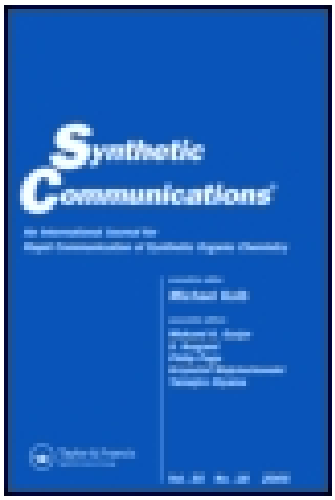

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A STEREOSELECTIVE SYNTHETIC ROUTE TO (Z)-α-STANNYL-α,β-UNSATURATED ESTERS

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A STEREOSELECTIVE SYNTHETIC ROUTE TO (*Z*)-α-STANNYL-α,β-UNSATURATED ESTERS

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ABSTRACT

Acetylenic stannanes **1** react with $Cp_2Zr(H)Cl$ ($Cp = \eta^5$-C_5H_5) and CO to give acylzirconocene chloride derivatives **2**, which are trapped with Br_2 in alcohol to afford (*Z*)-α-stannyl-α,β-unsaturated esters **3** in good yield.

Vinylstannanes that can lead to carbon-carbon bond formation under a variety of conditions are of increasing importance as intermediates in synthetic organic chemistry (1,2). The α- and β-stannyl vinylesters have also been used as synthetic intermediates to construct olefins (3). It was reported that, in the presence of palladium catalyst and 1 equivalent of tributyltin hydride, conjugated alkynoic esters led mainly to the corresponding (*E*)-α-(tributylstannyl)-α,β-unsaturated esters (3). Herein, we want to find a convenient approach to (*Z*)-α-stannyl-α,β-unsaturated esters from acetylenic stannanes.

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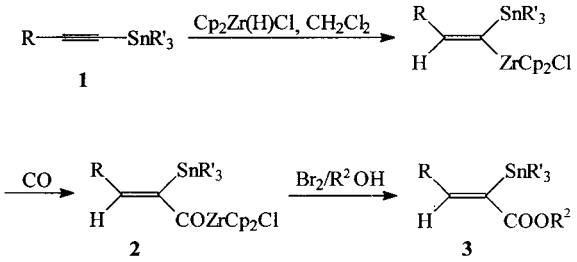

R = Ph, n-C_4H_9, n-C_5H_{11}; R^1 = Ph, n-C_4H_9; R^2 = CH_3, C_2H_5

Scheme 1.

Recently, it has become popular to transform acylzirconocene chlorides to other functional groups. It has been reported that Lewis acid-mediated reaction of acylzirconocene chlorides with aldehydes affords α-ketol derivatives (4). Coupling reactions of acylzirconocene chlorides with organic halides afforded corresponding ketones (5). However, to date, hydrozirconation of alkynylstannanes has been received less attention (6,7), and the corresponding coupling reaction of acylzirconocene chlorides has not been reported.

In this communication, we describe the reaction of acylzirconocene chlorides. Acetylenic stannanes **1** react with $Cp_2Zr(H)Cl$ (8) ($Cp = \eta^5$-C_5H_5) and CO in CH_2Cl_2 to give acylzirconocene chloride derivatives **2**, which are trapped with Br_2 in alcohol to afford (*Z*)-α-stannyl-α,β-unsaturated esters **3** (Scheme 1). Yields are modest to excellent (Table 1).

When the acetylenic stannanes **1** are acetylenic triphenyl stannanes, the yields are good to excellent, but the reaction of acetylenic tributyl stannanes only gave modest yields, due to the fact that the α-tributylstannyl conjugated carbonyl compounds are very sensitive to acidic conditions (3).

Table 1. Synthesis of Compound **3a–g**

Product	R	R^1	R^2	MP (°C)	Yield (%)[a]
3a	Ph	Ph	CH_3	106–108	78
3b	C_4H_9	Ph	CH_3	107–110	81
3c	C_5H_{11}	Ph	CH_3	112–114	85
3d	Ph	C_4H_9	CH_3	Oil	49
3e	Ph	Ph	C_2H_5	103–105	72
3f	C_4H_9	Ph	C_2H_5	110–112	76
3g	C_5H_{11}	Ph	C_2H_5	118–119	82

[a] Isolated yield.

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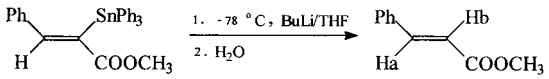


3a **4**

Scheme 2.

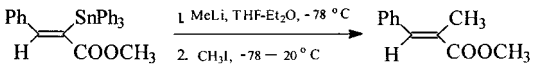
All the compounds **3** were purified by preparative TLC on silica gel and fully characterized by ^{1}H NMR, MS, and IR spectroscopy. The configuration of compound **3a** could be confirmed from compound **4**, which was obtained by treatment of **3a** with n-butyllithium in THF followed by hydrolysis; the reaction occurs with stereospecific lithiation (Scheme 2) (9,10). Particularly diagnostic for the stereochemistry of **4** was the coupling constant between the vicinal protons H_a and H_b, which show a typical value of J_{HH} of 16 Hz consistent with an *E* configuration. Therefore, we could confirm that the compounds **3** have *Z* configuration.

Vinylstannanes have recently emerged as valuable reagents for organic synthesis. For example, **3a** was transformed into (*E*)-2-methyl-3-phenyl-2-propenoic acid methyl ester **5** in 71% yield by treatment with an Et_2O solution of methyllithium at -78°C for 30 h, followed by treatment with a large excess of methyl iodide (Scheme 3) (11).

In conclusion, the hydrozirconation/CO insertion strategy provides a direct route to (*Z*)-α-stannyl-α,β-unsaturated esters from acetylenic stannanes. The method has some attractive advantages such as high yields, mild reaction conditions, simple procedure, short reaction time, and high regio- and stereoselectivity.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer with TMS as the internal standard in $CDCl_3$. Chemical shifts were reported in parts per million (δ, ppm). IR spectra were obtained on PE-683 instrument as neat films. Silica gel 60 GF254 was used for analytical and preparative TLC. All solvents were dried, deoxygenated, and redistilled before use. All reactions were carried out in pre-dried glassware (140°C, 4 h) and cooled under a stream of dry nitrogen.



3a **5**

Scheme 3.

General Procedure for the Synthesis of 3a–g

Under nitrogen atmosphere, to a suspension of $Cp_2Zr(H)Cl$ (1.5 mmol) in CH_2Cl_2 (10 mL) was added acetylenic stannane **1** (1.5 mmol) and the mixture was stirred at room temperature for 30 min to yield a clear solution. After the mixture had been stirred under an atmosphere of CO for 2 h, a solution of Br_2 (1.5 mmol) in 2 mL alcohol was added at room temperature, and the mixture was stirred for 1 h. The solvent was removed by rotary evaporator under reduced pressure to give a crude oil, which was purified by preparative TLC (silica gel, hexane: AcOEt = 20:1) to give **3**.

3a: a pale yellow solid, mp 106°–108°C (from methanol). ^{1}H NMR: $\delta = 3.60$ (s, 3H), 7.00–7.60 (m, 21H, Ph, C*H*=); IR (KBr) $\nu = 3095$, 3080, 2980, 2960, 1735, 1495, 1440 cm^{-1}; EIMS $m/z = 512$ (M^+, 4.1), 481 (M–CH_3O, 9.5), 435 (M–Ph, 100), 351 ($SnPh_3$, 23.5%). Anal. for $C_{28}H_{24}O_2Sn$, calc. %C 65.79, H 4.73; found C 65.55, H 4.70.

3b: a pale yellow solid, mp 108°–110°C (from methanol). ^{1}H NMR: $\delta = 0.60$–1.55 (m, 7H, C_3H_7), 2.00 (m, 2H, CH_2CH=), 3.48 (s, 3H, OCH_3), 6.33 (t, J = 6.5 Hz, 1H, C*H*=), 7.00–7.70 (m, 15H, Ph); IR (KBr): $\nu = 3095$, 2990, 2880, 1735 cm^{-1}; EIMS $m/z = 492$ (M^+, 3.2), 461 (M–CH_3O, 12.9), 415 (M–Ph, 100), 351 ($SnPh_3$, 14.8%). Anal. for $C_{26}H_{28}O_2Sn$, calc. %C 63.58, H 5.75; found C 63.65, H 5.77.

3c: a pale yellow solid, mp 112°–114°C (from methanol). ^{1}H NMR: $\delta = 0.60$–1.60 (m, 9H, C_4H_9), 2.10 (m, 2H, CH_2CH=), 3.47 (s, 3H, OCH_3), 6.25 (t, J = 6.5 Hz, 1H, C*H*=), 7.00–7.70 (m, 15H, Ph); IR (KBr) $\nu = 3095$, 2950, 2880, 1750 cm^{-1}; EIMS $m/z = 506$ (M^+, 1.0), 475 (M–CH_3O, 8.6), 429 (M–Ph, 100), 351 ($SnPh_3$, 24.6%). Anal. for $C_{27}H_{30}O_2Sn$, calc. %C 64.19, H 5.99; found C 64.35, H 6.02.

3d: oil. ^{1}H NMR: $\delta = 0.65$–1.65 (m, 27H, C_4H_9), 3.65 (s, 3H, OCH_3), 7.00–7.60 (m, 6H, Ph, C*H*=); IR (film) $\nu = 3065$, 2985, 2950, 2870, 1740 cm^{-1}; EIMS $m/z = 452$ (M^+, 23.5), 421 (M–CH_3O, 4.7), 291 ($SnBu_3$, 100%). Anal. for $C_{22}H_{36}O_2Sn$, calc. %C 58.56, H 8.04; found: C 58.74, H 8.02.

3e: a pale yellow solid, mp 103°–105°C (from methanol). ^{1}H NMR: $\delta = 1.30$ (t, J = 8.0 Hz, 3H), 4.00 (q, J = 8.0 Hz, 2H, OCH_2), 7.00–7.60 (m, 21H, Ph, C*H*=); IR (KBr) $\nu = 3090$, 2980, 2960, 1738, 1495, 1445 cm^{-1}; EIMS $m/z = 526$ (M^+, 4.5), 481 (M–C_2H_5O, 10.0), 449 (M–Ph, 100), 351 ($SnPh_3$, 25.5%). Anal. for $C_{29}H_{26}O_2Sn$, calc. %C 66.32, H 4.99; found C 65.95, H 4.78.

3f: a pale yellow solid, mp 110°–112°C (from methanol). ^{1}H NMR: $\delta = 0.60$–1.55 (m, 10H), 2.05 (m, 2H, CH_2CH=), 3.95 (q, J = 8.0 Hz, 2H, OCH_2), 6.35 (t, J = 6.5 Hz, 1H, C*H*=), 7.05–7.70 (m, 15H, Ph); IR (KBr) $\nu = 3090$, 2995, 2885, 1735 cm^{-1}; EIMS $m/z = 506$ (M^+, 3.6), 461 (M–C_2H_5O, 15.2), 429 (M–Ph, 100), 351 ($SnPh_3$, 18.5%). Anal. for $C_{27}H_{30}O_2Sn$, calc. %C 64.19, H 5.99; found C 63.85, H 5.87.

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3g: a pale yellow solid, mp 118°–119°C (from methanol). ^{1}H NMR: $\delta =$ 0.60–1.60 (m, 12H), 2.15 (m, 2H, CH_2CH=), 3.97 (q, J = 8.0 Hz, 2H, OCH_2), 6.25 (t, J = 6.5 Hz, 1H, CH=), 7.05–7.70 (m, 15H, Ph); IR (KBr) $\nu = 3090$, 2956, 2885, 1750 cm^{-1}; EIMS $m/z = 520$ (M$^+$, 3.7), 475 (M–C_2H_5O, 12.9), 443 (M–Ph, 100), 351 ($SnPh_3$, 27.9%). Anal. for $C_{28}H_{32}O_2Sn$, calc. %C 64.77, H 6.21; found C 64.23, H 6.12.

General Procedure for the Synthesis of 4

One mL BuLi (1.1 M hexane solution) was added to a THF (5.0 mL) solution of **3a** (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 ether to give **4** (yield: 82%).

4: oil. ^{1}H NMR: $\delta = 3.81$ (s, 3H, CH_3), 6.45 (d, J = 16.5 1H, CH=), 7.33–7.54 (m, 5H, Ph), 7.69 (d, J = 16.5, 1H, CH=); IR (film) $\nu = 2950$, 2890, 2740, 1700, 1640, 1600 cm^{-1}.

General Procedure for the Synthesis of 5

2.3 mL MeLi (1.1 M Et_2O solution) was added to a THF (5.0 mL) solution of **3a** (1.0 mmol) at −78°C. After stirring for 30 h, methyl iodide (3.5 mmol) was then added. The reaction mixture was allowed to warm to room temperature and stirred overnight. It was then poured into a large excess of brine 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 ether to give **5** (yield: 71%).

5: oil. ^{1}H NMR: $\delta = 2.45$ (s, 3H, CH_3CH=), 3.81 (s, 3H, OCH_3), 7.33–7.60 (m, 6H, Ph, CH=); IR (film) $\nu = 2950$, 2890, 2740, 1700, 1600 cm^{-1}.

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