

# Tin/mercury exchange in 1,2-distannyl-1-alkenes and 1-silyl-2-stannyl-1-alkenes

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## Abstract

1,2-Bis(chloromercuri)alkenes, 1-trimethylsilyl-2-chloromercuri-alkenes and 1-trimethylsilyl-2-organomercurialkenes can be readily made by transmetallation of the corresponding trimethyltin compounds with  $\text{HgCl}_2$  and  $\text{RHgCl}$ ; their structures have been confirmed by multinuclear NMR data. The new compounds are expected to have a large synthetic potential involving lithium/mercury exchange, and subsequent reaction with electrophilic reagents.

**Key words:** Mercury; Nuclear magnetic resonance; Tin; Silicon

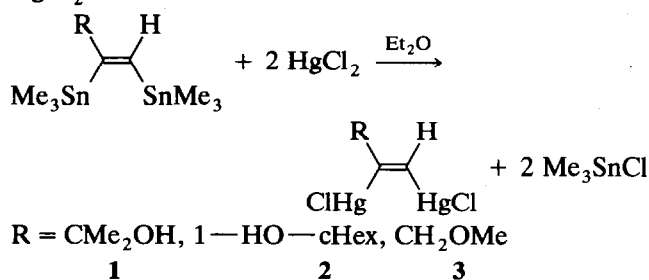
## 1. Introduction

Organomercury compounds are suitable precursors for vinyl anions (or anionoids), particularly in cases where lithiation of hydrocarbons or organotins leads only to equilibrium reactions. Thus, lithiation of cubane with  $\text{MeLi}$  gives only 3% of the lithiated species, whereas reaction of chloromercuricubane with  $\text{MeLi}$  gives complete lithiation [1]. 1,2-Distannylalkenes, which are readily available by Pd-catalyzed addition of  $\text{Me}_6\text{Sn}_2$  to terminal alkynes [2], do not undergo double lithiation with  $\text{MeLi}$  [3]. However, Maercker *et al.* demonstrated that 1,2-bis(chloromercuri)ethene is completely lithiated by  $\text{MeLi}$  and the carbanion can subsequently be trapped by dimethyl sulfate [4].

This prompted us to investigate the mercuriation of 1,2-distannylalkenes and 1-silyl-2-stannyl-alkenes in more detail. Nesmeyanow *et al.* have previously described the preparation of 1,2-bis(chloromercuri)ethene and 1-trimethylsilyl-2-chloromercuriethene, which were characterized only by elemental analysis and IR data [5].

## 2. Results and discussion

1,2-Distannylalkenes are readily converted into the corresponding dimercurated alkenes by reaction with  $\text{HgCl}_2$  in ether:

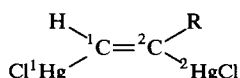


The products separate almost immediately as white air-stable solids, that are soluble in THF, slightly soluble in acetone, and insoluble in other common organic solvents.

The structure of the new mercury compounds is confirmed by multinuclear NMR spectroscopy (see Table 1). In the  $^1\text{H}$  NMR spectra the vinyl protons appear at considerably higher fields than for the ditin compounds, and show two pairs of satellites corresponding to  $^2J(\text{HgH})$  and  $^3J(\text{HgH})$ .

$^{13}\text{C}$  NMR spectra indicate a low-field shift for the quaternary vinyl carbon; each of the carbon atoms 1–3 (for numbering see Table 1) displays two  $\text{HgC}$  cou-

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TABLE 1. Multinuclear NMR data for compounds 1, 2 and 3<sup>a,b</sup>

R = CMe<sub>2</sub>OH, 1-HO-cHex, CH<sub>2</sub>OMe  
 1                      2                      3

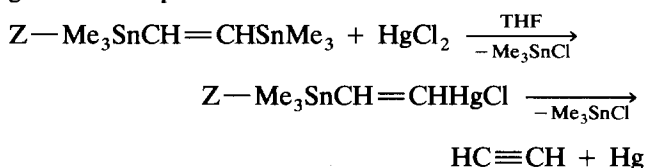
	1	2	3
$\delta(^1\text{Hg})$	-1205	-1212	
$\delta(^2\text{Hg})$	-1318	-1317	
$^3J(\text{HgHg})$	8820	8828	
$\delta(^1\text{C})$	141.8	142.2	143.8
$^1J(\text{Hg}^1\text{C})$	2568	2554	2540
$^2J(\text{Hg}^1\text{C})$	86	n.d.	92
$\delta(^2\text{C})$	187.8	188.5	171.3
$^1J(\text{Hg}^2\text{C})$	2470	2446	2464
$^2J(\text{Hg}^2\text{C})$	34	30	48
$\delta(^3\text{C})$	75.6	76.6	78.6
$^2J(\text{Hg}^3\text{C})$	114	114	n.d.
$^3J(\text{Hg}^3\text{C})$	346	326	n.d.
$\delta(\text{HC}=\text{C})$	6.23	6.39	6.46
$^2J(\text{HgH})$	232	224	253
$^3J(\text{HgH})$	662	672	641

<sup>a</sup>  $\delta$  in ppm relative to internal Me<sub>2</sub>Hg or TMS,  $J$  in Hz. <sup>b</sup> <sup>1</sup>H NMR spectra in acetone-d<sub>6</sub>, <sup>199</sup>Hg spectra in THF-d<sub>8</sub>, <sup>13</sup>C NMR data in THF/CDCl<sub>3</sub> (2:1).

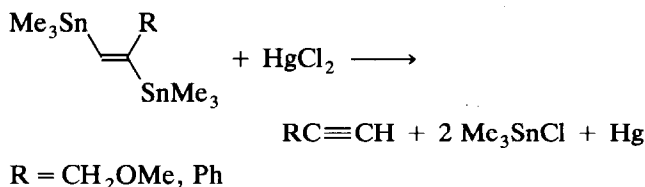
plings. As expected, the relative magnitudes fall in the order  $^1J(\text{HgC}) > ^3J(\text{HgC}) > ^2J(\text{HgC})$ .

We succeeded in showing  $^3J(\text{HgHg})$  to be *ca.* 8820 Hz; in the <sup>199</sup>Hg NMR spectrum the mercury satellites form an AB system.

Attempts to exchange only one tin moiety by mercury failed. With 1,2-bis(trimethylstannyl)ethene and HgCl<sub>2</sub> in a 1:1 ratio, a colourless solid forms which decomposes rapidly, generating elemental mercury. We assume that the transmetalation product is formed as an intermediate which is not stable and which undergoes a subsequent intramolecular reaction.

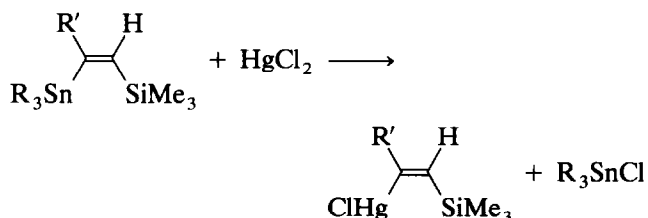


Efforts to avoid decomposition by using E-distannyl alkenes also proved to be unsuccessful. In these cases we were able to detect the alkyne by <sup>13</sup>C NMR.



As the vinyl silicon bond is much more stable towards electrophilic attack by mercury salts we extended

the reaction type to include 1-silyl-2-stannyl alkenes:



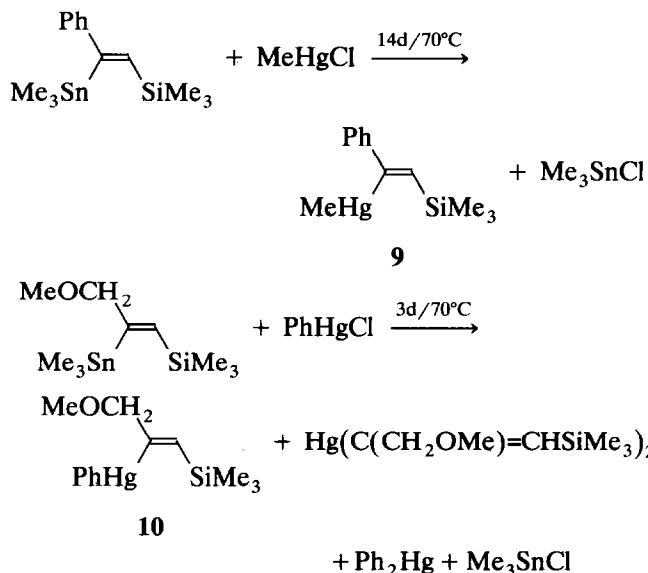
R = Bu,

R' = CH<sub>2</sub>OH, CH<sub>2</sub>OMe, Ph, CMe<sub>2</sub>OH, CH<sub>2</sub>NMe<sub>2</sub>  
 4                      5                      6                      7                      8

R = Me, R' = CH<sub>2</sub>OH, CH<sub>2</sub>OMe, Ph

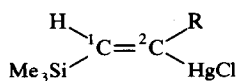
We advise the use of trimethylstannyl-substituted olefin rather than tributylstannyl analogues as starting materials because Me<sub>3</sub>SnCl can be removed much easier by precipitation with KF than can Bu<sub>3</sub>SnCl. Thus, after sublimation (80°C/10<sup>-2</sup> torr), the 1-silyl-2-mercuriethenes 4 and 5 are obtained, starting with the trimethylstannyl-substituted olefin as crystalline solids, while 6 was obtained in a pure state (according to the NMR spectra) but as a highly viscous oil which could not be crystallised. Compounds 7 and 8 were prepared from the tributylstannyl-substituted olefin, and could not be freed from Bu<sub>3</sub>SnF, so only NMR data are so far available.

Use of organomercury chlorides instead of HgCl<sub>2</sub> requires higher reaction temperatures, as well as longer reaction times.



In the case of transmetalation with PhHgCl, the metal exchange is followed by some disproportionation to give Ph<sub>2</sub>Hg as a by-product, as shown by the <sup>13</sup>C and <sup>199</sup>Hg NMR data [6].

In the mass spectra of 4 and 5 there are small peaks that indicate the formation of the divinyl compound

TABLE 2. Selected multinuclear NMR data for compounds 4–8<sup>a,b</sup>

R = CH<sub>2</sub>OH, CH<sub>2</sub>OMe, Ph, CMe<sub>2</sub>OH, CH<sub>2</sub>NMe<sub>2</sub>  
 4            5            6            7            8

	4	5	6	7	8
δ(Hg)	-1143	-1150	-1157	-1127	-1130
δ(Si)	-8.5	-8.8	-8.2	-8.2	-9.4
<sup>3</sup> J(SiHg)	185	186	182	n.d.	192
δ( <sup>1</sup> C)	139.5	140.1	143.0	134.1	141.3
<sup>1</sup> J(Si <sup>1</sup> C)	66	66	66	68	66
<sup>2</sup> J(Hg <sup>1</sup> C)	243	243	234	250	234
δ( <sup>2</sup> C)	170.5	168.3	168.8	181.1	170.8
<sup>1</sup> J(Hg <sup>2</sup> C)	n.d.	2212	2204	2232	2254
δ( <sup>3</sup> C)	70.9	80.4	144.0	75.7	72.1
<sup>2</sup> J(Hg <sup>3</sup> C)	178	153	183	n.d.	170
δ(HC=)	6.45	6.37	6.83	6.27	6.38
<sup>3</sup> J(HgH)	710	719	710	742	710

<sup>a</sup> δ in ppm relative to internal Me<sub>2</sub>Hg or TMS, *J* in Hz. <sup>b</sup> all spectra in CDCl<sub>3</sub>.

Hg(CR=CHSiMe<sub>3</sub>)<sub>2</sub>. This may explain why elemental analysis indicates the presence of more carbon and hydrogen than expected (see Section 3).

Within the group of the new 1-trimethylsilyl-2-chloromercuri-ethenes, the most characteristic NMR data, *i.e.* δ(<sup>199</sup>Hg), δ(<sup>29</sup>Si), δ(HC=), <sup>3</sup>J(<sup>199</sup>Hg<sup>29</sup>Si), <sup>n</sup>J(<sup>199</sup>Hg<sup>13</sup>C) and <sup>n</sup>J(HgH), hardly differ (see Table 2). As in the corresponding dimercury compounds, the vinyl protons appear considerably shifted to high field, while the value of <sup>3</sup>J(<sup>199</sup>Hg<sup>1</sup>H)<sub>trans</sub> confirms the assignment of the two sets of HgH-couplings in the 1,2-dimercury ethenes.

The values of <sup>3</sup>J(<sup>199</sup>Hg<sup>29</sup>Si) in 4–8, for which to our knowledge there is no precedent, range from 182 Hz to 192 Hz.

Further experiments are planned in order to extend the scope of this transmetallation process.

### 3. Experimental details

All manipulations involving organotin compounds were carried out under an inert atmosphere. NMR spectra were recorded on a Bruker AM-300 spectrometer, and the mass spectra were obtained on a Finnigan MAT 8230 instrument.

#### 3.1. General procedure for the preparation of 1,2-bis(chloromercuri)ethenes

The reaction of 3-hydroxy-3-methyl-1,2-bis(trimethylstannyl)-butene 1 is representative. Solid HgCl<sub>2</sub> (1.25 g, 4.6 mmol) was added at room temperature to a solution of the distannylalkene (0.95 g, 2.3 mmol) in

Et<sub>2</sub>O (20 mL). A white solid separated immediately. After 12 h stirring at room temperature, the solid was filtered off and washed with Et<sub>2</sub>O and CHCl<sub>3</sub>. Purification by dissolving in THF and subsequent precipitation with CHCl<sub>3</sub> yielded 3-hydroxy-3-methyl-1,2-bis(chloromercuri)butene 1 (0.75 g, 59%). M.p. 180°C (decomposition). Anal. calc. (found) for C<sub>5</sub>H<sub>8</sub>Cl<sub>2</sub>Hg<sub>2</sub>O: C, 10.8 (11.5); H, 1.5 (1.6)%. Compound 2: 64% yield, m.p. 189°C (decomposition). Anal. calc. (found) for C<sub>8</sub>H<sub>12</sub>Cl<sub>2</sub>Hg<sub>2</sub>O: C, 16.1 (16.1); H, 2.0 (2.0)%. Compound 3: 45% yield, m.p. 181°C (decomposition). Anal. calc. (found) for C<sub>4</sub>H<sub>6</sub>Cl<sub>2</sub>Hg<sub>2</sub>O: C, 8.9 (8.8); H, 1.1 (1.1)%.

#### 3.2. Reaction of Z-1,2-bis(trimethylstannyl)-ethene with HgCl<sub>2</sub> in a molar ratio 1:1

A solution of HgCl<sub>2</sub> (0.81 g, 3 mmol) in Et<sub>2</sub>O (20 mL) was added at room temperature during 20 min to a solution of 1,2-bis(trimethylstannyl)-ethene (1.06 g, 3 mmol) in Et<sub>2</sub>O (5 mL). A white solid separated immediately. Approximately 0.5 h later, elemental mercury separated. After removal of the solvent, Me<sub>3</sub>SnCl was detected by <sup>119</sup>Sn NMR spectroscopy. Analogous reactions with E-1-phenyl- and E-1-methoxymethyl-1,2-bis(trimethylstannyl)-ethene gave elemental mercury, Me<sub>3</sub>SnCl, and the corresponding alkynes.

#### 3.3. General procedure for the preparation of 1-trimethylsilyl-2-chloromercuri-ethenes

Solid HgCl<sub>2</sub> (1.35 g, 5 mmol) was added to a solution of the 1-trimethylsilyl-2-triorganostannyl-ethene (5 mmol) in THF (25 mL) at room temperature. After 20 h stirring, KF (2.9 g, 50 mmol) was added. After filtration and removal of the solvent, the residue was sublimed at 80°C/10<sup>-2</sup> torr. Separation of triorganotin chloride was only complete when 1-trimethylsilyl-2-trimethylstannyl-ethenes were used.

4: white solid, 73% (1.3 g) yield, m.p. 100–101°C. Mass spectrum (80 eV): 351 (4%, M<sup>+</sup>-Me); 201 (8%, Hg<sup>+</sup>); 129 (63%, M<sup>+</sup>-HgCl); 73 (83%, SiMe<sub>3</sub><sup>+</sup>); 45 (100%, SiMe<sup>+</sup>); a weak peak (0.1%) at *m/e* 458 is assigned to Hg(C(CH<sub>2</sub>OH)=CHSiMe<sub>3</sub>)<sub>2</sub>. Anal. calc. (found) for C<sub>6</sub>H<sub>13</sub>ClHgOSi: C, 19.7 (22.0); H, 3.6 (4.1)%.

5: white solid, 79% (1.5 g) yield, m.p. 80°C. Mass spectrum (80 eV): 365 (4%, M<sup>+</sup>-Me); 202 (7%, Hg<sup>+</sup>); 143 (53%, M<sup>+</sup>-HgCl); 73 (70%, SiMe<sub>3</sub><sup>+</sup>); 59 (63%, SiMe<sub>2</sub><sup>+</sup>); 45 (100%, SiMe<sup>+</sup>); a weak peak (0.4%) at *m/e* 488 is assigned to Hg(C(CH<sub>2</sub>OMe)=CHSiMe<sub>3</sub>)<sub>2</sub>. Anal. calc. (found) for C<sub>7</sub>H<sub>15</sub>ClHgOSi: C, 22.2 (23.1); H, 4.0 (4.2)%.

6: colourless highly viscous oil, 89% (1.8 g) yield. Anal. calc. (found) for C<sub>11</sub>H<sub>15</sub>ClHgSi: C, 32.1 (32.3); H, 3.7 (4.0)%.

While the reactions leading to **7** and **8** proceeded quantitatively, the products have so far been obtained only in an impure form, as complete separation from  $\text{Bu}_3\text{SnF}$  was not possible.

1-Trimethylsilyl-2-methylmercuri-2-phenyl-ethene **9** was prepared by the general procedure for compds. **4-8**; NMR yield after 14d/70°C ca. 75%.  $^{199}\text{Hg}$  NMR ( $\text{CDCl}_3$ )  $\delta = -380$ ;  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ )  $\delta = -9.4$ ;  $^3\text{J}(\text{SiHg}) = \text{not determined}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 1.0$ , ( $^1\text{J}(\text{SiC}) = 52$  Hz), 15.3 ( $^1\text{J}(\text{HgC}) = 730$  Hz), 126.4, 126.6, 128.4, 143.2 ( $\text{J}(\text{HgC}) = 127$  Hz, 56 Hz), 149.5 ( $^2\text{J}(\text{HgC}) = 86$  Hz), 199.2 ( $^1\text{J}(\text{HgC}) = 1058$  Hz);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.35$  (s, 9H), 0.62 (s, 3H),  $^2\text{J}(\text{HgH}) = 109$  Hz), 7.20 (s, 1H),  $^3\text{J}(\text{HgH}) = 280$  Hz), 7.33–7.40 (m, 5H).

Reaction of 3-methoxy-1-trimethylsilyl-2-trimethylstannyl-propene with  $\text{PhHgCl}$  by the general procedure used for compounds **4-8** led to a mixture of **10/11** in nearly equal amounts, and to formation of  $\text{Ph}_2\text{Hg}$ . The NMR signals of **10/11** could not be assigned unequivocally because of very small differences in chemical shifts of the corresponding signals.  $^{199}\text{Hg}(\text{CDCl}_3)$   $\delta = -723/-718$ ;  $^{29}\text{Si}(\text{CDCl}_3)$   $\delta = -10.5/-10.0$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.43/0.30$ , 57.8/57.6, 83.4 ( $^2\text{J}(\text{HgC})$

$= 84$  Hz)/84.2 ( $^2\text{J}(\text{HgC}) = 86$  Hz), 140.9 ( $^2\text{J}(\text{HgC}) = 137$  Hz)/140.6 ( $^2\text{J}(\text{HgC}) = 140$  Hz), 190.0 ( $^1\text{J}(\text{HgC}) = 1170$  Hz)/192.1 ( $^1\text{J}(\text{HgC}) = 1158$  Hz); 128.0 ( $\text{J}(\text{HgC}) = 22$  Hz), 128.6 ( $\text{J}(\text{HgC}) = 100$  Hz), 137.4 ( $\text{J}(\text{HgC}) = 86$  Hz), 172.5 ( $^1\text{J}(\text{HgC}) = 1166$  Hz);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.30/0.26$  (s,  $\text{SiMe}_3$ ), 3.42/3.36 (s, OMe), 4.28/4.23 (d,  $\text{CH}_2\text{O}$ ,  $^3\text{J}(\text{HH}) = 1.9$  Hz), 6.67/6.66 (t,  $\text{CH}=\text{}$ ), 7.34–7.53 (m, Ph).

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