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Z- and *threo*-Selective 1-Methyl-2-butenylation of Aldehydes by 4-(Tributylstannyl)-2-pentene

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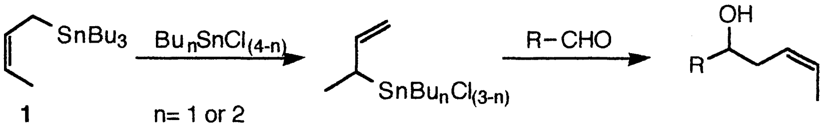
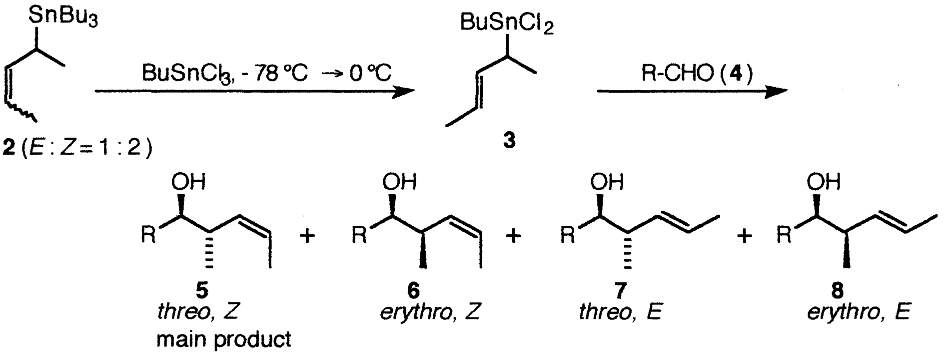
Transmetallation of an *E,Z*-mixture of 4-(tributylstannyl)-2-pentene with $BuSnCl_3$ proceeded stereoselectively to give (*E*)-4-(butyldichlorostannyl)-2-pentene (**3**). The subsequent addition of it to an aldehyde proceeded *Z*- and *threo*-selectively to give 1-methyl-2-butenylated product.

Transmetallation of allyltins is one of the most important procedures to prepare more reactive allyl metals.[1] Especially, the transmetallation of 1-(tributylstannyl)-2-butene (**1**) with Bu_2SnCl_2 or $BuSnCl_3$ and the subsequent addition to an aldehyde is a very useful method for (*Z*)-2-butenylation of the compound.[2] In this paper, we wish to report a *Z*- and *threo*-selective 1-methyl-2-butenylation of aldehyde *via* the transmetallation of 4-(tributylstannyl)-2-pentene (**2**) with $BuSnCl_3$.

Although the similar transformation can be accomplished by thermal reaction of **2** with aldehydes, it requires severe reaction conditions (150 °C, 18 h, for benzaldehyde).[3] The present method did not need a pure stereoisomer of **2**; an *E,Z*- mixture of **2**, which is readily available by Pd(0) catalyzed hydrostannation of 1,3-pentadiene,[4] will do. And both the transmetallation of **2** with $BuSnCl_3$ to give **3**, and the addition of **3** to aldehydes proceed smoothly under mild conditions. Although Lewis acid ($BF_3•OEt_3$) catalyzed reaction of **2** (*E*-isomer) with aldehydes proceeds under mild conditions, it proceeds *E*- and *erythro*-selectively.[3,5]



(1)



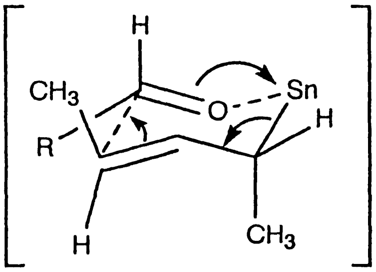
(2)

When **2** (*E*:*Z* = 1:2) was treated with $BuSnCl_3$ at -78 °C in CH_2Cl_2 and subsequent warming to 0 °C, the transmetallation was completed within 30 min to give 4-(butyldichlorostannyl)-2-pentene (**3**) and tributyltin chloride. The termination of the transmetallation can be checked easily by TLC analysis with disappearance of nonpolar **2**. Subsequent addition of aldehyde to the solution gave the mixture of **5-8**, which contains 96% of **5** in 91% yield in the case of benzaldehyde. The results are summarized in Table 1. The well-established chair-like transition state shown in Scheme 1 can explain this stereoselectivity. The configuration of **5** (R = Ph, *p*-Cl-C_6H_4, and *c*-Hex) was confirmed by comparison with the reported spectral data.[3] The reasons of the *E*-selectivity[6] of the transmetallation of **2** with $BuSnCl_3$ are under investigation.

Table 1. $BuSnCl_3$ mediated reaction of **2** with aldehydes

Run	R	Yield/%[a]	**5** : **6+7+8**[b]
1	Ph	91	96 : 4
2	*p*-Cl-C_6H_4	76	94 : 6
3	Hex	71	95 : 5
4	*i*-Bu	61	92 : 8
5	*c*-Hex	71	96 : 4

a) Isolated total yield of **5-8**.
b) Determined by GLC.



Chair-like transition state
Scheme 1.

A typical procedure for the synthesis of **5** is as follows. To a CH_2Cl_2 (3 ml) solution of **2** (0.54 g, 1.5 mmol), was added $BuSnCl_3$ (0.51 g, 1.8 mmol) in CH_2Cl_2 (1 ml) slowly at -78 °C. After stirring at -78 °C for 10 min, the mixture was warmed to 0 °C. After stirring at this temperature for 30 min, benzaldehyde (0.21 g, 2.0 mmol) in CH_2Cl_2 (1 ml) was added slowly to the mixture and stirred for 30 min. Then the reaction was quenched with water and extracted with ether. The organic layer was dried and evaporated under reduced pressure. The residue was purified by flash-chromatography on silica gel to give the mixture of **5-8** (R = Ph) (0.24 g, 1.36 mmol) in 91% yield.

References

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6) The *E*-selectivity was judged by NMR recorded at 25 °C.

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