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Stereoselective Synthesis of (Z)-α-Bromovinylstannanes and (E)-α-Iodovinylstannanes *via* Hydrozirconation of Alkynylstannanes

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Abstract: Alkynylstannanes **1** react with $Cp_2Zr(H)Cl$ ($Cp=\eta^5$-C_5H_5) giving (Z)-α-stannylvinylzirconium complexes **2**, which are trapped with NBS or iodine in THF at 0°C to stereoselectively afford (Z)-α-bromovinylstannanes and (E)- α-iodovinylstannanes **3**, respectively.

Keywords: Hydrozirconation, alkynylstannane, (Z)-α-bromovinylstannane, (E)- α-iodovinylstannane, stereoselective synthesis.

Difunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, play an important role in organic synthesis, especially in developing many convenient methods for the stereoselective synthesis of substituted Alkenes[1]. The stereoselective synthesis of difunctional group reagents containing halogen atoms is of considerable interest in recent years. The B-Br[2], S-Cl[3], Si-Br[4], Se-I[5], and Te-Br[6] combinations have already been described in the literature. Both vinylstannanes and alkenyl halides are important intermediates[7], but the difunctional group reagent containing tin and halogen atoms has not been reported. Hydrozirconation has emerged as a unique hydrometallation with some attractive features[8], such as the high regioselectivity and stereoselectivity observed with alkynes[9]. However, to date, hydrozirconation of alkynylstannanes has received less attention[10]. We now wish to report that (Z)-α-bromovinylstannanes and (E)- α-iodovinylstannanes could be synthesized by hydrozirconation of alkynylstannanes, followed by treatment with NBS or iodine.

Alkynylstannanes **1** were prepared according to literature procedure[11]. Hydrozirconation of alkynylstannanes **1** at room temperature in THF gave (Z)- α-stannylvinylzirconium complexes **2**, which were reacted with NBS or iodine to afford (Z)-α-bromovinylstannanes and (E)-α-iodovinylstannanes **3,** respectively. The yields were 69-83% (**Scheme 1**).

Investigations of the crude products **3** by ^{1}H NMR spectroscopy (300 MHz) showed isomeric purities of more than 97%. One olefinic proton signal of **3** was characteristically split into triplet with coupling constant J = 7.0 Hz, which indicated that

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the hydrozirconation of the alkynylstannanes has a strong preference for the addition of the zirconium atom at the carbon adjacent to the alkylstannyl group. The results of the reaction are summarized in **Table 1**.

Scheme 1

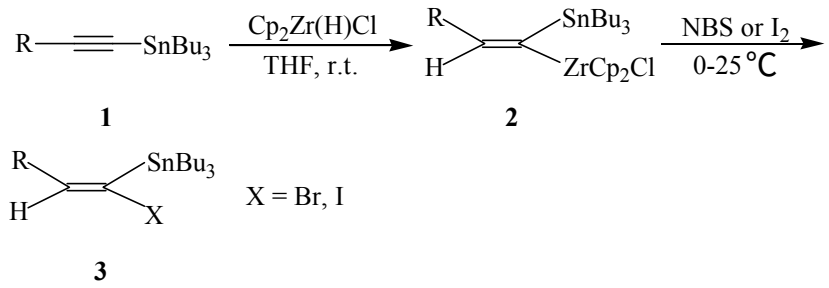

Table 1 Synthesis of (Z)-α-bromovinylstannanes and (E)-α-iodovinylstannanes

Entry	R	X	Product[a]	Yield[b](%)
1	*n*-C_4H_9	Br	**3a**	83
2	Ph	Br	**3b**	76
3	CH_3OCH_2	Br	**3c**	82
4	*n*-C_6H_{13}	Br	**3d**	79
5	*n*-C_4H_9	I	**3e**	81
6	Ph	I	**3f**	78
7	CH_3OCH_2	I	**3g**	69
8	*n*-C_6H_{13}	I	**3h**	76

[a]All products were characterized by IR, ^{1}H NMR and elemental analyses.
[b]Isolated yield based on the alkynylstannane used.

In conclusion, the hydrozirconation/halogenation strategy provides a direct route to (Z)-α-bromovinylstannanes and (E)-α-iodovinylstannanes from alkynylstannanes. The method has some attractive advantages such as mild reaction conditions, a simple procedure, shorter reaction times, good yields and high regio- and stereoselectivity. Investigations into the synthetic applications of (Z)-α-bromovinylstannanes and (E)-α-iodovinylstannanes are currently in progress.

Experimental

^{1}H NMR spectra were recorded on an AZ-300 spectrometer with TMS as internal standard (δ in ppm) using $CDCl_3$ as solvent. IR spectra were determined on a PE-683 instrument as neat films. Microanalysis were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in pre-dried glassware (140°C, 4 h) and cooled under a stream of dry nitrogen. THF was distilled from sodium-benzophenone ketyl before use.

*General procedure for the synthesis of **3a-h***

A mixture of $Cp_2Zr(H)Cl$ (1 mmol) and alkynylstannane **1** (1 mmol) in THF (5 mL) was stirred at room temperature for 40 min to yield a clear solution. Into the resulting solution was added NBS or iodine (1 mmol) at 0°C, and the mixture was stirred for 30 min, then at room temperature for 30 min. The solvent was removed by rotary evaporator under reduced pressure. The residue was extracted with light petroleum (3×10 mL) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel eluting with light petroleum.

*(Z)-1-Bromo-1-tributylstannyl-1-hexene **3a*** . ν (film)/cm^{-1}: 2957, 2928, 2872, 2855, 1596, 1463, 1377, 1073, 693; δ_H: 6.85 (t, 1H, *J* = 7.8 Hz), 1.97 (m, 2H), 1.67-0.85 (m, 34H); Anal. Calcd. for $C_{18}H_{37}SnBr$: C, 47.79; H, 8.19. Found: C, 47.54; H, 8.03.
*(Z)-1-Bromo-1-tributylstannyl-2-phenylethene **3b*** . ν (film)/cm^{-1}: 3058, 3023, 2956, 2921, 2871, 2853, 1600, 1489, 1463, 1376, 1072, 754, 722, 695; δ_H: 8.18 (s, 1H), 7.46-7.11 (m, 5H), 1.47-0.79 (m, 27H); Anal. Calcd. for $C_{20}H_{33}SnBr$: C, 50.85; H, 6.99. Found: C, 50.60; H, 6.83.
*(Z)-1-Bromo-1-tributylstannyl-3-methoxy-1-propene **3c*** . ν (film)/cm^{-1}: 2957, 2922, 2872, 2853, 1606, 1464, 1377, 1117; δ_H: 7.00 (t, 1H, *J* = 6.5 Hz), 3.79 (d, 2H, *J* = 6.4 Hz), 3.33 (s, 3H), 1.65-0.76 (m, 27H); Anal. Calcd. for $C_{16}H_{33}OSnBr$: C, 43.64; H, 7.50. Found: C, 43.42; H, 7.37.
*(Z)-1-Bromo-1-tributylstannyl-1-octene **3d*** . ν (film)/cm^{-1}: 2958, 2926, 2871, 2856, 1597, 1463, 1377; δ_H: 6.82 (t, 1H, *J* = 7.8 Hz), 1.99 (m, 2H), 1.50-0.75 (m, 38H); Anal. Calcd. for $C_{20}H_{41}SnBr$: C, 50.00; H, 8.54. Found: C, 49.82; H, 8.42.
*(E)-1-Iodo-1-tributylstannyl-1-hexene **3e*** . ν (film)/cm^{-1}: 2954, 2871, 1581, 1463, 1377; δ_H: 7.22 (t, 1H, *J* = 7.0 Hz), 2.23-1.91 (m, 2H), 1.78-0.66 (m, 34H); Anal. Calcd. for $C_{18}H_{37}SnI$: C, 43.29; H, 7.41. Found: C, 43.12; H, 7.26.
*(E)-1-Iodo-1-tributylstannyl-2-phenylethene **3f*** . ν(film)/cm^{-1}: 3057, 3022, 2955, 2871, 1598, 1488, 1463, 1377; δ_H: 8.47 (s, 1H), 7.41-7.08 (m, 5H), 1.70-0.69 (m, 27H); Anal. Calcd. for $C_{20}H_{33}SnI$: C, 46.24; H, 6.36. Found: C, 46.03; H, 6.27.
*(E)-1-Iodo-1-tributylstannyl-3-methoxy-1-propene **3g*** . ν (film)/cm^{-1}: 2956, 2923, 2871, 2854, 1590, 1463, 1376, 1106; δ_H: 7.42 (t, 1H, *J* = 7.0 Hz), 3.69 (d, 2H, *J* = 6.5 Hz), 3.29 (s, 3H), 1.74-0.70 (m, 27H); Anal. Calcd. for $C_{16}H_{33}OSnI$: C, 39.43; H, 6.78. Found: C, 39.21; H, 6.62.
*(E)-1-Iodo-1-tributylstannyl-1-octene **3h*** . ν (film)/cm^{-1}: 2956, 2924, 2872, 2855, 1585, 1463, 1376; δ_H: 7.20 (t, 1H, *J* = 7.0 Hz), 2.22-1.94 (m, 2H), 1.75-0.73 (m, 38H); Anal. Calcd. for $C_{20}H_{41}SnI$: C, 45.54; H, 7.78. Found: C, 45.32; H, 7.69.

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References

1. (a) T. N. Mitchell, R. Wickenkamp, A. Amamria, U. Schneider, *J. Org. Chem.*, **1987**, *52*, 4868.
   (b) P. A. Magrietis, M. E. Scott, K. D. Kim, *Tetrahedron Lett.*, **1991**, *32*, 6085.
   (c) X. Huang, Y. Ma, *Synthesis*, **1997**, 417.
2. G. Zweifel, R. P. Fisher, J. T. Snow, C. C. Whitney, *J. Am. Chem. Soc*.,**1971**, *93*, 6309.
3. V. Fiandanese, G. Marchese, F. Naso, L. Ronzini, *Synthesis*, **1987**, 1034.
4. C. Huynh, G. Linstrumelle, *Tetrahedron Lett.*, **1979**, 1073.
5. (a) L. S. Zhu, Z. Z. Huang, X. Huang, *J. Chem. Res.*, **1996**, 112.
   (b) X. Huang, L. S. Zhu, *Synthesis*, **1996**, 1191.
6. (a) X. Huang, Y. P. Wang, *Tetrahedron Lett.*, **1996**, *37*, 7417.
   (b) X. Huang, Y. P. Wang, *Synth. Commun*., **1996**, *26*, 3087.
7. J. K. Stille, *Angew. Chem. Int. Ed. Engl*., **1986**, *25*, 508.
8. J. Schwartz, *J. Organomet. Chem. Library*, **1976**, *1*, 461.
9. D. W. Hart, T. F. Blackburn, J. Schwartz, *J. Am. Chem. Soc.*, **1975**, *97*, 679.
10. (a) B. H. Lipshutz, R. Keil, J. C. Barton, *Tetrahedron Lett*., **1992**, *33*, 5861.
    (b) X. Huang, P. Zhong, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 1543.
11. Logue, K. Teng, *J. Org. Chem.*, **1982**, *47*, 2549.

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