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## UNRAVELLING THE HYDROLYSIS PATHWAY OF DIORGANOTIN DIHALIDES TOWARDS MOLECULAR DIORGANOTIN OXIDES

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### Abstract

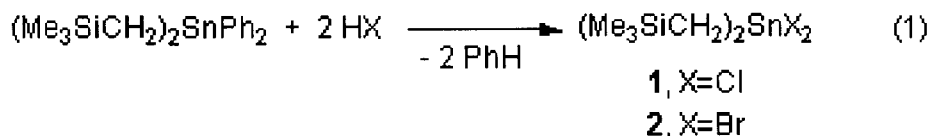
The synthesis and controlled hydrolysis is reported of  $(\text{Me}_3\text{SiCH}_2)_2\text{SnX}_2$  ( $\text{X} = \text{Cl}$  (**1**),  $\text{Br}$  (**2**)), which provided the water adduct  $(\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}$  (**1a**), and the symmetrically substituted dimeric tetraorganodistannoxanes  $[\text{R}_2(\text{X})\text{SnOSn}(\text{X})\text{R}_2]_2$  ( $\text{X} = \text{Cl}$  (**3**),  $\text{OH}$  (**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].

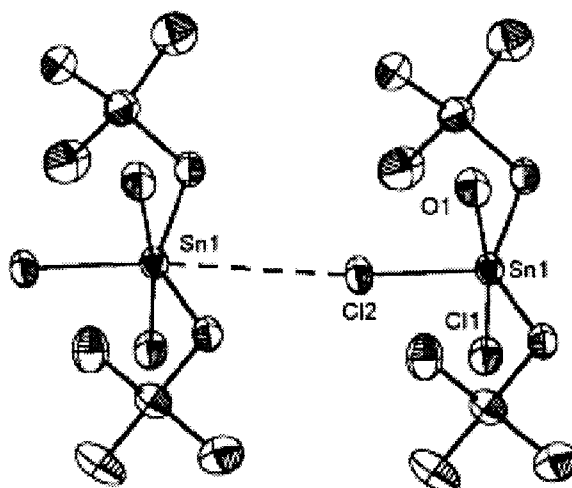
### Results and discussion

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



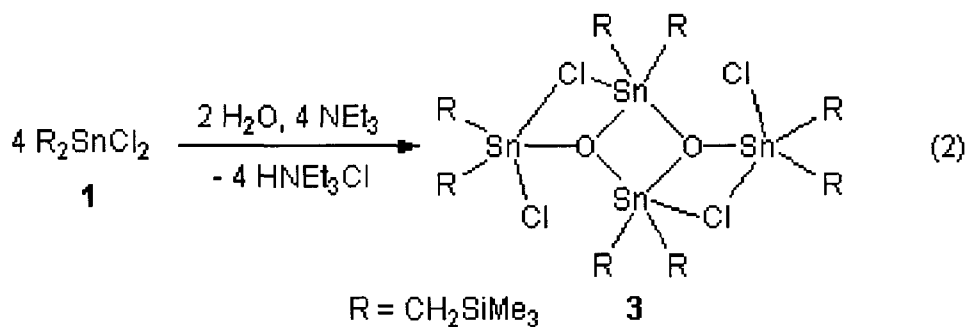
In the presence of moist air,  $(\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2$  (**1**) forms a water adduct,  $(\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}$  (**1a**) which can be regarded as first hydrolysis product along the hydrolysis pathway to diorganotin oxides. In contrast,  $(\text{Me}_3\text{SiCH}_2)_2\text{SnBr}_2$  (**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).

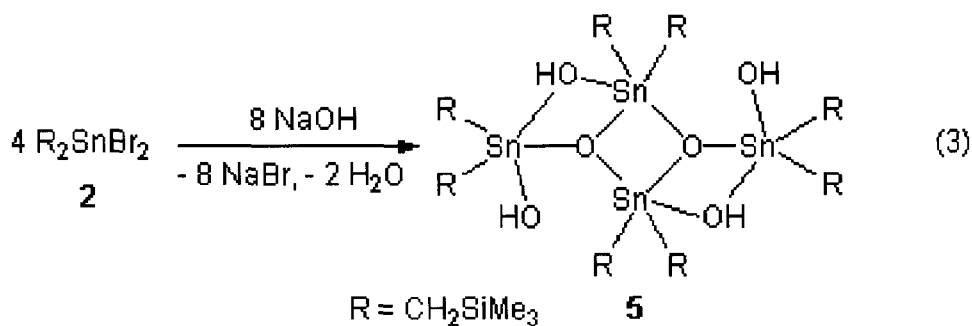


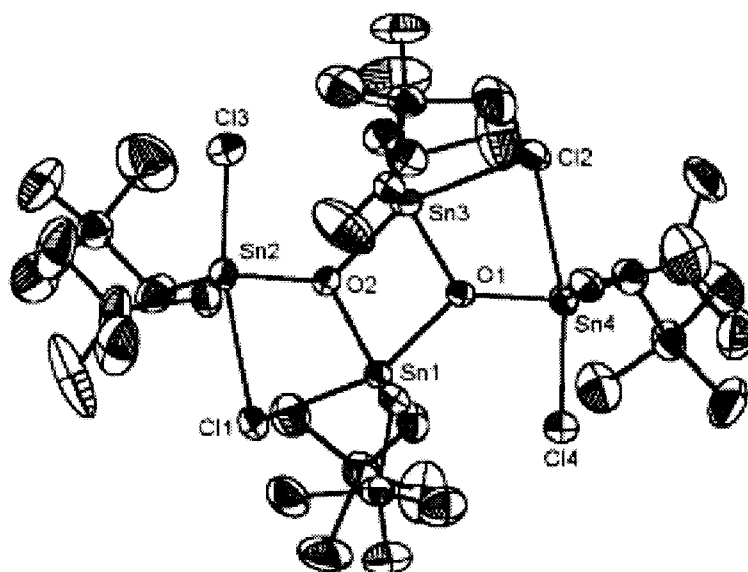
**Figure 1.** DIAMOND [12] presentation of  $(\text{Me}_3\text{SiCH}_2)_2\text{SnCl}_2 \cdot \text{H}_2\text{O}$  (**1a**). Selected bond lengths: Sn1-Cl1: 2.497(3), Sn1-Cl2: 2.375(2), Sn1...Cl2: 3.805(2), Sn1-O1: 2.404(8).

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.

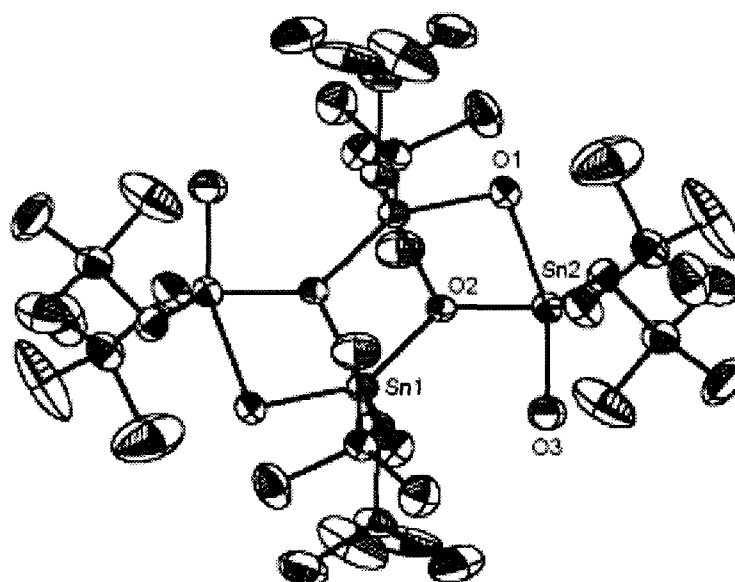


The hydrolysis of  $(\text{Me}_3\text{SiCH}_2)_2\text{SnBr}_2$  (**2**) with sodium hydroxide under reactions conditions comparable to those described by Puff et al. [6] for the preparation of  $[\text{R}_2(\text{Cl})\text{SnOSn}(\text{OH})\text{R}_2]_2$  (**4**,  $\text{R} = \text{CH}_2\text{SiMe}_3$ ) 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.



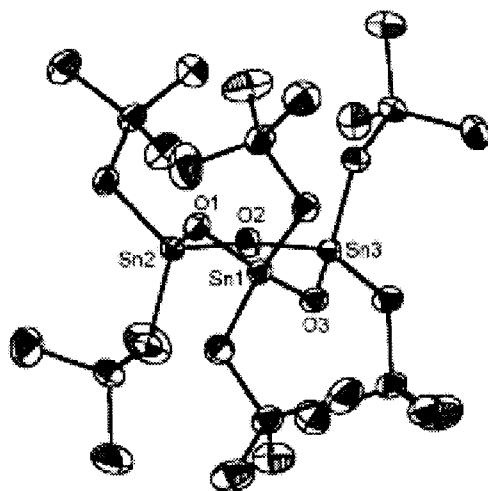
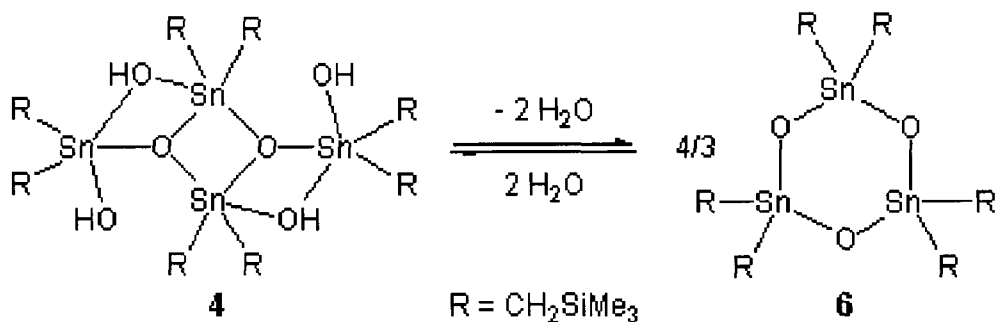


**Figure 2.** DIAMOND [12] presentation of  $[R_2(Cl)SnOSn(Cl)R_2]_2$  (**3**,  $R = CH_2SiMe_3$ ). Selected bond lengths: Sn1-Cl1: 2.577(2), Sn1 $\cdots$ Cl4: 3.648(2), Sn1-O1: 2.203(3), Sn1-O2: 2.054(3), Sn2-Cl1: 2.921(2), Sn2-Cl3: 2.395(2), Sn2-O2: 2.021(3), Sn3-Cl2: 2.586(2), Sn3 $\cdots$ Cl3: 3.616(2), 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).



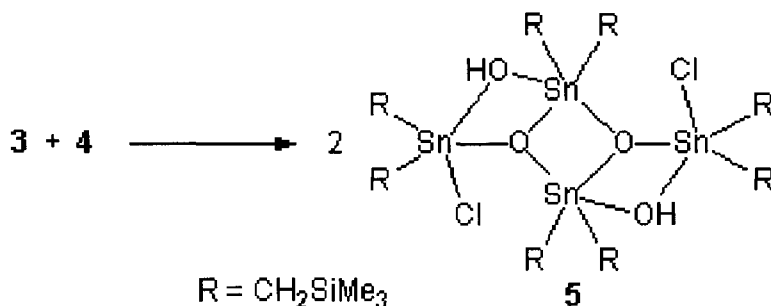
**Figure 3.** DIAMOND [12] presentation of  $[R_2(OH)SnOSn(OH)R_2]_2$  (**5**,  $R = CH_2SiMe_3$ ). Selected bond lengths: Sn1-O1: 2.147(4), Sn1-O2: 2.047(4), Sn1-O2a: 2.129(4), Sn1 $\cdots$ O3a: 3.583(5), Sn2-O1: 2.342(4), Sn2-O2: 2.019(4), Sn2-O3: 2.032(4).

In solution,  $[\text{R}_2(\text{HO})\text{SnOSn}(\text{OH})\text{R}_2]_2$  (**5**,  $\text{R} = \text{CH}_2\text{SiMe}_3$ ) is in equilibrium with the molecular diorganotin oxide,  $[(\text{Me}_3\text{SiCH}_2)_2\text{SnO}]_3$  (**6**) and water (Eq. 4). Addition of activated molecular sieve shifts the equilibrium completely to  $[(\text{Me}_3\text{SiCH}_2)_2\text{SnO}]_3$  (**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  $[(\text{Me}_3\text{SiCH}_2)_2\text{SnO}]_3$  (**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],  $[\text{R}_2(\text{HO})\text{SnOSn}(\text{Cl})\text{R}_2]_2$  (**4**,  $\text{R} = \text{CH}_2\text{SiMe}_3$ ) could be prepared by a redistribution reaction of the symmetrically substituted dimeric tetraorganodistannoxanes,  $[\text{R}_2(\text{X})\text{SnOSn}(\text{X})\text{R}_2]_2$  ( $\text{R} = \text{CH}_2\text{SiMe}_3$ ), **3** ( $\text{X} = \text{Cl}$ ) and **5** ( $\text{X} = \text{OH}$ ) (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].

#### Acknowledgement

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