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Synthesis, X-ray diffraction analysis and NMR studies of (Z)-2-methyl-3-triphenylstannyl-3-pentene-2-ol

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Abstract

The synthesis of (Z)-2-methyl-3-triphenylstannyl-3-pentene-2-ol and its characterization by an X-ray diffraction study and multinuclear NMR are reported. The tin atom exhibits a distorted tetrahedral SnC_4 geometry with the four Sn–C bond distances experimentally equivalent. The slight distortion from the ideal tetrahedral geometry is because of the presence of a weak intramolecular HO → Sn interaction of 3.012(3) Å which produces a loose four-membered ring. The title compound was characterized in solution by ^{1}H, ^{13}C and ^{119}Sn NMR, and the persistence of the weak intramolecular HO → Sn coordination in solution was revealed by ^{13}C and ^{119}Sn secondary isotope multiplet of partially labelled entities (SIMPLE-NMR) experiments.

Key words: Tin; Crystal structure; Mössbauer spectroscopy; Nuclear magnetic resonance

1. Introduction

Several compounds of the type (Z)–(Ph_3Sn)–CH=CH–C(OH)RR′ exhibit a weak intramolecular HO → Sn interaction giving rise to a five-membered ring [1–3]. Triphenylstannylvinyl compounds of this type can be conveniently prepared by addition of triphenyltin hydride to the appropriate terminal alkyne [4]. In general, addition of a triorganotin hydride to a non-symmetric internal alkyne can give rise to four isomeric alkenes [5]. The relative amounts of the various isomers generated depend on the structure of the triorganotin hydride and that of the alkyne, as well as on the experimental conditions [5].

We recently reported [1,2,6] that the phenyl–tin bonds are broken regiospecifically during the monoiododemetallation reaction of (Z)–(Ph_3Sn)–CH=CH–C(OH)RR′ as a consequence of the presence of the weak HO → Sn interaction. We report here the synthesis, with triethylborane as a catalyst [7], of (Z)–2-methyl-3-triphenylstannyl-3-pentene-2-ol (**1**). Compound **1** was characterized in the solid state by an X-ray diffraction study and Mössbauer spectroscopy and, in solution by multinuclear ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. Particular attention has been given to the existence of a weak intramolecular HO → Sn interaction and its possible influence upon the course of the monoiododemetallation reaction of compound **1**.

2. Synthesis

Compound **1** was obtained in 67% yield from the reaction shown in Scheme 1. After purification by column chromatography the (sole) product was purified by recrystallization from $CHCl_3$/petroleum ether.

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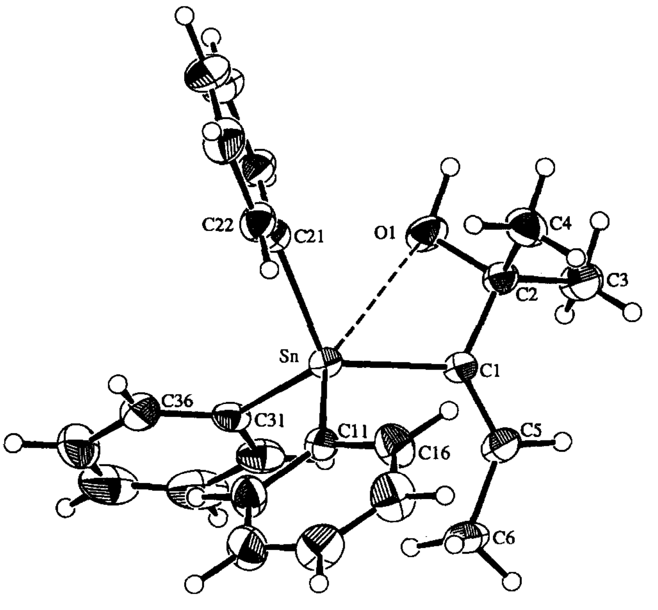


Fig. 1. The molecular structure of **1**.

TABLE 1. Selected bond distances (Å) and angles (deg.) for **1**

Sn–C(1)	2.125(3)	Sn–C(1)–C(2)	114.9(2)
Sn–C(11)	2.125(3)	Sn–C(1)–C(5)	121.1(3)
Sn–C(21)	2.129(3)	O(1)–Sn–C(1)	49.3(1)
Sn–C(31)	2.118(3)	O(1)–Sn–C(11)	149.5(1)
Sn–O(1)	3.012(3)	O(1)–Sn–C(21)	77.9(1)
O(1)–C(2)	1.438(4)	O(1)–Sn–C(31)	100.0(2)
C(1)–C(2)	1.491(4)	O(1)–C(2)–C(1)	102.7(3)
C(1)–C(5)	1.316(5)	C(1)–Sn–C(11)	107.8(1)
C(2)–C(3)	1.508(5)	C(1)–Sn–C(21)	118.0(1)
C(2)–C(4)	1.505(4)	C(1)–Sn–C(31)	110.8(1)
C(5)–C(6)	1.476(5)	C(1)–C(5)–C(6)	128.3(4)
		C(2)–C(1)–C(5)	123.8(3)
		C(11)–Sn–C(21)	103.9(1)
		C(11)–Sn–C(31)	108.2(1)
		C(21)–Sn–C(31)	107.7(1)

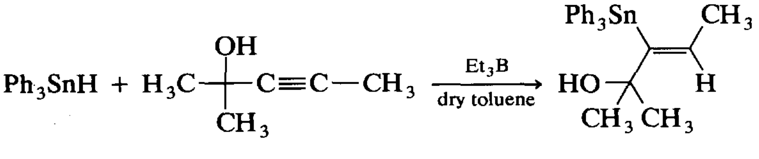
2.1. Solid-state structure determination by X-ray diffraction analysis

The molecular structure of **1** is shown in Fig. 1 and selected interatomic parameters are listed in Table 1. There are no significant intermolecular contacts in the lattice; the closest non-hydrogen contact of 3.339(4) Å, is between the O(1) and C(3′) atoms (symmetry operation: −x, 1 − y, 1 − z).

The geometry about the Sn atom is distorted tetrahedral, with the four almost equivalent Sn–C bond lengths falling in the narrow range 2.118(3)–2.129(3) Å. Except for the C(1)–Sn–C(21) angle [118.0(1)°], the C–Sn–C angles lie in the range 103.9(1)–110.8(1)°, indicating relatively minor deviations from the expected tetrahedral values. The expansion of the C(1)–Sn–C(21) angle is a result of the relatively close approach of the hydroxyl oxygen atom to the tin atom. The Sn...O(1) separation [3.012(3) Å] is significantly less than the sum of the van der Waals radii for these atoms [3.70 Å] [8]. The O(1)–Sn–C(1) angle is 49.3(1)°. In addition all the Ph–Sn–Ph angles are below the tetrahedral value of 109.5°, reflecting the influence of the O(1) atom on the overall geometry about the tin atom. From the values of the O(1)–Sn–C(11), O(1)–Sn–C(21), O(1)–Sn–C(31) angles, respectively 149.5(1)°, 77.9(1)° and 100.0(1)°, it is concluded that the Sn...O(1) interaction is a weak one, with only a slight but definite deviation towards trigonal bipyramid. In terms of this description the C(11) and O(1) atoms define the axial positions; it should be stressed, however, that the equivalent bond lengths Sn–C(11), Sn–C(21) and Sn–C(31) do not favour this view, apical Ph–Sn bonds usually being longer than equatorial ones [1]. Nevertheless, the small Sn–C(1)–C(2) angle of 114.9(2)° (compared with the expected angle of 120°) as well as the C(1)–C(2)–O(1) angle of 102.7(3)° suggest that the OH group is "pulled" towards the tin atom and that the interaction HO → Sn is real. The deviation of **1** towards trigonal bipyramidal geometry is less marked than in the analogous (Z)-17-[2-(triphenylstannyl)-vinyl]-4-estren-17*β*-ol structure [1], where it is the result of a much shorter intramolecular HO → Sn interaction, of 2.77(1) Å. The main difference between the strengths of the two O → Sn interactions is attributable to the fact that in the latter compound it generates a five-membered ring, while in the former it gives rise to a more strained four-membered one. The latter ring is not planar, the dihedral angle between the planes Sn–O(1)–C(2) and Sn–C(1)–C(2) being 135.7°. It is rather surprising that, despite the constraint involved in such a four-membered ring, the O → Sn interaction is still effective.

2.2. Mössbauer spectroscopy

The Mössbauer spectrum of compound **1** exhibits an isomer shift of 1.32 mm s^{-1} relative to $Ca^{119m}SnO_3$



Scheme 1.

TABLE 2. ^{1}H and ^{13}C resonance assignments and coupling data obtained for **1**

	^{1}H	^{13}C
C–OH	1.25 (s)	75.2 [32/33]
$(CH_3)_2$	1.38 (s)	30.6 [≈13] [a]
=C–H	6.51 (q, 7) [167/174]	132.8 [≈29] [a]
=C–Sn	–	152.8 [509/532]
CH_3	1.67 (d, 7) [≈13] [a]	20.0 [48/50]
ipso	–	141.1 [489/512]
ortho	complex pattern	137.0 [37/39]
meta	between	128.4 [48/51]
para	7.20–7.80	128.5 [≈12] [a]

The chemical shifts and coupling constant values are given in ppm and Hz respectively. The observed proton multiplicities (s = singlet; d = doublet; q = quartet) and ^{1}H–^{1}H coupling values are given between parentheses. $^{n}J(^{1}H-^{117/119}Sn)$ and $^{n}J(^{13}C-^{117/119}Sn)$ couplings are given between brackets. [a] unresolved satellites.

and a quadrupole splitting of 0.39 mm s^{-1}. These findings are in agreement with the structure obtained by X-ray diffraction. The small quadrupole splitting indicates a slight but significant deviation from spherical symmetry of the electron cloud around the tin atom, and is consistent with a weak intramolecular HO → Sn interaction in the solid state; in support of this proposal is the observation that Ph_3Sn vinyl compounds, in which such an interaction is impossible, do not exhibit quadrupole splitting [3].

2.3. *NMR spectroscopy*

The assignments of the ^{1}H and ^{13}C resonance for compound **1** together with the associated coupling data, are given in Table 2. The proton-proton coupling constant of 7 Hz between the methyl and the olefinic proton resonance is in agreement [9] only with a $^{3}J(^{1}H-^{1}H)$ coupling constant, which in turn is characteristic for their *gem* disposition. The high $^{3}J(^{1}H-^{119}Sn)$ coupling constant value of 174 Hz observed between the olefinic proton and the tin atom arises from the mutual *trans* disposition of the triphenylstannyl group and the olefinic hydrogen [10]. Also noteworthy is the rather high value of 13 Hz for $^{4}J(^{1}H-^{119}Sn)$ between the C=CH–CH_3 methyl protons and the tin atom.

All the resonances of the ^{13}C spectrum exhibit characteristic $^{117/119}Sn$ coupling satellites. The aromatic and olefinic ^{13}C resonances were assigned from the ^{13}C DEPT spectrum and from fully relaxed resonance intensities in the inverse gated decoupled ^{13}C spectrum, which enabled unambiguous characterization of the quaternary carbon atoms. The relationship [10] $|^{1}J(^{13}C-^{119}Sn)| > |^{3}J(^{13}C-^{119}Sn)| > |^{2}J(^{13}C-^{119}Sn)| > |^{4}J(^{13}C-^{119}Sn)|$ was used to assign the ^{13}C resonances of the phenyl moiety. The high $^{2}J(^{13}C{=}C-^{119}Sn)$ value of 29 Hz is noteworthy, because such coupling does not usually exceed 4 Hz in vinyltin compounds. The standard 1D ^{119}Sn spectrum of **1** exhibits a singlet at −146.8 ppm.

Evidence for the existence of a weak HO → Sn coordinative interaction in solution was obtained from ^{13}C and ^{119}Sn secondary isotope multiplet of partially labelled entities (^{13}C and ^{119}Sn SIMPLE-NMR) experiments [2,11,12]. Secondary isotopic effects on the ^{13}C chemical shift, $\delta(^{13}C^{2}H)-\delta(^{13}C^{1}H)$, of −0.05, −0.14, −0.01 and −0.01 ppm, resulting from the deuteration of the hydroxyl group, were observed for the carbon atoms =C–Sn, C–OH, $(CH_3)_2$ and C_{ipso}, respectively. The isotope shift for the *ipso* carbon of the phenyl moiety can reasonably only result from a three-bond effect through the $D-O \rightarrow Sn-C_{ipso}$ pathway. This is further confirmed by the secondary isotopic effect on the ^{119}Sn chemical shift, $\delta(^{119}Sn^{2}H)-\delta(^{119}Sn^{1}H)$, of +0.05 ppm observed in a ^{119}Sn SIMPLE-NMR experiment.

2.4. *Iododemetallation*

In general, the ease of carbon–tin bond cleavage by iodine in mixed organotin is comparable for aryl and vinyl groups, or slightly greater for the former [13]. Both types of group are more readily cleaved off than alkyl groups. Intramolecular HO → Sn coordination is known to influence the selectivity of the iododemetallation reaction of such compounds. Alkyl-tin bonds can be broken in preference to aryl–tin bonds when nucleophilic assistance at tin because of intramolecular coordination is possible [14].

The iododemetallation reaction of compound **1** reveals that the vinyl group can be cleaved off in contrast to the behaviour of (Z)-(Ph_3Sn)–CH=CH–C(OH)RR′ compounds [1,2,7]. Thus, when a dilute solution of iodine was mixed with a solution of **1**, the NMR spectrum of the crude reaction mixture no longer exhibited any $^{1}H-^{119}Sn$ coupling satellites for the olefinic proton resonances. This result indicates that the HO → Sn coordination is too weak in solution to promote phenyl–tin bond cleavage, confirming that none of the phenyl groups of **1** has a marked apical character, in contrast to the situation in (Z)-17-[2-(triphenylstannyl) vinyl]-4-estren-17β-ol and other related compounds [1,2,7].

3. Experimental details

3.1. *Synthesis*

Triphenyltin hydride was prepared as described by Kuivila [15] by treatment of triphenyltin chloride and $LiAlH_4$ in dry diethyl ether. The product mixture was purified by column chromatography on silica gel with benzene/petroleum ether (1/4) as eluent to yield the pure hydride ($R_f = 0.63$) in good yield (89%). 2-Methyl-3-pentyn-2-ol was purified by vacuum distillation (Bp. 48°C; 15 T) before use.

A 1 M solution of Et_3B in hexane (0.1 mL) was added under nitrogen to a solution of 2-methyl-3-pentyn-2-ol (0.0981 g 1 mmol) and triphenyltin hydride (0.4224 g, 1.2 mmol) in toluene (15 mL) at room temperature. The mixture was stirred for 20 h at room temperature under nitrogen and water was then added to the white suspension. The mixture was extracted three times with ethyl acetate, and the extract was washed with aqueous NaCl, dried over $MgSO_4$, and evaporated under vacuum to yield an oil. This was subjected to column chromatography on silica gel with chloroform as eluent ($R_f = 0.32$) followed by crystallisation from $CHCl_3$/petroleum ether. Yield: 0.30 g (67%); mp 135–136°C. The single crystal used for the X-ray diffraction study was obtained by slow evaporation of a cyclohexane solution of **1**.

A 14.9 mM solution of iodine (79.9 ml; 1.19 mmol) in $CHCl_3$ was added dropwise to a solution of 536.6 mg (1.19 mmol) of compound **1** in 15 mL of chloroform. The violet colour disappeared nearly immediately. The solvent was evaporated under vacuum at room temperature and the ^1H NMR spectrum of the product was recorded in $CDCl_3$.

3.2. *X-ray diffraction analysis*

Intensity data for a colourless crystal of **1** (0.05 × 0.21 × 0.31 mm) were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromatized Mo-Kα radiation; $\lambda = 0.71073$ Å. A total of 5097 reflections was collected by the $\omega : 2\theta$ scan technique to θ_{max} 27.5°, and of the reflections measured, 4834 were unique, and after correction for absorption 3713 (min. and max. transmission factors were 0.822 and 1.124, respectively [16]) satisfying the $I \geq 3.0\sigma(I)$ criterion and were used in the analysis.

Crystal data for $C_{24}H_{26}OSn$: $M = 449.2$, triclinic, space group $P\bar{1}$, $a = 10.813(3)$ Å, $b = 11.460(3)$ Å, $c = 9.888(2)$ Å, $\alpha = 94.43(2)°$, $\beta = 108.40(2)°$, $\gamma = 63.75(2)°$, $V = 1039.9(5)$ Å^3, $Z = 2$, $D_{max} = 1.434$ g cm^{-3}, μ(Mo-Kα) = 12.37 cm^{-1}, no. parameters/no. variables = 15.8.

The structure was solved by direct methods (SHELXS86 [17]) and refined by a full-matrix least-squares procedure based on F [18]. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model in calculated positions (C–H 0.97 Å); the hydrogen atom of the OH group was located in a difference map but not refined. The refinement converged with $R = 0.032$ and $R_w = 0.029$ (sigma weights [19]), the analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.44 e Å^{-3}. Final fractional atomic coordinates are listed in Table 3, and the numbering scheme employed is shown in Fig. 1, which was drawn with ORTEP [19]. Lists of thermal parameters and hydrogen atom parameters, and complete tables of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

TABLE 3. Fractional atomic coordinates for 1

Atom	x	y	z
Sn	0.12472(3)	0.21368(2)	0.37340(3)
O(1)	−0.0890(3)	0.4977(2)	0.3117(3)
C(1)	−0.1018(4)	0.3043(3)	0.2621(4)
C(2)	−0.1592(4)	0.4393(3)	0.1990(4)
C(3)	−0.3212(4)	0.5193(4)	0.1633(5)
C(4)	−0.1135(5)	0.4369(4)	0.0695(4)
C(5)	−0.1838(4)	0.2460(4)	0.2581(4)
C(6)	−0.1392(5)	0.1151(4)	0.3205(5)
C(11)	0.2139(4)	0.0241(3)	0.3003(4)
C(12)	0.3221(4)	−0.0816(4)	0.3880(4)
C(13)	0.3790(5)	−0.2028(4)	0.3384(6)
C(14)	0.3280(5)	−0.2203(4)	0.1982(6)
C(15)	0.2213(6)	−0.1180(5)	0.1092(5)
C(16)	0.1626(5)	0.0037(4)	0.1593(4)
C(21)	0.2534(4)	0.2998(4)	0.3426(4)
C(22)	0.3534(4)	0.2353(4)	0.2739(4)
C(23)	0.4395(5)	0.2882(5)	0.2534(5)
C(24)	0.4239(5)	0.4067(5)	0.3018(6)
C(25)	0.3259(5)	0.4723(4)	0.3718(5)
C(26)	0.2406(4)	0.4190(4)	0.3933(5)
C(31)	0.1636(4)	0.1935(3)	0.5961(4)
C(32)	0.0503(5)	0.2270(4)	0.6504(4)
C(33)	0.0797(7)	0.2143(5)	0.7962(6)
C(34)	0.2140(9)	0.1719(6)	0.8855(5)
C(35)	0.3259(7)	0.1388(5)	0.8345(5)
C(36)	0.3007(5)	0.1503(4)	0.6897(5)

3.3. *NMR experiments*

Solutions of about 100 mg of compound **1** in 0.5 mL $CDCl_3$ were used. All spectra were recorded on a Bruker AC250 NMR spectrometer at 250.13 MHz proton resonance frequency interfaced with an Aspect-3000 computer and equipped with a 5 mm QNP (^1H, ^{13}C, ^{19}F, ^{119}Sn) probe. ^{13}C and ^{119}Sn SIMPLE NMR experiments were run on a Bruker AMX500 spectrometer equipped with a 5 mm inverse detection broadband probe head at ^{13}C and ^{119}Sn frequencies of 125.76 and 186.41 MHz respectively. Chemical shifts were referenced to the residual solvent peak and converted to the standard TMS scale by adding 7.24 ppm and 77.0 ppm for ^1H and ^{13}C nuclei, respectively. The ^{119}Sn chemical shift is given with respect to neat external tetramethyltin ($\Xi(^{119}Sn) = 37.290665$) [20].

Totally deuterated samples were prepared by dissolving **1** in CD_3OD and evaporating subsequently the methanol under reduced pressure. The HO/DO ratio for the ^{13}C and ^{119}Sn SIMPLE-NMR experiments was adjusted to 60/40 by adding 40 mg of the totally deuterated sample to a 0.5 mL $CDCl_3$ solution containing 60 mg of the totally protonated one.

3.4. *Mössbauer spectroscopy*

The Mössbauer spectrum was recorded with the constant acceleration mode and with a $Ca^{119m}SnO_3$ source from Amersham, using a home built (INAN, Université Catholique de Louvain) instrument, designed by the "Instituut voor Kern- en Stralingsfysika" (IKS, Katholieke Universiteit Leuven). The probe was maintained at a temperature between 90–100 K, the source at room temperature. The digital data were treated with a least-square-iterative program deconvoluting the spectrum into a combination of Lorentzians.

4. Conclusion

This paper presents for the first time evidence of the existence of a weak intramolecular OSn interaction in a tetraorganotin compound that gives rise to a four-membered ring which is present in the solid state as well as in solution.

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