

# Intramolecular Carbostannylation of Allyl- and Vinylstannanes *via* a Radical Chain Process

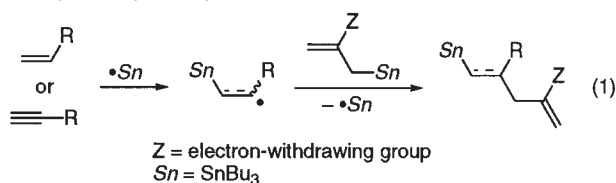
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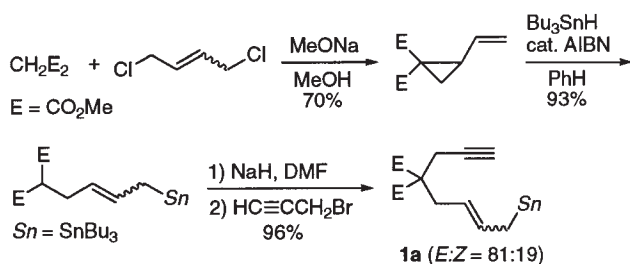
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In the presence of  $\text{Bu}_3\text{SnH}$  and AIBN, 8-tributylstannyl-6-octen-1-yne were efficiently cyclized to 2-allyl-1-(tributylstannylmethylene)cyclopentanes by intramolecular homolytic allylstannylation. 8-Tributylstannyl-1,6-octadienes as well underwent the radical cyclization in high efficiency. This radical-based method was applicable to the intramolecular vinylstannylation of alkynes and alkenes.

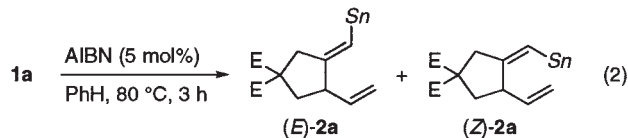
Intramolecular carbometalation provides a powerful tool for the stereoselective construction of a wide range of carbocycles and heterocycles.<sup>1,2</sup> A notable advantage of this cyclization is that the cyclized products can be easily utilized for further transformation by reaction with various electrophiles. With some exceptions,<sup>3,4</sup> most of the known intramolecular carbometalations proceed *via* a concerted path in which a reactive carbon-metal bond participates. Previously, we have reported intermolecular homolytic allylstannylation of alkenes and alkynes with allylstannanes bearing an electron-withdrawing group at the  $\beta$ -position (eq 1).<sup>5,6</sup> We herein describe an intramolecular version of the allylstannylation in addition to intramolecular homolytic vinylstannylation.<sup>7</sup>



Initially, 1,6-enyne **1a**, an allylstannane bearing an alkynyl group, was selected as a substrate. It could be easily prepared from dimethyl malonate in three steps (62% total yield) as shown in Scheme 1. The AIBN-initiated reaction of **1a** in benzene at 80 °C formed the desired allylstannylation product **2a** in only a poor yield (eq 2). However, addition of  $\text{Bu}_3\text{SnH}$  (10 mol%) to the reaction mixture effectively promoted the cycloisomerization to give (*E*)-**2a** in 82% isolated yield along with a small quantity of its geometrical isomer.<sup>8</sup> Thus, unlike the intermolecular homolytic allylstannylation (eq 1), the present intramolecular version does not require the substrate to have an electron-withdrawing group  $\beta$  to the stannyl group.



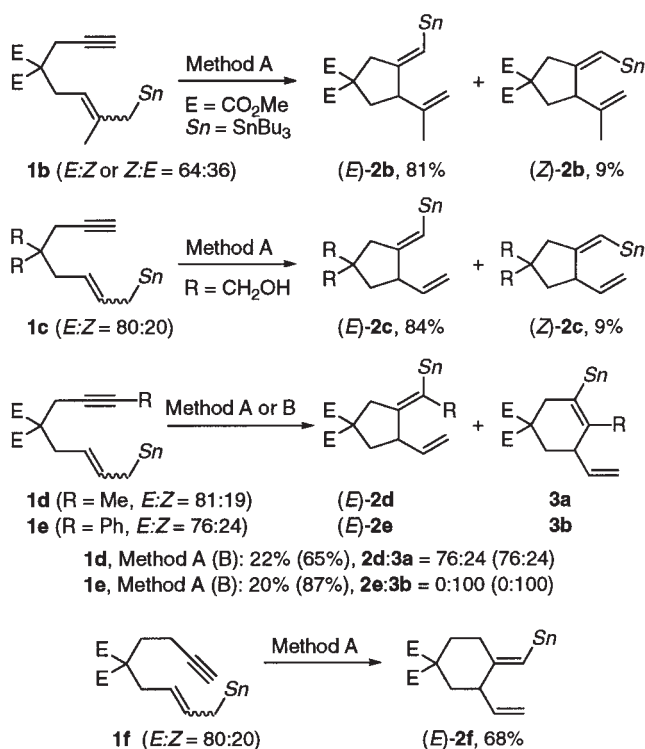
Scheme 1.



Without  $\text{Bu}_3\text{SnH}$ : <10%  
With 10 mol% of  $\text{Bu}_3\text{SnH}$ : 82%                      6%

Under the same reaction conditions using 10 mol% of  $\text{Bu}_3\text{SnH}$  (method A), allylstannanes **1b-f** as well underwent the intramolecular allylstannylation (Scheme 2). The result with **1c** indicates that the present cyclization is compatible with a hydroxy group as an advantage of radical process. The cyclization of **1d** ( $\text{R}=\text{Me}$ ), bearing an internal triple bond, formed a mixture of two regioisomers (*E*)-**2d** and **3a** in a poor yield. Increasing the amounts of AIBN and  $\text{Bu}_3\text{SnH}$  (method B) improved the yield without change in the isomeric ratio. In contrast with **1d**, **1e** ( $\text{R}=\text{Ph}$ ) was converted into **3b** exclusively. The complete regio-control is probably due to the high radical-stabilizing ability of the phenyl group. As shown in the case with **1f**, the intramolecular allylstannylation is applicable to a substrate with one more methylene tether.

We next investigated the radical-initiated allylstannylation of



Method A: AIBN (5 mol%),  $\text{Bu}_3\text{SnH}$  (10 mol%), PhH, 80 °C, 3 h.  
Method B: AIBN (20 mol%),  $\text{Bu}_3\text{SnH}$  (40 mol%), PhH, 80 °C, 3 h.

Scheme 2.

dienylstannanes **4**. The results are summarized in Table 1. The cyclization of **4a** was not observed without Bu<sub>3</sub>SnH, while its addition to the reaction system is quite effective in the formation of **5a** (entry 1). Introduction of the substituent R<sup>1</sup> increased the yield of **5** (entries 2–4). In contrast, substitution at the terminal sp<sup>2</sup> carbon and homologation of the methylene tether resulted in no cyclized products (entries 5 and 6).

Table 1. Cyclization of dienylstannanes **4**<sup>a</sup>

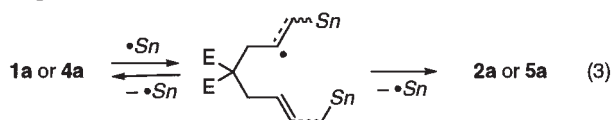
Method A

$E = \text{CO}_2\text{Me}$   
 $\text{Sn} = \text{SnBu}_3$

Entry	Dienylstannane <sup>b</sup>				Yield/%	<i>cis:trans</i> <sup>c</sup>
	R <sup>1</sup>	R <sup>2</sup>	n			
1	H	H	1	<b>4a</b>	88	82:18
2	Me	H	1	<b>4b</b>	90	42:58
3	Ph	H	1	<b>4c</b>	quant.	55:45
4	CN	H	1	<b>4d</b>	96	68:32
5	H	Me	1	<b>4e</b>	0	
6	H	H	2	<b>4f</b>	0	

<sup>a</sup>All reactions were carried out with 0.50 mmol of **4** according to method A. See Scheme 2. <sup>b</sup>*E:Z* = ca. 4:1. <sup>c</sup>The isomeric ratio and the relative configuration were determined by <sup>1</sup>H and <sup>13</sup>C NMR analysis.

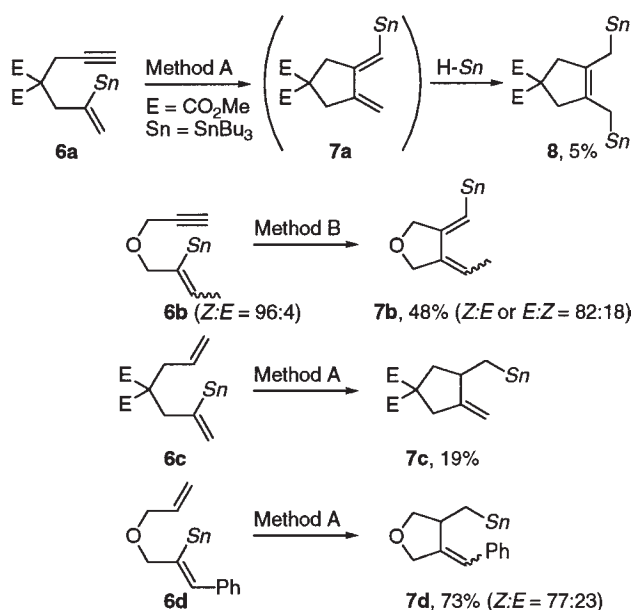
The propagation process of the present radical cyclization consists of the reversible addition of •SnBu<sub>3</sub> and the subsequent intramolecular homolytic substitution (eq 3).<sup>9</sup> The addition of Bu<sub>3</sub>SnH would promote the former step by increasing the concentration of •SnBu<sub>3</sub>. The latter radical cyclization, which is much faster than intermolecular homolytic allylation, allows the successful allylstannylation of unactivated allylstannanes. The *E*-selectivity in the cyclization of **1** results from the fact that the C–C bond formation takes place in the opposite side to the stannyl group to avoid its steric hindrance.<sup>5</sup>



We further attempted the intramolecular vinylstannylation of alkynes and alkenes (Scheme 3). The reaction of 2-stannyl-1,6-enyne **6a** by method A did not afford the desired product **7a**, but a small amount of bisstannylated carbocycle **8** was obtained. This product would be formed by hydrostannylation of **7a**, which should suppress the cycloisomerization of **6a** to **7a**. To retard the side reaction, 1-substituted 1,6-enyne **6b** was used as a substrate. As a result, the desired dienylstannane **7b** was obtained in a moderate yield by method B. 2-Stannyl-1,6-diene **6c** was converted into the desired product **7c** although the yield was rather low. The cyclization of 1-phenyl-substituted 1,6-diene **6d** smoothly proceeded even under the conditions of method A.

In conclusion, we have demonstrated that the intramolecular allylstannylation of alkynes and alkenes is effectively catalyzed by Bu<sub>3</sub>SnH-AIBN. The present radical-based carbometalation provides a new route to functionalized five- and six-membered rings.

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Scheme 3.

Research from the Japan Society for the Promotion of Science (JSPS).

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 75th birthday.

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