

When a CHCl_3 solution of an aldehyde (**1**) and BuSnCl_3 was treated with an *E,Z* mixture⁷⁾ of 1-(tributylstannyl)-2-alkene (**2**), the *Z*-selective 2-alkenylation of **1** proceed smoothly to give *Z* homoallyl alcohol (**3**). Results were summarized in Table 1. In all cases shown in Table 1, (*E*)-isomers were not detected in NMR analysis. However, small amount of the regioisomers (**4**) were obtained. The 2-alkenylation of **1f**, **1g**,

and **1h** proceeded with poor diastereoselectivity to give **3f**, **3g**, and **3h**, respectively, as a mixture of diastereomers. The configurations of the diastereomers were not determined.

Table 1. Z-Selective 2-alkenylation of **1**

	R ¹		R ²	Main product	Yield/% ^{a)}	3 : 4
1a	Ph	2a	Pn	3a	94	95 : 5 ^{b)}
1b	Et	2a	Pn	3b	81	97 : 3 ^{b)}
1c	Hex	2b	Pr	3c	86	98 : 2 ^{b)}
1d	AcO(CH ₂) ₅	2b	Pr	3d	92	98 : 2 ^{b)}
1e	AcO(CH ₂) ₉	2b	Pr	3e	87	98 : 2 ^{b)}
1f	MeCH(SPh)CH ₂	2c	Pn	3f	76	97 ^{d)} : 3 ^{c)}
1g	MeCHSPh	2a	Pn	3g	79	96 ^{e)} : 4 ^{c)}
1h	PhCH(SPh)CH ₂	2a	Pn	3h	79	97 ^{d)} : 3 ^{c)}
1i	CH ₂ =CH	2a	Pn	3i	75	93 : 7 ^{b)}

a) Total isolated yield of **3** and **4**. b) Determined by GLC. c) Determined by NMR.

d) About 5:4 mixture of diastereomers. e) About 3:2 mixture of diastereomers.

2-Methyl-2-butenylation also proceeded successfully under similar conditions by using (Z)-2-methyl-1-(tributylstannyl)-2-butene (**5**), which can be prepared easily by Pd(0) catalyzed hydrostannylation of isoprene.⁸⁾ Results were summarized in Table 2. In the case of **1a**, using 2 eq of **1a**, based on BuSnCl₃, is effective to improve the regioselectivity. However, the yield of **6a** decreased to some extent.

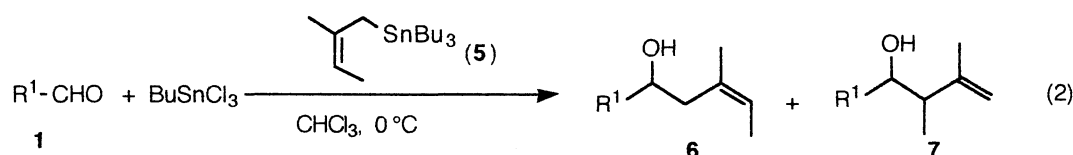


Table 2. Z-Selective 2-methyl-2-butenylation of **1**

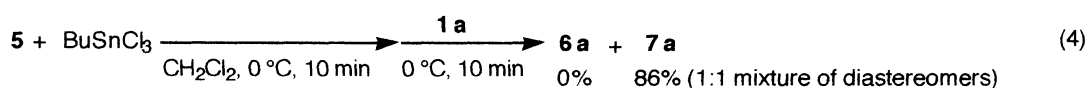
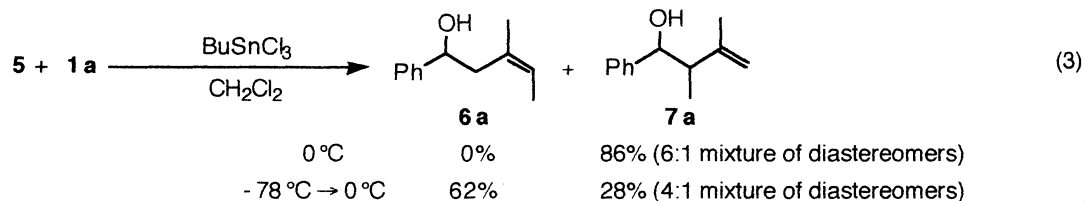
	R ¹	Main product	Yield/% ^{a)}	6 : 7 ^{b)}
1a	Ph	6a	79	90 : 10
1a	Ph	6a	64	93 : 7 ^{c)}
1c	<i>n</i> -Hex	6b	84	99 : 1
1j	<i>i</i> -Pr	6c	77	99 : 1
1k	<i>i</i> -Bu	6d	77	99 : 1
1l	<i>c</i> -Hex	6e	52	99 : 1

a) Total isolated yield of **6** and **7**. b) Determined by GLC.

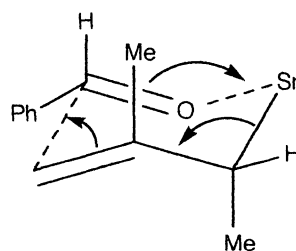
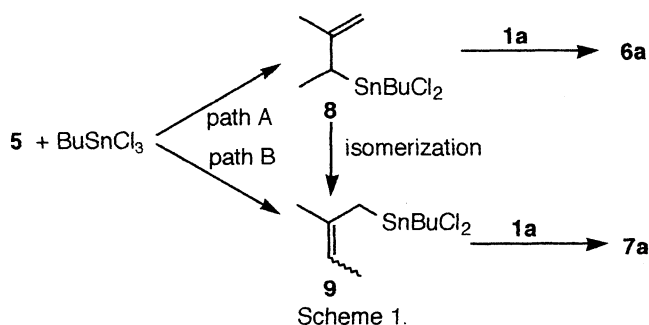
c) Molar ratio of **1a**:BuSnCl₃:**5** is 2.4:1.2:1.

It must be noted that 1-(tributylstannyl)-2-alkenes (**2** or **5**) must be added last. If **1** or BuSnCl₃ was added last, the regio selectivity of 2-alkenylation decreased considerably. For example, when BuSnCl₃ was added to a

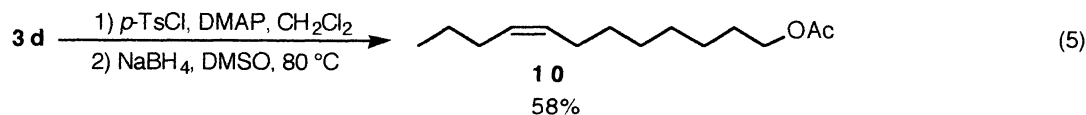
CH_2Cl_2 solution of **5** and **1a** at 0°C , **7a** was obtained in 86% yield, and **6a** was not obtained (Eq. 3). And even when BuSnCl_3 was added at -78°C , **6a** was obtained in 62% yield, and the regioisomer **7a** was obtained in 28% yield. Similarly, when **1a** was added last at 0°C , **6a** was not obtained (Eq. 4).

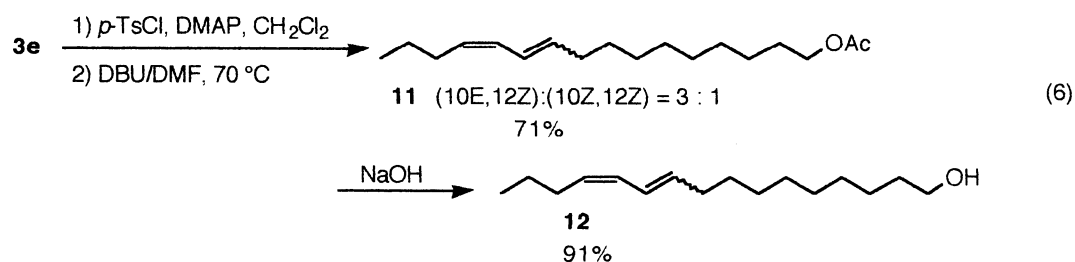


The mechanism of this reaction can be explained as follows. The transmetalation of allylic tin compound with BuSnCl_3 or Bu_2SnCl_2 is well-established reaction.^{5,6,9)} As we have reported recently, the regioselectivity of the transmetalation depends on the stereochemistry of the double bond.⁶⁾ When **5** is not added last, considerable amount of **5** reacts with BuSnCl_3 by path B in Scheme 1 to give **9**, and the alternative product **8** readily isomerize at 0°C to more stable **9**. The transmetalation product **8** and **9** react with **1a** to give **6a** and **7a**, respectively. The well-established cyclic chair-like transition state (Scheme 2) can explain it.^{5,6)} The reaction of **5** and **1a** at -78°C , the isomerization of **8** to **9** is slow enough to give considerable amount of **6a**. On the other hand, the corresponding reaction at 0°C , the isomerization is too fast to give **6a**. When **5** is added last, the oxygen atom of **1a** coordinates to BuSnCl_3 .¹⁰⁾ The coordination of **1a** reduces the electrophilicity of BuSnCl_3 , and it is effective to improve the regio-selectivity of the transmetalation. Further study on the transmetalation is now in progress.



The present method can be applied to a stereoselective synthesis of pheromones which have (*Z*)-double bonds. Tosylation of **3d** and the subsequent reduction by NaBH_4 in DMSO gave (*Z*)-8-dodecenyl acetate (**10**), sex pheromone of *Grapholitha molesta*, in 58% yield. Bombykol (**12**), sex pheromone of *Bombyx mori*, can also be synthesized from **3e**. Results are summarized as follows.





This method provides a new method for an introduction of (Z)-double bond from *E,Z*-mixture of 1-(tributylstannyl)-2-alkenes which can be prepared by various methods.

A typical procedure for the Z-selective 2-alkenylation is as follows. To a CHCl₃ (2 ml) solution of **1a** (0.21 g, 2.0 mmol), was added BuSnCl₃ (0.42 g, 1.5 mmol) in CHCl₃ (0.5 ml) at 0 °C. After stirring at this temperature for 2 min, **2a** (0.40 g, 1.0 mmol) in CHCl₃ (1 ml) was added slowly. The mixture was stirred at 0 °C for 30 min. Then it was poured into water and extracted with ether. The organic layer was separated and dried over MgSO₄, and evaporated. The crude product was purified with flash chromatography on silica gel to give a mixture of **3a** and **4a** (95:5, total 0.205 g, 0.94 mmol) in 94% yield.

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