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$BuSnCl_3$-Mediated Reaction of 3-(Tributylstannyl)cycloalkenes with Aldehydes. Highly *erythro*-Selective 2-Cyclopentenylation and 2-Cyclohexenylation of Aromatic Aldehydes

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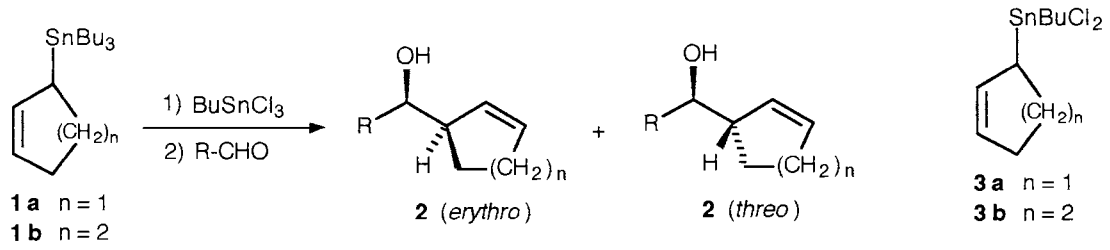
3-(Butyldichlorostannyl)cyclopentene and 3-(butyldichlorostannyl)cyclohexene, which are prepared by the transmetalation of corresponding 3-(tributylstannyl)cycloalkene with $BuSnCl_3$, react with aromatic aldehydes to give 2-cycloalkenylated products with excellent *erythro*-selectivity. However, the corresponding reaction with aliphatic aldehydes proceeded in only moderate *erythro*-selectivity.

Stereoselective allylation of aldehyde by allyltin compounds is well-studied.[1] We studied the diastereoselective 2-cycloalkenylation of aldehydes by 3-(tributylstannyl)cycloalkene (**1**). Although BF_3•OEt_2 mediated *erythro*-selective 1-methyl-2-propenylation of aldehydes by 2-butenyltin is well-established,[2] BF_3•OEt_2 mediated reaction of 2-cyclohexenyltin with benzaldehyde proceed with poor *threo*-selectivity, whereas that with aliphatic aldehyde proceed with good *erythro*-selectivity.[3] Recently, Issacs and coworkers have reported the *erythro*-selective 2-cycloalkenylation of benzaldehyde under high pressure (9 kbar) with 86-92% diastereoselectivity.[4] In this paper, we wish to report the $BuSnCl_3$-mediated highly *erythro*-selective 2-cycloalkenylation of aromatic aldehydes.



1a n = 1
1b n = 2

2 (*erythro*) **2** (*threo*)

3a n = 1
3b n = 2

When $BuSnCl_3$ was added to the CH_2Cl_2 solution of **1**, transmetalation of Bu_3Sn to $BuSnCl_2$ occurred smoothly to give **3**. And the following addition of aldehydes to the solution gave 2-cycloalkenylated products (**2**). $BuSnCl_3$-mediated reaction of allyltins with aldehydes generally proceed with the cyclic chair-like transition state,[5] and the diastereochemistry of the products depends on the stereochemistry of the double bonds of the allyltins. In the present cases, the stereochemistry of the double bond is fixed to be *cis* because of the 5 or 6 membered cyclic structure. This means that the $BuSnCl_3$ mediated reaction of **1** with aldehyde is expected to proceed *erythro*-selectively. When **3** was treated with aromatic aldehydes such as benzaldehyde, the cycloalkenylation proceeded with excellent *erythro*-selectivity; *threo* isomers were not detected by NMR analysis. However, unexpectedly, the reaction with aliphatic aldehydes, such as 3-methylbutanal and heptanal, proceeded with only moderate *erythro*-selectivity. These results cannot be explained satisfactorily by the

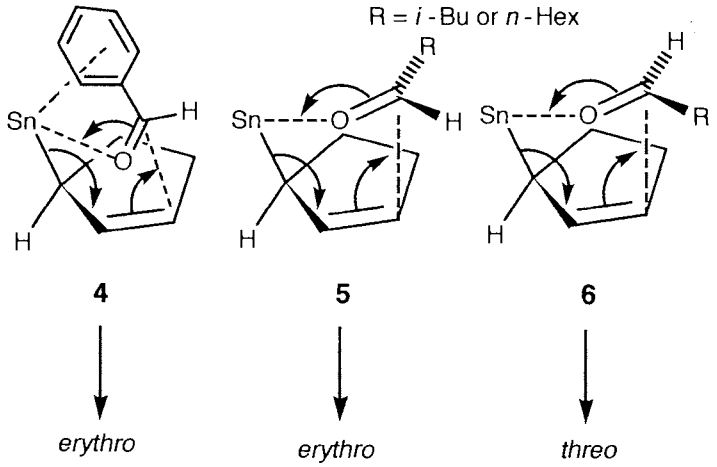
conventional cyclic chair-like transition state, and they suggest an interaction between Lewis basic aromatic ring and Lewis acidic tin atom. The plausible transition states of this reaction were shown in Scheme 1. In the cases of aromatic aldehydes, the interactions of aromatic ring and oxygen atom with tin atom make the transition states to be **4**, and it gives *erythro*-isomers. However, in the cases of aliphatic aldehydes, the conventional transition state such as **5** has only a little predominance over **6**, because the steric repulsion between R and cyclepentene or cyclohexene ring diminish the predominance of **5**.

The stereochemistry of **2** was determined by comparison with the ^{1}H and ^{13}C NMR data of the same or the similar compounds.[3,4,6]

Table 1. Cycloalkenylation of aldehyde

1	R	Product	Yield/%[a]
1a	Ph	**2a**	75[b]
1b	Ph	**2b**	84[b]
1a	*p*-Cl-C_6H_4	**2c**	84[b]
1b	*p*-Cl-C_6H_4	**2d**	88[b]
1a	*p*-CH_3-C_6H_4	**2e**	56[b]
1b	*p*-CH_3-C_6H_4	**2f**	67[b]
1a	*i*-Bu	**2g**	80[c]
1a	*n*-Hex	**2h**	85[c]
1b	*n*-Hex	**2i**	82[c]

a) Isolated yield. b) *threo*-Isomers were not detected by NMR analysis.
c) *erythro*:*threo*= 2:1.



Scheme 1

Typical procedures for the 2-cycloalkenylation were shown as follows. $BuSnCl_3$ (0.677 g, 2.4 mmol) was added to a solution of **1a** (0.714 g, 2.0 mmol) in CH_2Cl_2 (2 ml) at 0 °C. After 15 min at 0 °C, benzaldehyde (0.318 g, 3.0 mmol) was added to the solution and stirred at this temperature for 30 min. The solution was then quenched with water, and extracted with ether. The organic layer was dried ($MgSO_4$) and condensed. The crude product was purified by flash chromatography on silica gel to give **2a** (0.262 g, 1.50 mmol) in 75% yield.

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