

Synthesis and decomposition of bis(alkoxyethynyl)dimethyltin

Bernd Wrackmeyer ^{a,*}, Sergej V. Ponomarev ^b

^a *Laboratorium für Anorganische Chemie, Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, Postfach 101 251, Universitätstrasse 30, NW I, D-95440 Bayreuth, Germany*

^b *Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russia*

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Dedicated to Professor H. Vahrenkamp on the occasion of his 60th birthday.

Abstract

The reaction of bis(diethylamino)dimethyltin, $\text{Me}_2\text{Sn}(\text{NET}_2)_2$ with methoxy (**a**) and ethoxyethyne (**b**) at 0°C affords the bis(alkoxyethynyl)dimethyltin derivatives $\text{Me}_2\text{Sn}(\text{C}\equiv\text{COR})_2$ (**5a**, **b**) without side products in high yield. Both **5a** and **5b** decompose slowly at room temperature or much faster at 60–70°C almost quantitatively into an unidentified polymer, small amounts of numerous unidentified methyltin compounds, and mainly 1,1-bis(alkoxy)-2,2-bis[(alkoxyethynyl)dimethyl-stannyl]ethene. The new compounds were characterised by ¹H-, ¹³C- and ¹¹⁹Sn-NMR spectroscopy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkynes; Alkenes; NMR; Tin

1. Introduction

The inherent instability of alkoxyethynes and their enhanced reactivity when compared with non-functionalised alkynes is of interest for organic synthesis [1]. Organometallic-substituted ethoxyethynes of type **1** [2] are known to eliminate ethene upon heating and rearrange into ketene **2** (Scheme 1).

Although **2** had not been detected in the case of $\text{M} = \text{Sn}$ and $\text{R} = \text{Me}$, its intermediacy could be assumed, since bis(trimethylstannyl)ketene (**3**) had been isolated instead of **2** [3]. Recently, we have reinvestigated the decomposition of ethoxyethynyl(trimethyl)tin by ¹³C- and ¹¹⁹Sn-NMR spectroscopy [4] and found that the ester **4** is also formed, as a second major product (Scheme 2).

One way to explain the formation of **4** is to assume that another product arising from the decomposition of $\text{Me}_3\text{SnC}\equiv\text{COEt}$ is Me_3SnOEt , which then traps the unstable ketene **2** (with $\text{M} = \text{Sn}$) to give the ester **4**. Considering this assumption, it was of interest to study the behaviour of bis(alkoxyethynyl)dimethyltin (**5**).

Therefore, we report on the synthesis of these hitherto unknown tin compounds and on their decomposition as studied by ¹H-, ¹³C- and ¹¹⁹Sn-NMR spectroscopy.

2. Results and discussion

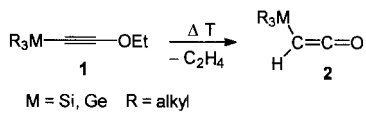
2.1. Synthesis of bis(alkoxyethynyl)dimethyltin (**5a**, **b**)

Two routes to the compounds **5** appear to be feasible: reaction of Me_2SnCl_2 with two equivalents of $\text{LiC}\equiv\text{COR}$ or treatment of $\text{Me}_2\text{Sn}(\text{NET}_2)_2$ with two equivalents of the alkoxyethyne [5]. The route via $\text{LiC}\equiv\text{COR}$ can be applied to prepare the more stable germanium analogues of **5** [6]. If these reactions were carried out at room temperature, the mixture of products, in each case, contained mainly two tin compounds, one of which has ¹¹⁹Sn-NMR parameters fitting to **5**. The second compound could be a decomposition product of **5**. Repetition of the reactions according to Scheme 3 at 0°C, and working up the reaction mixture also at 0°C or below, affords only one compound in each case, which could be identified as **5a** or **5b** (see Table 1 for NMR parameters).

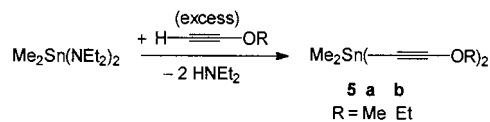
The compounds **5** are colourless solids at 0°C and can be stored as such or better as hexane solutions

* Corresponding author. Tel./fax: +49-921-552542.

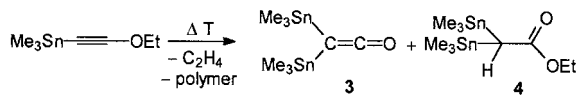
E-mail address: b.wrack@uni-bayreuth.de (B. Wrackmeyer)



Scheme 1.



Scheme 3.



Scheme 2.

under Ar for prolonged time at -18°C without decomposition.

2.2. Decomposition of bis(alkoxyethynyl)dimethyltin (**5a, b**)

If the compounds **5** are dissolved in C_6D_6 and the solutions are heated at $60\text{--}70^\circ\text{C}$ for 5 h, the colour of the solution turns to dark brown and the NMR signals of **5** disappear. Instead new sets of signals appear, representing ca. 85–90% of all intensities (see Fig. 1). These NMR signals (Table 2) corroborate the proposed structure of the new compound **6**. The possible route to **6** is shown in Scheme 4; it involves the formation of a tinalkoxide as an intermediate, in analogy to the explanation of the decomposition of $\text{Me}_3\text{SnC}\equiv\text{COEt}$ [4]. However, in the course of the decomposition of **5**, there is no indication of a ketene as an intermediate or a final product (checked by IR and NMR). Thus, elimination of ethene must be of minor importance in the case of **5b**, since the decomposition of **5a** mimics that of **5b**. Samples containing **5** in different concentrations show that the compounds **6** are formed at approximately the same rate. Thus, the decomposition of **5** starts as an intramolecular process.

2.3. NMR spectroscopic results

The NMR data of **5a, b** (Table 1) fit exactly into the well-known pattern of 1-alkynyl tin compounds [7]. The changes in the isotope-induced chemical shifts in going from $\text{Me}_3\text{SnC}\equiv\text{COEt}$ [4] to **5b** are fully in accordance with analogous data observed for other mono- and bis(1-alkynyl)tin compounds [8].

The structures of **6a, b** are proposed on the basis of the NMR data in Table 2. There are typical data sets for a $\text{C}\equiv\text{COR}$ and a $\text{C}=\text{C}(\text{OR})_2$ group, and the $^{119}\text{Sn}\text{--}^{117}\text{Sn}$ spin–spin coupling indicates the presence of two tin atoms in the same molecule. The coupling constants $J(^{119}\text{Sn}, ^{13}\text{C})$ were measured both from the ^{119}Sn - and ^{13}C -NMR spectra. The ^{13}C resonances of the olefinic carbon atom at 81.3 (**6a**) or 82.6 (**6b**) are difficult to observe owing to slow nuclear spin relaxation. In these cases, the refocused INEPT pulse sequence [9], based on $^3J(^{13}\text{C}, \text{Sn}, \text{C}, ^1\text{H}) = 1.8$ [10], can be applied successfully, which allows us to detect the $^{119/117}\text{Sn}$ satellites within reasonable time (see Fig. 2). The $\delta^{119}\text{Sn}$ values of **6** lie just outside of the range known for non-cyclic bis(alkenyl)dimethyltin in the direction of that known for bis(1-alkynyl)-dimethyltin compounds [11]. The magnitude of the coupling constants $^2J(\text{Sn}, \text{Sn})$ (**6a**: 348.0 Hz; **6b**: 349.0 Hz) is somewhat smaller than observed for other 1,1-bis(trimethylstannyl)alkenes [11]. This is due to the influence of two electronegative alkoxy substituents at the $\text{C}=\text{C}$ bond. The absolute sign of $^2J(\text{Sn}, \text{Sn})$ in **6** is positive, the same as in other 1,1-bis(trimethylstannyl)alkenes [12].

Table 1
 ^1H -, ^{13}C - and ^{119}Sn -NMR data ^a of bis(alkoxyethynyl)dimethyltin compounds (**5a, b**) and $\text{Me}_3\text{SnC}\equiv\text{COEt}$ [4]

Compound	$\delta^{13}\text{C}$ ($\delta^1\text{H}$) Me_2Sn [$J(^{119}\text{Sn}, ^{13}\text{C})$] { $J(^{119}\text{Sn}, ^1\text{H})$ }	$\delta^{13}\text{C}$ ($\delta^1\text{H}$) OR [$J(^{119}\text{Sn}, ^{13}\text{C})$]	$\delta^{13}\text{C}$ Sn–C≡C [$J(^{119}\text{Sn}, ^{13}\text{C})$]	$\delta^{119}\text{Sn}$
5a	–5.4 [503.5] (0.26) {68.2}	65.0 (3.18)	32.1 [690.0] 113.6 [168.0]	–131.1
5b	–5.8 [508.7] (0.34) {69.0}	74.4 [8.5] 14.8 (3.60, 0.86)	33.2 [708.2] 112.5 [171.0]	–130.9 ^b
$\text{Me}_3\text{SnC}\equiv\text{COEt}$	–7.8 [406.3]	74.2 [6.9] 14.2	33.8 [545.7] 112.1 [130.3]	–61.5

^a In C_6D_6 at 25°C . Coupling constants ± 0.3 Hz.

^b Isotope-induced shifts (± 0.5 ppb) $^1J^{12/13}\text{C}(^{119}\text{Sn}) = +18$ ppb (SnMe); -27 ppb (C≡); $^2J^{12/13}\text{C}(^{119}\text{Sn}) = -0.3$ ppb (see Refs. [4,8,11] for other $^1J^{12/13}\text{C}(^{119}\text{Sn})$ values); e.g. $\text{Me}_3\text{SnC}\equiv\text{COEt}$: $^1J^{12/13}\text{C}(^{119}\text{Sn}) = +1.3$ ppb (SnMe); -51.0 ppb (C≡); $^2J^{12/13}\text{C}(^{119}\text{Sn}) = -8.4$ ppb.

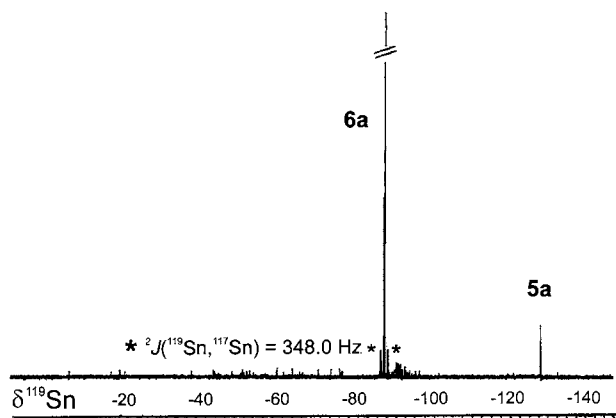


Fig. 1. 186.5 MHz ^{119}Sn -NMR spectrum (recorded by using the refocused INEPT pulse sequence with ^1H decoupling [9,11]) of the reaction mixture containing **6a** and a small amount of **5a** after heating the solution of pure **5a** for 5 h at 65°C in C_6D_6 . There are numerous small signals of other unidentified methyl tin compounds (the intensity distribution is the same, within experimental error if the ^{119}Sn -NMR spectrum is measured directly by inverse gated ^1H decoupling). The ^{117}Sn satellites of the parent ^{119}Sn -NMR signal of **6a** are marked by asterisks.

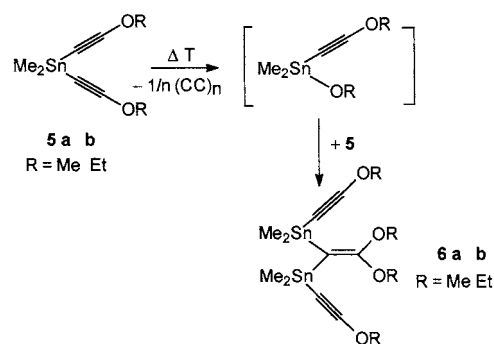
3. Conclusions

Apparently the more labile Sn–C \equiv bonds in alkoxyethynyltin derivatives are responsible for the different behaviour when compared with analogous germanium or silicon compounds. Thus, the germanium analogue of **5b** was prepared [6], and it can be distilled without decomposition. On the other hand, the instability of the tin compounds **5** offers attractive new aspects since the decomposition products **6** are formed in high yield and possess numerous reactive sites for reactions with nucleophilic and electrophilic reagents.

4. Experimental

4.1. General

The compounds were handled in an atmosphere of Ar and oven-dried glass ware was used. Starting materi-



Scheme 4.

als such as methoxyethyne [13], ethoxyethyne [14], $\text{Me}_2\text{Sn}(\text{NET}_2)_2$ [15] were prepared following the literature procedures. IR spectra were measured using a Perkin–Elmer 983G instrument. NMR spectra were run on Bruker ARX 250 and DRX 500 spectrometers. Chemical shifts are given relative to Me_4Si [$\delta^1\text{H}$ (C_6D_6) = 7.15; $\delta^{13}\text{C}$ (C_6D_5) = 128.0] and Me_4Sn [$\delta^{119}\text{Sn}$ = 0 for $\Xi(^{119}\text{Sn})$ = 37.290665 MHz]. In order to measure accurate isotope-induced chemical shifts $\Delta^{12/13}\text{C}(^{119}\text{Sn})$ [11] from ^{119}Sn -NMR spectra, all pulse angles for ^1H , and ^{119}Sn were carefully calibrated, shim parameters were optimised, and low-power selective ^1H decoupling was used in order to keep temperature gradients in the sample at a minimum. The absolute sign of $^2J(\text{Sn}, \text{Sn})$ in **6b** was determined by 2D $^{119}\text{Sn}/^1\text{H}$ HETCOR experiments based on $^4J(^{119}\text{Sn}, \text{C}, \text{Sn}, \text{C}, ^1\text{H}) \approx 1$ Hz, as described [16].

4.2. Synthesis of bis(alkoxyethynyl)dimethyltin (**5a, b**)

A solution of $\text{Me}_2\text{Sn}(\text{NET}_2)_2$ (0.68 g; 2.3 mmol) in ether (3 ml) is cooled to 0°C , and ethoxyethyne (6 mmol as a 50% solution in hexane) is added in one portion. After stirring the mixture at 0°C for 8 h, all readily volatile material is removed in vacuo, leaving **5a** (75% yield) and **5b** (70% yield) as colourless solids. These can be dissolved in hexane and stored at -30°C without decomposition for several months. **5a**: IR: $\nu(\text{C}=\text{C}) = 2167$ cm^{-1} ; **5b**: IR: $\nu(\text{C}=\text{C}) = 2158$ cm^{-1} .

Table 2
 ^1H -, ^{13}C - and ^{119}Sn -NMR data^a of the 1,1-bis(alkoxy)-2,2-bis[(alkoxy-ethynyl)dimethylstannyl]ethenes (**6a, b**)

Compound	$\delta^{13}\text{C}$ ($\delta^1\text{H}$) Me_2Sn [$J(^{119}\text{Sn}, ^{13}\text{C})$] [$J(^{119}\text{Sn}, ^1\text{H})$]	$\delta^{13}\text{C}$ ($\delta^1\text{H}$) OR [$J(^{119}\text{Sn}, ^{13}\text{C})$]	$\delta^{13}\text{C}$ Sn–C \equiv C [$J(^{119}\text{Sn}, ^{13}\text{C})$]	$\delta^{13}\text{C}$ Sn–C=C [$J(^{119}\text{Sn}, ^{13}\text{C})$]	$\delta^{119}\text{Sn}$ [$^2J(^{119}\text{Sn}, ^{117}\text{Sn})$]
6a	–6.0 [433.5] [6.8] (0.48) {62.0}	65.0 (3.35) $\equiv\text{COMe}$; 56.7 (3.20) $=\text{C}(\text{OMe})_2$	34.8 [535.2] 113.7 [126.2]	81.3 [432.3] 166.2 [2.1]	–89.6 [348.0] ^b
6b	–5.0 [430.7] [7.3] (0.56) {62.0}	74.1 [6.5], 14.2 (3.71, 0.94) $\equiv\text{COEt}$ 65.4, 14.8 (3.63, 1.05) $=\text{C}(\text{OEt})_2$	36.0 [537.7] 112.4 [126.8]	82.6 [437.0] 164.9 [<2]	–89.0 [349.0]

^a In C_6D_6 at 25°C . Coupling constants ± 0.3 Hz.

^b Isotope-induced shifts (± 0.5 ppb) $^1\Delta^{12/13}\text{C}(^{119}\text{Sn}) = +10$ ppb (SnMe); -41 ppb (C \equiv); -14 ppb (C=C); $^2\Delta^{12/13}\text{C}(^{119}\text{Sn}) = -0.5$ ppb (see Refs. [4,8,11] for other $^1\Delta^{12/13}\text{C}(^{119}\text{Sn})$ values).

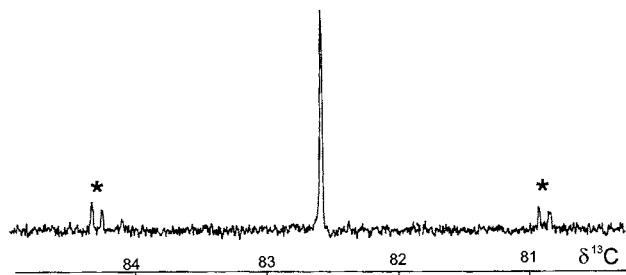


Fig. 2. 125.8 MHz ^{13}C -NMR spectrum of **6b** in C_6D_6 showing the region for the $^{13}\text{C}=\text{C}(\text{OEt})_2$ NMR signal [recorded by using the refocused INEPT pulse sequence, based on $^3J(^{13}\text{C}, \text{Sn}, \text{C}, ^1\text{H}) = 1.8$ Hz, with ^1H decoupling [9,10]; result of 400 transients, 30 min of spectrometer time. The $^{119/117}\text{Sn}$ satellites [$^1J(^{119}\text{Sn}, ^{13}\text{C}) = 437.0$ Hz] are marked by asterisks, and their intensities correspond to the presence of two tin atoms.

Acknowledgements

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