

**Unexpected fragmentation of bis(triarylstannanethiocarbonyl)disulfides, formation and X-ray structure of triarylstannyl triarylstannanecarbodithioates.**

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The synthesis of bis(triarylstannanethiocarbonyl)disulfides was attempted by oxidation of lithium triarylstannanecarbodithioates with molecular iodine. Unexpectedly, the desired compounds are highly unstable and undergo subsequent fragmentation giving triarylstannyl triarylstannanecarbodithioates. The proposed mechanism for this transformation assumes intramolecular nucleophilic substitution with formation of six-membered ring transition complex, stabilized by interaction between tin and thiocarbonyl sulfur atom. Obtained compounds were identified by mass-spectrometry and NMR spectroscopies, and their structures were analyzed by X-ray diffraction. These molecules show the existence of intramolecular non-bonding interactions between the sulfur atoms of the thiocarbonyl moieties and tin atoms. These interactions reflect the tin - sulfur affinity and are the main driving force in the fragmentation of bis(triarylstannanethiocarbonyl)disulfides.

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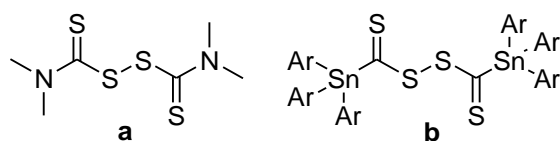
### **Introduction**

Processed natural latex from the Castilla elastic tree was used by Mesoamericans as early as 1600 B.C. for the manufacture of elastic balls, human figurines and other rubber artifacts [1]. However historically the discovery of vulcanization using elemental sulfur has been credited to Charles Goodyear [2]. Nowadays the vulcanization of natural or synthetic rubber is

one of the most important industrial processes. Generally, it involves the cross-linking of individual polymer chains with sulfide and polysulfide chains. Sulfur, by itself, is a slow vulcanizing agent and does not vulcanize synthetic elastomers. Even with natural rubber, large amounts of sulfur, as well as high temperatures and long heating periods are necessary to lead to even ineffective crosslinking, with unsatisfactory

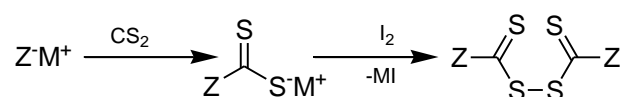
strength and ageing properties. The high level performance required by today's rubber industry can only be provided by vulcanization accelerators such as dithiocarbamates, thiurams, thioureas, thiazoles and sulfenamides [3]. Among these, thiuram disulfides such as tetramethylthiuramdisulfide (TMTD) (chemical structure **a** in **Chart 1**) are some of the most effective candidates for rubber vulcanization because of a low S-S homolytic bond dissociation energy and high stability of generated radicals.

Recently, main group element-substituted bis(thiocarbonyl)disulfides have attracted significant attention as potential vulcanization accelerators [4]. Meanwhile, organotin chemistry has been strongly developed over the last century, mainly because the derived molecules are extremely important from a biological standpoint and have a rich free-radical chemistry [5,6]. The combination of these two facts led us to examine the access to tin substituted bis(thiocarbonyl)disulfides (Structure **b** in **Chart 1**), with triaryl tin substituents.



**Chart 1.** Structures of tetramethylthiuramdisulfide (TMTD) (**a**); bis(triarylstannanethiocarbonyl)disulfides (**b**) with Ar = Phenyl, *p*-Tolyl.

Bis(thiocarbonyl)disulfides can be easily prepared by oxidation of the carbodithioate salts with molecular iodine which generally proceeds in quantitative yield [7]. The overall synthetic pathway is depicted in **Scheme 1**.



**Scheme 1.** Synthesis of bis(thiocarbonyl)disulfides through carbodithioate salts. Z = alkyl, aryl, OR, SR, NRR', M = alkali metal.

Unexpectedly, treatment of lithium triarylstannanedithioates with iodine leads to formation of triarylstannyl triarylstannanecarbodithioates as depicted in **Scheme 2**. Herein we describe this reaction, and the related structures of the corresponding products.

## Results and discussion

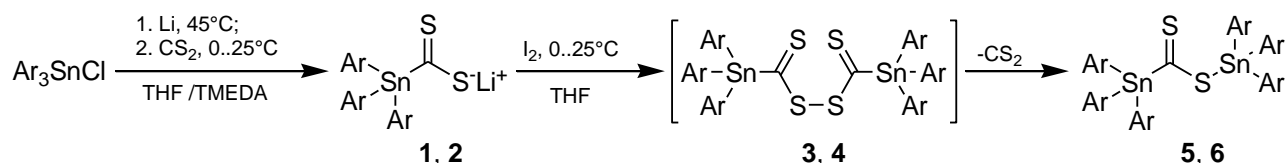
A limited number of stannanedithioesters have been reported in the literature [8-13]. The stannyl group connected to the thiocarbonylthio function is usually triphenylstannane moiety, but also two triarylstannanes with *ortho*- and *para*-tolyl [8] groups have been studied. Finally, the only described trialkyltin dithioester possessed a tricyclohexylstannyl group [9]. This class of compounds was studied in the eighties but not to a great extent, and only two crystal structures were determined [8, 13], namely for methyl and benzyl triphenylstannanecarbodithioates. In this study we describe a new access to this type of compounds.

Lithium triarylstannanecarbodithioates **1**, **2** (**Scheme 2**) were prepared according to a slightly modified literature procedure [8] by addition of triaryl tin anion **3** to carbon disulfide in presence of TMEDA (**Scheme 2**).

Treatment of lithium triphenylstannanedithioate **1** with one equivalent of molecu-

lar iodine led after treatment to a pink crystalline solid insoluble in water and slightly soluble in organic solvents.  $^{119}\text{Sn}$  NMR indicated the presence of two non-equivalent tin nuclei in the obtained molecule, with chemical shifts of -177.3 and -105.0 ppm. Detailed investigation with NMR and X-ray crystallographic studies allowed the product to be identified as previous-

ly described triphenylstannyl triphenylstannanecarbodithioate **5** [9]. Analogous treatment of lithium tri(*p*-tolyl)stannanecarbodithioate **2** allowed tri(*p*-tolyl)stannyl tri(*p*-tolyl)stannanedithioate **6** to be isolated. All these transformations are depicted in **Scheme 2**. Both compounds are formed in good yields, without significant formation of side products.

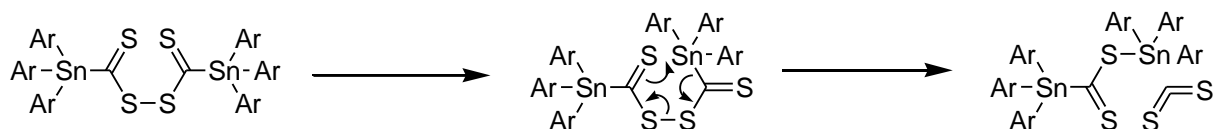


**Scheme 2.** Formation of triarylstannyl triarylstannanecarbodithioates with Ar = Ph (**1, 3, 5**), *p*-Tolyl (**2, 4, 6**).

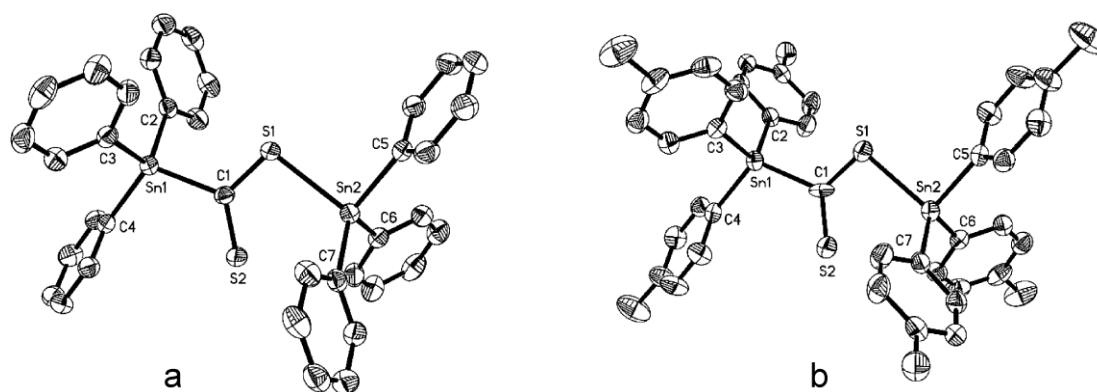
Compounds **5, 6** were also prepared by reaction of lithium triarylstannanecarbodithioates **1, 2** with the corresponding triaryltin chlorides. The desired compounds were isolated in good yields and are identical to those formed by reaction of **1, 2** with iodine. Compounds **5, 6** were fully characterized by mass spectrometry and spectroscopic methods. Characteristics obtained for **5** are conformed to those previously described in literature [9].

Due to the high yield of esters **5** and **6**, and negligible formation of hexaaryldistannanes, we assumed that the mechanism proceeds via the formation of the

bis(triarylstannanethiocarbonyl)disulfides **3, 4** as unstable intermediates. It is known that tin – sulfur bond formation can be the driving force for some chemical transformations such as Barton-McCombie deoxygenation [14] or intramolecular nucleophilic substitution ( $\text{S}_{\text{Ni}}$ ) in triphenyltinchlorothioformate [15]. The proposed mechanism of transformation of **3, 4** into **5, 6** respectively assumes  $\text{S}_{\text{Ni}}$  with formation of six-membered ring transition complex, stabilized by Sn-S coordination, synchronous cleavage of S-S and Sn-C bonds and formation of new Sn-S bond and  $\text{CS}_2$  (**Scheme 3**).



**Scheme 3.** Proposed mechanism for the fragmentation of the bis(stannylthiocarbonyl)disulfides.



**Figure 1.** The molecular structure of **5** (a) and **6** (b) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and disordered atoms have been omitted for clarity.

The crystallographic data of compounds **5**, **6** are summarized in **Table 1** and molecular views are reported in **Figure 1**.

**Table 1.** Crystallographic data for **5** and **6**

	<b>5</b>	<b>6</b>
chemical formula	C <sub>37</sub> H <sub>30</sub> S <sub>2</sub> Sn <sub>2</sub>	C <sub>43</sub> H <sub>42</sub> S <sub>2</sub> Sn <sub>2</sub>
<i>M<sub>r</sub></i>	776.11	860.27
crystal system	trigonal	monoclinic
space group	<i>R</i> $\bar{3}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> [Å]	31.8036(7)	10.7591(4)
<i>b</i> [Å]	31.8036(7)	16.4867(5)
<i>c</i> [Å]	10.9295(5)	11.6250(4)
$\alpha$ [°]	90	90
$\beta$ [°]	90	105.298(2)
$\gamma$ [°]	120	90
<i>V</i> [Å <sup>3</sup> ]	9573.8(5)	1989.00(12)
<i>Z</i>	12	2
$\rho_{calc}$ [g cm <sup>-3</sup> ]	1.615	1.436
$\lambda$ [Å]	0.71073	0.71073
<i>T</i> [K]	193(2)	193(2)
$\mu$ (MoK $\alpha$ ) [mm <sup>-1</sup> ]	1.721	1.388
crystal size (mm <sup>3</sup> )	0.20 x 0.20 x 0.20	0.18 x 0.16 x 0.04
GOF on F <sup>2</sup>	1.017	1.247
<i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0318	0.0264
<i>wR</i> <sup>2</sup> (all data)	0.0695	0.1142
Largest difference peak and hole [e Å <sup>-3</sup> ]	0.860 and -1.368	0.704 and -0.850

These compounds exist in two different space groups, but the inequality in crystalline system does not generate any significant differences in the geometry. Selected parameters of

planar SnCS<sub>2</sub> unit for compounds **5** and **6** and previously described methyl [8] and benzyl [13] triphenylstannyldithioesters are collected in **Table 2**. Almost all the key bond lengths and angles are similar in the listed compounds. The only remark concerns the angle around the  $\sigma$ -bonded sulfur S1. This angle decreases when one moves from carbon, in the case of the methyl and the benzyl groups, to the tin atom of the compounds **5** or **6**. This observation can be explained by the existence in these last compounds of an intramolecular coordination between sulfur S2 of the thiocarbonyl group and Sn2 atom. Indeed, the Sn2 – S2 distances observed in **5** (3.246 Å) and **6** (3.227 Å) are longer than the sum of their covalent bond radii (2.44 Å) [16], but significantly less than the sum of van der Waals radii of both atoms (3.96 Å) [17]. A similar interaction has been reported in the model compound *p*-TolylCS<sub>2</sub>SnPh<sub>3</sub> [18] with penta-coordinated tin which showed a S2-Sn bond length of 3.207(2) Å and a C1-S1-Sn angle of 100.4(2). Formation of C1-S1-Sn2-S2 four-membered cycle can be assumed to be an addi-

tional driving force in the fragmentation of disulfides **3** and **4**.

**Table 2.** Selected bond lengths (Å) and angles (°) from the Ar<sub>3</sub>SnCS<sub>2</sub>R structures. R = Me [8], benzyl [13] and triarylstannyl groups (**5**, **6**).

	[8]	[13]	<b>5</b>	<b>6</b>
Sn1-C1	2.139(9)	2.181(4)	2.161(5)	2.187(1)
C1-S2	1.66(2)	1.629(4)	1.632(6)	1.619(9)
C1-S1	1.64(2)	1.695(4)	1.714(6)	1.656(8)
S1-Sn2	-	-	2.530(2)	2.551(3)
S2-Sn2	-	-	3.246	3.227
S1-C'2	1.79(5)	1.820(5)	-	-
Sn1-C1-S2	120.8(8)	122.0(2)	119.3(3)	117.5(4)
Sn1-C1-S1	118.6(6)	112.3(2)	117.4(3)	116.1(6)
S1-C1-S2	121(1)	125.7(3)	123.3(3)	126.4(8)
C1-S1-Sn2	-	-	99.9(2)	98.4(5)
C1-S1-C'2	105(2)	105.9(2)	-	-

### Conclusions

Bis(triphenylstannanethiocarbonyl)disulfide synthesis was attempted by oxidation of lithium triarylstannanecarbodithioates with molecular iodine. Unexpectedly, the desired compounds are highly unstable and undergo subsequent fragmentation giving triarylstannyl triarylstannanecarbodithioates. The proposed mechanism of this transformation assumes intramolecular nucleophilic substitution with formation of six-membered ring transition complex, stabilized by interaction between the tin and the sulfur atom of the thiocarbonyl group.

The obtained compounds were identified by mass spectrometry and NMR spectroscopies, and their structures were analyzed by X-ray diffraction. Their molecules show the existence of intramolecular non-bonding interactions between the sulfur atom of the thiocarbonyl and

tin. These non-bonding interactions reflect the tin - sulfur affinity and are the main driving force in the fragmentation of the bis(triphenylstannanethiocarbonyl)disulfides.

The synthesized products could potentially be used in free radical transformations as reagents for radical reduction [19] or regulators in RAFT polymerization [20, 21]. These features will be subject to future investigation.

### Experimental part

NMR spectra were recorded using a Bruker AMX 300 spectrometer at 298K. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR). The external chemical shift reference for <sup>119</sup>Sn is Me<sub>4</sub>Sn. IR spectra were recorded using a Thermo Fischer Nexus 6700 FTIR spectrometer in ATR mode. High resolution mass spectra were measured with a Waters GCT Premier in the chemical ionisation mode (CH<sub>4</sub>). Diffraction measurements of single crystals were made at low temperature on a Bruker-AXS SMART APEX II diffractometer (**5**) or on a Bruker-AXS APEX II QUAZAR diffractometer (**6**) equipped with a 30W air-cooled micro-focus source, using MoK $\alpha$  radiation ( $\lambda = 0.71073\text{Å}$ ). Phi- and omega- scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied [22]. The structures were solved by direct methods (SHELXS-97) and refined using the least-squares method on  $F^2$  [23]. All non-H

atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically at calculated positions using a riding model.

CCDC-1011600 (**5**) and CCDC-1011601 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre [24].

THF, 1,4-dioxane and CS<sub>2</sub> were purified by conventional methods before use. Tri(*p*-tolyl)tin chloride was prepared by literature method [25]. Li wire (Aldrich, ≥98%), *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, Aldrich, ≥99.5%), triphenyltin chloride (Fluka, 95%) and iodine (Aldrich, 99.7%) were used as received.

All the syntheses were carried out using standard Schlenk and high vacuum line techniques under an argon atmosphere.

**Preparation of lithium triarylstannanecarbodithioates 1, 2:** A solution of triaryltin chloride (6 mmol) and TMEDA (1 mL, 6.67 mmol) in 20 mL of dry THF was stirred with Li wire (84 mg, 12 mmol) at 45 °C until it has totally dissolved. Then CS<sub>2</sub> (1.08 mL, 18 mmol) was added dropwise at 0 °C and stirred for 30 min at room temperature. The resulting brown-red solution was evaporated under reduced pressure and solid was dissolved in 30 ml of dry THF (resulting concentration ~0.2 M). This solution was used in the next syntheses as it is.

**Reaction of lithium triarylstannanecarbodithioates 1, 2 with iodine:** Lithium triarylstannanecarbodithioate solution (10 ml, 2 mmol) was added at once to cooled solution of iodine (2.54 g, 1 mmol) in 10 ml of dry THF with vigorous stirring. Temperature of the reaction mixture instantly elevated up to 25-30 °C and colour was changed into pink. Reaction mixture was concentrated under reduced pressure and chromatographed over silica gel using first petroleum ether as eluent to remove impurities and then dichloromethane to collect the pink fraction. Product was recrystallized from appropriate solvent (dichloromethane for **5** and pentane for **6**). Yields: **5** (0.65 g, 84%), **6** (0.66 g, 77%).

**Triphenylstannyl triphenylstannanecarbodithioate 5.** Pink crystals. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>, 333K): δ = 7.05-7.20 (*m*, 18H, 3H, 4H-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn), 7.5-7.85 (*m*, 12H, 2H-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn); <sup>13</sup>C{<sup>1</sup>H} NMR (75.47 MHz, C<sub>6</sub>D<sub>6</sub>, 333K): δ = 129.19, 129.74, 129.78, 137.18, 137.47, 138.83, 140.00, 234.06; <sup>119</sup>Sn{<sup>1</sup>H} NMR (98.2 MHz, C<sub>6</sub>D<sub>6</sub>, 333K, external Me<sub>4</sub>Sn): δ = -177.3, -105.0, IR: 1038.5 cm<sup>-1</sup> (C=S). HRMS: M<sup>+</sup> found 777.9904, calc. 777.9932.

**Tri(*p*-tolyl)stannyl tri(*p*-tolyl)stannanecarbodithioate 6.** Pink crystals. <sup>1</sup>H NMR (300.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 2.04 (*t*, <sup>6</sup>J<sub>Sn,H</sub> = 2.1 Hz, 9H, (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnS), 2.06 (*t*, <sup>6</sup>J<sub>Sn,H</sub> = 2.1 Hz, 9H, (4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnC=S), 6.92-7.08 (*m*, 12H, 3H-(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn), 7.55-

7.85 (*m*, 12H, 3H-(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn); <sup>13</sup>C{<sup>1</sup>H} NMR (75.47 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 21.42, 21.46, 130.02, 135.20, 136.26, 137.25, 137.48, 139.43, 226.21; <sup>119</sup>Sn{<sup>1</sup>H} NMR (98.2 MHz, C<sub>6</sub>D<sub>6</sub>, 298K, external Me<sub>4</sub>Sn): δ = -169.2, -96.9. IR: 1038 cm<sup>-1</sup> (C=S). HRMS: M<sup>+</sup> found 860.0794, calc. 860.0766.

**Reaction of 1, 2 with corresponding triaryltin chlorides :** Lithium triarylstannane-carbodithioate solution (10 ml, 2 mmol) was added dropwise to cooled solution of corresponding triaryltin chloride (2 mmol) in 10 ml of dry THF with vigorous stirring. Reaction mixture was additionally stirred for 30 min at ambient temperature. Product was isolated as described above. Yields: **5** (1.37 g, 88%), **6** (1.21 g, 70%).

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