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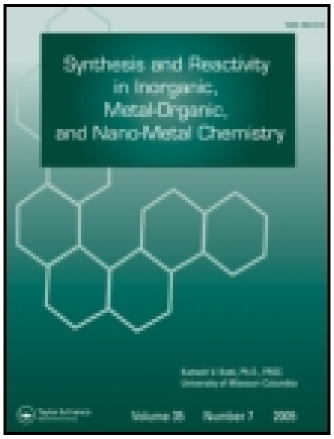

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Synthesis and Characterization of (Z)-1-[2-(Tribenzylstannyl)vinyl]-1-cycloheptanol and its Benzylhalostannyl Derivatives

Yujie Ren [a] , Cuiying Jia [a] , Peng Liang [a] , Xuefeng Yang [a] & Huilin Chen [b]
[a] Chemistry Department , Dalian University of Technology , Dalian, 116024, P.R. China
[b] Dalian Institute of Chemical Physics , The Chinese Academy of Science , Dalian, 116023, P.R. China

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis and Characterization of (Z)-1-[2-(Tribenzylstannyl)vinyl]-1-cycloheptanol and Its Benzylhalostannyl Derivatives

**Yujie Ren,[1,*] Cuiying Jia,[1] Peng Liang,[1]
Xuefeng Yang,[1] and Huilin Chen[2]**

[1]Chemistry Department, Dalian University of Technology,
Dalian, P.R. China
[2]Dalian Institute of Chemical Physics, The Chinese Academy of Science,
Dalian, P.R. China

ABSTRACT

1-Ethynyl-1-cycloheptanol reacts with tribenzylstannylhydride, $(C_6H_5CH_2)_3SnH$, and generates the corresponding (Z)-1-[2-(tribenzylstannyl)vinyl]-1-cycloheptanol. The product obtained reacts with one or two equivalents of halogen (I_2, Br_2 or ICl) to form the associated (Z)-1-[2-(dibenzylhalostannyl)vinyl]-1-cycloheptanol or (Z)-1-[2-(benzyldihalostannyl)-vinyl]-1-cycloheptanol, respectively. All compounds were characterized by elemental analyses, IR, ^{1}H NMR. The X-ray diffraction analysis of (Z)-1-[2-(tribenzylstannyl)vinyl]-1-cycloheptanol shows the presence of an intramolecular coordination of oxygen to the tin atom

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[*] Correspondence: Yujie Ren, Chemistry Department, Dalian University of Technology, Dalian 116024, P.R. China; E-mail: yujie_ren@163.com.

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giving rise to a five-membered ring in which the metal exhibits a distorted trigonal-bipyramidal geometry. This may explain that a benzyl group, probably the apical one, is cleaved more easily by halogen than the vinyl substituent.

Key Words: Synthesis; Characterization; Organotin compound.

INTRODUCTION

It has been reported[1] that Ph_3SnH adds to 17-ethynyl-4-estren-17β-ol to give (Z)-17-[2-(triphenylstannyl)vinyl]-4-estren-17β-ol. This triphenylvinyltin derivative reacts smoothly with one or two equivalents of iodine, leading exclusively to the cleavage of one or two phenyl-tin bonds, respectively. A 1:1 molar ratio gives rise to (Z)-17-[2-(iododi-phenylstannyl)-vinyl]-4-estren-17β-ol, a 2:1 molar ratio, (Z)-17-[2-(diiodophenylstannyl)-vinyl]-4-estren-17β-ol, which exhibits interesting antitumour activities.[2]

Thus, the vinyl-tin bond is not cleaved at all. The intramolecular coordination bond from oxygen to tin in this compound is likely to be responsible for this high regioselectivity in the phenyl-tin bond cleavage.

In order to check the general validity of this assumption, we prepared model compounds in which the same intramolecular coordination bond is present, giving rise to the same cyclic, tin-containing unit, but without the steroid moiety of (Z)-17-[2-(triphenylstannyl)vinyl]-4-estren-17β-ol.[1] Moreover, we examined the influence of benzyl substitution on the phenyl ring in order to find out whether this modification induces a noticeable change in the reactivity with iodine. We synthesized (Z)-1-[2-(tribenzylstannyl)vinyl]-1-cycloheptanol and corresponding mono-and dihalides.

EXPERIMENTAL

Materials

1-Ethynyl-1-cycloheptanol was prepared according to Verkruijsse et al.,[3] b.p 81–83 °C/26 mm Hg; yield: 47%. Tribenzyltin hydride was prepared according to the procedure of Kuivila et al.,[4] mp 102–104 °C, yield: 45%, $\nu(Sn-H)$: 1835 cm^{-1}, and was directly used without seperation.

Physical Measurements

IR spectra were recorded on a Nicolet 360 FT-IR spectrometer, ^1H NMR spectra were obtained on a Varian Unity-400 NMR spectrometer at

400 MHz proton resonance frequency. The chemical shifts of the proton NMR spectra are reported with TMS as internal standard and $CDCl_3$ as solvent. The elemental analysis data for C and H were obtaind on a PE 2400 C–H–N automatic element analyzer. The content of Sn was determined on a VRA-20 X-ray fluorescence spectrometer.

Synthesis of (Z)-1-[2-(Tribenzylstannyl)vinyl]-1-cycloheptanol (1)

Tribenzyltin hydride (15.74 g, 40 mmol) and 1-ethynyl-1-cycloheptanol (5.56 g, 40 mmol) were placed into a two-necked flask equipped with a condenser on top of which was placed a $CaCl_2$ tube. 30 mL of diethyl ether and 20 mg of dibenzoyl peroxide were added to this mixture which was kept under nitrogen. After magnetic stirring for 20 h, diethyl ether was evaporated and the residue was recrystallized from ethanol, The main product (Z)-1-[2-(tribenzylstannyl)vinyl]-1-cycloheptanol (**1**) was obtained in 55.4% (11.77 g) yield; mp 74–75 °C. Anal. Calcd. for $C_{30}H_{36}OSn$ (531): C, 67.79; H, 6.78; Sn, 22.41%. Found: C, 67.35; H, 6.65; Sn, 22.61%. IR (KBr), ν_{max} cm^{-1}: 3571.7 (s, OH), 1084.0 (s, CO), 529.0 (Sn←O). ^1H NMR ($CDCl_3$) δ ppm: 0.67 (1H, s, OH), 1.54 (12H, br, C_7H_{12}), 2.28 (6H, s, $3CH_2$), 5.55 (d, J = 13 Hz, =CH – cycloheptyl), 6.58 (d, J = 13 Hz, CH – Sn), 6.83–7.17 (15H, m, $3C_6H_5$). Hexabenzylditin, obtained as an insoluble byproduct, was filtered off; 11.2% (3.5 g) yield.

Synthesis of (Z)-1-[2-(Dibenzylhalostannyl)vinyl]-1-cycloheptanols (2), (3) and (4) and (Z)-1-[2-(Benzyldihalostannyl)vinyl]-1-cycloheptanols (5), (6), and (7)

Typically, a solution of 1.6 g (10 mmol) of Br_2 in 100 mL of CCl_4 was added drop-wise under magnetic stirring to a solution of 5.3 g (10 mmol) of (**1**) in 100 mL of the same solvent. The color of Br_2 disappeared immediately. After having added the last drop of bromine a colorless solution was obtained. The reaction mixture was kept for 4 h at room temperature; then the solvent was evaporated. The residue was recrystallized from cyclohexane. A solid, (Z)-1-[2-(dibenzylbromostannyl)vinyl]-1-cycloheptanol (**3**), was obtained in 71.2% (3.69 g) yield.

Analogous procedures were used for the synthesis of compounds (**2**) and (**4**)–(**7**).

(**2**) Yellow pasty compound, yield 54.1%. Anal. Calcd. for $C_{23}H_{29}IOSn$ (567): C, 48.68; H, 5.11; Sn, 20.99%. Found: C, 48.26; H, 5.10; Sn, 20.88%. IR (KBr), ν_{max} cm^{-1}: 3416.7 (s, OH), 1041.3 (s, CO), 526.0 (Sn←O). ^1H NMR ($CDCl_3$) δ ppm: 2.24 (1H, s, OH), 1.53 (12H, br, C_7H_{12}), 2.28 (4H, s,

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$2CH_2$), 6.37 (d, J = 12 Hz, =CH – cycloheptyl), 6.81 (d, J = 12 Hz, =CH – Sn), 6.73–7.21 (15H, m, $3C_6H_5$).

(**3**) Colorless solid, yield 71.2%, mp 106–108 °C. Anal. Calcd. for $C_{23}H_{29}BrOSn$ (520): C, 53.08; H, 5.58; Sn, 22.88%. Found: C, 53.01; H, 5.46; Sn, 22.68%. IR (KBr), ν_{max} cm^{-1}: 3403.6 (s, OH), 1050.4 (s, CO), 535.0 ($Sn \leftarrow O$). ^1H NMR ($CDCl_3$) δ ppm: 2.35 (1H, s, OH), 1.53 (12H, br, C_7H_{12}), 2.28 (4H, s, $2CH_2$), 6.31 (d, J = 12 Hz, =CH–cycloheptyl), 6.89 (d, J = 12 Hz, =CH – Sn), 6.83–7.17 (15H, m, $3C_6H_5$).

(**4**) Colorless solid, yield 81.2%, mp 145–146 °C. Anal. Calcd. for $C_{23}H_{29}ClOSn$ (475.5): C, 58.04; H, 6.10; Sn, 25.03%. Found: C, 58.00; H, 6.01; Sn, 24.98%. IR (KBr), ν_{max} cm^{-1}: 3411.0 (s, OH), 1051.3 (s, CO), 520.0 ($Sn \leftarrow O$). ^1H NMR ($CDCl_3$) δ ppm: 2.41 (1H, s, OH), 1.54 (12H, br, C_7H_{12}), 2.28 (4H, s, CH_2), 6.26 (d, J = 12 Hz, =CH–cycloheptyl), 6.92 (d, J = 12 Hz, =CH – Sn), 6.70–7.28 (15H, m, $3C_6H_5$).

(**5**) Colorless solid, yield 60.1%, mp 64–66 °C. Anal. Calcd. for $C_{16}H_{22}I_2OSn$. (603): C, 31.88; H, 3.68; Sn, 19.69%. Found: C, 31.82; H, 3.63; Sn, 19.68%. IR (KBr), ν_{max} cm^{-1}: 3420.6 (s, OH), 1048.1 (s, CO), 520.0 ($Sn \leftarrow O$). ^1H NMR ($CDCl_3$) δ ppm: 2.54 (1H, s, OH), 1.62 (12H, br, C_7H_{12}), 2.28 (2H, s, CH_2), 6.40 (d, J = 10 Hz, =CH–cycloheptyl), 6.64 (d, J = 10 Hz, =CH – Sn), 6.80–7.17 (15H, m, $3C_6H_5$).

(**6**) Colorless solid, yield 81.8%, mp 152–154 °C. Anal. Calcd. for $C_{16}H_{22}Br_2OSn$. (509): C, 37.76; H, 4.36; Sn, 23.33%. Found: C, 37.72; H, 4.31; Sn, 23.29%. IR (KBr), ν_{max} cm^{-1}: 3417.2 (s, OH), 1054.6 (s, CO), 539.0 ($Sn \leftarrow O$). ^1H NMR ($CDCl_3$) δ ppm: 2.89 (1H, s, OH), 1.63 (12H, br, C_7H_{12}), 2.28 (2H, s, CH_2), 6.33 (d, J = 10 Hz, =CH–cycloheptyl), 6.89 (d, J = 10 Hz, =CH – Sn), 6.79–7.27 (15H, m, $3C_6H_5$).

(**7**) Colorless solid, yield 85.8%, mp 144–145 °C. Anal. Calcd. for $C_{16}H_{22}Cl_2OSn$. (420): C, 45.76; H, 5.28; Sn, 28.27%. Found: C, 45.71; H, 5.20; Sn, 28.23%. ν_{max}: 3411.1 (s, OH), 1054.9 (s, CO), 529.0 ($Sn \leftarrow O$). ^1H NMR ($CDCl_3$) δ ppm: 3.20 (1H, s, OH), 1.61 (12H, br, C_7H_{12}), 2.28 (2H, s, CH_2), 6.26 (d, J = 10 Hz, =CH – cycloheptyl), 6.98 (d, J = 10 Hz, CH – Sn), 6.83–7.17 (15H, m, $3C_6H_5$).

X-Ray Structure Determination of Compound (1)

A crystal, dimensions 0.15 mm × 0.25 mm × 0.50 mm, was used to collect data on a MAC DIP-2030K automatic diffractometer. The structure of (Z)-1-[2-(tribenzylstannyl)-vinyl]-1-cycloheptanol (**1**) has been determined by X-ray diffraction analysis and is shown in Figure 1. Unit cell dimensions a = 9.474(1), b = 25.858(2), c = 10.717(1) Å, β = 92.988(4)°, V = 2621.9(3) $Å^3$, Z = 4, D_c = 1.346 $g.cm^{-3}$. Data were collected by the ω

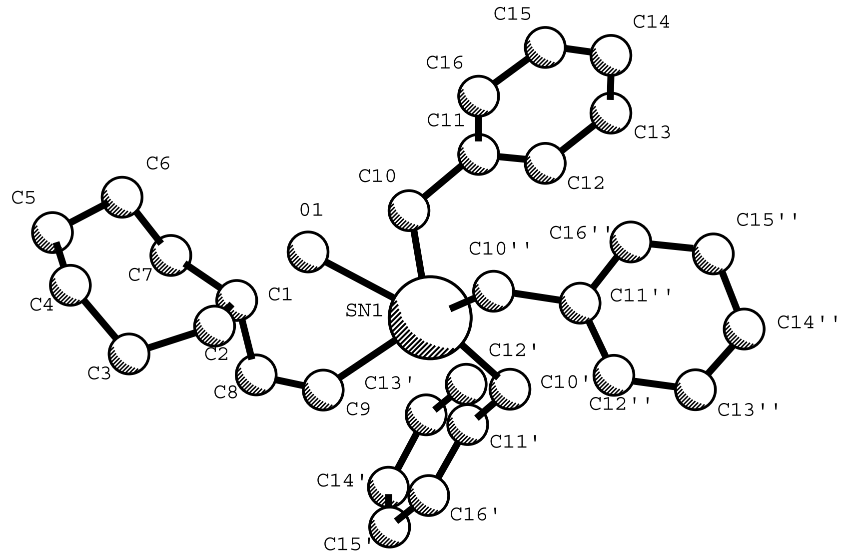


Figure 1. Structure of compound (**1**).

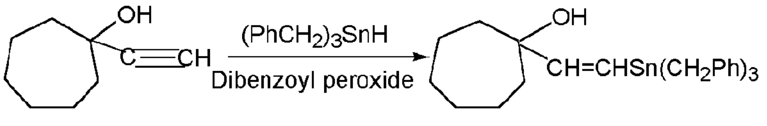
scan technique with $2\theta \leq 50.0°$. During data collection no decay was found. The intensities were corrected for Lorentz, polarization and absorption effects [$\mu(M_0\ K_\alpha) = 10.48\ cm^{-1}$]. The scan range was 0–180°. Calculations were carried out with the SHELXS-86 system of computer programs. Systematic absences showed the space group to be $p2_1/c$. The position of the tin atom and all the non-hydrogen atoms was determined from a three dimensional Patterson map followed by the use of Fourier technique. They were refined anisotropically by least-squares methods and the positions of all the hydrogen atoms could be located from geometric and difference Fourier calculations. Final R = 0.079 for 3631 observed reflections ($|F|^2 \geq 8\sigma\ |F|^2$) $R_w = 0.075$, $w = 1/\sigma|F|^2$.

RESULTS AND DISCUSSION

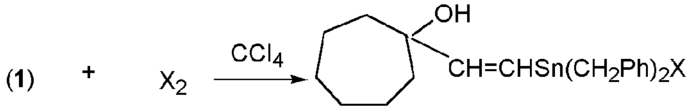
Synthesis

The (Z)-1-[2-(tribenzylstannyl)vinyl]-1-cycloheptanol (**1**) was synthesized by the addition of tribenzyltin hydride to the triple bond of 1-ethynyl-1-cycloheptanol (Eq. 1).

The reactions of (**1**) with halogens in a 1:1 or 1:2 molar ratio yield the corresponding mono- and di-halides (**2**)–(**7**), respectively (Eqs. 2 and 3).

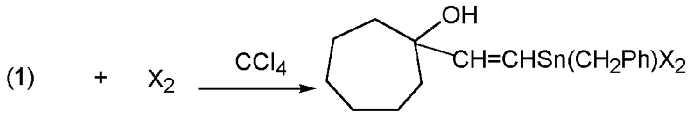


(1)



(2)

$X_2 = I_2, Br_2, ICl$ molar ratio 1:1 (**2**), (**3**), (**4**) (For (**4**) X = Cl)



(3)

$X_2 = I_2, Br_2, ICl$ molar ratio 1:2 (**5**), (**6**), (**7**) (For (**7**) X = Cl)

The reaction conditions are described in Table 1. The physical properties of the new products are described in the experimental details.

Table 1. Reaction conditions and recrystallization solvents during the synthesis of compounds (**2**) to (**7**).

Starting compound	Halogen	Molar ratio	Product	Reaction time (h)	Reaction temp (°C)	Recrystallization solvent
(**1**)	I_2	1:1	(**2**)	6	18	cyclohexane
(**1**)	Br_2	1:1	(**3**)	4	− 10	cyclohexane
(**1**)	ICl	1:1	(**4**)	4	− 5	cyclohexane/ CCl_4[a]
(**1**)	I_2	1:2	(**5**)	48	− 10	cyclohexane/ CCl_4[a]
(**1**)	Br_2	1:2	(**6**)	10	− 10	cyclohexane
(**1**)	ICl	1:2	(**7**)	8	0	cyclohexane/ CCl_4[a]

[a] 1:1, v/v.

^{1}H NMR Spectra

The proton NMR spectrum of compound (**1**), obtained after the addition of one equivalent of tribenzyltin hydride to the triple bond of 1-ethynyl-1-cycloheptanol, no longer exhibits the signal of the acetylenic proton at 2.55 ppm, characteristic of the starting material. Rather, compound (**1**) shows characteristic ethylenic proton signals at 5.55 and 6.58 ppm, namely two doublets with $^3J_{HC=CH}$ = 13 Hz.

When compound (**1**) reacts with one equivalent of halogen, the vinylic protons appear at 6.37 and 6.81 ppm (**2**); 6.31 and 6.89 ppm (**3**); 6.26 and 6.92 ppm (**4**), respectively, again as doublets $^3J_{HC=CH}$ = 12 Hz. The presence of vinylic protons clearly shows that the benzyl-tin bond is cleaved by halogen and the −CH=CH−Sn bond remains intact. Indeed, no other signals from the vinylic −CH=CH−X (X = Cl; Br; I) protons could be detected in the proton NMR spectrum. Therefore, compounds (**2**)−(**4**) were identified as (Z)-1-[2-(dibenzylhalo-stannyl)vinyl]-1-cycloheptanol.

After the addition of a second equivalent of halogen, the vinylic protons change to 6.40 and 6.64 ppm (**5**); 6.33 and 6.89 ppm (**6**); 6.26 and 6.98 ppm (**7**) as doublets $^3J_{HC=CH}$ = 10 Hz. This shows that the second group cleaved by halogen is again a benzyl group, thus, compounds (**5**)**−**(**7**) are (Z)-1-[2-(benzyldihalostannyl) vinyl]-1-cycloheptanols.

In addition, we have separated the side product benzyl bromide, and have obtained its ^{1}H NMR spectrum, it showed the correct data for the ^{1}H NMR spectrum of benzyl bromide.

The coupling constant $^3J_{HC=CH}$ = 13 Hz observed for compound (**1**) is rather larger than *cis* coupling constants in five-membered rings which usually amount to 8 Hz or even less. However, this ring, containing a tin

Table 2. Selected bond lengths (Å) and angles (°).

O(1)−Sn	2.728(1)	Sn(1)−C(9)	2.153(9)
Sn(1)−C(10)	2.174(10)	Sn(1)−C(10″)	2.176(9)
Sn(1)−C(10′)	2.176(9)	O(1)−C(1)	1.456(11)
C(1)−C(8)	1.521(13)	C(2)−C(3)	1.532(16)
C(8)−C(9)	1.324(13)	C(10)−C(11)	1.492(14)
C(10′)−C(11′)	1.534(13)	C(10″)−C(11″)	1.478(12)
C(9)−Sn(1)−C(10)	114.5(4)	C(9)−Sn(1)−C(10′)	103.8(4)
C(9)−Sn(1)−C(10″)	116.4(3)	C(10)−Sn(1)−C(10′)	105.8(4)
C(10)−Sn(1)−C(10″)	109.8(4)	C(10′)−Sn(1)−C(10″)	105.4(4)

atom, is characterized by rather abnormal bond angles. This coupling constant decreases from compound (**1**) to compound (**7**).

Molecular Structure of Compound (1)

The structure of compound (**1**) has been determined by X-ray diffraction and is shown in Figure 1. As shown in Figure 1, compound (**1**) has a distorted trigonal bipyramidal geometry which is similar to that of (Z)-17-[2-(triphenylstannyl)vinyl]-4-estren-17β-ol.[1] Selected bond lengths and angles are given in Table 2.

The central tin atom has a strongly distorted trigonal-bipyramidal geometry with O and C(10′) atoms in apical positions and the C(9), C(10) and C(10″) atoms in equatorial positions. Even if we do not take into account the tin-oxygen interaction, a tetrahedral environment around tin is not credible because the angles C(9)–Sn–C(10) (114.5°) and C(9)–Sn–C(10″) (116.4°) indicate a distorted trigonal-bipyramidal geometry. The fact that the *Z* isomer is obtained rather than the *E* isomer generally formed in this type of reaction might be attributed to the intramolecular O → Sn coordination observed experimentally.

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Referee I: M. Ehses
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