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$BuSnCl_3$ Mediated *Z*-Selective 2-Butenylation and *erythro*-Selective 1-Methyl-2-propenylation of Aldehydes by 1-(Tributylstannyl)-2-butene

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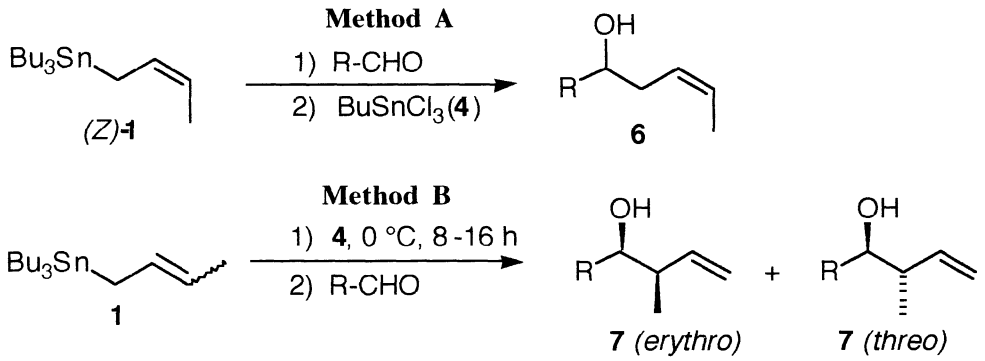
Butyltin trichloride mediated reaction of 1-(tributylstannyl)-2-butene with aldehydes is described. This reaction is useful as a stereoselective method for *(Z)*-2-butenylation and *erythro*-1-methy-2-propenylation of aldehydes.

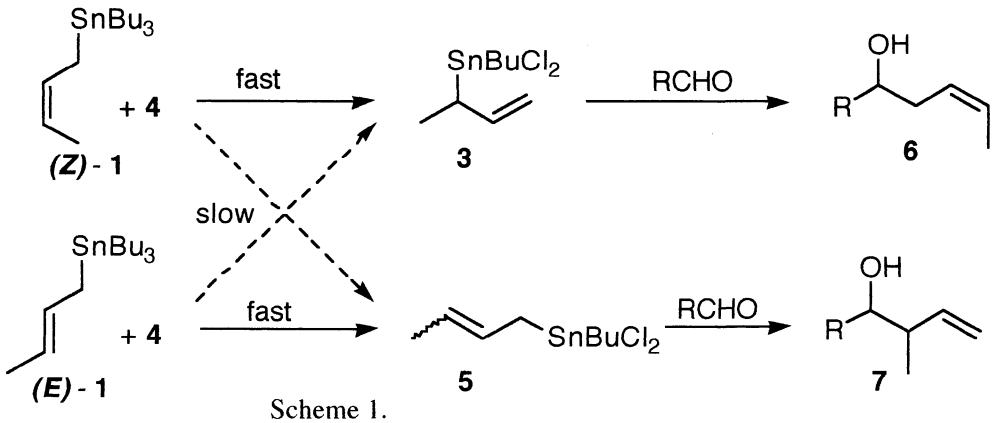
The utility of 1-(tributyistannyl)-2-butene(**1**) is well-established.[1] Lewis acid catalyzed reaction and thermal reaction of **1** with aldehydes give 1-methyl-2-propenylated products.[2] On the other hand, 2-butenylation by **1** can be accomplished by a transmetalation method.[3,4] For example, Bu_2SnCl_2 mediated reaction of **1** with aldehydes proceeds regio- and stereoselectively to give *(Z)*-2-butenylated products predominantly.[4] This reaction contains 3-(dibutylchlorostannyl)-1-butene(**2**) as an intermediate. Although 3-(butyldichlorostannyl)-1-butene(**3**), prepared from **1** and $BuSnCl_3$ (**4**), is more reactive than **2**,[5] the utility of **3** in organic synthesis has not been studied extensively. In this paper, we wish to report the **4** mediated stereoselective *(Z)*-2-butenylation and *erythro*-1-methyl-2-propenylation of aldehydes by **1**.



Regio- and stereoselectivity of **4** mediated reaction of **1** with aldehydes depends on the stereochemistry of **1** and the reaction conditions. Especially, the order of the addition of **1**, **4**, and aldehydes is important. When *(Z)*-1-(tributylstannyl)-2-butene(***(Z)*-1**)[6] was used and **4** was added last, *(Z)*-2-butenylated product(**6**) was obtained predominantly (Method A).[7] In this method, the initially formed **3** reacts immediately with aldehydes without isomerization to 1-(butyldichlorostannyl)-2-butene(**5**) to give **6**.

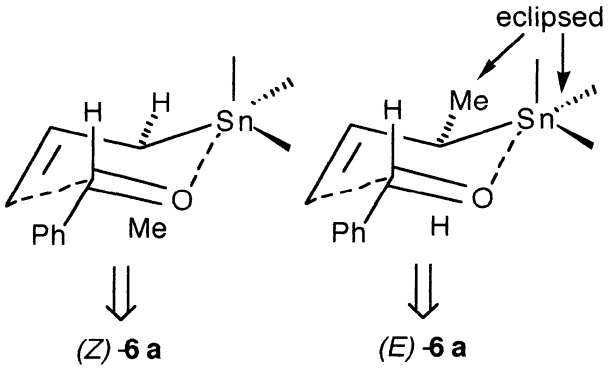
When **4** was added to a solution of **1**, the transmetalation of Bu_3Sn to $BuSnCl_2$ proceeded immediately to give **3** and **5**, and the former slowly isomerized to **5**. When aldehyde was added after sufficient time elapsed for the isomerization of **3**, 1-methy-2-propenylated product(**7**) was obtained predominantly (Method B,[8] Runs 8-17 in Table 1).

When *E,Z* mixture of **1** was used in Method A, a considerable amount of **7** was obtained (Runs 2 and 5). Similar results were obtained in Method B with short reaction time at low temperature (Runs 6 and 7). When **4** was added to the solution of **1**, transmetalation of Bu_3Sn to $BuSnCl_2$ proceeded immediately even at -78 °C. These results suggest that the transmetalation of *(Z)*-**1** proceeds with migration of the double bond, and that of *(E)*-**1** proceeds without it (Scheme 1). The reasons for these results are under investigation.

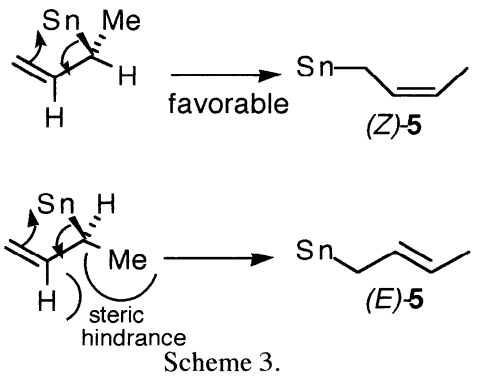


Scheme 1.

The *Z*-selectivity of the reaction of **3** with aldehydes can be explained by the well-established chairlike cyclic transition state.[4] (Scheme 2)



Scheme 2.

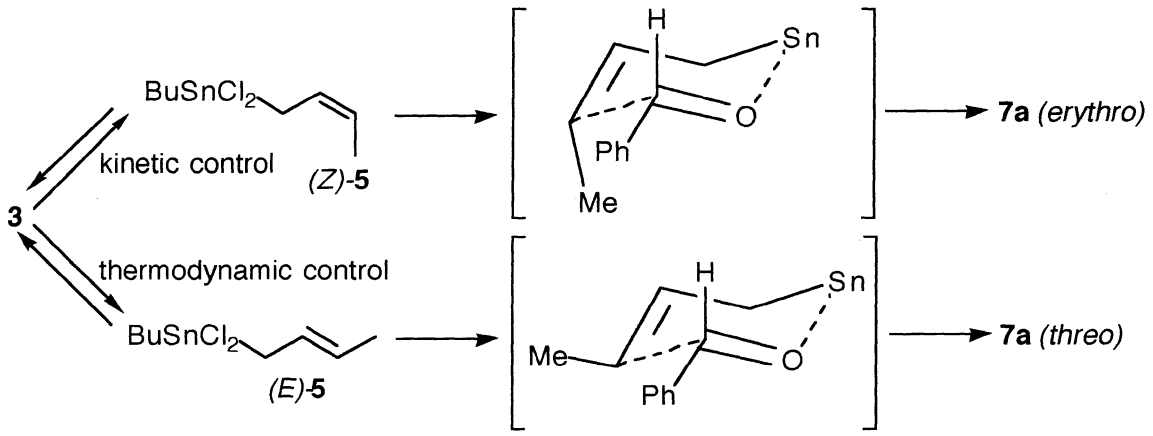


Scheme 3.

In Method B, the ratios of **6**, **7***(erythro)*, and **7***(threo)* depend on the reaction time and temperature. When CH_2Cl_2 was used as solvent, the reaction at 0°C for 8 hs gave the best *erythro* selectivity. Longer reaction time and higher temperature increase the ratio of *threo* isomer. These results can be explained as follows. When the initially formed **3** slowly isomerizes to **5**, isomerization to *(Z)*-**5** is faster than that to *(E)*-**5**, because of the steric effect shown in Scheme 3.[9] However, *(E)*-**5** is thermodynamically more stable than *(Z)*-**5**. The ratio of *(E)*-**5** slowly increases at higher temperature. *(Z)*-**5** is the kinetically controlled product, and *(E)*-**5** is the thermodynamically controlled product. *(Z)*-**5** and *(E)*-**5** form the chairlike transition state shown in Scheme 4 by the reaction with benzaldehyde to give **7***(erythro)* and **7***(threo)*, respectively.[10]

Table 1. $BuSnCl_3$ Mediated Reaction of **1** with Aldehydes

Run	*E*/*Z* ratio of **1**	R	Method	Solvent	Temp/°C, Time	Yield/%	**6**	: **7**(*erythro*)	: **7**(*threo*)
1	0 / 10	Ph	A	CH_2Cl_2	-78	96	96	: 3	: 1
2	6 / 4	Ph	A	CH_2Cl_2	-78	96	44	: 34	: 22
3	0 / 10	Ph	A	CH_2Cl_2	0	95	80	: 16	: 4
4	0 / 10	Hex	A	CH_2Cl_2	-78	94	95	: 5 (*threo* + *erythro*)	
5	6 / 4	Hex	A	CH_2Cl_2	-78	90	69	: 31 (*threo* + *erythro*)	
6	0 / 10	Ph	B	CH_2Cl_2	-10, 1 min	92	96	: 3	: 1
7	6 / 4	Ph	B	CH_2Cl_2	-10, 1 min	95	54	: 23	: 23
8	0 / 10	Ph	B	CH_2Cl_2	0, 8 h	93	6	: 80	: 14
9	6 / 4	Ph	B	CH_2Cl_2	0, 8 h	68	trace	: 69	: 31
10	0 / 10	Ph	B	CH_2Cl_2	0, 15 h	75	4	: 74	: 22
11	6 / 4	Ph	B	CH_2Cl_2	0, 15 h	80	0	: 69	: 31
12	0 / 10	Ph	B	CH_2Cl_2	reflux, 30 min	93	trace	: 75	: 25
13	0 / 10	Ph	B	$CHCl_3$	0, 16 h	86	0	: 82	: 18
14	0 / 10	Ph	B	$CHCl_3$	30, 3 h	90	4	: 65	: 31
15	0 / 10	Ph	B	$CHCl_3$	reflux, 1 h	95	trace	: 50	: 50
16	0 / 10	Ph	B	toluene	reflux, 1 h	65	trace	: 48	: 52
17	6 / 4	Ph	B	$CHCl_3$	0, 14 h	80	trace	: 77	: 23



Scheme 4.

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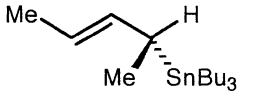
6) Typical procedure of Method A (Run 1 in Table 1) is as follows: To a solution of **1** (0.690 g, 2.0 mmol) and benzaldehyde (0.233 g, 2.2 mmol) in CH_2Cl_2 (10 ml) under nitrogen atmosphere at -78 °C, was added **4** (0.564 g, 2.0 mmol) in CH_2Cl_2 (5 ml) slowly. The mixture was allowed to warm to 0 °C, and stirred at that temperature for 30 min. The reaction mixture was quenched with H_2O and extracted with ether. The organic phase was dried, condensed, and purified by column chromatography on silica gel to give the mixture of **6a**, **7a** *(erythro)*, and **7a** *(threo)* (total 0.302 g, 1.84 mmol, 92% yield). The ratio of **6a** : **7a** *(erythro)* : **7b** *(threo)* was determined by ^1H NMR.

7) Typical procedure of Method B (Run 8 in Table 1) is as follows: To a solution of **1** (0.690 g, 2.0 mmol) in CH_2Cl_2 (10 ml) at -10 °C under nitrogen atmosphere, was added **4** (0.564 g, 2.0 mmol) in CH_2Cl_2 (5 ml) slowly. After stirring at 0 °C for 8 h, benzaldehyde (0.254 g, 2.4 mmol) in CH_2Cl_2 (2 ml) was added slowly to the mixture. After stirring at 0°C for 30 minutes, the reaction mixture was quenched and purified in a similar manner to Method A. The total yield of **6a**, **7a** *(erythro)*, and **7a** *(threo)* was 95% (0.301g, 0.186 mmol).

8) Stereoselective synthesis of *(Z)*-(**1**); H. Miyake and K. Yamamura, *Chem. Lett.*, **1992**, 507.

9) ^{13}C NMR data of *(E)*-3-(tributylstannyl)-2-pentene suggest its most stable conformation to be **8**. This result supports the most stable conformation of **3** to be **9**: H. Miyake and K. Yamamura, *Chem. Lett.*, **1992**, in press.



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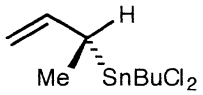

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