Syntheses of Monomeric Bis(Dialkoxyorganylsiloxy)Dibutylstannanes
Bu$_2$Sn[OSi(R')(OR)]$_2$ (R\(=\)C$_3$H$_7$, C$_4$H$_9$, i-C$_4$H$_9$, C$_5$H$_{11}$; 
R' =Vi, Ph)

Alexander V. Alikovskii · Victoria V. Vasileva · 
Elena T. Dan’ko · Svetlana G. Krasitskaya · 
Mikhail I. Balanov

Received: 30 April 2014 / Accepted: 22 October 2014 / Published online: 16 December 2014
© Springer Science+Business Media Dordrecht 2014

Abstract The reaction of dibutyltin (IV) oxide with poly-
organosiloxanes in the presence of aliphatic alcohols is 
shown to lead to the formation of both monomeric and 
polymeric functional heterosiloxanes. The composition and 
yield of the final products are defined by the character of 
the organic radical of the silicon atom and the reagents mole 
ratio.

Keywords Tin · Stannanes · Heterosiloxanes · 
Stannasiloxanes

1 Introduction

Stannasiloxanes are of increasing interest as models in catalysis [1–6] or might serve as molecular precursors for well-defined inorganic polymers, therefore, a better understanding of their chemistry is welcome. Thus far, stannasiloxanes have been prepared by the reaction of organosilanols with organochlorostannanes in the presence of a base, by the reaction of organosilanols with organotin oxides or by lithium halide elimination from organosilanolates and organohalostannanes. The formation of Si-O-Sn linkages has also been achieved by making use of the high Bronsted acidity of silica surfaces, which allows the cleavage of Sn-C and Sn-H bonds [7].

Usually, to form a Sn-O-Si fragment, highly reactive silicon compounds and tin are used, which in turn makes the process of preparing the object compounds highly demanding [7–10].

One of the most universal and convenient preparative methods for polymetalloorganosiloxanes synthesis is the reaction of waterless chlorides of metals with phenylsiloxanolates of sodium. The classical variant of this method uses n-butanol as one of the solvents. In all subsequent works, n-butanol is considered only as a solvent, and its impact on the structure and character of the products is not studied [11, 12]. However, during the synthesis of poly(dibutylstanno)phenylsilsesquioxane (1) by a classical technique [13], bis(dibutoxyphenylsiloxy)dibutylstannane (2) was isolated along with polymer (1). The treatment of 1 with n-butanol led to the same result (1 was obtained by reaction between Bu$_2$SnCl$_2$ and [PhSi(O)ONa]$_n$ in the presence of DMSO, according to the published method [14]).

It was established that 1 can be obtained with practical quantitative yield when dibutyltin (IV) oxide (DBO) reacts with polyphenylsilsesquioxane (PPS) in boiling toluene [15]. The latter circumstance indicates the interesting possibility of synthesising bis(dialkoxyorganylsiloxy) dibutylstannanes in one step, avoiding the obtaining and isolation of polymers, if one uses aliphatic alcohols as one of the solvents. The objective of this research is to determine the factors influencing the character and yield of the products.
2 Materials and Methods

2.1 Materials

Phenyltrichlorosilane, vinyltrichlorosilane, methyltrichlorosilane, tetraethoxysilane, dibutyltin (IV) oxides, n-butanol, n-propanol, iso-butanol, n-pentanol, diethyl ether and toluene were purchased from Sigma-Aldrich. Poly(dibutylstanno)phenylsilsesquioxane was obtained by the method given in reference [15].

2.2 Methods

Gel permeation chromatography. The technique uses a glass tube of 1000 mm in length with an internal diameter of 10 mm, filled with copolymer of styrol and 2 % divinylbenzol, with granules of diameter 0.08-0.10 mm. Toluene serves as the eluent, and the flow rate is 1 ml/minute. The free volume is determined by the volume at the peak maximum of high-molecular silicone rubber of approximately 20000 molecular weight. The free volume of the glass tube is 30 ml. The weighed portion is 0.15–0.25 g.

The detection is conducted by a weight method according to the maintenance of the dry residue in 3 ml fractions. Tributyltin acetate with M = 596, tris(tributylstannoxy) phenylsilane with M = 1023 and methylphenylcyclotrisiloxane with M = 408 were used for calibration.

The \(^{29}\text{Si NMR}\) spectra were registered by a MX 260 spectrometer with working frequency of 65.38 MHz and a Bruker WM-250 spectrometer with a working frequency of 250 MHz, in CDCl\(_3\) solution, with TMS as the internal standard.

The \(^{29}\text{Si NMR}\) spectra were registered by a Bruker Ultrashield 400 Plus spectrometer with a working frequency of 400 MHz, in CDCl\(_3\) solution, with TMS as the internal standard.

IR-spectra were registered by a Specord 75-IR device in CH\(_2\)Cl\(_2\) and a Spectrum 1000 BX-II in CH\(_2\)Cl\(_2\) and on a thin layer.

Mass-spectra were registered by a LKB-SOOS spectrometer (70 eV).

2.3 Synthesis of Polyphenylsilsesquioxane

A mixture of PhSiCl\(_3\) (200 ml, 1.253 mol) and diethyl ether (200 ml) was added dropwise with vigorous stirring to a biphasic mixture of water/diethyl ether (600 ml, 2:1) in a 2 l round bottomed flask cooled in an ice bath. After the addition was complete, the mixture was stirred for a further 30 min. The upper organic layer was separated and washed with water until neutral, then dried with anhydrous MgSO\(_4\). The organic solvent was removed under reduced pressure. 159.2 g (98.5 %) of PPS is isolated.

2.4 Syntheses of Polyvinylsilsesquioxane and Polymethylsilsesquioxane

These syntheses were analogous to the synthesis of PPS using ViSiCl\(_3\), MeSiCl\(_3\) and the addition of n-butanol (200 ml) to a biphasic mixture of water/diethyl ether.

2.5 Synthesis N\(_2\) 1

Fifty millilitres of n-butanol is added to a poly(dibutylstanno)phenylsilsesquioxane solution of 10.1 g (0.020 mol), structure \([\text{Bu}_2\text{SnO}[\text{PhSiO}_1\text{]}_2\text{]}\) in 100 ml of toluene. The synthesis was conducted at the boiling temperature of the solvents until complete water collection into a Dean-Stark trap over 10 hours. As a result, 7.7 g (50.5 % in tin) of bis(dibutoxyphenylsiloxyl) dibutylstannane, structure \([\text{Bu}_2\text{Sn}[\text{OSi}(\text{Ph})(\text{OC}_4\text{H}_9\text{})_2]\text{]}\) was isolated after vacuum distillation at b.p. 107-109 °C/0.01 mm Hg. Found (%): Si, 7.2; Sn, 15.3. Calculated (%): Si, 7.3; Sn, 15.5. IR (CCl\(_4\), \(\nu\text{cm}^{-1}\)) : 1040 (Si-O from Si-O-(Sn)), 1090 (Si-O from Si-O-(C)), 1132 (Si-O + Si-Ph), 980 (Sn-O), 1429 (Si-Ph), 1464 (Sn-C), 2800-3000 (C-H from C\(_6\)H\(_5\)). \(^{13}\text{C NMR}\) (CDCl\(_3\), ppm from TMS): 135.0, 130.4, 128.0 (C\(_6\)H\(_5\)-); 63.0 (-CH\(_2\)C), 1132 (Si-O + Si-Ph), 980 (Sn-O), 1429 (Si-Ph), 1464 (Sn-C), 2800-3000 (C-H from C\(_6\)H\(_5\)). \(^{29}\text{Si NMR}\) (CDCl\(_3\), ppm from TMS): -57.7. MS (m/z): 709 \(\{\text{Bu}_2\text{Sn}[\text{OSi}(\text{Ph})(\text{OC}_4\text{H}_9\text{})_2]\}\) : 251 \{ Si(Ph)(OC\(_4\text{H}_9\text{})_2\}\}; 232 \{ \text{Bu}_2\text{Sn}\} .

The bottoms residue yield was 4.5 g (45.0 % tin), structure \([\text{Bu}_2\text{SnO}[\text{PhSiO}_1\text{]}_2\text{]}\). Found (%): Si, 11.1; Sn, 23.7. Calculated (%): Si, 11.0; Sn, 23.5.

2.6 Synthesis N\(_2\) 2

For this synthesis, 10.0 g (0.040 mol) of DBO and 100 ml of n-butanol were added to a solution of 10.3 g (0.080 mol) PPS in 50 ml of toluene. The synthesis was conducted in conditions analogous to the previous (synthesis N\(_2\) 1). As a result, 16.4 g (53.5 % tin) of the target product, structure \([\text{Bu}_2\text{Sn}[\text{OSi}(\text{Ph})(\text{OC}_4\text{H}_9\text{})_2]\text{]}\) was isolated after deep-vacuum distillation at b.p. 107-109 °C/0.01 mm Hg. Found (%): Si, 7.5; Sn, 15.4. Calculated (%): Si, 7.3; Sn, 15.5.

The bottoms residue yield was 9.3 g (45.8 % tin), structure \([\text{Bu}_2\text{SnO}[\text{PhSiO}_1\text{]}_2\text{]}\). Found (%): Si, 11.1; Sn, 23.8. Calculated (%): Si, 11.0; Sn, 23.5.

2.7 Synthesis N\(_2\) 3

This procedure was analogous to synthesis N\(_2\) 2 with the solvent ratio of toluene and n-butanol changed to 2:1. First, 2.5 g (0.010 mol) of DBO and 15 ml of n-butanol were added to 2.6 g (0.020 mol) of PPS in 30 ml of toluene.