UNRAVELLING THE HYDROLYSIS PATHWAY OF DIORGANOTIN DIHALIDES TOWARDS MOLECULAR DIORGANOTIN OXIDES

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Abstract

The synthesis and controlled hydrolysis is reported of $(\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2$ ($\text{X} = \text{Cl}$ (**1**), 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 $[\text{R}_2(\text{X})\text{SnOSn}(\text{X})\text{R}_2]_2$ ($\text{X} = \text{Cl}$ (**3**), OH (**5**); $\text{R} = \text{CH}_2\text{SiMe}_3$). The asymmetrically substituted dimeric tetraorganodistannoxanes $[\text{R}_2(\text{HO})\text{SnOSn}(\text{Cl})\text{R}_2]_2$ (**4**, $\text{R} = \text{CH}_2\text{SiMe}_3$) was prepared by a redistribution reaction of **3** and **5**. Dehydration of **5** using activated molecular sieve afforded the trimeric diorganotin oxide, $[(\text{Me}_3\text{SiCH}_2)_2\text{SnO}]_3$ (**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 ($\text{R} = \text{alkyl, aryl}$; $\text{X} = \text{Cl, Br}$) gives rise to the formation of different molecular products, such as dimeric tetraorganodistannoxanes, $[\text{R}_2(\text{X})\text{SnOSn}(\text{Y})\text{R}_2]_2$, dimeric diorganotin hydroxide halides, $[\text{R}_2\text{Sn}(\text{OH})\text{X}]_2$, or trimeric diorganotin oxides, $(\text{R}_2\text{SnO})_3$ ($\text{R} = \text{alkyl, aryl}$; $\text{X, Y} = \text{Cl, Br, OH}$) [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 $(\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2$ ($\text{X} = \text{Cl, Br}$) including four fully characterized new compounds, $\text{R}_2\text{SnCl}_2 \cdot \text{H}_2\text{O}$, $[\text{R}_2(\text{Cl})\text{SnOSn}(\text{Cl})\text{R}_2]_2$, $[\text{R}_2(\text{HO})\text{SnOSn}(\text{OH})\text{R}_2]_2$, $(\text{R}_2\text{SnO})_3$ with the same organic group, $\text{R} = \text{CH}_2\text{SiMe}_3$ [11]. This series is supplemented by another hydrolysis product, $[\text{R}_2(\text{HO})\text{SnOSn}(\text{Cl})\text{R}_2]_2$ ($\text{R} = \text{CH}_2\text{SiMe}_3$), for which the molecular structure was previously published by Puff et al. [6].

Results and discussion

The synthesis of the starting materials $(\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2$ ($\text{X} = \text{Cl}$ (**1**), 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).

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 $[\text{R}_2(\text{Cl})\text{SnOSn}(\text{Cl})\text{R}_2]_2$ (**3**, $\text{R} = \text{CH}_2\text{SiMe}_3$) (Eq. 2).

Figure 1. DIAMOND [12] presentation of $(\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}$ (**1a**). Selected bond lengths: Sn1-Cl1: 2.497(3), Sn1-Cl2: 2.375(2), Sn1...Cl2: 3.805(2), Sn1-O1: 2.404(8).

Notably, the hydrolysis of $(\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2$ (**1**) with sodium hydroxide under different reaction conditions providing the dimeric tetraorganodistannoxane $[\text{R}_2(\text{Cl})\text{SnOSn}(\text{OH})\text{R}_2]_2$ (**4**, $\text{R} = \text{CH}_2\text{SiMe}_3$) was already reported by Puff et al. [6]. An alternative method for the preparation of **4** is given below. The molecular structure of $[\text{R}_2(\text{Cl})\text{SnOSn}(\text{Cl})\text{R}_2]_2$ (**3**, $\text{R} = \text{CH}_2\text{SiMe}_3$) is shown in Figure 2.

The hydrolysis of $(\text{Me}_3\text{SiCH}_2)_2\text{SnBr}_2$ (**2**) with sodium hydroxide under reactions conditions comparable to those described by Puff et al. [6] for the preparation of $[\text{R}_2(\text{Cl})\text{SnOSn}(\text{OH})\text{R}_2]_2$ (**4**, $\text{R} = \text{CH}_2\text{SiMe}_3$) gave the dimeric tetraorganodistannoxane $[\text{R}_2(\text{HO})\text{SnOSn}(\text{OH})\text{R}_2]_2$ (**5**, $\text{R} = \text{CH}_2\text{SiMe}_3$) (Eq. 3), for which the molecular structure is presented in Figure 3.

Figure 2. DIAMOND [12] presentation of $[R_2(Cl)SnOSn(Cl)R_2]_2$ (**3**, $R = CH_2SiMe_3$). Selected bond lengths: Sn1-Cl1: 2.577(2), Sn1...Cl4: 3.648(2), Sn1-O1: 2.203(3), Sn1-O2: 2.054(3), Sn2-Cl1: 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 $[R_2(OH)SnOSn(OH)R_2]_2$ (**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, $[(Me_3SiCH_2)_2SnO]_3$ (**6**) and water (Eq. 4). Addition of activated molecular sieve shifts the equilibrium completely to $[(Me_3SiCH_2)_2SnO]_3$ (**6**), which could be isolated and investigated by X-ray diffraction. The molecular structure is depicted in Figure 4.

Figure 4. DIAMOND [12] presentation of $[(Me_3SiCH_2)_2SnO]_3$ (**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. [6], $[R_2(HO)SnOSn(Cl)R_2]_2$ (**4**, $R = CH_2SiMe_3$) could be prepared by a redistribution reaction of the symmetrically substituted dimeric tetraorganodistannoxanes, $[R_2(X)SnOSn(X)R_2]_2$ ($R = CH_2SiMe_3$), **3** ($X = Cl$) and **5** ($X = OH$) (Eq. 5).

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].

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