}_2\), \(\text{R}_2\text{SnO}\), with the same organic group, \(R = \text{CH}_3\text{SiMe}_3\) [11]. This series is supplemented by another hydrolysis product, \([\text{R}_2(\text{HO})\text{SnOSnCl}]_2\) (\(R = \text{CH}_3\text{SiMe}_3\)), for which the molecular structure was previously published by Puff et al. [6].

Results and discussion

The synthesis of the starting materials \((\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2\) (\(X = \text{Cl} \ (1), \text{Br} \ (2)\)) was achieved by cleaving the phenyl groups in \((\text{Me}_3\text{SiCH}_2)_2\text{SnPh}_2\) using hydrogen chloride or bromide, respectively (Eq. 1).

\[
(\text{Me}_3\text{SiCH}_2)_2\text{SnPh}_2 + 2\text{HX} \rightarrow (\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2 - 2\text{PhH}
\]

\(1, X = \text{Cl}\)

\(2, X = \text{Br}\)

In the presence of moist air, \((\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2\) (1) forms a water adduct, \((\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2\cdot\text{H}_2\text{O} \ (1a)\) which can be regarded as first hydrolysis product along the hydrolysis pathway to diorganotin oxides. In contrast, \((\text{Me}_3\text{SiCH}_2)_2\text{SnBr}_2\) (2) forms no such water adduct. The molecular structure of \((\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2\cdot\text{H}_2\text{O} \ (1a)\) is shown in Figure 1.

The reaction of \((\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2\) (1) with water in the presence of the appropriate amount of triethylamine afforded the dimeric tetraorganodistannoxane \([\text{R}_2(\text{Cl})\text{SnOSnCl}]_2\) (3, \(R = \text{CH}_3\text{SiMe}_3\)) (Eq. 2).
Figure 1. DIAMOND [12] presentation of (Me₂SiCH₂)₂SnCl₂·H₂O (1a). Selected bond lengths: Sn1-Cl1: 2.497(3), Sn1-Cl2: 2.375(2), Sn1-C1: 3.805(2), Sn1-O1: 2.404(8).

Notably, the hydrolysis of (Me₂SiCH₂)₂SnCl₂ (1) with sodium hydroxide under different reaction conditions providing the dimeric tetraorganodistannoxane [R₂(Cl)SnOSn(OH)R₄]₂ (4, R = CH₂SiMe₃) was already reported by Puff et al. [6]. An alternative method for the preparation of 4 is given below. The molecular structure of [R₂(Cl)SnOSn(Cl)R₄]₂ (3, R = CH₂SiMe₃) is shown in Figure 2.

\[
4 \text{R}_2\text{SnCl}_2 + 2 \text{H}_2\text{O}, 4 \text{NEt}_3 \rightarrow 4 \text{HNEt}_3\text{Cl}
\]

\[
\text{R} = \text{CH}_2\text{SiMe}_3
\]

The hydrolysis of (Me₂SiCH₂)₂SnBr₂ (2) with sodium hydroxide under reactions conditions comparable to those described by Puff et al. [6] for the preparation of [R₂(Cl)SnOSn(OH)R₄]₂ (4, R = CH₂SiMe₃) gave the dimeric tetraorganodistannoxane [R₂(HO)SnOSn(OH)R₄]₂ (5, R = CH₂SiMe₃) (Eq. 3), for which the molecular structure is presented in Figure 3.

\[
4 \text{R}_2\text{SnBr}_2 + 8 \text{NaOH} \rightarrow 8 \text{NaBr} - 2 \text{H}_2\text{O}
\]

\[
\text{R} = \text{CH}_2\text{SiMe}_3
\]
Figure 2. DIAMOND [12] presentation of $[R_2(Cl)SnOSn(Cl)R_2]_2$ (3, $R = CH_2SiMe_3$). Selected bond lengths: Sn1-C11: 2.577(2), Sn1···Cl4: 3.648(2), Sn1-O1: 2.203(3), Sn1-O2: 2.054(3), Sn2-C11: 2.921(2), Sn2-Cl3: 2.395(2), Sn2-O2: 2.021(3), Sn3-Cl2: 2.586(2), Sn3-Cl3: 3.616(2), Sn3-O1: 2.051(3), Sn3-O2: 2.191(3), Sn4-Cl2: 2.857(2), Sn4-Cl4: 2.414(2), Sn4-O1: 2.015(3).

Figure 3. DIAMOND [12] presentation of $[R_2(HO)SnOSn(OH)R_2]_2$ (5, $R = CH_2SiMe_3$). Selected bond lengths: Sn1-O1: 2.147(4), Sn1-O2: 2.047(4), Sn1-O2a: 2.129(4), Sn1···O3a: 3.583(5), Sn2-O1: 2.342(4), Sn2-O2: 2.019(4), Sn2-O3: 2.032(4).
In solution, \([R_2(HO)SnOSn(OH)R_2]_2\) (5, \(R = CH_2SiMe_3\)) is in equilibrium with the molecular diorganotin oxide, \([\{Me_3Sn(CH_2)_2SnO\}_2\] (6) and water (Eq. 4). Addition of activated molecular sieve shifts the equilibrium completely to \([\{Me_3Sn(CH_2)_2SnO\}_2\] (6), which could be isolated and investigated by X-ray diffraction. The molecular structure is depicted in Figure 4.

![Equilibrium Diagram](image)

**Figure 4.** DIAMOND [12] presentation of \([\{Me_3Sn(CH_2)_2SnO\}_2\] (6). Selected bond lengths: Sn1-O1: 1.961(2), Sn1-O3: 1.966(3), Sn2-O1: 1.966(3), Sn2-O2: 1.965(3), Sn3-O2: 1.962(3), Sn3-O3: 1.980(2).

Alternatively to the hydrolysis method reported by Puff et al. [5], \([R_2(HO)SnOSn(Cl)R_2]_2\) (4, \(R = CH_2SiMe_3\)) could prepared by a redistribution reaction of the symmetrically substituted dimeric tetraorganodistannoxanes, \([R_3(X)SnOSn(X)R_3]_2\) (R = CH_2SiMe_3), 3 (X = Cl) and 5 (X = OH) (Eq. 5).

![Redistribution Reaction](image)

**Equation 5:**

3 + 4 → 2

\(R = CH_2SiMe_3\)
The compounds 1 – 6 were also characterized by multinuclear NMR spectroscopy in solution and in the solid state, as well as by electrospray mass spectroscopy. However, these results will be published in a forthcoming paper [11].

Acknowledgement
We thank the Deutsche Forschungsgemeinschaft, the Fonds der chemischen Industrie, and the Australian Research Council for financial support.

References