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Note

Stereoselective preparation of (*Z*)-α-stannyl-1-alkenyl sulfoxides via hydrozirconation of acetylenic stannanes

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Abstract

Acetylenic stannanes (**1**) react with $Cp_2Zr(H)Cl$ ($Cp = \eta^5$-C_5H_5) giving (*Z*)-α-stannylvinylzirconium complexes (**2**), which are trapped with sulfinyl chlorides (**3**) in THF at room temperature to afford (*Z*)-α-stannyl-1-alkenyl sulfoxides (**4**). The yields are 63–81%. The coupling of **4h** with diphenyliodonium chloride in the presence of $Pd(PPh_3)_4$ and CuI afford (*E*)-α-phenyl unsaturated sulfoxide **5** in 75% yield.

Keywords: Alkynylstannane; Organozirconocene compound; Hydrozirconation; Sulfinyl chloride; Sulfoxidation; (*Z*)-α-Stannyl-1-alkenyl sulfoxide

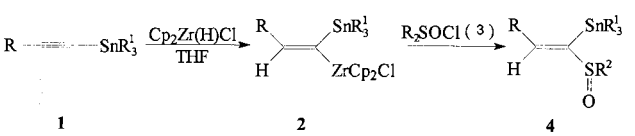
1. Introduction

Alkenyl sulfoxides [1–3] and alkenyl stannanes [4] have been used as synthetic intermediates to construct some olefins. The reaction of 1-hexynyl-1-(4-methylphenyl)sulfoxide with tributyltin hydride afforded a mixture of (*E*)-1-hexenyl-1-(4-methylphenyl)-sulfinyl tributyl stannane and its (*Z*)-stereoisomer [5]. Herein, we want to find a convenient approach to (*Z*)-1-hexenyl-1-(4-methylphenyl)sulfinyl tributyl stannane from acetylenic stannanes. Hydrozirconation has emerged as a unique hydrometallation with some attractive features [6], such as the high regioselectivity and stereoselectivity observed with alkynes [7]. However, to date, hydrozirconation of alkynylstannanes has been receiving less attention [8,9]. Therefore, we now wish to report that (*Z*)-α-stannyl substituted α,β-unsaturated sulfoxides could be synthesized by hydrozirconation of the alkynylstannanes, followed by treatment with sulfinyl chlorides, although the sulfoxidation of vinylzirconium complexes has not been reported.

2. Results and discussion

Alkynylstannanes (**1**) and sulfinyl chlorides (**3**) were prepared according to the literature, respectively [10,11]. Hydrozirconation of alkynylstannanes at room temperature (r.t.) in THF gave (*Z*)-α-stannylvinylzirconium complexes (**2**), which reacted with sulfinyl chlorides to afford (*Z*)-α-stannyl substituted α,β-unsaturated sulfoxides (**4**). The yields were 63–81% (Scheme 1).

Investigations of the crude products **4** by ^{1}H-NMR spectroscopy (300 MHz) showed isomeric purities of more than 96%. One olefinic proton signal of **4** was characteristically split into one triplet with coupling constant $J = 7.0$ Hz, which indicated that the hydrozirconation of the alkynylstannes has a strong preference for the addition of the zirconium atom at the carbon adjacent to the alkylstannyl group. The results of the reaction were summarized in Table 1.



1 2 4

Scheme 1.

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Table 1
Synthesis of α-stannyl-α,β-unsaturated sulfoxides

Entry	R	R^1	R^2	Product [a]	Yield [b] (%)
a	C_6H_5	C_6H_5	C_6H_5	**4a**	80
b	$^nC_5H_{11}$	C_6H_5	C_6H_5	**4b**	75
c	$^nC_4H_9$	C_6H_5	C_6H_5	**4c**	81
d	CH_3OCH_2	C_6H_5	C_6H_5	**4d**	68
e	C_6H_5	C_6H_5	p-MeC_6H_4	**4e**	77
f	$^nC_5H_{11}$	C_6H_5	p-MeC_6H_4	**4f**	70
g	$^nC_4H_9$	C_6H_5	p-MeC_6H_4	**4g**	79
h	C_6H_5	C_6H_5	CH_3	**4h**	65
i	$^nC_4H_9$	C_6H_5	CH_3	**4i**	63
j	CH_3OCH_2	$^nC_4H_9$	C_6H_5	**4j**	69

[a] All the compounds were characterized using ^{1}H-NMR, IR, MS or elemental analyses.
[b] Isolated yield based on the alkynylstannanes.

We also tried to carry out the coupling reaction of compound **4h** at 0°C in CH_2Cl_2 with diphenyliodonium chloride in the presence of $Pd(PPh_3)_4$ (0.1 equivalents) and CuI (0.8 equivalents) for 2 h to give (*E*)-α-phenyl unsaturated sulfoxide (**5**) [12] in 75% yield with high stereroselectivity (Scheme 2).

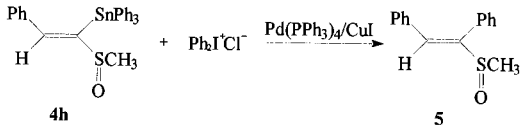
In summary, our results showed that the hydrozirconation/sulfoxidation sequence of the alkynylstannanes has advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and high yields. The investigation on the synthetic applications of these α-stannyl α,β-unsaturated sulfoxides is in progress.

3. Experimental

^{1}H-NMR spectra were recorded on an AZ-300 MHz spectrometer with TMS as an internal standard. Mass spectra were determined using a Finigan 8230 mass spectrometer. IR spectra were obtained by use of neat capillary cells on a Shimadzu IR-408 instrument. Elemental analyses were performed using a Carlo Erba 1106 analyzer. The reactions were carried out in predried (150°C, 4 h) glassware and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use.

*3.1. General procedure for the synthesis of (Z)-α-stannyl-α,β-unsaturated sulfoxides (**4a–j**)*

To a suspension of zirconocene hydrochloride (1.2 mmol) in THF (6 ml) was added a solution of the alkynylstannanes (1.0 mmol) in THF at r.t. with stirring. After 30 min of stirring, the reaction mixture turned to a clear green solution, and the sulfinyl chloride (1.2 mmol) was added. The reaction mixture was



Scheme 2.

stirred at r.t. for about 2 h. The solvent was removed by a rotary evaporator under reduced pressure. The residue was extracted with a mixed solvent (ether–EtOAc, 2:1) and filtered though a short plug of silica gel. After the removal of the solvent, the oily residue was purified by flash column chromatography silica gel (1:10 EtOAc–hexane) to give **4a–j**.

Characterisation data of **4a–g** are as follows.

*3.1.1. Compound **4a***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 8.15$–7.90 (m, 2H), 7.75–7.00 (m, 24H). IR ν (cm^{-1}): 3095, 1695, 1595, 1075. MS: m/z 578 [M^+, 2.3], 351 (47.6), 154 (100%). Anal. Calc. for $C_{32}H_{26}OSSn$: C, 66.58; H, 4.54. Found: C, 65.87; H, 4.61%.

*3.1.2. Compound **4b***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.80$–7.15 (m, 20H), 6.75 (t, $J = 7.3$ Hz, 1H), 2,40–2.05 (m, 2H), 1.50–0.70 (m, 9H). IR ν (cm^{-1}): 3095, 1665, 1145, 1080, 1020. MS: m/z 572 [M^+, 1.9], 515 (4.6), 351 (8.6), 154 (100%). Anal. Calc. for $C_{31}H_{32}OSSn$: C, 65.17; H, 5.65. Found: C, 65.38; H, 5.76%.

*3.1.3. Compound **4c***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.80$–7.10 (m, 20H), 6.85 (t, $J = 7.3$ Hz, 1H), 2.25–1.90 (m, 2H), 1.30–0.60 (m, 7H). IR ν (cm^{-1}): 3080, 1590, 1075, 1022. MS: m/z 558 [M^+, 1.5], 515 (3.1), 351 (36.5), 154 (100%). Anal. Calc. for $C_{30}H_{30}OSSn$: C, 64.65; H, 5.42. Found: C, 65.01; H, 5.66%.

*3.1.4. Compound **4d***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.80$–7.10 (m, 20H), 6.15 (t, $J = 7.5$ Hz, 1H), 4.10 (d, $J = 7.5$ Hz, 2H), 3.25 (s, 3H). IR ν (cm^{-1}): 3070, 1585, 1075, 1022. MS: m/z 546 [M^+, 1.1], 515 (6.4), 351 (28.6), 154 (100%). Anal. Calc. for $C_{28}H_{26}O_2SSn$: C, 61.68; H, 4.80. Found: C, 61.49; H, 4.65%.

*3.1.5. Compound **4e***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 8.05$–7.90 (m, 2H), 7.75–7.15 (m, 23H), 2.25 (s, 3H). IR ν (cm^{-1}): 3095, 1580, 1070, 1025. MS: m/z 592 [M^+, 0.9], 351 (63), 154 (100%). Anal. Calc. for $C_{33}H_{28}OSSn$: C, 67.03; H, 4.77. Found: C, 67.26%; H, 4.68%.

*3.1.6. Compound **4f***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.80–7.20$ (m, 19H), 6.73 (t, $J = 7.0$ Hz, 1H), 2.30 (s, 3H), 2.25–2.10 (m, 2H), 1.45–0.70 (m, 9H). IR ν (cm^{-1}): 3095, 1590, 1070, 1020. MS: m/z 586 [M^+, 0.9], 529 (3.6), 351 (21.0), 77 (100%). Anal. Calc. for $C_{32}H_{34}OSSn$: C, 65.66; H, 5.85. Found: C, 64.78; H, 5.76%.

*3.1.7. Compound **4g***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.90–7.10$ (m, 19H), 6.75(t, $J = 6$ Hz, 1H), 2.35 (s, 3H), 2.25–1.95 (m, 2H), 1.50–0.80 (m, 7H). IR ν (cm^{-1}): 3080, 1595, 1075, 1040. MS: m/z 572 [M^+, 1.8], 529 (3.6), 351 (21.3), 77 (100%). Anal. Calc. for $C_{31}H_{32}OSSn$: C, 65.17; H, 5.64. Found: C, 65.39; H, 5.72%.

*3.1.8. Compound **4h***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 8.10–7.20$ (m, 21H), 2.70 (s, 3H). IR ν (cm^{-1}): 3090, 1590, 1070, 1022. MS: m/z 516 [M^+, 2.7], 351 (71), 154 (100%). Anal. Calc. for $C_{27}H_{24}OSSn$: C, 62.94; H, 4.69. Found: C, 63.83; H, 4.78%.

*3.1.9. Compound **4i***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.80–7.10$ (m, 15H), 6.80 (t, $J = 7.0$ Hz, 1H), 2.60 (s, 3H), 2.25–1.97 (m, 2H), 1.80–0.80 (m, 7H). IR ν (cm^{-1}): 3090, 1595, 1075, 1025. MS: m/z 496 [M^+, 2.8], 453 (4.4), 351 (11.2), 77 (100%). Anal. Calc. for $C_{25}H_{28}OSSn$: C, 60.63; H, 5.70. Found: C, 60.33; H, 5.57%.

*3.1.10. Compound **4j***

Oil. ^{1}H-NMR ($CDCl_3$, δ ppm): $\delta = 7.70–7.20$ (m, 5H), 6.40 (t, $J = 7.0$ Hz, 1H), 4.05 (d, 2H), 3.30 (s, 3H), 1.80–0.80 (m, 27H). IR ν (cm^{-1}): 3080, 2970, 2930, 1590, 1075, 1020. MS: m/z 486 [M^+, 0.32], 455 (4.3), 291 (31.0), 45 (100%). Anal. Calc. for $C_{22}H_{38}O_2SSn$: C, 54.45; H, 7.89. Found: C, 54.66; H, 7.86%.

*3.2. The synthesis of (E)-α-phenyl unsaturated sulfoxide (**5**)*

Compound **4h** (0.5 mmol) and diphenyliodonium chloride (0.5 mmol) were dissolved in CH_2Cl_2 (5 ml) under nitrogen at 0°C. $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.4 mmol) were then added. The mixture was stirred at 0°C and monitored by TLC for the disappearance of the stating 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 flash column chromatography silica gel (1:10 EtOAc–hexane) to give **5** in 75% yield.

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