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(*Z*)-1-[2-(Tribenzylstannyl)vinyl]-1-cyclooctanol: Synthesis, Characterization, Halodebenzylation, and Crystal Structure

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ABSTRACT

The synthesis and properties of (*Z*)-1-[2-(tribenzylstannyl)vinyl]-1-cyclooctanol (**1**) are described. Compound (**1**) crystallizes from alcohol in the monoclinic space group $P2_1/c$ with unit-cell dimensions $a = 9.348(1)$ Å, $b = 26.143(1)$ Å, $c = 10.705(1)$ Å, $\beta = 95.09(1)°$, $V = 2605.9(1)$ Å^3, $Z = 4, D_c = 1.390\,\mathrm{g\,cm^{-3}}, \mu = 10\,\mathrm{cm^{-1}}$, final $R = 0.033$ for 3165 observed reflection ($|F|^2 \geq 8\sigma|F|^2$). The x-ray diffraction analysis of this compound shows intramolecular coordination of oxygen to the tin atom giving rise to a five-membered ring in which the metal exhibits a distorted trigonal

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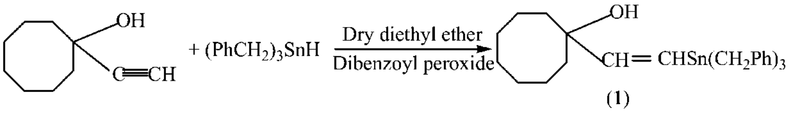
bipyramidal geometry. Compound (**1**) by halodebenzylation by Br_2 or ICl forms the corresponding (*Z*)-1-[2-(dibenzylhalostannyl)vinyl]-1-cyclooctanol or (*Z*)-1-[2-(benzyldi-halostannyl)vinyl]-1-cyclooctanol, respectively. All compounds were characterized by elemental analyses, IR, ^{1}H NMR.

Key Words: Halodebenzylation; Crystal sturcutre; (*Z*)-1-[2-(tribenzylstannyl)vinyl]-1-cyclooctanol.

INTRODUCTION

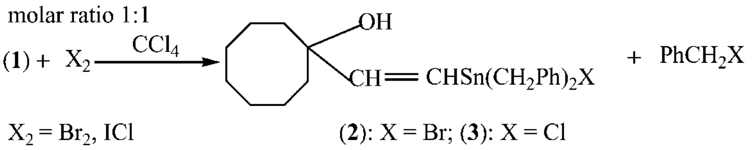
It was recently reported[1–4] that $(C_6H_5CH_2)_3SnH$ adds to 1-ethynylcyclo-heptanol to give (*Z*)-1-[2-(tribenzylstannyl)vinyl]-1-cycloheptanol. This tribenzylvinyltin derivative reacts with one or two equivalents of halogen (Br_2 or ICl), leading exclusively to the cleavage of one or two benzyl-tin bonds, respectively. A 1 : 1 molar ratio gives rise to (*Z*)-1-[2-(dibenzylhalostannyl)-vinyl]-1-cycloheptanol, a 2 : 1 molar ratio, (*Z*)-1-[2-(benzyldihalostannyl)-vinyl]-1-cycloheptanol, which exhibits interesting results against P388 lymphocytic leukemia in mice and BEL-7402 liver cancer in humans (the results will be reported elsewhere).

To enable us to further study this structure/activity relationship, we synthesized (*Z*)-1-[2-(tribenzylstannyl)vinyl]-1-cyclooctanol (**1**) and corresponding mono- and dihalides (**2**)–(**5**) as shown in Eqs. (1), (2) and (3).



(1)

(**1**)



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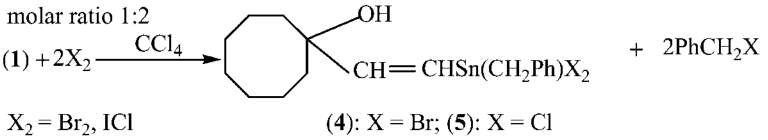

(3)

EXPERIMENTAL

Materials

1-Ethynyl-1-cyclooctanol was prepared by the literature method,[5] b.p. 78–80 °C/10 mmHg; yield: 78% and was recrystallized with pentane before use (m.p. 43–44 °C, lit. 44–44.5 °C). Tribenzyltin hydride was prepared according to the procedure of Kuivila,[6] m.p. 102–104 °C, yield: 45%, ν(Sn–H): 1835 cm^{-1} (lit. ν(Sn–H): 1835 cm^{-1}). It was used directly without separation.

Physical Measurements

A crystal, dimensions 0.24 mm × 0.32 mm × 0.38 mm, was used to collect data on a Rigaku R-AXIS RAPID IP automatic diffractometer. IR spectra were recorded on a Nicolet Instrument Corporation 360 FT-IR ESP spectrometer, ^{1}H NMR spectra were obtained on a DRX-400 spectrometer in $CDCl_3$ with TMS as internal standard. The data for the content of C and H were recorded on a PE 2400 C-H-N automatic element analyzer. The content of Sn was determined on a VRA-20 x-ray fluorescence spectrometer.

Reaction of 1-Ethynyl-1-cyclooctanol with Tribenzyltin Hydride

To 30 mL of a dry diethyl ether solution of tribenzyltin hydride (15.74 g, 40 mmol) in a three-necked flask equipped with a condenser on top of which was a $CaCl_2$ tube, 1-ethynyl-1-cyclooctanol (6.08 g, 40 mmol) and dibenzoyl peroxide (20 mg) were added. This mixture was kept under nitrogen. After 20 hr at room temperature with stirring, diethyl ether was evaporated, the residue was recrystallized from ethanol to give 12.46 g (57.2%) of a colorless solid, (*Z*)-1-[2-(tribenzylstannyl)vinyl]-1-cyclooctanol (**1**). m.p. 84–86 °C. Anal. calcd. for $C_{31}H_{38}OSn$ (FW 545): C, 68.26; H, 6.97; Sn, 21.83. Found C, 68.22; H, 6.92; Sn, 21.78. IR: ν(O–H): 3579; ν(C–O): 1083; $\nu(O \rightarrow Sn)$: 522 cm^{-1}. ^{1}H NMR δ_H: 0.61 (1H, s, OH), 1.56 (14H, br, C_8H_{14}), 2.28 (2H, s, CH_2), 5.59, 6.65 (2H, d, $J = 13$ Hz, CH=CH), 6.84–7.22 (15H, m, $3C_6H_5$) ppm. Hexabenzylditin was obtained as an insoluble by-product.

Reaction of Compound (1) with Bromine or Iodine Monochloride (Molar Ratio 1 : 1)

Bromine (0.1 mL, 1.98 mmol) dissolved in carbon tetrachloride (10 mL) was added slowly to compound (**1**) (1.079 g, 1.98 mmol) dissolved in CCl_4 (12 mL) at $-5\,^\circ$C. The color of bromine disappeared immediately. The solvent was evaporated and the residue was recrystallized from cyclohexane to give (*Z*)-1-[2-(dibenzylbromostannyl)vinyl]-1-cyclooctanol (**2**), as white crystals, yield 0.78 g (73.4%), m.p. 56–58 °C. Anal. Calcd for $C_{24}H_{31}BrOSn$ (FW 534): C, 53.93; H, 5.81; Sn, 22.28. Found: C, 53.88; H, 5.76; Sn, 22.21. IR: ν(O–H): 3577; ν(C–O): 1085; $\nu(O \rightarrow Sn)$: 545 cm^{-1}. ^1H NMR δ_H: 2.28 (1H, s, OH), 1.47 (14H, br, C_8H_{14}), 2.36 (2H, s, CH_2), 5.59, 6.63 (2H, d, $J = 10$ Hz, CH=CH), 7.07–7.37 (10H, m, $2C_6H_5$) ppm. From the mother liquor, benzyl bromide was separated and 0.5 mL $CDCl_3$ was added to determine its ^1H NMR spectrum. ^1H NMR δ_H: 4.56 (2H, s, CH_2), 7.06–7.14 (5H, m, C_6H_5) ppm. It confirmed benzyl bromide.

An analogous procedure was used for the synthesis of (*Z*)-1-[2-(dibenzylchlorostannyl)vinyl]-1-cyclooctanol (**3**), white crystals, yield 0.55 g (56.7%), m.p. 112–114 °C. Anal. Calcd for $C_{24}H_{31}ClOSn$ (FW 489.5): C, 58.84; H, 6.33; Sn, 24.31. Found: C, 58.80; H, 6.28; Sn, 24.29. IR: ν(O–H): 3421; ν(C–O): 1054; $\nu(O \rightarrow Sn)$: 546 cm^{-1}; ^1H NMR δ_H: 2.65 (1H, s, OH), 1.55 (14H, br, C_8H_{14}), 2.79 (2H, s, CH_2), 6.03, 6.64 (2H, d, $J = 13$ Hz, CH=CH), 7.04–7.24 (10H, m, $2C_6H_5$) ppm.

Reaction of Compound (1) with Bromine or Iodine Monochloride (Molar Ratio 1 : 2)

Bromine (0.2 mL, 3.96 mmol) dissolved in carbon tetrachloride (20 mL) was added slowly to compound (**1**) (1.079 g, 1.98 mmol) dissolved in CCl_4 (25 mL) at $-10\,^\circ$C. When the solution became almost colorless, carbon tetrachloride was evaporated. The residue was recrystallized from cyclohexane to give (*Z*)-1-[2-(benzyldibromostannyl)vinyl]-1-cyclooctanol (**4**), as white needles, yield 0.75 g (72.3%), m.p. 126–128 °C. Anal. Calcd for $C_{17}H_{24}Br_2OSn$ (FW 523): C, 39.01; H, 4.59; Sn, 22.75. Found: C, 38.98; H, 4.51; Sn, 22.70. IR: ν(O–H): 3422; ν(C–O): 1050 cm^{-1}; $\nu(O \rightarrow Sn)$: overlapped. ^1H NMR δ_H: 3.13 (1H, s, OH), 1.54 (14H, br, C_8H_{14}), 3.02 (2H, s, CH_2), 6.07, 6.96 (2H, d, $J = 12$ Hz, CH=CH), 7.20–7.86 (5H, m, C_6H_5) ppm.

An analogous procedure was used for the synthesis of (*Z*)-1-[2-(benzyldichlorostannyl)vinyl]-1-cyclooctanol (**5**), white crystals, yield 0.58 g (68.2%), m.p. 160–161 °C. Anal. Calcd for $C_{17}H_{24}Cl_2OSn$ (FW 434): C, 47.00; H, 5.53; Sn, 27.42. Found: C, 46.98; H, 5.50; Sn, 27.40. IR: ν(O–H): 3409;

ν(C–O): 1083; ν(O → Sn): 520 cm^{-1}; ^{1}H NMR δ_H: 3.18 (1H, s, OH), 1.65 (14H, br, C_8H_{14}), 3.10 (2H, s, CH_2), 6.26, 6.97 (2H, d, $J = 10$ Hz, CH═CH), 7.23–7.72 (5H, m, C_6H_5) ppm.

RESULT AND DISCUSSION

Syntheses

The addition of ethyne to cyclooctanone in the presence of *t*-BuOK according to the literature method[5] yielded 1-ethynylcyclooctanol in good yield (78%). Hydrostannation of this alkyne with tribenzyltin hydride using dibenzoyl peroxide as a catalysts yielded compound (**1**) [Eq. (1)]. Compound (**1**) was purified by crystallization from ethanol. Compound (**1**) shows characteristic ethylenic proton signals at 5.59 and 6.65 ppm, namely two doublets with $^3J_{HC=CH} = 13$ Hz.

The reaction of compound (**1**) with halogens (Br_2 or ICl) in 1 : 1 or 1 : 2 molar ration yielded compounds (**2**)–(**5**) quantitatively [Eqs. (2) and (3)]. Hence, the benzyl-tin bond is cleaved regiospecifically. Such regiospecific cleavages have been observed previously in organotin compounds containing donor groups.[2] Compound (**1**) reacts with one equivalent of halogen, the vinylic protons appear at 5.59 and 6.63 ppm (**2**); 6.03 and 6.64 ppm (**3**), respectively, again as doublets $^3J_{HC=CH} = 10$ Hz and $^3J_{HC=CH} = 13$ 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. Therefore, compounds (**2**) and (**3**) are identified as (*Z*)-1-[2-(dibenzylhalostannyl)vinyl]-1-cyclooctanols. After the addition of a second equivalent of halogen, the vinylic protons change to 6.07 and 6.96 ppm (**4**); 6.26 and 6.97 ppm (**5**) as doublets $^3J_{HC=CH} = 12$ Hz and $^3J_{HC=CH} = 10$ Hz. This shows that the second group cleaved by halogen again is a benzyl group. Thus, compounds (**4**) and (**5**) are (*Z*)-1-[2-(benzyldihalostannyl)-vinyl]-1-cyclooctanols.

In addition, we have separated the side product benzyl bromide, and have recorded its ^{1}H NMR spectrum confirming it as of benzyl bromide.

X-ray Structure Analysis of Compound (1)

The structure of (*Z*)-1-[2-(tribenzylstannyl)vinyl]-1-cyclooctanol (**1**) has been determined by x-ray diffraction analysis and is shown in Fig. 1. Compound (**1**) crystallizes from alcohol in the monoclinic space group $P2_1/c$ with $a = 9.348(1)$ Å, $b = 26.143(1)$ Å, $c = 10.705(1)$ Å, $\beta = 95.09(1)°$, $V = 2605.9(1)$ Å^3, $Z = 4$, $D_c = 1.390$ g cm^{-3}, $\mu = 10$ cm^{-1}, final $R = 0.033$

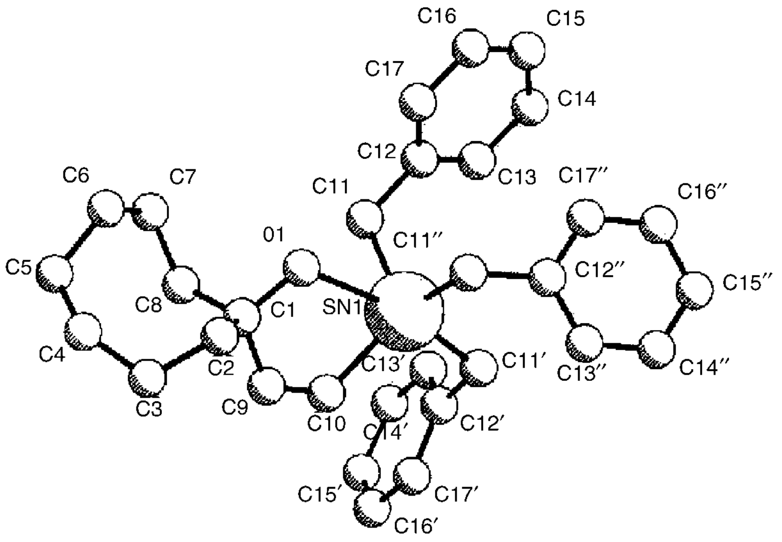

Figure 1. Structure of compound (**1**).

for 3165 observed reflection ($|F|^2 \geq 8\sigma|F|^2$). Selected bond lengths and angles are given in Tables 1 and 2. Crystal data and details of the x-ray studies are listed in Table 3.

The tin atom is coordinated by the C(10) and O(1) atoms of the 1-ethynyl-1-cyclooctanol ligand, and three benzyl groups. The Sn···O(1) bond length of 2.807(5) Å for (**1**), clearly represents significant bonding interactions. The geometry about the atom is thus best described as being based on a distorted trigonal bipyramid with the axial positions occupied by the C(11′) and O(1) atoms; O(1)–Sn(1)–C(11′) 167.9(1)°. The tin atom is five-coordinate, being bonded to three benzyl groups, the vinyl C(10) atom

Table 1. Selected bond lengths (Å) in compound (**1**).[a]

O(1)–Sn	2.807(5)	Sn(1)–C(11′)	2.182(5)
Sn(1)–C(10)	2.137(5)	Sn(1)–C(11″)	2.168(5)
Sn(1)–C(11)	2.180(5)	O(1)–C(1)	1.425(6)
C(1)–C(9)	1.509(7)	C(2)–C(3)	1.554(8)
C(9)–C(10)	1.328(7)	C(11)–C(12)	1.492(8)
C(11′)–C(12′)	1.495(7)	C(11″)–C(12″)	1.500(7)

[a] Standard deviations are given in parentheses.

Table 2. Selected bond angles (deg) in compound (**1**).[a]

O(1)–Sn(1)–C(10)	65.7(1)	O(1)–Sn(1)–C(11)	85.1(1)
O(1)–Sn(1)–C(11′)	167.9(1)	O(1)–Sn(1)–C(11″)	75.9(1)
C(11)–C(12)–C(13)	120.9(5)	C(10)–Sn(1)–C(11)	115.7(1)
C(10)–Sn(1)–C(11′)	103.1(1)	Sn(1)–O(1)–C(1)	110.0(2)
C(11′)–Sn(1)–C(11″)	110.4(2)	C(11)–Sn(1)–C(11″)	104.6(2)

[a] Standard deviations are given in parentheses.

Table 3. Date collection and structure refinement parameters.

Formula unit	$C_{31}H_{38}OSn$
Crystal size	0.24 mm × 0.32 mm × 0.38 mm
No. and 2θ range, degree of reflections for lattice parameter	4458, 55
Space group	$P2_1/c$
a, (Å)	9.348(1)
b, (Å)	26.143(1)
c, (Å)	10.705(1)
β, °	95.09(1)
V, (Å^3)	2605.9(1)
Z	4
D_{calc} (g cm^{-3})	1.390
$\mu_{\mathrm{MoK}\alpha}$ (cm^{-1})	10
Radiation	MoKα
λ, (Å)	0.71073
Monochromator	graphite
$2\theta_{\max}$, (deg)	55
Index range (h, k, l)	0–12, 0–33, −13–13
No. of ind rflns	
Meads	4458
Obsd($\|F\|^2 > 8\sigma\|F\|^2$)	3165
Method used to solve structure	Direct methods (SHELX86)
Refinement	Anisotropic least squares (SHELXS86) using F^2
Weighting scheme	$W = 1/\sigma\|F\|^2$
H atoms	All hydrogen atoms were obtained from geometric and difference Fourier calculations.
R, R_w, S	0.033, 0.042, 0.203
Max height in final ΔF map	0.47

[2.137(5) Å] and the O(1) atom of the hydroxyl group [2.807(5) Å]. The equatorial plane is being defined by the three carbon atoms C(10), C(11), and C(11″).

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