An Easy Access to Stereodefined 2-Pentenyltins by Partial Hydrogenation of 2,4-Pentadienyltins with Diazene

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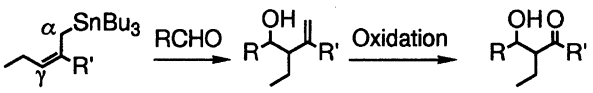
Synopsis. Tributyl-(2-pentenyl)tins were readily prepared in high yield by hydrogenation of tributyl-(2,4-pentadienyl)tins with diazene generated from 2,4,6-triisopropylbenzenesulfonohydrazide. The terminal double bond was selectively hydrogenated in the conjugated diene system. The stereochemistry of the internal double bond was completely retained.

Since it has become well-established that allylic tin compounds are of great synthetic importance,[1] various preparative methods of these compounds are known; however, there are few for the facile preparation of stereodefined ones,[2—5] in spite of their potential importance. In the thermal reaction with aldehydes, (*E*)- and (*Z*)-allylic tins preferentially gave *anti*- and *syn*-products, respectively.[6] In the photoreaction with benzil[7] and aldehydes,[8] (*E*)- and (*Z*)-allylic groups were introduced regio-reversely at the α-position of allylic tins, while retaining their stereochemistry. Under these circumstances, while 2-butenyltin (crotyltin) is particularly famous, especially due to its stereoselective reaction,[6] homologous 2-pentenyltins, which should also be useful reagents for organic synthesis (e.g. Eq. 1), have not yet been well mentioned.[9]

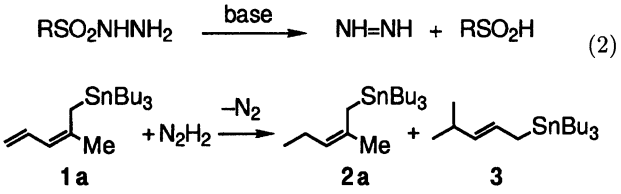


(1)

In this paper, we wish to report that stereodefined tributyl-(2-pentenyl)tins can be readily synthesized by a partial hydrogenation of the corresponding tributyl-(2,4-pentadienyl)tins (PDT) with the use of diazene, while retaining their internal double-bond geometry.

Results and Discussion

Because the facile stereoselective preparation of PDTs has already been reported,[10] they can be good precursors for the stereodefined synthesis of 2-pentenyltins. Knowing that diazene can hydrogenate less congested olefins selectively,[11,12] we first applied *p*-toluenesulfonohydrazide as a source of diazene for the considered reaction (Eq. 2. R=*p*-MeC_6H_4). However, the reaction conditons necessary to generate diazene (reflux in ethanol)[13] were found to be unsuitable, since the yield of pentenyltin **2a** from PDT **1a** was disappointing (26%) with a considerable contamination of the rearranged product **3**[14] (13%) (Eq. 3).



(2)

(3)

Thus, we next attempted the reaction in an aprotic solvent and at a lower temperature, finding that 2,4,6-triisopropylbenzenesulfonohydrazide (**4**)[15] is suitable for the source of diazene.

The results are listed in Table 1. (*Z*)-PDT was successfully hydrogenated by Method A (1.7 mol of **4** and 2 mol of K_2CO_3 in ether at room temperature for 27 h). As for the 2-substituent, its bulkiness and functionality did not disturb the reaction. (*E*)-PDTs required slightly forced conditions, such as Method B (**4** was increased to 3 mol) or Method C (temperature was raised at 35 °C), due to their lower reactivity. Even if a little (*E*)-PDT remained unreacted, it could be removed by the Diels–Alder reaction with maleic anhydride.[10] After this treatment, 80% of (*E*)-**2e** was recovered without any contamination of (*E*)-**1e**.

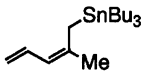
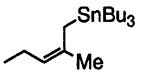
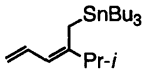
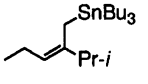
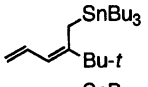
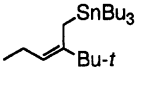
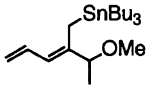
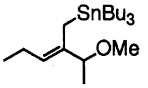
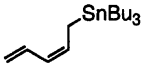
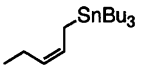
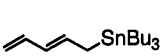
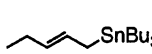
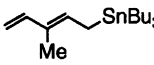
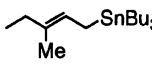
In every case listed, the terminal double bond of **1** was selectively hydrogenated to afford the corresponding pentenyltin **2** with high yield, irrespective of the double-bond geometry and the substituent at the 2- or 3-position of PDT. It is also worth mentioning that the stereochemistry of **2** completely agreed with that of the parent PDT **1**, as shown in Table 1. Thus, (*Z*)-**2** were obtained with complete stereoretention in spite of the tendency of (*Z*)-allylic tins to isomerize to the (*E*)-form.[3,14] No rearranged pentenyltin like **3** was contaminated, either. These facts indicate the mildness of the present reaction conditons. However, hydrogenation of tributyl-(2,4-dimethyl-2,4-pentadienyl)tin and tributyl-(2,4-hexadienyl)tin failed, even under forced conditons; the hydrogenation was very slow.

In conclusion, variously substituted and unsubstituted 2-pentenyltins have been prepared in a facile and stereodefined manner. Such pentenyltins can be widely utilized for synthetic and mechanistic studies.

Experimental

General. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a JEOL GX-270 spectrometer. Tetramethylsilane (δ=0.00) for ^1H and chloroform-*d* (δ=77.03) for ^{13}C were used as internal standards. An ^{119}Sn NMR measurement was performed using a double-sample tube technique; a

Table 1. Hydrogenation of PDT by Diazene

PDT (E/Z)		Product (E/Z)		Method[a)]	Yield/%[b)]
	**1a** (<1/99)		**2a** (<1/99)	A	86
	**1b** (<1/99)		**2b** (<1/99)	A	90
	**1c** (<1/99)		**2c** (<1/99)	A	88
	**1d** (<1/99)		**2d** (<1/99)	A	93
	(*Z*)-**1e** (7/93)		(*Z*)-**2e** (7/93)	A	87
	(*E*)-**1e** (85/15)		(*E*)-**2e** (85/15)	B	81[c)]
	**1f** (86/14)		**2f** (85/15)	B (C)	89 (88)

a) See text. b) Determined by ^{1}H NMR analysis. Yield in parentheses was obtained by Method C. c) (*E*)-**1e** (13%) remained.

sample compound in CCl_4 was in the outer tube and tetramethyltin in acetone-d_6 as an external standard (δ=0.00) was in the inner tube. The IR spectra were obtained with a Hitachi 260-50 spectrometer.

PDTs **1a**—**c**[10] (E/Z<1/99), **1d**[16] (E/Z<1/99), (*Z*)-**1e**[17,18] (E/Z=7/93), and (*E*)-**1e**[19,20] (E/Z=85/15) were prepared while referring to the reported methods. PDT **1f** (E/Z=86/14) was similarly prepared from 3-methylpentadienyl-lithium[21] and tributyltin chloride in THF.

Preparation of 2-Pentenyltins. Method A. Hydrogenation of PDT **1b** is representative. A mixture of PDT **1b** (1.46 g, 3.6 mmol), anhydrous K_2CO_3 (1.00 g, 7.2 mmol), and 2,4,6-triisopropylbenzenesulfonohydrazide (**4**)[15] (1.86 g, 6.2 mmol) in anhydrous ether (30 cm^3) was stirred for 27 h at room temperature under an atmosphere of dry nitrogen. After being added to a solution of 1 mol dm^{-3} NaOH in methanol (40 cm^3), the mixture was stirred for 2 h. It was partitioned between hexane and water. The organic layer was separated, washed with saturated brine, dried (anhydrous Na_2SO_4), and concentrated under reduced pressure to leave pentenyltin **2b** as a colorless oil. The yield was determined 90% by ^{1}H NMR using *p*-nitrobenzaldehyde as an internal standard.

Method B. A mixture of PDT (1 mol), anhydrous K_2CO_3 (3.5 mol), and **4** (3 mol) in ether was stirred for 27 h in a similar way to that mentioned above. The work-up procedure was the same as Method A.

Method C. A mixture of PDT (1 mol), anhydrous K_2CO_3 (2 mol), and **4** (1.7 mol) in ether was refluxed for 4 h. The work-up procedure was the same as Method A.

(*Z*)-Tributyl-(2-methyl-2-pentenyl)tin (2a): IR (neat) 2950, 2900, 2860, 2840, 1640, 1450, 1370, 1065, and 865 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.84 (6H, m, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 0.89 (9H, t, J=7.2 Hz, (CH$_2$)$_3$C$\underline{H}_3$), 0.94 (3H, t, J=7.5 Hz, C$\underline{H}_3$CH$_2$CH=), 1.30 (6H, sext, J=7.1 Hz, CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.48 (6H, m, CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.64 (3H, q, J = 1.2 Hz, J_{Sn-H} = 11.0 Hz, =CCH$_3$), 1.69 (2H, s, J_{Sn-H} = 61.0 Hz, C$\underline{H}_2$SnBu$_3$), 1.93 (2H, quint, J=7.3 Hz, CH$_3$C$\underline{H}_2$CH=), and 4.81 (1H, t, J= 6.7 Hz, CH$_3$CH$_2$C$\underline{H}$=); ^{13}C NMR ($CDCl_3$) δ = 9.7 (3C, J_{Sn-C} = 311.1 and 297.4 Hz, $\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 13.7 (3C, (CH$_2$)$_3$$\underline{C}H_3$), 14.5 ($\underline{C}H_3CH_2$CH=), 15.3 ($J_{Sn-C}$ = 249.2 and 238.0 Hz, $\underline{C}$H$_2$SnBu$_3$), 21.6 (CH$_3$$\underline{C}H_2$CH=), 26.0 (=C$\underline{C}H_3$), 27.5 (3C, J_{Sn-C} = 54.8 Hz, CH$_2$$\underline{C}H_2CH_2CH_3$), 29.2 (3C, J_{Sn-C} = 19.6 Hz, CH$_2$CH$_2$$\underline{C}H_2CH_3$), 122.0 ($J_{Sn-C}$ = 42.1 Hz, CH$_3$CH$_2$$\underline{C}$H=), and 134.4 ($J_{Sn-C}$ = 45.0 Hz, =$\underline{C}$CH$_2$Sn); ^{119}Sn NMR (CCl_4) δ = −15.83.

(*Z*)-Tributyl-(2-isopropyl-2-pentenyl)tin (2b): IR (neat) 2950, 2910, 2860, 2840, 1635, 1450, 1370, 1065, and 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.83 (6H, m, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 0.89 (9H, t, J=7.2 Hz, (CH$_2$)$_3$C$\underline{H}_3$), 0.95 (3H, t, J=7.6 Hz, C$\underline{H}_3$CH$_2$CH=), 1.00 (6H, d, J=6.8 Hz, *i*-Pr-CH$_3$), 1.30 (6H, sext, J=7.3 Hz, CH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.47 (6H, m, CH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.68 (2H, s, J_{Sn-H}=63.0 Hz, C$\underline{H}_2$SnBu$_3$), 1.90 (2H, quint, J=7.3 Hz, CH$_3$C$\underline{H}_2$CH=), 2.02 (1H, quint, J=6.8 Hz, *i*-Pr-C$\underline{H}$), and 4.83 (1H, t, J=6.3 Hz, CH$_3$CH$_2$C$\underline{H}$=); ^{13}C NMR ($CDCl_3$) δ=9.9 (3C, J_{Sn-C}=310.1 and 296.4 Hz), 13.1 (J_{Sn-C}=256.6 and 242.6 Hz), 13.7 (3C), 14.4, 21.5, 22.1 (2C), 27.5 (3C, J_{Sn-C}=53.8 Hz), 29.2 (3C, J_{Sn-C} = 19.6 Hz), 35.9, 118.5 (J_{Sn-C} = 40.1 Hz), and 144.4 (J_{Sn-C} = 44.0 Hz); ^{119}Sn NMR (CCl_4) δ = −16.70.

(*Z*)-Tributyl-(2-*t*-butyl-2-pentenyl)tin (2c): IR (neat) 2970, 2940, 2880, 1635, 1470, 1380, 1360, 1070, and 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.84 (6H, m, C$\underline{H}_2$CH$_2$CH$_2$CH$_3$), 0.89 (9H, t, J=7.1 Hz, (CH$_2$)$_3$C$\underline{H}_3$), 0.97 (3H, t, J=7.6 Hz, C$\underline{H}_3$CH$_2$CH=), 1.02 (9H, s, *t*-Bu),

1.30 (6H, sext, J=7.2 Hz, $CH_2CH_2C\underline{H}_2CH_3$), 1.47 (6H, m, $CH_2C\underline{H}_2CH_2CH_3$), 1.67 (2H, s, $C\underline{H}_2SnBu_3$), 1.82 (2H, quint, J=7.6 Hz, $CH_3C\underline{H}_2CH$=), and 4.89 (1H, t, J=6.3 Hz, $CH_3CH_2C\underline{H}$=); ^{13}C NMR ($CDCl_3$) δ=10.2 (3C, J_{Sn-C}=311.0 and 297.4 Hz), 11.3 (J_{Sn-C}=261.3 and 251.0 Hz), 13.7 (3C), 14.3, 22.1 (J_{Sn-C}=10.8 Hz), 27.5 (3C, J_{Sn-C}=55.8 Hz), 29.2 (3C, J_{Sn-C}=19.6 Hz), 29.7 (3C), 36.2, 118.8 (J_{Sn-C}=39.1 Hz), and 146.5 (J_{Sn-C}=46.0 Hz); ^{119}Sn NMR (CCl_4) δ=−19.21.

(*Z*)-Tributyl-[2-(1-methoxyethyl)-2-pentenyl]tin (2d): IR (neat) 2960, 2930, 2875, 2860, 2820, 1650, 1460, 1380, 1300, 1120, 1100, and 865 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84 (6H, m, $C\underline{H}_2CH_2CH_2CH_3$), 0.89 (9H, t, J=7.1 Hz, $(CH_2)_3C\underline{H}_3$), 0.98 (3H, t, J=7.6 Hz, $C\underline{H}_3CH_2CH$=), 1.20 (3H, d, J=6.4 Hz, $CH(OCH_3)C\underline{H}_3$), 1.30 (6H, sext, J=7.1 Hz, $CH_2CH_2C\underline{H}_2CH_3$), 1.48 (6H, m, $CH_2C\underline{H}_2CH_2CH_3$), 1.61 (2H, AB, $C\underline{H}_2SnBu_3$), 1.93 (2H, m, $CH_3C\underline{H}_2CH$=), 3.19 (3H, s, OCH_3), 3.55 (1H, q, J=6.35 Hz, $C\underline{H}OCH_3$), and 5.06 (1H, t, J=6.6 Hz, $CH_3CH_2C\underline{H}$=); ^{13}C NMR ($CDCl_3$) δ=8.8 (J_{Sn-C}=255.7 and 241.6 Hz), 10.1 (3C, J_{Sn-C}=315.0 and 301.6 Hz), 13.7 (3C), 14.1, 19.9, 21.2, 27.4 (3C, J_{Sn-C}=55.8 Hz), 29.1 (3C, J_{Sn-C}=19.6 Hz), 55.7, 82.5, 123.4 (J_{Sn-C}=39.1 Hz), and 139.3 (J_{Sn-C}=45.0 Hz); ^{119}Sn NMR (CCl_4) δ=−16.95.

(*Z*)-Tributyl-(2-pentenyl)tin ((*Z*)-2e): IR (neat) 2950, 2910, 2860, 2840, 1630, 1450, 1370, 1065, and 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.82 (6H, m, $C\underline{H}_2CH_2CH_2CH_3$), 0.89 (9H, t, J=7.3 Hz, $(CH_2)_3C\underline{H}_3$), 0.96 (3H, t, J=7.3 Hz, $C\underline{H}_3CH_2CH$=), 1.31 (6H, sext, J=7.1 Hz, $CH_2CH_2C\underline{H}_2CH_3$), 1.49 (6H, m, $CH_2C\underline{H}_2CH_2CH_3$), 1.71 (2H, d, J=8.5 Hz, J_{Sn-H}=61.8 Hz, $C\underline{H}_2SnBu_3$), 2.01 (2H, ddq, J=8.9, 1.7, and 7.1 Hz, $CH_3C\underline{H}_2CH$=), 5.05 (dtt, J=10.7, 7.1, and 1.2 Hz, $CH_3CH_2C\underline{H}$=), and 5.51 (1H, dtt, J=10.7, 9.0, and 1.7 Hz, =$C\underline{H}CH_2Sn$); ^{13}C NMR ($CDCl_3$) δ=9.3 (3C, J_{Sn-C}=313.0 and 299.3 Hz), 10.4 (J_{Sn-C}=252.0 and 241.7 Hz), 13.7 (3C), 14.3, 20.2, 27.4 (3C, J_{Sn-C}=52.8 Hz), 29.2 (3C, J_{Sn-C}=19.6 Hz), 126.2 (J_{Sn-C}=45.0 Hz), and 127.6 (J_{Sn-C}=44.0 Hz); ^{119}Sn NMR (CCl_4) δ=−16.59.

(*E*)-Tributyl-(2-pentenyl)tin ((*E*)-2e): IR (neat) 2960, 2925, 2875, 2850, 1635, 1460, 1375, 1070, 960, and 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84 (6H, m, $C\underline{H}_2CH_2CH_2CH_3$), 0.89 (9H, t, J=7.1 Hz, $(CH_2)_3C\underline{H}_3$), 0.94 (3H, t, J=7.3 Hz, $C\underline{H}_3CH_2CH$=), 1.29 (6H, sext, J=7.1 Hz, $CH_2CH_2C\underline{H}_2CH_3$), 1.48 (6H, m, $CH_2C\underline{H}_2CH_2CH_3$), 1.68 (2H, dd, J=8.3 and 0.9 Hz, $C\underline{H}_2SnBu_3$), 1.97 (2H, quint, J=7.6 Hz, $CH_3C\underline{H}_2CH$=), 5.24 (1H, dt, J=15.1 and 6.4 Hz, $CH_3CH_2C\underline{H}$=), and 5.51 (1H, dtt, J=15.1, 8.3, and 1.2 Hz, =$C\underline{H}CH_2Sn$); ^{13}C NMR ($CDCl_3$) δ=9.2 (3C, J_{Sn-C}=314.0 and 300.3 Hz), 9.5 (J_{Sn-C}=330.4 and 313.6 Hz), 13.7 (3C), 14.1, 25.8, 27.4 (3C, J_{Sn-C}=50.9 Hz), 29.2 (3C, J_{Sn-C}=19.6 Hz), 127.6 (J_{Sn-C}=46.0 Hz), and 128.0 (J_{Sn-C}=44.0 Hz); ^{119}Sn NMR (CCl_4) δ=−19.73.

(*E*)-Tributyl-(3-methyl-2-pentenyl)tin (2f): IR (neat) 2950, 2920, 2860, 2850, 1620, 1460, 1370, 1290, 1065, and 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.83 (6H, m, $C\underline{H}_2CH_2CH_2CH_3$), 0.89 (9H, t, J=7.3 Hz, $(CH_2)_3C\underline{H}_3$), 0.96 (3H, t, J=7.3 Hz, $C\underline{H}_3CH_2C$=), 1.29 (6H, sext, J=7.1 Hz, $CH_2CH_2C\underline{H}_2CH_3$), 1.48 (6H, m, $CH_2C\underline{H}_2CH_2CH_3$), 1.57 (3H, s, CCH_3=), 1.66 (2H, d, J=9.0 Hz, J_{Sn-H}=60.3 Hz, $C\underline{H}_2SnBu_3$), 1.97 (2H, q, J=7.6 Hz, $CH_3C\underline{H}_2C$=), and 5.31 (1H, tq, J=8.8 and 1.5 Hz, =$C\underline{H}CH_2Sn$); ^{13}C NMR ($CDCl_3$) δ=9.4 (3C, J_{Sn-C}=309.1 and 295.4 Hz), 10.7 (J_{Sn-C}=264.0 and 252.0 Hz), 13.2 (J_{Sn-C}=15.7 Hz), 13.7 (3C), 15.5, 27.4 (3C, J_{Sn-C}=52.8 Hz), 29.3 (3C, J_{Sn-C}=19.6 Hz), 32.5, 121.5 (J_{Sn-C}=46.0 Hz), and 131.0 (J_{Sn-C}=47.5 Hz); ^{119}Sn NMR (CCl_4) δ=−19.73.

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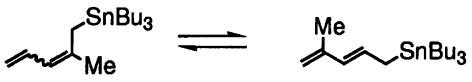

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