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Pd(0) Catalyzed Hydrostannation of Conjugated Dienes. A Facile and Highly Regio- and Stereoselective Synthesis of *(Z)*-2-Alkenylstannanes

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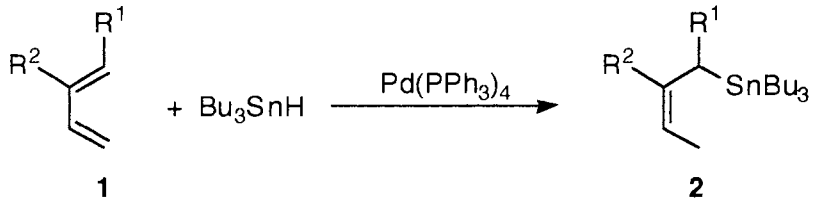
Tetrakis(triphenylphosphine)palladium(0) catalyzes the hydrostannation of conjugated dienes. The reaction proceeds highly regio- and stereoselectively to give *(Z)*-2-alkenyltributylstannanes. This method is convenient for the stereoselective synthesis of allyltin compounds.

The synthetic utility of allylic stannane as allyl anion equivalent is well-established.[1] On the other hand, the stereoselective synthesis of allylic stannanes has not been extensively studied,[2] in spite of the potential importance of allylic stannanes of defined stereochemistry in organic synthesis. Although the transition metal catalyzed hydrostannation of alkynes was reported,[3] that of conjugated diene has not been reported. In this paper, we wish to report the Pd(0) catalyzed hydrostannation of conjugated dienes as a facile method for the regio- and stereoselective synthesis of allylic stannanes.

When dienes (**1**) were treated with tributyltin hydride in the presence of $Pd(PPh_3)_4$, allylic stannanes were obtained regio- and stereoselectively. The results are shown in Table 1.



1 **2**

Table 1. Allylic Stannanes **2** from Conjugated Dienes **1**

Diene	R^1	R^2	Product	Yield/%	*E*	/	*Z*
1a	H	H	**2a**	91	0	/	100
1b	H	Me	**2b**	61	0	/	100
1c	Me	H	**2c**	45	36	/	64
1d	H	OAc	**2d**	72	100	/	0
1e	1,3-cyclohexadiene		**2e**	78	0	/	1

Pd(0) catalyzed hydrostannation of dienes (**1**), with exception of 1,3-pentadiene (**1c**), proceeded stereoselectively, probably because of s-cis type coordination of **1** to Pd(0). The hydrostannation of **1c** gave considerable amount of *(E)*-4-(tributylstannyl)-2-pentene. The results has not been clearly understood. Sterically hindered dienes such as 2,3-dimethyl-1,3-butadiene and 1,3-cyclooctadiene could not be hydrostannated under similar conditions. These results suggest that the steric factor is important to this reaction. Pd(0) catalyzed hydrostannation of substituted butadienes such as 2-methyl-1,3-butadiene (**1b**) proceeded with high regioselectivity to give **2b** in 61% yield, and the regioisomer 3-methyl-1-(tributylstannyl)-2-butene (**3**) was not detected by NMR analysis.[4)]

A typical procedure for the hydrostannation of **1d** is as follows. To a solution of **1d** (0.672 g, 6.0 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) in benzene (10 ml) under nitrogen atmosphere, was added Bu_3SnH (0.582 g, 2.0 mmol) in benzene (5 ml) dropwise at room temperature and stirred for 10 minutes. After the solvent was removed under reduced pressure, the product was purified by column chromatography on silica gel to give **2d** (0.580 g, 1.44 mmol) in 72% yield.

References

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3) Y. Ichinose, H. Oda, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **60**, 3468 (1987); K. Kikukawa, H. Umekawa, F. Wada, and T, Matsuda, *Chem. Lett.*, **1988**, 881; H. Miyake and K. Yamamura, *ibid.*, **1989**, 981.

4) ^1H and ^{13}C NMR data of **2b** and **3**, prepared from 3-methyl-2-butenylmagnesium chloride and Bu_3SnCl, were as follows. **2b**: ^1H NMR ($CDCl_3$) δ= 0.7-1.0 (m, 15H), 1.2-1.8 (m, 20H), and 4.91 (q, 1H, J =6 Hz); ^{13}C NMR ($CDCl_3$) δ= 9.69 (t, 3C), 13.70 (q, 4C), 14.97 (t), 25.89 (q), 27.43 (t, 3C), 29.24 (t, 3C), 113.36 (d), and 136.10 (s). **3**: ^1H NMR ($CDCl_3$) δ= 0.7-1.0 (m, 15H), 1.2-1.7 (m, 20H), and 5.25 (t, 1H, J = 9 Hz); ^{13}C NMR ($CDCl_3$) δ= 9.44 (t, 3C), 10.72 (t), 13.74 (q, 3C), 17.38 (q), 25.54 (q), 27.45 (t, 3C), 29.28 (t, 3C), 122.96 (d), and 125.31 (s).

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