

Stereospecific Preparation of (*E*)- α -Stannyl-1-alkenylphosphonates and their Application in Stille Reaction

Zheng Chang XIONG¹, Lu Ling WU¹, Xian HUANG^{1,2*}

¹Department of Chemistry, Zhejiang University, Xixi Campus, Hangzhou 310028

²State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032

Abstract: The palladium catalyzed hydrostannation of 1-alkenylphosphonates gives the (*E*)- α -stannyl 1-alkenylphosphonates **2** stereospecifically. Compounds **2** can occur Stille coupling reaction to afford α , β -disubstituted vinylphosphonates with the retention of the configuration.

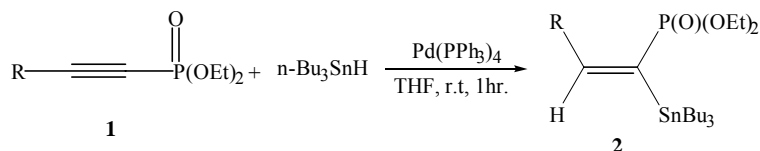
Keywords: 1-Alkenylphosphonate, hydrostannation, Stille reaction.

1-Alkenylphosphonates are very useful compounds for organic transformations¹ and for the synthesis of biological active compounds². On the other hand, alkenylstannanes are of particular synthetic interest and have attracted a great deal of attention in recent years³. For this reason, we anticipate the α -stannyl-1-alkenylphosphonates, a new class of 1, 1-difunctional reagents which combined α -stannyl and phosphonate groups in one molecule, will play an important role in organic synthesis. They can be regarded as a synthetic equivalent of a vinylphosphonates carbanion which may react with various electrophiles to afford the α , β -disubstituted vinylphosphonates. For this purpose, we started to synthesize the α -stannyl-1-alkenylphosphonates and to explore their application in organic synthesis

We firstly examined the palladium (0)-catalyzed hydrostannation of 1-alkenyl phosphonates. It shows that the hydrostannation of 1-alkenylphosphonates with Bu₃SnH occurred readily in the presence of Pd (PPh₃)₄ catalyst in THF at room temperature. The Bu₃SnH was added to the 1-alkenylphosphonates in a *syn*-addition way with the stannyl moiety directed to the carbon of the double bond bearing the phosphonate functionality. The stereochemistry of products **2** (**Scheme 1**, **Table 1**) was assigned according to the ³J_{HP} coupling constant measurement in their ¹H NMR spectra,⁴ which varied from 58-65 Hz for *E*-isomers and from 31-34 Hz for *Z*-isomers. The products are stable to moisture and air and can be handled conveniently.

The (*E*)- α -stannyl-1-alkenylphosphonates **2** can occur the palladium-catalyzed cross-coupling reaction with diaryliodonium salts. For example, the coupling of compound **2a** with diphenyliodonium chloride at room temperature in the presence

* E-mail: huangx@mail.hz.zj.cn

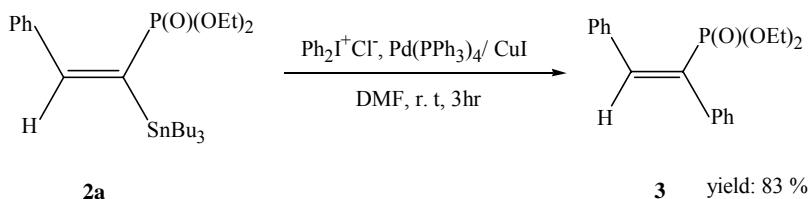
Scheme 1

a, R=Ph; b, R=n-C₄H₉; c, R=C₅H₁₁; d, R=MeOCH₂.

Table 1 Synthesis of products **2a-d**.

Entry	R	Product	Yield (%) ^a
1	Ph	2a	87
2	C ₄ H ₉	2b	83
3	C ₅ H ₁₁	2c	79
4	MeOCH ₂	2d	72

a: Purified yield after column chromatography.

Scheme 2

of Pd(PPh₃)₄ and CuI in DMF affords (*E*)- α -phenyl-phenylethenylphosphonate **3** in 83% yield (**Scheme 2**).

In conclusion, we have developed a facile route for the synthesis of (*E*)- α -stannyl 1-alkenylphosphonates **2**, which can occur Stille reaction smoothly.

Acknowledgments

We thank the Doctoral Foundation of the National Education Ministry of China for financial support of this research.

References

- For a recent review, see: I. T. Minami, J. Motoyosiya, *Synthesis*, **1992**, 333.
- (a) M. R. Harndn, M. J. Parrat, R. M. Perkin, *J. Med. Chem.*, **1993**, *36*, 1343. (b) S. Magati, S. Phadtare, J. Zemlica, *J. Org. Chem.*, **1992**, *57*, 2320.
- (a) D. Seyforth, M. A. Weiner, *J. Am. Chem. Soc.*, **1961**, *83*, 7585. (b) V. Farina, S. I. Hauck, *J. Org. Chem.*, **1991**, *56*, 4317. (c) J. K. Stille, *Angew. Chem Ed. Eng.*, **1986**, *25*, 508. (d) J. K. Stille, *Pure & Appl. Chem.*, **1985**, *57*, 1771. (e) W. J. Scott, J. K. Stille, *J. Am. Chem. Soc.*, **1986**, *108*, 3033.
- (a) G. L. Kenyon, F. H. Westheimer, *J. Am. Chem. Soc.*, **1966**, *88*, 3557. (b) C. Benzra, S. Nseic, G. Qurisson, *Bull. Soc. Chim. Fr.*, **1967**, 1140

Received 3 January, 2003