A useful method in organotin chemistry: diimine hydrogenation of 1,2-bis(trimethylstannyl)-1-alkenes, 1-trimethylsilyl-2-trimethylstannyl-1-alkenes and some distannacyclopentenes

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Abstract

The title compounds can be readily hydrogenated by diimine produced *in situ* from commercial 80% hydrazine hydrate, 30% hydrogen peroxide and a 1% copper sulphate solution. Replacement of the methyl groups on tin by butyl groups causes the consumption of the alkene to fall dramatically under standard reaction conditions.
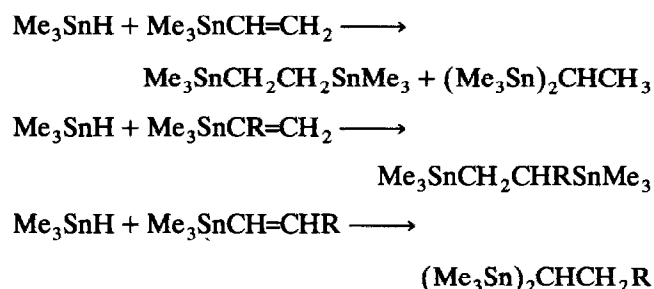
1. Introduction

No general method for the preparation of 1,2-bis(trimethylstannyl)alkanes (**1**) and 1-trimethylsilyl-2-trimethylstannylalkanes (**2**) has so far been described.

$$Me_3SnCH_2CHRSnMe_3 \qquad Me_3SiCH_2CHRSnMe_3$$
$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$
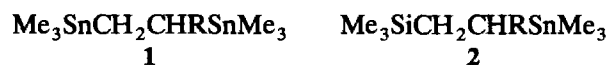
The potentially feasible routes to compounds **1** which are not in fact successful include reactions between 1,2-dihaloethanes and trimethylstannyllithium or -sodium (which lead to elimination) [1] and the palladium-catalysed addition of hexamethylditin to olefins (no reaction using a selection of catalysts) [2]. The hydrostannylation of vinyltins can be used in a few cases: thus the reaction of trimethyltin hydride and vinyltrimethyltin gives a 60:40 mixture of 1,2- and 1,1-bis(trimethylstannyl)ethane [3], and 2-trimethyl-stannyl-1-alkenes indeed afford compounds **1** [4]: however, 1-trimethylstannyl-1-alkenes generally react to give 1,1-bis(trimethylstannyl)-1-alkenes [5].

$$Me_3SnH + Me_3SnCH=CH_2 \longrightarrow$$
$$Me_3SnCH_2CH_2SnMe_3 + (Me_3Sn)_2CHCH_3$$
$$Me_3SnH + Me_3SnCR=CH_2 \longrightarrow$$
$$Me_3SnCH_2CHRSnMe_3$$
$$Me_3SnH + Me_3SnCH=CHR \longrightarrow$$
$$(Me_3Sn)_2CHCH_2R$$

Since the preparation of the 2-trimethylstannyl-1-alkenes is somewhat tedious an easier approach is required, while methods for the preparation of compounds **2** are almost unknown. The obvious method of choice would be catalytic hydrogenation of 1,2-bis(trimethylstannyl)-1-alkenes and 1-trimethylsilyl-2-trimethylstannyl-1-alkenes. However, vinyltins do not normally undergo hydrogenation, presumably because the catalyst is poisoned by the tin compounds. One exception has recently been described by Lautens *et al.*

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[6], but this rhodium-catalysed reaction is limited to stannylsubstituted allylic alcohols:
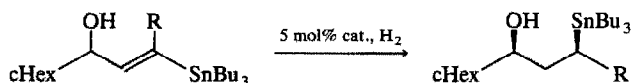

catalyst: ((dppb)Rh(nbd))BF$_4$; dppb = diphenylphos-phinobutane; nbd = norbornadiene.

Attempts to extend the reaction to include a corresponding distannyl compound were unsuccessful [7]. We thus had recourse to reduction via diimine (prepared *in situ* from hydrazine hydrate). Only two examples of this reaction have to our knowledge been reported in organotin chemistry: in 1973 Kuivila *et al.* carried out the reduction of 2-trimethylstannylnorbornene to endo-2-trimethylstannylnorbornane [8], while in 1985 Rahm *et al.* described the reduction of the corresponding 2-triphenylstannyl compound [9]. The former authors generated diimine from 95% hydrazine, 30% hydrogen peroxide and a 1% solution of CuSO$_4$ · 5H$_2$O, while the latter used potassium azodicarboxylate and acetic acid in dioxane. Since the first procedure appeared simpler, we attempted to apply it to the preparation of the title compounds. Our results are described below.

2. Results and discussion

The reaction between diimine produced in this manner and Z-1,2-bis(trimethylstannyl)ethene occurred in a quantitative manner, thus affording the first route to 1,2-bis(trimethylstannyl)ethane free from its regioisomer. We then found that it was possible to replace 95% hydrazine by commercially available 80% hydrazine hydrate, thus making the procedure more attractive. Although it has been observed that increasing substitution leads to decreasing yields in diimine hydrogenation of olefins (in the case of trisubstituted olefins the yields fall to around 50% [10]), we had no problems in hydrogenating bis-1,2-(trimethylstannyl)-1-alkenes quantitatively. The following reactions have been carried out:

Z-Me$_3$SnCR=CHSnMe$_3$ + "N$_2$H$_2$" ⟶

Me$_3$SnCHR-CH$_2$SnMe$_3$
1
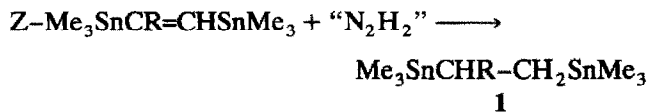
R = Ph, CH$_2$OH, CH$_2$OCH$_2$Ph, CH$_2$OMe,

CHMeOH, CMe$_2$OH, 1-HO-c-C$_6$H$_{11}$, CH$_2$NMe$_2$

However, the procedure reaches its limits when applied to bis-1,2-(tributylstannyl)ethene, the consumption of which under standard conditions is only 30%.

1-Trialkylsilyl-2-trimethylstannyl-1-alkenes can readily be prepared by the palladium-catalysed addition of

compounds R$_3$SnSiMe$_3$ (R = Me,Bu) to 1-alkynes [11–13].

R$_3$SnSiMe$_3$ + R'C ≡ CH ⟶

Z-Me$_3$SnCR'=CHSiMe$_3$
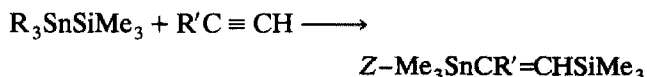
In cases where R = Me the diimine hydrogenation occurs in a quantitative manner (R' = Ph, CH$_2$OH, CH$_2$OMe, CHMeOH, CMe$_2$OH, CH$_2$NMe$_2$). However, under the standard conditions the consumption of the alkenes is reduced to 20–30% in corresponding cases where R = n-Bu (R' = CH$_2$OMe, CMe$_2$OH, CH$_2$NMe$_2$). The palladium-catalysed reaction between 1,2,4,5-tetrastannacyclohexanes and 1-alkynes leads to 1,4-distannacyclopent-2-enes [14].
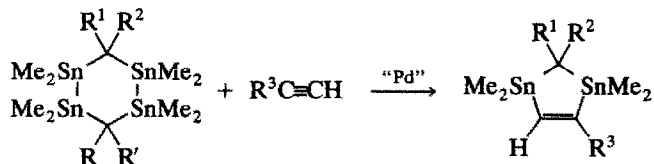
However, our original observations [14] regarding reaction times and yields in reactions between terminal alkynes and tetrastannacyclohexanes have since been found to be only poorly reproducible due to variations in the quality of our original catalyst, Pd(PPh$_3$)$_4$. We have now found that the generally more active catalyst system Pd(dba)$_2$/P(OEt)$_3$ is also more active in this reaction, although it has limitations; thus propargyl alcohol does not react even with this catalyst system. We could however obtain two new distannacyclopentenes (R, R' = H, R'' = CH$_2$OMe; R = Me, R' = SiMe$_3$, R'' = CMe$_2$OH); their spectral data, together with reaction times and yields for the preparation of compounds known previously, using the improved catalyst system, are given in the Experimental section.

TABLE 1. Conditions and yields for reactions between tetrastannacyclohexanes RR'C-SnMe$_2$-SnMe$_2$-CRR'-SnMe$_2$-SnMe$_2$ and Alkynes R''C = CH

| R, R'	R''	Catalyst [a]	Conditions (days and temperature)	Yield (%) [b]
H, H	CMe$_2$OH	B	2/80°C	69
H, H	CH$_2$NMe$_2$	A	2/80°C	51
H, H	CH$_2$OMe	A	2/80°C	26 [c]
H, H	Ph	A	2/70°C	29
H, Me	CMe$_2$OH	B	3/75°C	65
H, Me	CH$_2$OMe	B	3/80°C	61
H, Me	CH$_2$NMe$_2$	A	2/80°C	48
H, Me	Ph	A	3/70°C	50
Me, Me	CMe$_2$OH	A	4/70°C	52
Me, SiMe$_3$	CMe$_2$OH	B	4.5/70°C	42 [c]

[a] A: Pd(dba)$_2$/P(OEt)$_3$, B: Pd(PPh$_3$)$_4$. In all cases where catalyst A is used there is no reaction in the presence of catalyst B; [b] after distillation; [c] new compound.

TABLE 2. Tin-119 and Carbon-13 NMR data for compounds 1 of the type $Me_3Sn_AC^1H_AH_BC^2RH_XSn_BMe_3$

Compound	R	$\delta(Sn_{A/B})$	$^3J(^{119}Sn, ^{119}Sn)$	$\delta(SnMe_3)$ $[^1J(SnC)]$	$\delta(C^1)$ $[^1J(SnC^1)]/$ $[^2J(Sn,C^1)]$	$\delta(C^2)$ $[^1J(Sn,C^2)]/$ $[^2J(Sn,C^2)]$	$\delta(C^R)$ [a] $[^2J(Sn,C_R)]/$ $[^3J(Sn,C_R)]$
1a	H	0.4	1124	−10.6 [308]	i 6.9 [356]/[38]		
1b	CH_2OH	−2.2/−1.4	894	−10.6/−9.2 [310/308]	12.1 [346]/[25]	28.1 [376]/[36]	67.9 [36]
1c	CHMeOH	−5.8/−1.7; −7.6,/−1.9 [b]	886, 846	−9.2/−9.1; −9.1/−8.9 [b] [305/n.d.]/[n.d./313]	12.2/12.2 [b] [346/25]	35.2/35.3 [b] [376]/[33]	73.2/73.3 [b] [31]/[33] [b]
1d	CMe_2OH	−6.2,/−4.5	788	−8.4/−8.3 [320/308]	11.1 [366]/[n.d.]	39.6 [379]/[36]	75.2 [30]
1e	$1\text{-}c\text{-}C_6H_4OH$	−7.8/−5.1	736	−8.3/−7.9 [320/305]	10.0 [369]/[22]	39.9 [387]/[33]	75.5 [28]
1f	CH_2OMe	−3.4/0.4	964	−10.6/−9.1 [320/313]	13.1 [351]/[28]	25.4 [371]/[38]	78.7 [31]
1g	CH_2OBz	−2.8/0.2	944	−10.4/−9.1 [309/309]	13.0 [345]/[28]	25.6 [375]/[38]	76.5 [31]/[13]
1h	CH_2NMe_2	−5.4/−2.9	1098	−10.4/−9.0 [305/305]	13.8 [348]/[33]	24.7 [410]/[38]	66.5 [31]/[13]
1j	Ph	0.1/9.1	1048	−10.6/−9.3 [305]/[308]	14.2 [336]/[28]	31.5 [379][33]	147.7 [31]/[21]

[a] Refers to α-carbon of the group R. [b] Two isomers present. n.d. = not determined.

The diimine hydrogenation of these distannacyclopentenes should lead to the corresponding distannacyclopentanes (3), which have not so far been described in the literature. We did indeed observe that in the cases studied the diimine hydrogenation occurred in a quantitative manner. In those cases where R = H and R' = Me or R = Me, R' = SiMe$_3$ the hydrogenation creates a second chiral centre, and the formation of two diastereomeric products in a ratio close to unity was detected by NMR spectroscopy; we have not attempted to identify these unequivocally, but we assume that the compound formed in slightly greater yield is that in which the substituents R' and R" are *trans* to one another. The *cis/trans* nomenclature is used in this sense in the tables.
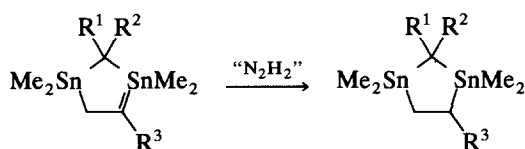
3. Experimental section

All manipulations involving organotin compounds were carried out in an argon atmosphere. Multinuclear NMR data were obtained using a Bruker AM-300 spectrometer (solvent: CDCl$_3$, standards TMS (^{1}H, ^{13}C, ^{29}Si), Me$_4$Sn). Reaction conditions and yields for the formation of distannacyclopentenes are collected in Table 1.

Two new distannacyclopentenes were prepared according to the following general procedure: the 1,2,4,5-tetrastannacyclohexane (10 mmol) and the alkyne (21 mmol) were dissolved in toluene (20 ml) and treated with 2% of the catalyst. The reaction mixture

was heated for 2–4 days at 70–80°C (see Table 1), after which the toluene was removed at the water pump and the resulting oil fractionated. Spectroscopic data for the two new compounds are given below.

a) 1,1,4,4,5-Pentamethyl-2-(1-hydroxyisopropyl)-5-trimethylsilyl-1,4-distannacyclopent-2-ene (b.p. 125°C/0.005 mm Hg); δ(^{119}Sn): 64.7, 76.4 ppm, ^{2+3}J(Sn, Sn) 282 Hz. δ(^{13}C): −9.3, −6.9, −5.8, −3.5 (SnMe_2); −1.4(CMeSiMe$_3$); 0.2 (SiMe_3); 16.9 (CMeSiMe$_3$); 30.6 (CMe_2OH); 77.4 (CMe_2OH), ^{3+4}J(Sn, C) 91.6 Hz; 138.0 (=CH), ^1J(SnC) 470.4, ^2J(Sn, C) 109.4 Hz; 179.8 (=C <), ^1J(SnC) 462.8, ^2J(Sn, C) 68.6 Hz. δ(^{1}H): 0.00 (s, SiMe_3); 0.12, 0.20, 0.21, 0.31 (s, SnMe_2); 1.29 (s, CMe_2OH); 1.71 (s, OH); 7.00 (s, =CH), ^3J(Sn, H) 205.4, ^2J(Sn, H) 133.2 Hz.

b) 1,1,4,4-Tetramethyl-2-methoxymethyl-1,4-distannacyclopent-2-ene (b.p. 55°C/0.001 mm Hg). δ(^{119}Sn) 61.3, 69.5 ppm, ^{2+3}J(Sn, Sn) 231 Hz. δ(^{13}C): −18.6 (SnCH$_2$Sn), ^1J(SnC) 292.4, 274.6 Hz, −7.3, −7.2, −6.9 (SnMe_2); 57.7 (OMe); 80.8 (CH$_2$OMe), ^{3+4}J(Sn, C) 109.4, ^2J(Sn, C) 63.6 Hz; 142.1 (=CH), ^1J(SnC) 488.4, ^2J(Sn, C) 99.2 Hz; 170.1 (=C <), ^1J(SnC) 478.2, ^2J(Sn, C) 79.8 Hz. δ(^{1}H): −0.45 (s, SnCH_2Sn), ^2J(Sn, H) 40.6 Hz; 0.18, 0.22 (s, SnMe_2); 3.30 (s, OMe); 4.17 (s, CH_2OMe); 7.21 (s, =CH), ^3J(Sn, H) 193.6, ^2J(Sn, H) 139.8 Hz.

The general procedure used for the diimine reduction is illustrated for the hydrogenation of 2,3-bis(trimethylstannyl)-prop-2-en-1-ol: the alkene (1.92 g, 5 mmol) was dissolved in absolute ethanol (15 ml) and treated with 80% hydrazine hydrate (7.5 ml) and a 1% solution of copper sulphate (0.78 ml). A 30% hydrogen peroxide solution (2.0 ml) was added at 0°C at such a rate that there was a steady evolution of nitrogen. The solvent was removed at the water pump and the product extracted with chloroform. 2,3-bis(trimethylstan-

TABLE 3. Silicon-29, Tin-119 and Carbon-13 NMR data for compounds 2 of the type Me$_3$SiC^{1}H$_A$H$_B$C^{2}RH$_X$SnMe$_3$

Compound	R	δ(Si)	δ(Sn)	^3J(^{29}Si, ^{119}Sn)	δ(SiMe_3) [^1J(SiC)]	δ(SnMe_3) [^1J(SnC)]	δ(C^1) [^1J(SiC^1)]/ [^2J(Sn, C^1)]	δ(C^2) [^1J(Sn, C^2)]	δ(C^R) [a] [^2J(Sn, C^R)]
2a	CH$_2$OH	1.5	3.9	61	−1.0 [51]	−10.2 [313]	16.5 [51]/[19]	25.3 [389]	67.7 [20]
2b	CHMeOH	1.7	−1.1,−3.1 [b]	59	−0.9/−1.1 [b] [51]	−8.8 [310]	15.7 [50]/[19]	32.4 [383]	72.5 [18]
2c	CMe$_2$OH	1.4	−2.2	24	−1.2 [51]	−7.4 [310]	15.5 [n.d.]/[15]	37.7 [402]	75.3 [15]
2d	CH$_2$OMe	1.6	5.8	71	−0.9 [50]	−10.2 [313]	17.1 [n.d.]/[22]	22.6 [392]	78.4 [22]
2e	CH$_2$NMe$_2$	1.6	−1.8	89	−0.7 [51]	−10.1 [308]	17.8 [n.d.]/[28]	22.2 [430]	65.6 [22]
2f	Ph	2.3	1.2	91	−1.0 [51]	−10.7 [305]	18.7 [51]/[24]	28.6 [333]	148.0 [33]

[a] Refers to α-carbon of the group R; [b] Two isomers present. n.d. = not determined.

nyl)-propan-1-ol was obtained as a colourless oil in 95% yield. Distillation without decomposition was possible (b.p. 70°C/0.01 mm Hg), but the isolated yield was low (50%). Anal. Found: C, 28.0; H, 6.7. $C_9H_{24}OSn_2$ calc.: C, 28.0; H, 6.3%.

All other alkenes were hydrogenated according to this general procedure using corresponding amounts of reagents. Alkene consumption was complete in all cases when trimethylstannyl compounds were hydrogenated and NMR spectra showed the absence of any by-products. Hydrogenation products were characterised by elemental analysis (C, H) and multinuclear NMR analysis. Distillation was generally not carried out because of the loss of product involved.

TABLE 4. Structure-relevant Tin-119 and Carbon-13 NMR data for compounds 3 of the type $Me_2Sn-C^1RR'-SnMe_2-C^2H_AH_BC^3R''H_X$

Compound	R	R'	R''	δ(Sn)	^{2+3}J(Sn, Sn)	δ(C¹) [¹J(SnC)] [²J(Sn, C)]	δ(C²) [¹J(SnC)] [²J(Sn, C)]	δ(C³) [¹J(Sn, C)] [²J(Sn, C)]	δ(C^R) [a] [³J(Sn, C^R)] [²J(Sn, C^R)]
3a	H	H	CMe₂OH	59.7/75.3	98	−17.7 [239, 252] [23]	10.6 [356] [9]	44.3 [400]	75.7 [71]
3b(cis)	H	Me	CMe₂OH	60.2/71.1	234	−4.8 [272] [20]	10.3 [341] [n.o.]	44.2 [381]	75.8 [69]
3b(trans)	H	Me	CMe₂OH	55.8/73.6	228	−4.7 [275] [19]	10.6 [341] [n.o.]	43.1 [381]	75.8 [69]
3c(cis)	Me	SiMe₃	CMe₂OH	70.6/83.0	98	−2.1 [n.o.] [20]	9.9 [336] [n.o.]	45.2 [387]	75.6 [75]
3c(trans)	Me	SiMe₃	CMe₂OH	68.3/84.1	85	−1.7 [n.o.] [22]	11.6 [336] [n.o.]	43.1 [388]	75.7 [76]
3d	Me	Me	CMe₂OH	51.0/64.3	442	8.0 [313,300] [15]	10.4 [331] [n.o.]	43.6 [389]	75.5 [67]
3e	H	H	CH₂OMe	80.2/80.9	199	−17.8 [262] [23]	14.1 [373] [13]	28.1 [389]	79.9 [51]
3f(cis)	H	Me	CH₂OMe	78.1/78.9	362	−5.0 [297] [n.o.]	14.6 [364] [n.o.]	28.5 [374]	79.8 [41]
3f(trans)	H	Me	CH₂OMe	75.9/76.8	356	−4.9 [292] [n.o.]	14.2 [359] [n.o.]	28.0 [374]	79.9 [48]
3g	H	H	CH₂NMe₂	70.6/77.7	240	−18.6 [220,258] [33]	13.6 [362] [14]	27.9 [423]	67.5 [81]
3h(cis)	H	Me	CH₂NMe₂	71.1/71.7	394	−5.8 [n.o.] [15]	13.3 [351] [10]	27.8 [404]	67.8 [76]
3h(trans)	H	Me	CH₂NMe₂	67.6/76.4	401	−5.7 [n.o.] [13]	13.6 [348] [13]	27.4 [404]	67.5 [79] [19]
3i	H	H	Ph	75.0/80.7	92	−16.9 [234,247] [18]	14.6 [361] [15]	34.1 [331]	149.9 [66] [20]
3j(cis)	H	Me	Ph	71.7/80.1	238	−3.1 [264] [18]	14.1 [348] [13]	34.1 [318]	150.0 [68] [20]
3j(trans)	H	Me	Ph	72.9/74.9	208	−3.3 [264] [15]	14.3 [347] [15]	33.5 [318]	150.0 [68] [20]

[a] Refers to α-carbon of the group R. n.o. = not observed.

TABLE 5. Proton NMR data for the ABX spin systems in compounds of types 1, 2 and 3

Compound	$\delta(H_A)$	$\delta(H_B)$	$\delta(H_X)$	$^2J(AB)$	$^3J(AX)$	$^3J(BX)$
1a	0.97					
1b	1.03	1.11	1.64	−13.5	11.2	5.6
1d	1.10	0.95	1.61	−13.6	9.6	6.2
1e	1.10	0.93	a	−13.5	8.8	6.2
1f	1.02	1.11	1.70	−13.5	11.5	4.6
1h	0.90	1.18	1.69	−12.8	12.8	4.3
1j	1.62	1.39	2.76	−13.5	13.8	4.3
2a	0.70	0.72	1.45	−14.0	8.0	4.5
2c	0.76	0.76	1.37	−14.5	8.5	5.0
2d	0.72	0.77	1.55	−14.5	8.5	5.0
2e	0.58	0.81	1.59	−15.1	10.0	4.6
2f	1.02	1.35	2.62	−14.8	12.1	3.9
3a	hidden	0.66	1.41	−13.5	5.6	13.5
3b(cis)	1.20	0.76	1.50	n.d.	n.d.	n.d.
3b(trans)	1.20	0.68	1.50	−12.1	n.d.	14.1
3c(cis)	1.33	0.83	1.55	−12.1	6.2	15.1
3c(trans)	1.33	0.70	1.55	−12.1	6.2	15.1
3d	1.27	0.79	1.52	−12.1	5.6	14.4
3e	1.12	0.79	1.79	−12.8	6.6	8.5
3f(cis)	1.07	0.91	1.82	−12.8	6.8	7.5
3f(trans)	1.19	0.78	1.82	−12.8	6.5	8.5
3g	1.27	0.54	1.58	−12.5	6.5	12.5
3h(cis)	1.25	0.67	1.60	−12.1	6.2	12.1
3h(trans)	1.33	0.54	1.60	−12.5	6.6	12.5
3i	1.50	1.27	2.70	−12.8	5.6	12.8

n.d. = not determined.

Structure-relevant multinuclear NMR parameters are presented in Tables 2–5. An interpretation of the NMR data will be published separately.

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