Intramolecular O→Sn Coordination in (*Z*)-17-[2-(Triphenylstannyl)vinyl]-4-estren-17-ol: Evidence by X-ray Diffraction Analysis and Iodo Demetalation

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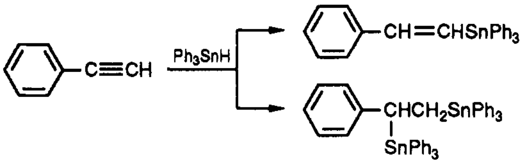
Received April 9, 1990

Summary: The synthesis and properties of (*Z*)-17-[2-(triphenylstannyl)vinyl]-4-estren-17-ol (**1**) are described. Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ ($Z = 4$) with $a = 8.007$ (2) Å, $b = 15.152$ (1) Å, and $c = 26.807$ (2) Å. The X-ray diffraction analysis of this compound shows the presence of an intramolecular coordination to the tin atom giving rise to a five-membered ring in which the metal exhibits a distorted-trigonal-bipyramidal geometry; as a consequence, a phenyl group, probably the apical one, is cleaved more easily by iodine than the vinyl substituent.

Only a few tetraorganotin compounds exhibit a geometry which approaches that of a trigonal bipyramid. Such a five-coordinated structure has been evidenced when intramolecular coordination of a nucleophile to tin can occur.[1] On the other hand, it is well established that the intramolecular coordination also dramatically influences the selectivity of electrophilic cleavages of carbon–tin bonds.[2]

We present experimental evidence for such types of intramolecular coordination and selectivity changes in (*Z*)-17-[2-(triphenylstannyl)vinyl]-4-estren-17-ol.

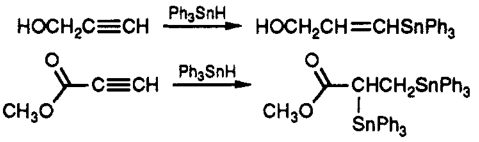
Results and Discussion. Synthesis and Characterization of (*Z*)-17-[2-(Triphenylstannyl)vinyl]-4-estren-17-ol (1). It is well-known that triphenyltin hydride adds to acetylenic triple bonds.[3] Thus, it reacts with phenylacetylene to yield either triphenylstyryltin or 1-phenyl-1,2-bis(triphenylstannyl)ethane depending on the molar ratio of the reagents:



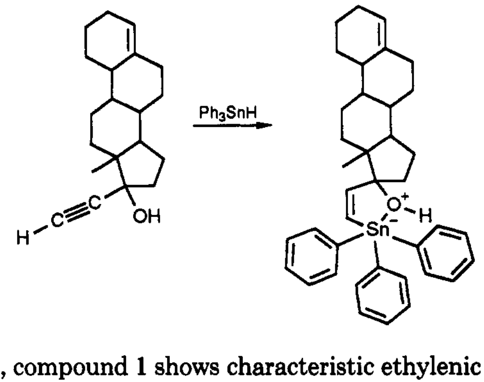
It reacts with acetylene to yield 1,2-bis(triphenylstannyl)ethane:[3]

$$HC{\equiv}CH \xrightarrow{Ph_3SnH} Ph_3SnCH_2CH_2SnPh_3$$

Triphenyltin hydride also reacts with propargyl alcohol and with the methyl ester of propiolic acid to yield (3-hydroxy-1-propenyl)triphenyltin and 1-(methoxycarbonyl)-1,2-bis(triphenylstannyl)ethane, respectively:[3]



The proton NMR spectrum of the product 1 obtained after the addition of 1 equiv of triphenyltin hydride to the triple bond of 17-ethynyl-4-estren-17-ol 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 6.17 and 6.98, ppm, namely two doublets with $^3J(^1H{-}C{=}C{-}^1H) = 13$ Hz, with additional $^1H{-}^{117/119}Sn$

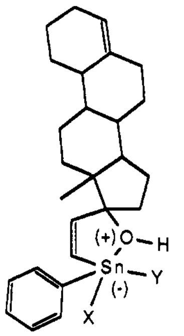


Figure 1. Structure of compounds 1 (X = Y = C_6H_5), 2 (X = I, Y = C_6H_5), and 3 (X = Y = I).

Table I. Selected Bond Lengths (Å) in Compound 1[a]

O1–Sn1	2.77 (1)	C5–C4	1.57 (2)	C15–C10	1.55 (2)
C1–Sn1	2.13 (1)	C6–C5	1.54 (2)	C12–C11	1.57 (2)
C21–Sn1	2.16 (1)	C7–C6	1.54 (2)	C13–C12	1.54 (2)
C27–Sn1	2.12 (1)	C11–C6	1.54 (2)	C14–C13	1.50 (2)
C33–Sn1	2.19 (1)	C8–C7	1.54 (2)	C15–C14	1.54 (2)
C3–O1	1.45 (1)	C20–C7	1.56 (2)	C19–C14	1.30 (2)
C2–C1	1.36 (2)	C9–C8	1.58 (2)	C16–C15	1.55 (2)
C3–C2	1.51 (2)	C10–C9	1.52 (2)	C17–C16	1.51 (2)
C4–C3	1.54 (2)	C11–C10	1.55 (2)	C18–C17	1.46 (3)
C7–C3	1.56 (2)			C19–C18	1.59 (3)

[a] Standard deviations are given in parentheses.

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Table II. Selected Bond Angles (deg) in Compound 1[a]

C21-Sn1-C1	117 (1)	C27-Sn1-C1	121 (1)	C27-Sn1-C21	105 (1)
C33-Sn1-C1	104 (1)	C33-Sn1-C21	105 (1)	C33-Sn1-C27	103 (1)
C2-C1-Sn1	127 (1)	O1-Sn1-C21	87 (1)	O1-Sn1-C27	77 (1)
O1-Sn1-C33	168 (1)	O1-Sn1-C1	67 (1)	C3-C2-C1	127 (1)
C2-C3-O1	106 (1)	C4-C3-O1	112 (1)	C4-C3-C2	109 (1)
C7-C3-O1	113 (1)	C7-C3-C2	112 (1)	C7-C3-C4	106 (1)
C5-C4-C3	107 (1)	C6-C5-C4	102 (1)	C7-C6-C5	106 (1)
C11-C6-C5	118 (1)	C11-C6-C7	112 (1)	C6-C7-C3	101 (1)
C8-C7-C3	116 (1)	C8-C7-C6	110 (1)	C20-C7-C3	107 (1)
C20-C7-C6	113 (1)	C20-C7-C8	111 (1)	C9-C8-C7	108 (1)
C10-C9-C8	116 (1)	C11-C10-C9	113 (1)	C15-C10-C9	112 (1)
C15-C10-C11	110 (1)	C10-C11-C6	109 (1)	C12-C11-C6	110 (1)
C12-C11-C10	112 (1)	C13-C12-C11	106 (1)	C14-C13-C12	118 (1)
C15-C14-C13	115 (1)	C19-C14-C13	120 (1)	C19-C14-C15	126 (1)
C14-C15-C10	111 (1)	C16-C15-C10	112 (1)	C16-C15-C14	110 (1)
C17-C16-C15	112 (1)	C18-C17-C16	111 (1)	C19-C18-C17	112 (2)
C18-C19-C14	120 (2)	C22-C21-Sn1	126 (1)	C26-C21-Sn1	117 (1)
		Sn1-O1-C3	112 (1)		

[a] Standard deviations are given in parentheses.

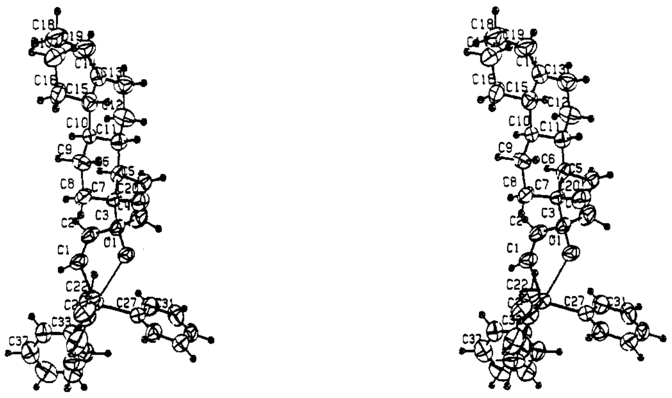

Figure 2. Molecular structure and numbering scheme of compound **1**. Non-hydrogen thermal ellipsoids are drawn at 50% probability.

Table III. Data Collection and Structure Refinement Parameters

formula unit	$C_{38}H_{44}OSn$
cryst shape	colorless needle (0.09 × 0.12 × 0.25 mm)
no. and 2θ range, deg, of rflns for lattice params	30, 11-46
orthorhombic space group	$P2_12_12_1$
a, Å	8.007 (2)
b, Å	15.152 (1)
c, Å	26.807 (2)
V, Å^3	3252.3 (9)
Z	4
D_{calc}, g cm^{-3}	1.30
$\mu_{Cu\,K\alpha}$, cm^{-1}	62.30
radiation	Cu Kα
λ, Å	1.541 78
monochromator	graphite
$2\theta_{max}$, deg	135
θ–2θ scan (scan width), deg	2.6
index range (h,k,l)	0-9, 0-18, 0-31
no. of ind rflns	
measd	3343
obsd ($I > 2.5\sigma$)	2570
empirical abs cor (ψ scan)	
min abs cor	0.73
max abs cor	1.12
method used to solve structure	direct methods (SHELX86[7])
refinement	anisotropic least squares (SHELX76[8]) using F
weighting scheme	$w = (\sigma^2 + gF^2)^{-1}$, $g = 0.000\,87$
H atoms	in calc position, with 2 diff isotropic temp factors (one for the H atoms of the phenyl groups, one for the other H atoms)
R, R_w, S	0.061, 0.066, 1.962 (for 2570 rflns)
max height in final ΔF map	0.49

coupling satellites $^{2}J(^{1}H{-}C{-}^{117/119}Sn) = 98/102$ Hz and $^{3}J(^{1}H{-}C{=}C{-}^{117/119}Sn) = 178/188$ Hz. Another olefinic singlet, with the same chemical shift as that of the starting material (5.38 ppm), is assigned to the proton on the double bond of the steroidal moiety.

X-ray Structure Analysis of Compound 1. The structure of 17-[2-(triphenylstannyl)vinyl]-4-estren-17-ol (**1**) has been determined by X-ray diffraction and is shown in Figures 1 and 2. Selected bond lengths and angles are given in Tables I and II. Crystal data and details of the X-ray studies are listed in Table III.

The central tin atom has a strongly distorted trigonal bipyramidal geometry with the O1 and C33 atoms in apical positions and the C1, C21, and C27 atoms in equatorial positions. Even if we do not take the tin–oxygen interaction into account, a tetrahedral environment around tin is not credible because the angles C1–Sn–C21 and C1–Sn–C27 are typically trigonal bipyramidal. 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. The C–Sn–O angle is quite small (67°), although it is not very different from the analogous C–Sn–O angle (also from a five-membered ring) observed for $Cl_2Sn(CH_2CH_2CH_2)_2O$ (71°).[5]

Reactivity of Compound 1 toward Iodine. This intramolecular coordination also has the consequence that a phenyl group, probably the apical one, is cleaved more easily by iodine than the equatorial vinyl substituent. Indeed, when compound **1** is allowed to react with 1 equiv of iodine, the NMR spectrum of the compound **2** obtained still exhibits the signal at 5.38 ppm of the steroidal vinylic proton, but the other two are shifted by the replacement of a phenyl group by iodine, as expected. They now appear at 6.38 and 6.77 ppm instead of 6.17 and 6.98 ppm, again as doublets ($^{3}J(^{1}H{-}C{=}C{-}^{1}H) = 12$ Hz) with the typical coupling satellites $^{2}J(^{1}H{-}C{-}^{117/119}Sn) = 126/132$ Hz and $^{3}J(^{1}H{-}C{=}C{-}^{117/119}Sn) = 240/251$ Hz. The presence of these vinylic proton–tin couplings in compound **2** clearly shows that the phenyl–tin bond is preferentially cleaved by iodine and that the (steroid—CH=CH)—Sn bond remains intact. Indeed, no other signals from the vinylic

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steroid—CH═CH—I protons could be detected in the proton NMR spectrum, and the patterns of iodobenzene clearly appear in the aromatic region overlapping partially with the tin-phenyl protons. Therefore, compound **2** is identified as (*Z*)-17-[2-(diphenyliodostannyl)vinyl]-4-estren-17-ol.

After the addition of a second equivalent of iodine, the steroidal vinyl resonance is again nearly unchanged (5.40 ppm), while the two other resonances, again changed to 6.40 and 6.01 ppm, appear as doublets ($^{3}J(^{1}\mathrm{H{-}C{=}C{-}}^{1}\mathrm{H})$ = 11 Hz) further coupled to tin with $^{2}J(^{1}\mathrm{H{-}C{-}}^{117/119}\mathrm{Sn})$ = 195/204 Hz and $^{3}J(^{1}\mathrm{H{-}C{=}C{-}}^{117/119}\mathrm{Sn})$ = 306/317 Hz. Again, no vinylic steroid—CH═CH—I signals are visible. The observation of vinylic tin-proton couplings unambiguously shows that the second group cleaved by iodine is again a phenyl one, allowing compound **3** obtained after the addition of 2 equiv of iodine to be identified as (*Z*)-17-[2-(phenyldiiodostannyl)vinyl]-4-estren-17-ol.

The coupling constant $^{3}J(^{1}\mathrm{H{-}C{=}C{-}}^{1}\mathrm{H})$ = 13 Hz observed for compound **1** is rather large since cis coupling constants in five-membered rings usually amount to 8 Hz or even less.[4] However, this ring, containing a tin atom, is characterized by rather abnormal bond angles. This coupling constant decreases from compound **1** to compound **3**.

Experimental Section. Chemicals. 17-Ethynyl-4-estren-17-ol ("lynestrenol") was supplied by Organon, Oss, The Netherlands. Triphenyltin hydride was prepared according to Kuivila:[6] bp 161-165 °C/0.5 Torr (lit.[6] bp 162-168 °C/0.3 Torr); n_{D}^{25} = 1.6343; IR ν(Sn-H) = 1835 cm^{-1}; yield 75%.

Equipment: X-ray diffractometer, Huber automated four-circle diffractometer, data collection at room temperature (ca. 21 °C); NMR, Bruker AM 270 instrument; IR, Perkin-Elmer 298 instrument; melting point microscope, Thermopan.

Reactions. Reaction of 17-Ethynyl-4-estren-17-ol with Triphenyltin Hydride. A 1.42-g amount of 17-ethynyl-4-estren-17-ol (5 mmol) and 1.76 g of triphenyltin hydride (5 mmol) were dissolved in 30 mL of dry ether in a two-necked flask and 10 mg of dibenzoyl peroxide was added. After 20 h at room temperature, ether was evaporated and the viscous material obtained was crystallized from ethanol, yielding 2.06 g of a crystalline solid, compound **1**: mp 133-135 °C; yield 65%. A 0.25-g amount of hexaphenylditin (mp 231-232 °C), only slightly soluble in ethanol, was obtained as a side product. Compound **1** was recrystallized three times from ethanol, yielding white needles (mp 134-135 °C), one of which was used for the single-crystal X-ray diffraction study.

Reaction of (*Z*)-17-[2-(Triphenylstannyl)vinyl]-4-estren-17-ol with Iodine. A 50.8-mg amount of iodine (0.2 mmol) dissolved in 5 mL of chloroform was added to 134.8 mg of **1** (0.2 mmol) dissolved in 2 mL of $\mathrm{CHCl_3}$. The color of iodine disappeared immediately. The solvent was evaporated, and 0.5 mL of $\mathrm{CDCl_3}$ was added for recording a ^{1}H NMR spectrum.

After the NMR study, an additional 50.8 mg of iodine dissolved in 5 mL of ethanol was added to this solution. The color disappeared much more slowly. When the solution had become almost colorless, the mixture was prepared as explained above for recording a further ^{1}H NMR spectrum.

Acknowledgment. We are grateful to the National Science Foundation of the People's Republic of China and to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" for financial support (Grant No. FKFO 20127.90; M.G., R.W.). We thank Mr. Willy Verbist for recording the NMR spectra.

Registry No. **1** (coordination compound entry), 127973-41-5; **1** (stannane entry), 127973-42-6; **2**, 127973-39-1; **3**, 127973-40-4; $\mathrm{Ph_3SnH}$, 892-20-6; lynestrenol, 52-76-6.

Supplementary Material Available: Tables of positional parameters, thermal parameters, angles between normals to least-squares planes, least-squares planes and deviations therefrom, and bond angles and a stereoview of **1** (23 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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A General, High-Yield Reaction for the Formation of (Chloromethyl)oligosilanes

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Received April 12, 1990

Summary: (Chloromethyl)oligosilanes are conveniently synthesized in high yield (>75%) via the reaction between chlorooligosilanes and (chloromethyl)lithium generated in situ from bromochloromethane and *n*-butyllithium at -60 °C. Bis(chloromethyl)silanes are also produced from the appropriate dichlorosilanes.

The chloromethyl group attached to silanes represents one of the most useful functional groups in organosilicon chemistry. It has been widely used as a synthon for the formation of silylmethyl Grignard or alkali-metal reagents and has also demonstrated much utility for functionalizing silanes via direct halogen displacement reactions.[1,2,3,5] There are several diverse routes available for the formation of such a group, and two popular chlorination procedures are outlined in eqs 1 and 2.[4,5]

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