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SYNTHESIS AND STRUCTURE CHARACTERIZATION OF (TRITOLYLSTANNYLTHIO)(TRIPHENYLSTANNYL)METHYL TRIPHENYLSTANNANECARBODITHIOATE

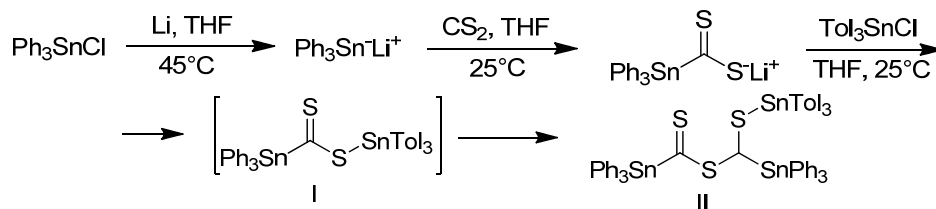
The title compound $\text{Ph}_3\text{SnCS}_2\text{CH}(\text{SSnTol}_3)\text{SnPh}_3$ has been isolated as major product after the attempted alkylation of lithium triphenylstannanecarbodithioate by tri(*p*-tolyl)tin chloride in THF as solvent and characterized by NMR spectroscopy and elemental analysis. The pink crystals of this compound have been grown from pentane/dichloromethane solution. The solid state structure has been established by X-ray crystallography analysis.

Keywords: organotin, thiocarbonyl, crystal structure, triphenylstannanecarbodithioate

Introduction. Molecules derived from organotin chemistry are extremely important from a biological standpoint and have a rich free-radical chemistry [1]. Recently, triarylstannanecarbodithioates have attracted our attention as potential reagents for free radical reduction [2] or as regulators in Radical Addition Fragmentation chain Transfer(RAFT) polymerization [3,4]. Only a limited number of stannanecarbodithioates are reported in the literature [5–11], and this class of compounds has not been studied to a great extent, with only four crystal structures determined so far [5,10,11]. In a recent study, we discussed the preparation and crystal structure of symmetrical triarylstannyl triarylstannanecarbodithioates with phenyl and *p*-tolyl aryl groups [11]. These structures reveal a strong non-bonded Sn-S interaction. Therefore we decided

to investigate this phenomenon further for non-symmetrical triarylstannyl triarylstannanecarbodithioates.

Herein, we describe an attempted synthesis of tri(*p*-tolyl)stannyl triphenylstannanecarbodithioate (I) according to a previously described method [11]. Lithium triphenylstannanecarbodithioate was prepared by interaction between triphenyltin lithium and carbon disulfide in dry THF. Alkylation of this salt with tri(*p*-tolyl)tin chloride afforded to isolate pink crystalline solid. Unexpectedly, the NMR spectra of isolated product did not correspond to those expected for the desired product. In particular, ^{119}Sn NMR showed the presence of three different signals. The actual structure (II) was definitively identified by X-ray diffraction measurements and confirmed by NMR experiments. The overall transformation is represented in Scheme 1:



Scheme 1. Synthetic pathway

The molecular structures of II and its central fragment are depicted in Figure 1a and b respectively. Selected bond lengths and bond angles are listed in Table 1.

The key parameters of the planar $\text{Sn}(1)\text{-CS}_2\text{-C}(2)$ fragment for the synthesized product and previously described triphenylstannyl dithioformates are compared in

Table 2. Almost all the key lengths and angles are similar, except the slightly shortened $\text{C}(1)\text{-S}(1)$ double bond and $\text{S}(2)\text{-C}(2)$ single bond and the elongated single $\text{C}(1)\text{-S}(2)$ single bond. These changes can be explained by steric hindrance around the $\text{C}(2)$ center.

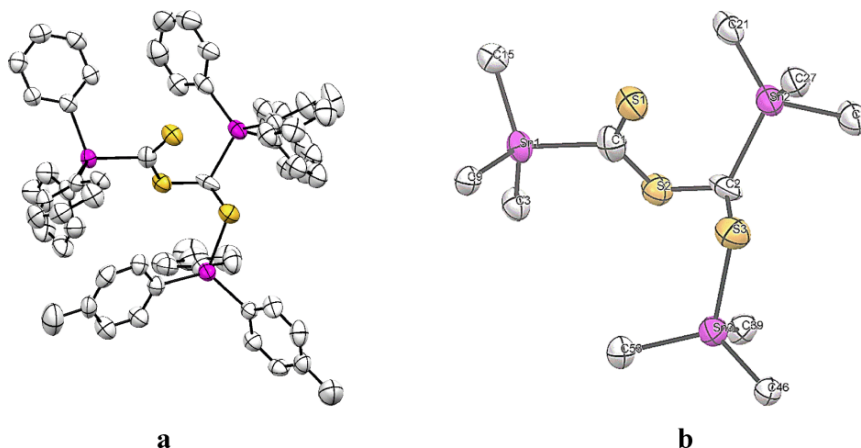


Fig. 1. (a) Molecular structure of II: Numeration and hydrogen atoms are omitted to clarify the view. (b) Structure of the central fragment: Atoms of the aromatic rings are omitted

Table 1

Bond	Selected bond lengths (Å) and bond angles (°)		
	Distance, Å	Angle	Value, °
Sn(1)-C(1)	2.162(7)	Sn(1)-C(1)-S(1)	120.7(4)
C(1)-S(1)	1.591(8)	Sn(1)-C(1)-S(2)	112.8(4)
C(1)-S(2)	1.734(8)	S(1)-C(1)-S(2)	126.5(4)
S(2)-C(2)	1.688(8)	C(1)-S(2)-C(2)	107.6(3)
C(2)-Sn(2)	2.222(6)	S(2)-C(2)-Sn(2)	120.1(4)
C(2)-S(3)	1.949(8)	S(2)-C(2)-S(3)	113.4(4)
S(3)-Sn(3)	2.426(2)	Sn(2)-C(2)-S(3)	105.8(4)
		C(2)-S(3)-Sn(3)	98.2(2)

Table 2

Selected bond lengths (Å) and angles (°) from the Ph₃SnCS₂R structures: R = Me[5], Bn[10], SnPh₃[11] and C(2) for the title compound.

	R = Me	R = Bn	R=SnPh ₃	R = C(2)
Sn(1)-C(1)	2.139(9)	2.181(4)	2.161(5)	2.162(7)
C(1)-S(1)	1.66(2)	1.629(4)	1.632(6)	1.591(8)
C(1)-S(2)	1.64(2)	1.695(4)	1.714(6)	1.734(8)
S(2)-R	1.79(5)	1.820(5)	2.530(2)	1.688(8)
Sn(1)-C(1)-S(2)	120.8(8)	122.0(2)	119.3(3)	120.7(4)
Sn-C1-S1	118.6(6)	112.3(2)	117.4(3)	112.8(4)
S1-C1-S2	121(1)	125.7(3)	123.3(3)	126.5(4)
C1-S1-R	105(2)	105.9(2)	99.9(2)	107.6(3)

While we do not have a complete mechanism for this transformation, we can assume that the principal step involves radical dimerization of the starting compound. The detailed investigation of this mechanism will be the subject of further investigation.

The ¹H NMR spectrum shows a characteristic deshielded signal for the Ph₃SnCHS₂ group with chemical shift of 5.12 ppm. The pronounced coupling into a pseudotriplet confirms the proximity of these protons to the tin ($J_{Sn,H} = 37 - 45$ Hz). The ¹¹⁹Sn{¹H} NMR gives three signals with chemical shifts characteristic of the triarylstannanecarbodithioacetate fragment (-192.3 ppm), triarylstannanedithioacetate (-133.0 ppm) and triarylstannylsulfide (-38.8 ppm) fragments. Definitive signal assignments were obtained using a ¹H-¹¹⁹Sn HMBC experiment.

In conclusion, we have identified a new and unexpected transformation of non-symmetrical triarylstannyl triarylstannanecarbodithioates, isolated the product of this transformation and fully characterized it with NMR spectroscopy and X-ray diffraction measurements. The mechanism of the transformation and chemical properties of the title product will form the subject of a future study.

Experimental section. Solvents were purified by conventional methods before use. Tri(*p*-tolyl)tin chloride was prepared according to the literature method [12]. Li wire (Aldrich, ≥98%), *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, Aldrich, ≥99.5%), CS₂ (Aldrich, ≥99%) and triphenyltin chloride (Fluka, 95%) were used as received. All syntheses were carried out using standard Schlenk and high vacuum line techniques under an argon atmosphere. NMR spectra were recorded using a Bruker AMX 300 spectrometer at 298 K in CDCl₃. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (¹H NMR). The external chemical shift reference for ¹¹⁹Sn is Me₄Sn. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O elemental analyzer.

Synthetic procedure. A solution of triphenyltin chloride (1.16 g, 3 mmol) and TMEDA (0.5 mL, 3.33 mmol) in 10 mL of dry THF was stirred with Li wire (42 mg, 6 mmol) at 45 °C until it had totally dissolved. Then CS₂ (0.54 mL, 9 mmol) was added dropwise at 0 °C and stirred for 30 min at room temperature. The resulting brown-red solution was added dropwise to cooled solution of tri(*p*-tolyl)tin chloride (1.29 g, 3 mmol) in 10 mL of dry THF with vigorous stirring. The reaction mixture was stirred overnight at ambient

temperature, concentrated under reduced pressure and chromatographed over silica gel using first petroleum ether as eluent to remove impurities and then CH₂Cl₂ to collect the pink fraction. The product was crystallized from pentane-CH₂Cl₂. Yield: 0.95 g (52%). ¹H NMR (300.13 MHz, C₆D₆, 333K): δ = 7.65-7.4 (*m*, 6H, 2H-(4-CH₃C₆H₄)₃Sn), 7.43-7.19 (*m*, 30H, (C₆H₅)₃Sn), 7.06-6.98 (*m*, 6H, 3H-(4-CH₃C₆H₄)₃Sn), 5.12 (*s*, 1H, CH), 2.30 (*s*, 9H, (4-CH₃C₆H₄)₃Sn); ¹¹⁹Sn{¹H} NMR (98.2 MHz, C₆D₆, 333K, external Me₄Sn): δ = -192.3 (Ph₃SnCS₂), -133.0 (Ph₃SnCH), -38.8(*p*-Tol₃Sn). Anal. Calcd. (%) for C₅₉H₅₂S₃Sn₃: C, 58.40; H, 4.32; S, 7.93. Found (%): C, 58.52; H, 4.36; S, 7.84.

Crystal structure determination. Diffraction measurements of single crystals were made at 193(2) K on a Bruker-AXS SMART APEX II diffractometer equipped with a 30W air-cooled microfocus source, using MoK α radiation ($\lambda = 0.71073$ Å). Phi- and omega- scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied [13]. The structures were solved by direct methods (SHELXS-97) and refined using the least-squares method on F^2 [14]. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically at calculated positions using a riding model.

Crystal data. C₅₉H₅₂S₃Sn₃, $M_r = 1212.25$, pink block, crystal size 0.18 mm x 0.16 mm x 0.08 mm, triclinic, space group P-1, $a = 10.0018(5)$ Å, $b = 13.0978(8)$ Å, $c = 20.4583(12)$ Å, $\alpha = 87.130(3)^\circ$, $\beta = 87.053(3)^\circ$, $\gamma = 79.071(3)^\circ$, $V = 2625.8(3)$ Å³, $T = 193(2)$ K, $Z = 2$, $\rho_{\text{calc}} = 1.533$ g·cm⁻³, $\mu = 1.572$ mm⁻¹ (for MoK α , $\lambda = 0.71073$ Å), absorption correction: semi-empirical from equivalents, $F(000) = 1206$, $T_{\text{min}} = 0.7651$, $T_{\text{max}} = 0.8864$, 50057 reflections measured, 10698 unique ($R_{\text{int}} = 0.0608$), θ range 2.94° to 26.37°, data = 10698, parameters = 620, restraints = 213, the final $R = 0.0547$, $wR^2 = 0.1292$ ($I > 2\sigma(I)$), Goodness-of-fit on $F^2 = 1.035$, ($\Delta\rho_{\text{max}}$) = 3.0033 and ($\Delta\rho_{\text{min}}$) = -1.561 e Å⁻³.

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СИНТЕЗ І СТРУКТУРНА ХАРАКТЕРИЗАЦІЯ (ТРИТОЛІЛСТАНИЛТІО)(ТРИФЕНІЛСТАНИЛ)МЕТИЛ ТРИФЕНІЛСТАНАНКАРБОДИТІОАТУ

(Тритолілстанілтіо)(трифенілстаніл)метил трифенілстананкарбодитіоат був ізольований, в якості головного продукту, при спробі алкілювання трифенілсананкарбодитіоату літію хлоридом тритолілолова в тетрагідрофурані, і охарактеризований за допомогою ЯМР спектроскопії та елементного аналізу. Рожеві кристали отриманої сполуки було вирощено з розчину в суміші пентану та дихлорометана. Кристалічна структура була встановлена за допомогою рентгеноструктурного аналізу.

Ключові слова: стануморганічний, тіокарбоніл, кристалічна структура, трифенілстананкарбодитіоат

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СИНТЕЗ И СТРУКТУРНАЯ ХАРАКТЕРИЗАЦИЯ (ТРИТОЛИЛСТАНИЛТИО)(ТРИФЕНИЛСТАНИЛ)МЕТИЛ ТРИФЕНИЛСТАНАНКАРБОДИТІОАТА

(Тритолілстанілтіо)(трифенілстаніл)метил трифенілстананкарбодитіоат был изолирован, в качестве главного продукта, при попытке алкилирования трифенілсананкарбодитіоата лития хлоридом тритолілолова в ТГФ, и охарактеризован при помощи ЯМР спектроскопии и элементного анализа. Розовые кристаллы полученного вещества были выращены из раствора в смеси пентана и дихлорометана. Кристаллическая структура была установлена с помощью рентгеноструктурного анализа.

Ключевые слова: стануморганический, тиокарбонил, кристаллическая структура, трифенілстананкарбодитіоат

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SYNTHESIS OF NEW *BIS*-MICHAEL ADDUCTS AND REARRANGED MICHAEL-DIELS-ALDER ADDUCTS OF THE SECOND TYPE BY REACTION OF 1-AMINOISOINDOLE WITH FUNCTIONALIZED MALEIMIDES

Optimal method for synthesis of the corresponding maleimides found. Six maleimides with necessary aliphatic chains, ester fragments and aminoacid residues were obtained. By the reaction of functionalized maleimides with 1-aminoisoindole new bis-Michael adducts were acquired. Through interaction of the bis-Michael adducts with acetylacetone in the acetic acid, saturated with hydrogen chloride, new rearranged adducts of the second type were obtained. Structure of all compounds was proved by spectral data.

Keywords: synthesis, Michael reaction, Diels-Alder reaction, cycloaddition, 1-aminoisoindole, functionalized maleimides.

Introduction. Until recently, chemistry of isoindole could be divided into two almost independent sections: 1) isoindoles with isoindole major tautomer form, main reaction is [4+2] cycloaddition; 2) isoindoles with isoindoline tautomer form and thus don't have o-quinoid structure and should not participate in [4+2] cycloaddition [1, 2, 3]. Reaction of [4+2] cycloaddition was methodically studied in our scientific group, among other results we discovered three new rearrangements, each is unique method of synthesis of the rearranged Michael-Diels-Alder adducts of the first [4], second [5] and third [6] type for condensed isoindoles. Also it was shown that some condensed isoindoles can give adducts of the first and of

the third type [7]. The last scientific experiments of our group proved Curtin-Hammett principle for the reactivity of 1-aminoisoindole [8]. For it Michael *bis*-adducts were obtained with 1:2 composition and reaction mechanism was proved. Also was shown that 1-aminoisoindole, as well as pirimidoisoindole, can form rearranged adducts of the second type [8, 9].

Goal of this work is study of the possibility for directed synthesis of compounds with preset properties on the example of 1-aminoisoindole by the introduction of aliphatic chains and aminoacid residues into corresponding 1:2 *bis*-Michael adducts and rearranged adducts of the second type. This is important from both theoretical and practical