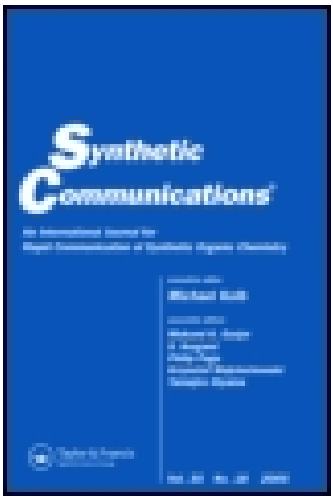

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A Stereoselective Synthetic Route to (Z)-α-Organostannyl-α,β-Unsaturated Carbonyl Compounds

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A STEREOSELECTIVE SYNTHETIC ROUTE TO (*Z*)-α-ORGANOSTANNYL-α,β-UNSATURATED CARBONYL COMPOUNDS

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ABSTRACT: Hydrozirconation of acetylenic stannanes **1** affords *gem*-stannazirconocene alkenes **2**. Intermediates **2** are treated with acyl halides to obtain (*Z*)-α-organostannyl-α,β-unsaturated carbonyl compounds **3** *via* Zr-Cu transmetallation.

Vinylstannanes which can lead to carbon-carbon bond formation under a variety of conditions are of increasing importance as intermediates in synthetic organic chemistry.[1] (*Z*)-α-organostannyl-α,β-unsaturated carbonyl compounds are important synthons in organic chemistry, but few convenient routes to such compounds are known. For example, the hydrostannation of conjugated alkynones gives (*E*)-α-organostannyl-α,β-unsaturated carbonyl compounds or a mixture of *E* and *Z* isomers.[2]

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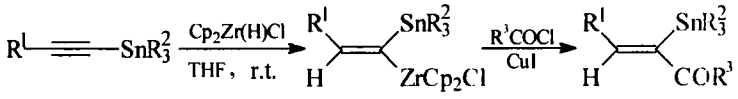
Recently, it was reported that *syn*-addition of Schwartz's reagent onto a alkyne followed by treatment with electrophiles provides access to functionalized alkenes with a high level of stereochemical purity.[3] For example, treatment of acetylenic stannanes, which can be synthesized in good yield according to the method of Bottaro,[4] with $Cp_2Zr(H)Cl$[5] followed by treating with α,β-unsaturated enones or allylic halides afforded polysubstituted alkenes.[6] But the coupling of *gem*-stannazirconocene alkenes with acyl halides has not been reported. Considering the electrophilicity of acyl halides, we managed to treat them with the *gem*-stannazirconocene alkenes (**2**) produced by hydrozirconation of acetylenic stannanes (**1**).

$Cp_2Zr(H)Cl$ adds to acetylenic stannanes (**1**) in THF at room temperature stereospecifically with high regioselectivity to yield (*Z*)-vinylic Zr(IV) complexes (**2**) which react with acyl halides in the presence of CuI to afford (*Z*)-α-organostannyl-α,β-unsaturated carbonyl compounds **3**.



1 **2** **3**

R^1 = Ph, n-C_5H_{11}, CH_3OCH_2; R^2 = Ph, Bu; R^3 = Ph, CH_3

Scheme 1

When the acetylenic stannanes **1** are acetylenic triphenyl stannanes, the yields are good (see table 1). However, the reaction of acetylenic tributyl stannanes hardly proceeded under similar conditions. The reason is that the α-tributylstannyl conjugated enones are very sensitive to acidic conditions, and attempted purification by preparative TLC on silica gel resulted in complete protodestannylation.[2]

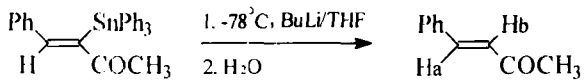
Table 1 Synthesis of Compounds **3a-g**

Product	R^1	R^2	R^3	Mp(°C)	Yield(%)[a]
3a	Ph	Ph	CH_3	95-96	61
3b	n-C_5H_{11}	Ph	CH_3	113-114	68
3c	CH_3OCH_2	Ph	CH_3	105-106	73
3d	Ph	Ph	Ph	95-96	62
3e	n-C_5H_{11}	Ph	Ph	89-90	70
3f	CH_3OCH_2	Ph	Ph	99-100	58
3g	CH_3OCH_2	Ph	4-MeC_6H_4	102-103	55
3h	CH_3OCH_2	Bu	CH_3	-	-

a. Isolated yields based on acetylenic stannanes.

All compounds **3** were purified by preparative TLC on silica gel and fully characterized by NMR, MS and IR spectroscopy. The stereochemistry of (*Z*)- α-organostannyl-α,β-unsaturated carbonyl compounds was easily established by consideration of tin-vinylic hydrogen coupling constants in the ^1H NMR spectra of products **3** (average value 130 Hz, *trans* Sn^{117}/Sn^{119}).[2] For comparison, the average *cis* coupling constant of Sn^{117}/Sn^{119} - vinylic hydrogen in **3** is 60 Hz.[3]

The configuration of compound **3a** could be confirmed *via* compound **4** which was obtained by treatment of **3a** with n-butyllithium in THF followed by hydrolysis; the reaction occurs stereoselectively (Scheme 2).[7,8] Particularly diagnostic for the stereochemistry of **4** was the coupling constant between the

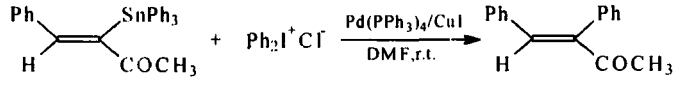


3a **4**

Scheme 2

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 could confirm that the compounds **3** have *Z* configuration.

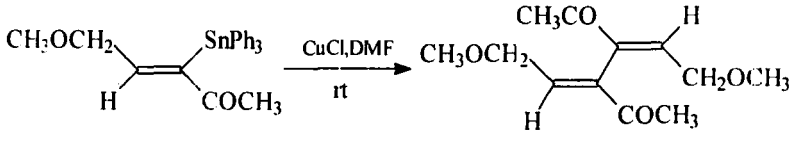
(*Z*)-α-organostannyl-α,β-unsaturated carbonyl compounds (**3**) are important useful synthetic intermediates and are effective precursors for the preparation of conjugated enones. For example, the coupling of compound **3a** with diphenyliodonium chloride at room temperature in the presence of $Pd(PPh_3)_4$ and CuI affords (*E*)-3,4-diphenyl-3-buten-2-one **5** in 80% yield. (Scheme 3)



3a **5**

Scheme 3

Intermolecular coupling of two alkenyltriphenylstannane groups can be effected by CuCl in DMF. For example, treatment of compound **3c** with CuCl in DMF at room temperature gave the coupled product **6** in 74% yield. (Scheme 4)



3c **6**

Scheme 4

The hydrozirconation/coupling stategy provides a direct route to (*Z*)-α-organostannyl-α,β-unsaturated carbonyl compounds from acetylenic stannanes. The method has some attractive advantages such as mild reaction conditions, simple procedure, short reaction time and high regio- and stereoselectivity.

EXPERIMENTAL

^{1}H NMR spectra were recorded on 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 suspension of zirconocene hydrochloride (0.31g, 1.2 mmol) in THF (2 mL) was stirred at room temperature under nitrogen. A solution of acetylenic stannanes (1.0 mmol) in THF (2 mL) was added. After being stirred for 30 min, this reaction mixture was transferred to the solution of acyl halide (1.5 mmol) and CuI (0.19g, 1.0 mmol) in THF (4 mL). After being stirred for 8 h at room temperature, the mixture was quenched by pouring it into saturated aqueous NH_4Cl (10 mL) and was extracted with Et_2O (3 × 8 mL). Normal handing and chrimatography afforded (*Z*)-α-organostannyl-α,β-unsaturated carbonyl comounds **3.**

(*Z*)-4-phenyl-3-triphenylstannyl-3-buten-2-one 3a: a pale yellow solid, mp 95 - 96 °C (from methanol). (Found: C, 68.03; H, 4.90. Calc. for $C_{28}H_{24}OSn$: C, 67.92; H, 4.88); ν_{max} (KBr)/cm^{-1}: 3080, 1760, 1605, 1580, 1500, 1490, 1440; δ_H (300 MHz; $CDCl_3$): 7.60 - 6.90 (m, 21H, Ph, *H*C=), 2.00 (s, 3H, C*H*$_3$); m/z: 479 (M - 17, 3.85%), 453 (M - CH_3CO, 6.32), 419 (M - Ph, 6.41), 377 (100), 351 ($SnPh_3$, 58.97), 197 (SnPh, 58.87).

(*Z*)-3-triphenylstannyl-3-nonen-2-one 3b: a white solid, mp 113 – 114 °C (from methanol). (Found: C, 66.41; H, 6.21. Calc. for $C_{27}H_{30}OSn$: C, 66.29; H, 6.18); ν_{max} (KBr)/cm^{-1}: 3080, 2980, 2950, 2870, 1760, 1490, 1440, 1375, 1245; δ_H (300 MHz; $CDCl_3$): 7.50 - 7.00 (m, 15H, Ph), 6.10 (t, 1H, *J* 7Hz, *H*C=), 1.90 (s, 3H, COC*H*$_3$), 1.85 (m, 2H, C*H*$_2$CH=), 1.40 - 0.65 (m, 9H, C$_4$*H*$_9$); m/z: 447 (M - CH_3CO, 1.36%), 351 ($SnPh_3$, 100).

(*Z*)-4-methoxy-3-triphenylstannyl-3-penten-2-one 3c: a white solid, mp 105 - 106 °C (from methanol). (Found: C, 61.97; H, 5.24. Calc. for $C_{24}H_{24}O_2Sn$: C, 62.24; H, 5.22); ν_{max} (KBr)/cm^{-1}: 3080, 1755, 1490; δ_H (300 MHz; $CDCl_3$): 7.25 - 6.90 (m, 15H, Ph), 6.30(t, 1H, *J* 7Hz, *H*C=), 3.85(d, 2H, *J* 7Hz, CH_2O), 2.75 (s, 3H, OCH_3), 1.85 (s, 3H, COCH_3); m/z: 421 (M - CH_3CO, 2.10 %), 351 ($SnPh_3$, 100).

(*Z*)-1,3-diphenyl-2-triphenylstannyl-2-propen-2-one 3d: a pale yellow solid, mp 95-96 °C (from methanol). (Found: C, 71.15; H, 4.74. Calc. for $C_{33}H_{26}OSn$: C, 71.13; H, 4.70); ν_{max} (KBr)/cm^{-1}: 3090, 3088, 1740, 1490, 1440, 1280; δ_H (300 MHz; $CDCl_3$): 8.20 (s, 1H, *H*C=), 7.45 - 7.00 (m, 25H, Ph); m/z: 453 (M - PhCO, 7.10%), 351 ($SnPh_3$, 100), 77 (12.94).

(*Z*)-1-phenyl-2-triphenylstannyl-2-octen-1-one 3e: a white solid, mp 89 - 90 °C (from methanol). (Found: C, 69.89; H, 5.88. Calc. for $C_{32}H_{32}OSn$: C, 69.72; H, 5.85); ν_{max} (KBr)/cm^{-1}: 3080, 2980, 2940, 2870, 1615, 1490, 1440, 1080; δ_H (300 MHz; $CDCl_3$): 7.50 - 7.00 (m, 20H, Ph), 6.53 (t, 1H, *J* 7Hz, *H*C=), 1.85 (m, 2H, CH_2CH=), 1.40 - 0.65 (m, 9H, C_4H_9); m/z: 447 (M - PhCO, 23.33%), 351 ($SnPh_3$, 100), 77 (20.00).

(*Z*)-4-methoxy-1-phenyl-2-triphenylstannyl-2-buten-1-one 3f: a white solid, mp 99 - 100°C (from methanol). (Found: C, 66.53; H, 4.97. Calc. for $C_{29}H_{26}O_2Sn$: C, 66.32; H, 4.99); ν_{max} (KBr)/cm^{-1}: 3010, 1745, 1500, 1445, 1290; δ_H (300 MHz; $CDCl_3$): 7.40 - 6.90 (m, 20H, Ph), 6.20 (t, 1H, *J* 7Hz, *H*C=), 3.85 (d, *J* 7.0 Hz, 2H, OCH_2). 2.70 (s, 3H, CH_3); m/z: 526 (M^+, 3.75%), 351 ($SnPh_3$, 100).

(*Z*)-4-methoxy-1-(4-methylphenyl)-2-triphenylstannyl-2-buten-1-one 3g: a pale yellow solid, mp 102 - 103°C (from methanol). (Found: C, 66.76; H, 5.20. Calc. for $C_{30}H_{28}O_2Sn$: C, 66.82; H, 5.23); ν_{max} (KBr)/cm^{-1}: 3085, 1740, 1625, 1490, 1440, 1285, 1000,730,700; δ_H (300 MHz; $CDCl_3$): 7.60 - 6.90 (m, 19H, Ph),

6.25 (t, 1H, *J* 7Hz, *H*C=), 3.85 (d, *J* 7.0 Hz, 2H, C*H*$_2$O), 2.80 (s, 3H, OC*H*$_3$), 2.20 (s, 3H, C*H*$_3$); m/z: 539 (M - 1, 8.89%), 351 ($SnPh_3$, 100), 77 (27.78).

The synthesis of (*E*)-4-phenyl-3-buten-2-one 4: 1 mL BuLi (1.1 M hexane solution) was added to a THF (5.0 mL) solution of **3a** (0.50g, 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 *vacuum*. The residue was purified by column chromatography over silica gel, eluting with petroleum to give (*E*)-4-phenyl-3-buten-2-one **4.** (0.12g, yield: 85%) as a pale yellow solid, mp 40 - 41 °C (lit.[9] 41 °C); ν_{max} (film)/cm^{-1}: 1665; δ_H (300 MHz; $CDCl_3$) 7.42(d, *J* 16 Hz, 1H, *H*C=), 7.10 - 7.70 (m, 5H, Ph), 6.58 (d, 1H, *J* 16 Hz, =C*H*), 2.27 (s, 3H, C*H*$_3$).

The synthesis of (*E*)-3,4-diphenyl-3-buten-2-one 5: (*Z*)-4-phenyl-3-triphenylstannyl-3-buten-2-one **3a** (0.25g, 0.5 mmol) and diphenyliodonium chloride[10] (0.16g, 0.5 mmol) were dissolved in DMF (5 mL) under nitrogen at room temperature. $Pd(PPh_3)_4$ (0.06g, 0.05 mmol) and CuI (0.08g, 0.4 mmol) were then added. The mixture was 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 light petroleum to give compound **5** (0.089g, yield: 80%) as a solid, mp 53-54 °C (lit.[11] 54-55 °C); ν_{max} (film)/cm^{-1}: 1670; δ_H (300 MHz; $CDCl_3$): 7.60(s, 1H, *H*C=), 6.90 - 7.40 (m, 10H, Ph), 2.23 (s, 3H, C*H*$_3$).

The synthesis of (*E,E*)-3,4-di(2-methoxyethylidene)-2,4-hexanedione 6: To a stirred suspension CuCl (0.19g, 2 mmol) in dry DMF (8 mL) at room temperature was added a solution of **3c** (0.46g, 1 mmol) in dry DMF (4 mL). The resulting mixture was stirred for 12hr. Saturated aqueous NH_4Cl (12 mL) and water (12 mL)

were added and the mixture was stirred, opened to the atmosphere, until the aqueous phase turned bright blue. The mixture was extracted with ether (3 × 8 mL) and the combined organic layers were washed with brine (2 × 5 mL) and water (2 × 5 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel, eluting with light petroleum to give compound **6** (0.167g, yield: 74%) as a pale yellow oil. (Found: C, 63.56; H, 8.00. Calc. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02); ν_{max} (film)/cm^{-1}: 3090, 1755, 1665; δ_H (300 MHz; $CDCl_3$) 7.10 (t, *J* 7.0 Hz, 2H, *H*C=), 3.85 (d, *J* 7.0 Hz, 4H, CH_2O), 3.25 (s, 6H, OCH_3) 1.85 (s, 6H, CH_3CO); m/z: 226 (M^+, 0.89%), 183 (M - CH_3CO, 34.66), 55 (100).

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