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On the Transmetallation of (*E*)-1-Phenyl-3-(tributylstannyl)propene and 3-Phenyl-3-(tributylstannyl)propene with $BuSnCl_3$

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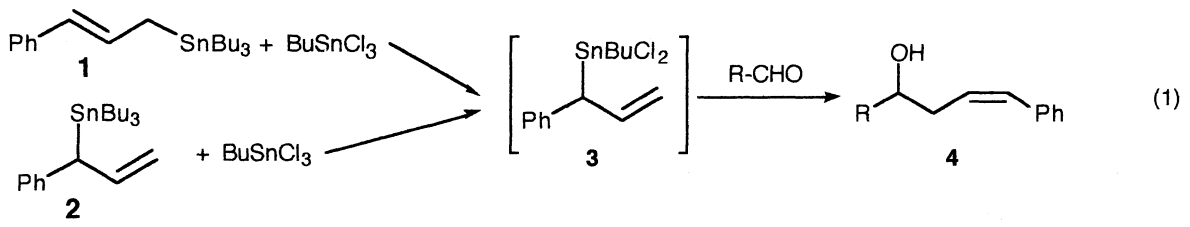
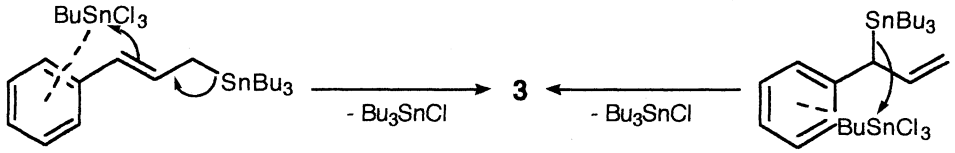
Transmetallation of *(E)*-1-phenyl-3-(tributylstannyl)propene and 3-phenyl-3-(tributylstannyl)propene with $BuSnCl_3$, and the isomerization of the transmetallated product are described. The application of the reactions to stereoselective *(Z)*-3-phenyl-2-propenylation and *threo*-1-phenyl-2-propenylation of aldehydes is also described.

Transmetallation of allyltins is a very useful procedure in organic synthesis to obtain more reactive allyl metal compounds.[1] The transmetallation of allyltins with Bu_nSnCl_{4-n} (n=0,1,2) usually proceeds with a migration of the double bond.[2] However, transmetallation of *(E)*-1-(tributylstannyl)-2-butene with $BuSnCl_3$ proceeds mainly without migration of the double bond, while that of *(Z)*-1-(tributylstannyl)-2-butene proceeds with it,[3] probably because of the difference in the steric hindrance of the α and γ carbons. In this paper, we wish to report the transmetallation of *(E)*-1-phenyl-3-(tributylstannyl)propene (**1**) and 3-phenyl-3-(tributylstannyl)propene[4] (**2**) with $BuSnCl_3$ in which the phenyl group plays a very important role in determining the regioselectivity of the transmetallation.



(1)

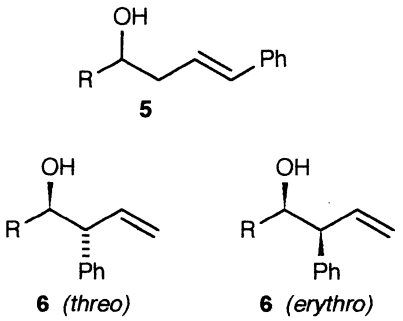
When **1** or **2** was treated with $BuSnCl_3$ in the presence of aldehydes, *(Z)*-3-phenyl-2-propenylation of the aldehydes proceeded with excellent stereoselectivity. These results and the mechanisms of similar reactions suggest that the transmetallation of **1** with $BuSnCl_3$ proceeded with a migration of the double bond, while that of **2** proceeded without it, to give **3** in both cases. These results can be explained as follows.



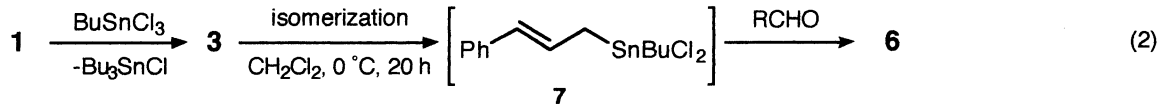
Initially, the phenyl group of **1** or **2** coordinates to Lewis acidic $BuSnCl_3$,[5] causing transmetallation to occur at the adjacent site of the phenyl group to give benzylic tin **3**, regardless of the initial positions of the Bu_3Sn groups of the starting allyltins. The coordination of a tin atom to aromatic ring was supported by the diastereo-selectivity of the reaction of 3-(butyldichlorostannyl)cycloalkenes with aldehydes.[5] Subsequent addition to aldehydes with a well-established six-membered cyclic transition state gave **4** diastereo-selectively.[6]

Table 1. Reaction of **1** and **2** with aldehydes

Allyltin	R	Solvent	Yield/%	**4** : **5**+**6**
1	Ph	$CHCl_3$	57	98 : 2
		CH_2Cl_2	86	97 : 3
1	*i*-Pr	$CHCl_3$	60	98 : 2
1	*i*-Bu	$CHCl_3$	65	99 : 1
1	*n*-Hex	$CHCl_3$	69	98 : 2
		CH_2Cl_2	92	96 : 4
1	*c*-Hex	$CHCl_3$	58	98 : 2
		CH_2Cl_2	67	96 : 4
2	Ph	$CHCl_3$	40	98 : 2



It must be noted that the transmetallation of **1** or **2** to give **3** is not a thermodynamically controlled reaction but a kinetically controlled reaction. Allyltin **3** slowly isomerize to give **7** which is thermodynamically more stable than **3**. Although McNeill and Thomas reported the similar effects of a benzyloxy group in the regioselective transmetallation of δ-benzyloxyallyltin with $SnCl_4$,[6] the isomerization of the product is not described in it. Subsequent addition of **7** to an aldehyde gave **6**(*threo*) in excellent diastereoselectivity. This reaction is useful as a new method for the *threo*-selective 1-phenyl-2-propenylation of aldehydes (Eq. 2).



(2)

R = Ph 68% *threo*:*erythro* = 98 : 2
R = *i*-Bu 58% *threo*:*erythro* = 98 : 2
R = *n*-Hex 75% *threo*:*erythro* = 98 : 2

A typical procedures for the synthesis of **4** is as follows. To a solution of **1** (0.61 g, 1.5 mmol) and heptanal (0.26 g, 2.25 mmol) in CH_2Cl_2 (2 ml), was added $BuSnCl_3$ (0.85 g, 3.0 mmol) in CH_2Cl_2 (2 ml) slowly at 0 °C. The mixture was stirred at this temperature for 1 h. Then it was poured into water and extracted with ether. The organic layer was separated and dried over $MgSO_4$, and evaporated. The crude product was purified with flush chromatography on silica gel to give a mixture of **4**, **5**, and **6** (total 0.32 g, 1.38 mmol) in 92% yield.

References

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