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A Stereoselective Synthetic Route to (*Z*)-1-Arylthio Vinylstannanes†

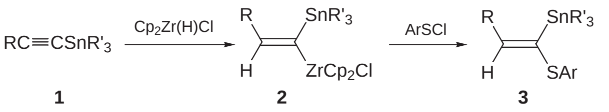
Xian Huang* and Ping Zhong‡

Department of Chemistry, Zhejiang University, at Xixi Campus, Hangzhou, 310028, P.R. China

Acetylenic stannanes react with $Cp_2Zr(H)Cl$ ($Cp = \eta^5\text{-}C_5H_5$) to give organozirconium(IV) complexes, which are trapped with arylsulfenyl chloride to afford (*Z*)-l-arylthio vinylstannanes.

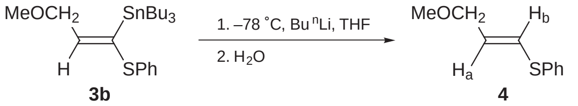
Vinyl sulfides[1–3] and vinylstannanes[4] have been used as synthetic intermediates to construct some olefins. (*E*)-1-Phenylthiovinylstannanes can be prepared by the reaction of 1-phenylthio-1-alkynes with tributyltin hydride,[5] but the *Z*-stereoisomers have not been reported. Herein, we report a convenient approach to (*Z*)-1-phenylthiovinylstannanes from acetylenic stannanes.

Recently, it has become popular to transform alkenylzirconium(IV) complexes to other functional groups with a high level of stereochemical purity.[6] Vinylzirconium complexes react with phenyltellurenyl iodide or arylselenenyl bromides readily to afford (*E*)-vinylic tellurides[7] or (*E*)-vinylic selenides.[8] Considering the high electrophility of arylsulfenyl chlorides, we tried to react them with the vinylzirconium complexes **2**[9] produced by hydrozirconation of acetylenic stannanes **1**. Experimental results show that $Cp_2Zr(H)Cl$[10] adds to acetylenic stannananes[11] in THF at room temperature stereospecifically with high regioselectivity to yield the vinylic Zr^{IV} complex **2** which react with arylsulfenyl chlorides[12] rapidly at 0 °C to afford vinylstannanes **3**. Yields are good to excellent (Scheme 1 and Table 1).



Scheme 1 R = Ph, Bu, $MeOCH_2$; R′ = Et, Bu; Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$

1-Phenylthio vinylstannanes can be transformed into vinylic sulfides. As the reaction occurs steroselectively,[13] it can be used to confirm the configuration of arylthio vinylstannanes **3**. For example, the configuration of vinylstannane **3b** could be confirmed from compound **4** which was obtained by treatment of **3b** with *n*-butyllithium in THF followed by hydrolysis; the reaction occurs stereoselectively (Scheme 2).[13] Particularly diagnostic for the stereochemistry of **4** is the coupling constant between the vicinal protons H_a and H_b which show a typical value of J_{HH} of 16 Hz which is consistent with an *E*-configuration. Therefore, we can confirm that the arylthio vinylstannanes **3** have *Z* configuration.



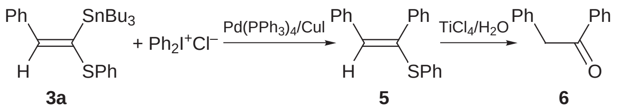
Scheme 2

Table 1 Synthesis of compounds **3a–g**[a]

Product	R	R′	Ar	Yield(%)
3a	Ph	Bu	Ph	80
3b	$MeOCH_2$	Bu	Ph	76
3c	Bu	Bu	Ph	70
3d	Ph	Bu	$4\text{-}MeC_6H_4$	74
3e	$MeOCH_2$	Bu	$4\text{-}MeC_6H_4$	69
3f	MePh	Bu	$4\text{-}ClC_6H_4$	76
3g	OCH_2	Et	Ph	68

[a] The products were identified by MS, ^1H NMR and IR spectroscopy.

The 1,1-difunctional compounds **3** have recently emerged as valuable reagents for organic synthesis. For example, palladium-catalyzed coupling reaction of **3a** with diphenyliodonium chloride affords (*E*)-1-phenyl-1-phenylthiostyrene (**5**) in 78% yield. Vinylsulfide **5** is readily hydrolyzed in the presence of $TiCl_4$ to afford 1-phenylacetophenone (**6**) in 96% yield.[4] This synthetic route, in which **3a** is equivalent to the synthon $PhCH_2C^- = O$, also provides a new method to obtain the ketone **6** (Scheme 3).



Scheme 2

Experimental

^1H NMR spectra were recorded on a AZ-300 spectrometer with TMS as internal standard. Mass spectra were obtained on Finigan 8230 mass spectrometer. IR spectra were determined on PE-683 instrument as neat films. All reactions were carried out in pre-dried glassware (140 °C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use.

General Procedure for the Synthesis of **3a–g**.—A mixture of $Cp_2Zr(H)Cl$ (1 mmol) and **1** (1 mmol) in THF (5 ml) was stirred at room temperature for 40 min. The resulting solution was cooled to 0 °C and ArSCl (1 mmol) was injected and the mixture was stirred at 0–10 °C for 40 min. The solvent was then removed by rotary evaporation under reduced pressure. The residue was extracted with light petroleum (3 × 6 ml) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel eluting with light petroleum.

3a: oil. IR (film): ν/cm^{-1} 3160, 1590, 1585, 1485, 1095, 810; $\delta_H(CDCl_3)$ 7.50–7.10 (m, 10 H), 6.75 (s, 1 H), 1.40–0.70 (m, 27 H); MS: *m/z* 502 (M^+, 26.00), 470 (20.12), 359 (23.25), 251 (100), 216 (74.09), 184 (54.99), 108 (29.33%); Calc. for $C_{26}H_{38}SSn$: C, 62.29; H, 7.64. Found: C, 62.44, H, 7.67%.

3b: oil. IR (film): ν/cm^{-1} 3095, 1590, 1470, 1020, 735; $\delta_H(CDCl_3)$ 7.43–7.10 (m, 5 H), 6.44 (t, *J* 6.0 Hz, 1 H), 3.70 (d, *J* 6.0 Hz, 2 H), 3.22 (s, 3 H), 1.35–0.70 (m, 27 H); MS: *m/z* 469 (M^+, 5.15), 255 (12.48), 177 (22.01), 147 (100), 103 (18.69), 45 (17.35%); Calc. for $C_{22}H_{38}OSSn$: C, 56.31; H, 8.16. Found: C, 56.45, H, 8.19%.

3c: oil. IR (film): ν/cm^{-1} 3090, 1595, 1485, 1025, 870; $\delta_H(CDCl_3)$ 7.40–7.16 (m, 5 H), 6.25 (t, *J* 6.0 Hz, 1 H), 2.45–2.32 (m, 2 H); 1.65–0.68 (m, 34 H); MS: *m/z* 482 (M^+, 3.11), 291 (76.64), 190 (81.31), 147 (64.96), 103 (46.35), 81 (100%). Calc. for $C_{24}H_{42}SSn$: C, 59.89; H, 8.79. Found: C, 60.01, H, 8.82%.

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* To receive any correspondence.

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡ *Permanent address*: Department of Chemistry, Yichun Normal Institute, Yichun, 336000, P.R. China.

3d: oil. IR (film): ν/cm^{-1} 3150, 1605, 1485, 1020, 825 δ_H(CDCl$_3$) 7.45–7.00 (m, 10 H), 2.28 (s, 3 H), 1.60–0.70 (m, 27 H); MS: *m/z* 515 (M$^+$, 6.52), 459 (100), 246 (49.47), 226 (36.01), 123 (32.06), 91 (28.62%); Calc. for $C_{27}H_{40}SSn$: C, 62.93; H, 7.82. Found: C, 62.98, H, 7.80%.

3e: oil. IR (film): ν/cm^{-1} 3140, 1600, 1420, 285 δ_H(CDCl$_3$) 7.30–6.90 (m, 4 H), 6.40 (t, *J* 6.0 Hz, 1 H), 3.80 (d, *J* 6.0 Hz, 2 H), 3.20 (s, 3 H), 2.28 (s, 3 H), 1.55–0.70 (m, 27 H); MS: *m/z* 483 (M$^+$, 3.35), 289 (30.17), 283 (59.85), 161 (100), 117 (13.26), 45 (11.03%); Calc. for $C_{23}H_{40}OSSn$: C, 57.16; H, 8.34. Found: C, 57.33, H, 8.38%.

3f: oil. IR (film): ν/cm^{-1} 3150, 1605, 1485, 1015, 820 δ_H(CDCl$_3$) 7.45–7.05 (m, 9 H), 7.00 (s, 1 H), 1.60–0.65 (m, 27 H); MS: *m/z* 534$^+$, 1.30), 479 (31.39), 386 (33.65), 262 (41.26), 244 (100), 210 (53.8), 57 (39.33%). Calc. for $C_{23}H_{37}ClSSn$: C, 58.29; H, 6.96. Found: C, 58.26, H, 6.96%.

3g: oil. IR (film): ν/cm^{-1} 3080, 1590, 1480, 1385, 1190, 1020, 740 δ_H(CDCl$_3$) 7.40–7.10 (m, 4 H), 6.40 (t, *J* 6.0 Hz, 1 H), 4.10 (d, *J* 6.0 Hz, 2 H), 3.18 (s, 3 H), 1.30 (s, 3 H), 1.30–0.65 (m, 15 H); MS: *m/z* 385 (M$^+$, 3.76), 321 (25.18), 291 (19.57), 255 (100), 177 (35.86), 147 (47.77), 45 (29.49%). Calc. for $C_{16}H_{26}OSSn$: C, 49.90; H, 6.804. Found: C, 49.97, H, 6.76%.

Synthesis of (E)-*Vinylsulfide* (**4**).—BuLi (1 ml, 1 M hexane solution) was added to a THF (5.0 ml) solution of **3b** (1.0 mmol) at −78 °C. After stirring for 30 min, the mixture was hydrolyzed with saturated aq. NH_4Cl and extracted with CH_2Cl_2 (2 × 10 ml). The organic extract was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel, eluting with petroleum to give (*E*)-vinylsulfide **4** (yield: 90%).

4. oil. IR (film): ν/cm^{-1} 3080, 1595, 1488, 950; δ_H(CDCl$_3$) 7.00–7.50 (m, 5 H), 6.30 (d, 1 H, *J* 16 Hz), 5.70 (dd, *J* 16, 6 Hz, 1 H), 3.82 (d, 2 H, *J* 6 Hz), 3.20 (s, 3 H).

Synthesis of (E)-1-*Phenyl*-1-*phenylthioethene* (**5**).—Vinyltributylstannane **3a** (0.5 mmol) and diphenyliodonium chloride[15] (0.5 mmol) were dissolved in DMF (5 ml) under nitrogen at room temperature. Pd(PPh$_3$)$_4$ (0.05 mmol) and Cu (0.4 mmol) were then added and the mixture stirred at room temperature and monitored by TLC for the disappearance of the starting organostannane. The reaction mixture was diluted with CH_2Cl_2 (15 ml), filtered and stirred with 20% aqueous KF (10 ml) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel, eluting with petroleum to give **5** (yield: 78%).

5. mp 76–77 °C (lit.,[16] 77–78 °C) IR (KBr): ν/cm^{-1} 3080, 1625, 1580, 1480, 1075, 1020, 730; δ_H(CDCl$_3$) 7.45–7.06 (m, 16 H).

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