CHEMISTRY LETTERS, pp. 1099-1100, 1992.

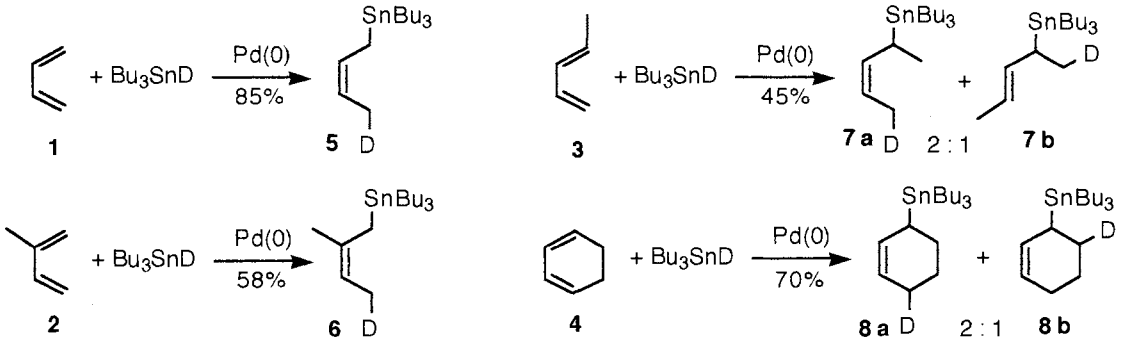
Study on the Mechanism of Pd(0) Catalyzed Hydrostannation of Conjugated Dienes by Deuterostannation

Hideyoshi MIYAKE* and Kimiaki YAMAMURA
Department of Chemistry, College of General Education, Kobe University, Nada, Kobe 657

The mechanism of Pd(0) catalyzed hydrostannation of conjugated dienes was studied by deuterostannation. In this reaction, η^3-allyl complex intermediate plays an important role. This mechanism can explain the reason of the stereoselectivity and the regioselectivity of this reaction.

Recently, we have reported the Pd(0) catalyzed hydrostannation of conjugated dienes.[1] The hydrostannation of 1,3-butadiene(**1**) and 2-methyl-1,3-butadiene(**2**) proceeded highly regio- and stereoselectively to give *(Z)*-2-alkenylstannanes. However, unexpectedly, that of 1,3-pentadiene(**3**) gave the *E,Z* mixture of 2-alkenylstannanes. In this paper, we wish to elucidate the reasons of those results by deuterostannation.

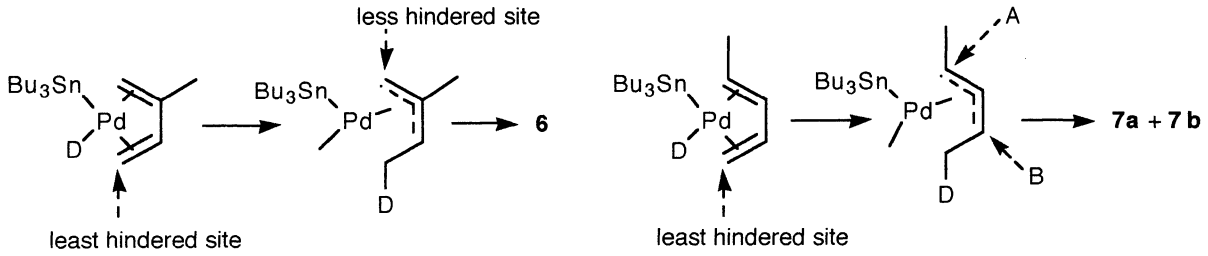
When dienes **1**, **2**, **3**, and 1,3-cyclohexadiene (**4**) were treated with tributyltin deuteride in the presence of $Pd(PPh_3)_4$, deuterostannated products were obtained. Results are shown as follows.



The deuterostannation of **1** and **2** gave 1,4-adducts **5** and **6** respectively. However, that of **3** and **4** gave the mixture of 1,4-adducts (**7a** and **8a**) and 1,2-adducts (**7b** and **8b**). It is very interesting that the 1,4-adduct of **3** has *Z*-geometry, and 1,2-adduct has *E*-geometry. These results were explained by the mechanism shown as follows.

Initially, dienes coordinate to Pd(0) in s-cis conformation,[2] and Bu_3SnD added oxidatively to Pd(0).[3] The deuterium on Pd attacks the least hindered site of the coordinated diene to give η^3-allyl complex. Then, Bu_3Sn group migrates to the less hindered site of the allyl group. When **2** was used, **6** was obtained as major product. However, when **3** was used, the difference between the steric hinderance of site A and that of site B was not serious. The attack of Bu_3Sn group to site A gives **7a**, and that to site B gives **7b**. This mechanism can explain why the hydrostannation of **1** gives *Z*-isomer of 2-alkenylstannanes exclusively, and that of **3** gives

E, *Z* mixture. The excellent regioselectivity of this reaction can be explained at the same time.

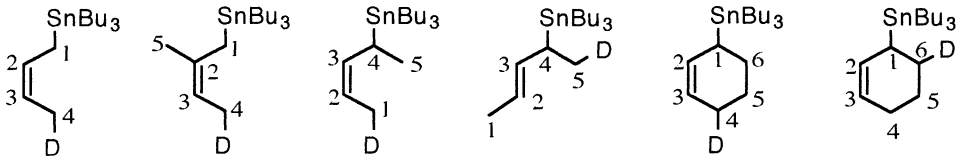


The stereochemistry of the **8a** and **8b** could not be determined by 250 MHz NMR analysis. The ^{13}C NMR data of **5-8** and corresponding non-deuterated compounds were summarized in Table 1.

Table 1. ^{13}C NMR chemical shifts of allyl stannanes[a)]

	C-1	C-2	C-3	C-4	C-5	C-6
5	10.10(10.08)	129.28(129.15)	117.86(117.88)	---[b)] (12.40)		
6	14.98(14.97)	136.10(136.10)	113.36(113.36)	---[b)] (13.70)	25.92(25.89)	
7a	---[b)] (13.06)	116.10(116.13)	137.22(137.22)	20.13(20.12)	18.54(18.53)	
7b	18.03(18.03)	116.76(116.77)	137.12(137.12)	23.98(24.00)	---[b)] (16.86)	
8a	26.09(26.03)	131.62(131.58)	121.41(121.47)	---[b)] (25.02)	23.20(23.27)	26.83(26.83)
8b	25.96(26.03)	131.56(131.58)	121.49(121.47)	25.02(25.02)	23.20(23.27)	---[b)] (26.83)

a) Chemical shifts of non-deuterated compounds are shown in parentheses. b) The signals of deuterated carbons could not be detected.



Scheme 1. Numbering of carbons of allyl stannanes for Table 1.

A typical procedure for the deuterostannation of **2** is as follows. To a solution of **2** (0.34 g, 5.0 mmol) and $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol) in benzene (5 ml), was added Bu_3SnD (0.29 g, 1.0 mmol) in benzene (3 ml) dropwise at room temperature and the mixture was stirred for 10 minutes. After the solvent was removed, the product was purified by column chromatography on silica gel to give **6** (0.21 g, 0.58 mmol) in 58% yield.

The authors wish to express their thanks to Professor Shinichi Ueji of Kobe University for helpful discussions on the structure of deuterated allylstannanes.

References

1) H. Miyake and K. Yamamura, *Chem. Lett.*, **1992**, 507.

2) H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 4330 (1967); R. P. Hughes and J. Powell, *J. Am. Chem. Soc.*, **94**, 7723 (1972); A. D. Josey, *J.Org. Chem.*, **39**, 139 (1972); T. Mitsuyasu and J. Tsuji, *Tetrahedron*, **30**, 831 (1974).

3) Y. Ichinose, H. Oda, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **60**, 3468 (1987).

(Received March 27, 1992)