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Reaction Pathways towards Novel Open Chain and Cyclic Stannasilanes

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Cyclic stannasilaalkanes are formed by rearrangement reactions of open chain and branched Si-Sn derivatives. Furthermore, we report on first attempts towards three membered Si-Sn rings via lithio or potassio substituted stannanes.

Keywords: silicon-tin compounds; stannanes; oligosilanes

INTRODUCTION

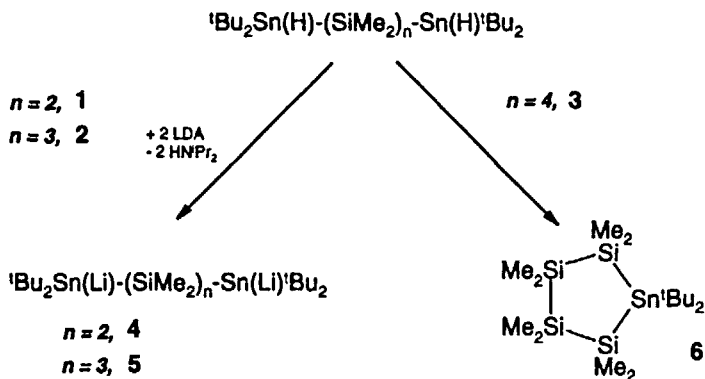
Recently, we reported on cyclic Si-Sn compounds^[1, 2] which were synthesized using 'one pot' reactions of oligomeric silanes with chlorostannanes in the presence of magnesium or stepwise syntheses via hydrido and chloro substituted Si-Sn chains^[3].

Here we describe base-catalyzed ring closing reactions of linear and branched stannasilane chains yielding unusual five or six membered rings containing tin atoms in addition to silicon.

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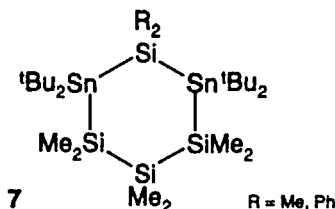
RESULTS AND DISCUSSION

As in recent reactions, hydrido-substituted α,ω -stannaoigosilanes ($n=2$, 1; $n=3$, 2; $n=4$, 3) were used as precursors. Reacting 1 with two equivalents of lithium diisopropyl amide (LDA) results in α,ω -dimetallated species 4 and 5 with Si chain lengths of two and three atoms. Surprisingly, in case of the tetrasilane chain the reaction quantitatively yields the stannatetrasilacyclopentane 6.

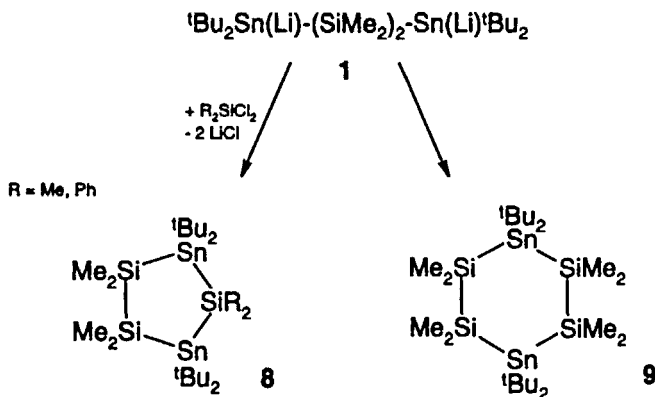


Scheme 1: Reactions of 1-3 with 2 equiv. of LDA

Up to now, it was not possible to clarify the reaction mechanism for the cleavage of the di-tert.butylstannyl group. The α,ω -dimetallated species 5 with three Si atoms in the chain is then reacted with R_2SiCl_2 yielding the expected six-membered ring 7; no byproducts are observed.

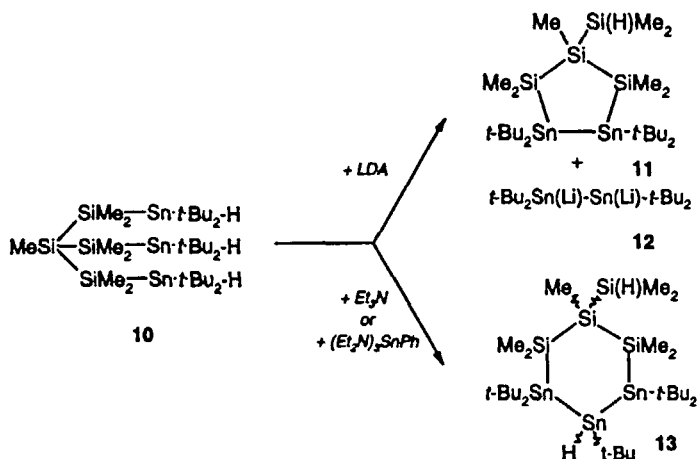


When reacting the 1,4-dilithio-substituted stannasilane chain **4** with $R_2\text{SiCl}_2$, we find compound **8** which is accompanied by the unexpected byproduct **9**. Seemingly, a reaction similar to the preparation of **6** takes place. In contrast to the four-membered silicon chain, the shorter two-membered chain cannot react on an intramolecular reaction pathway, therefore two Sn-Si-Si fragments combine to compound **9**.



Scheme 2: Formation of **8** and **9**

Reactions of the branched stannasilane **10** with three equivalents of LDA yield the cyclopentane **11** and the distannide **12**. Similar to the reaction of the open chain tetrasilane, no lithiated Si-Sn products can be observed.^[4]

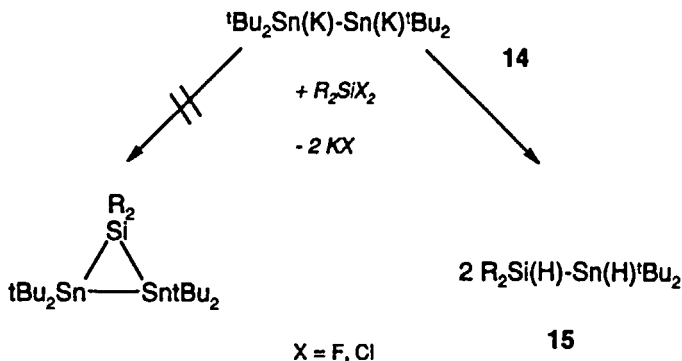


Scheme 3: Base-catalyzed rearrangement of **10**

Treatment of **10** with amines lead to an amine-catalyzed intramolecular ring closing reaction yielding the six membered ring **13**. The formation of **13** is the result of a silicon-tin, and surprisingly a tin-carbon bond cleavage; in addition, two tin-tin bonds have been formed.^[4]

First attempts towards three-membered Si-Sn rings by reacting the dipotassio distannide **14** with diorganodichloro- or difluorosilanes did not

result in the expected ring systems. Surprisingly, the 1,2-dihydridostannasilanes **15** are formed in nearly quantitative yield.



Scheme 4: Reaction of **14** with diorganodichlorosilanes

Further studies towards the new 1,3-dichloro substituted disilylstannes **16** and 1-sila-2,3-distannapropanes **17** are in progress and will be reported later.



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