

Synthesis of Peralkylpolysilanes and Peralkyoligostannanes

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Introduction

Polysilanes, $(-RR'Si-)_n$, the silicon analogs of polyalkenes are of considerable synthetic interest due to their commercial potential. Polymers of this nature have been studied extensively and their applications as electro-optical coatings on semiconductor substrates and a photoresists in microlithography is known.¹ Theoretically, polymers of this nature, with heavier atoms such as germanium or tin in the backbone are expected to have a higher photochemical sensitivity and narrower band gaps.² Recent synthesis of the high molecular weight polystannanes has allowed for the examination of their structural and electronic properties. For example, Dr. T. D. Tilley and V. Y. Lu have shown that the σ - σ^* transitions for poly(dialkyl)stannanes are red-shifted by ca. 30-70 nm with respect to those for comparable polysilanes.^{3,4}

While the electronic and chemical properties of the peralkylpolysilanes and peralkyoligostannanes is known, little is known about derivatives containing more than one Si-Sn bond. These compounds are of commercial interest because of their potential to

¹ N. R. Neale, T. D. Tilley, *Tetrahedron* **2004**, *60*, 2407.

² Pitt, C. G. In *Homoaromatic Rings, Chains, and Macromolecules of Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier: New York, 1977; Chapter 8.

³ *Ibid.*

⁴ Lu, V. Y.; Tilley, T. D.; *Macromolecules* **2000**, *33*, 2403.

precursors for novel polymeric materials, catalytic systems, or the modification of surfaces. They are also of considerable interest due to their novel structural behavior.⁵

The goal of this project was to synthesize and study per-*tert*-butylated polysilane and per-*tert*-butylated oligostannanes with a chain length of varying from 1 to 4. The compounds would then be analyzed via ²⁹Si-NMR, ¹¹⁹Sn-NMR, and Ultraviolet Spectroscopy. The data would then be compared to Si-Sn bonded chains with the same substituents and a chain length of 2.

Reaction Scheme

The attempted syntheses of the previously mentioned compounds were done by employing the Wurtz Coupling reaction scheme. This scheme can be classified as a classic organic chemistry reaction and it involves the use of two alkyl-halides to produce a dimer. The reaction proceeds with the following mechanism⁶:

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

The benefit of this reaction is that it is a single-pot reaction minimizing the exposure to the atmosphere that can occur during transfers. After a period of about 4 hours, the compounds that are being studied decompose in the atmosphere.

General Experimental

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk line techniques. Dry, oxygen-free solvents were used throughout. Cyclohexane

⁵ Fischer, R; Uhlig, F.; *Coordination Chemistry Reviews* **2005**, 249, 2075.

⁶ <http://www.organic-chemistry.org/frames.htm>

was dried over sodium/benzophenone. All other solvents were dried in the same manner through the university's distillation system. $\text{Cl}(\text{Si}^t\text{Bu}_2)_2\text{Cl}$ and $\text{ClSi}^t\text{Bu}_2\text{Cl}$ was purchased commercially and used as received.

$\text{Cl}(\text{Sn}^t\text{Bu}_2)_4\text{Cl}^7$: a solution of *tert*-butylmagnesium chloride was prepared from magnesium and *tert*-butyl chloride in tetrahydrofuran. Methyl iodide was added in trace amounts as a starter. The resulting solution was filtered and treated with *tert*-butyltin dichloride in portions over 20 minutes while stirring. The resulting mixture was then refluxed for 4 hours. After cooling to room temperature the mixture was filtered, affording a yellow powder. The resulting ring cleaved by adding a Cl_2/CCl_4 solution drop wise.

$\text{H}(\text{Si}^t\text{Bu}_2)_2\text{H}^8$: *t*Bu₂SiHCl and an equimolar quantity of potassium were refluxed in cyclohexane for 3 hours. The potassium was first cut into small pieces in a pentane bath and then added to the cyclohexane in a 3-neck flask equipped with mechanical stirrer, dropping funnel, and nitrogen inlet. The potassium was then heated to reflux, affording a light blue solution. Once reflux commenced, the silane was added drop wise to the reaction mixture. After 3 hours of reflux, the solution was caramel colored. The product was isolated via fractional distillation.

$\text{H}(\text{Si}^t\text{Bu}_2)_4\text{H}^9$: A solution of 2 equivalents Li is prepared in 40ml THF. The Li was prepared by taking a Li rod and hammering it into a thin sheet, which was then rolled up and added to the schlenk-tube. After cooling the mixture in an ice water bath, *t*Bu₂SiCl₂ is added and the solution is stirred while slowly warming to room temperature. The

⁷ Farrar, W. V.; Skinner, H. A. *J. Organometal. Chem.* **1964**, *1*, 434.

⁸ Triplett, K.; Curtis, M. D. *J. Organomet. Chem.* **1980**, *107*, 23.

⁹ *Ibid.*

resulting solution is then extracted in 30ml cyclohexane affording a light yellow solution. The resulting mixture is then concentrated, treated with water, and extracted in cyclohexane. The solvent was then removed under vacuum.

Results

The experiments did not proceed as expected. Although the first two compounds were known syntheses, I was unable to reproduce the achieved results. Each trial of the experiment gave the same product mixture, none of which was the desired product. This led me to the conclusion that the researchers who published the known syntheses of these compounds may or may not have excluded vital information from their journal article. This may have either been an oversight on their part or a blatant exclusion to keep the results and compound to themselves.

The third compound I attempted to make is a compound that has as of now, not yet been synthesized. The procedure was adopted from one used to make a similar compound. Unfortunately, this procedure did not lead to the desired products. However, a valuable lesson was learned from this endeavor because the literature that clearly stated that the method I would be employing does not yield the target compound. Unfortunately, because I did not take the time to thoroughly read the last page of the article and I took the previous information for granted. The products I did get when running that reaction were the products expected for that specific reactions. Due to the bulk of the reactants, the ring is not formed in the expected manner.

Conclusions

Although the experiments did not proceed as expected, I was still able to learn a lot this summer. I was able to refine and develop new schlenk-line techniques. The

chemical processes were very similar, however, the glassware that was employed in the lab was different, necessitating the new techniques. In addition to the new techniques, I also learned how to analyze different sets of data. Previously, I had never had exposure to ^{29}Si -NMR or ^{119}Sn -NMR or Ultraviolet Spectroscopy.

Also, valuable lessons were learned as far as how to best gather information from journal articles and how to report attained results properly. In the future, when it is time to publish results in a journal, I will know how to do it correctly and accurately.