

Esters from carbonyl-functionalized organostannanes *via* Stille coupling¹

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Dedicated to Prof. Alfred Hassner on the occasion of his 70th birthday

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Abstract

The palladium-catalyzed cross coupling of organostannanes with chloroformates has been expanded to provide an improved route to unsaturated esters (63-85%), including β -methoxylated derivatives, through a mild one-pot procedure.

Keywords: Organostannanes, unsaturated esters, palladium-catalyzed cross coupling, Stille coupling

Introduction

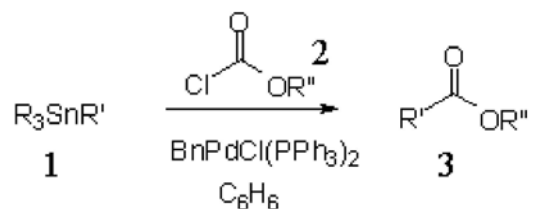
Organostannanes provide the synthetic chemist with a wide variety of versatile reagents for both functional group conversions and carboskeletal construction.⁵ Stable enough to be isolable in pure form, they are sufficiently reactive to undergo a variety of highly selective transformations. Moreover, they are available from a range of organometallic procedures as well as from hydrostannylation.⁶ In addition to their well-known transmetalation and free-radical chemistry, the pioneering work of the late John K. Stille demonstrated their amazing versatility in the Pd-catalyzed cross coupling of these organometallics with electrophilic carbon substrates (Stille Coupling).⁵ Spawning numerous subsequent studies, sustained interest in this coupling process has resulted, not only in better procedures,^{5d,7} but also, in its providing the key step in the synthesis of numerous important natural products and useful intermediates.⁸

Over two decades ago, Hassner and Soderquist described the preparation of α -methoxyvinyltin compounds and related metalloidal derivatives.^{6b} These functionalized organometallics later proved to be remarkably efficient partners in the Stille protocol providing, for example, α -methoxyenones and, subsequently, α -diketones from acid chlorides and (α -methoxyvinyl)trimethyltin.⁹ Since that time others have since utilized this coupling with chloroformates and carbamoyl chlorides for the preparation of esters and amides, respectively,

from vinyl, aryl and heterocyclic organotin derivatives.¹⁰ While acceptable yields (*ca.* 70%) have been generally obtained through this process, the conditions employed are generally harsh and the examples described include only a single example of this coupling with (α -alkoxyvinyl)tins.^{10b} We felt that because such functionalized organotins are normally isolable, stable compounds which are available from numerous methods, the (α -alkoxyvinyl)tins and related compounds deserved more study.

Results and Discussion

Representative functionalized stannanes were selected^{5,11} which would extend the method to include the preparation of pyruvate ester derivatives and stereodefined synthetic intermediates. These were coupled to either ethyl or menthyl chloroformate using the original Stille conditions with neither AsPh_3 nor CuI additives required. Efficient coupling was obtained in all of the examples examined (Table 1). The conditions ($\text{BnPdCl}[\text{PPh}_3]_2$ (1-2%); PhH , reflux) which had been previously employed for the acid chloride couplings⁹ also proved to be quite successful for these substrates (*cf.* **3a**, 85% vs PhMe/HMPA : ($\text{R}'' = i\text{-Pr}$), 66%).^{10a}



The protected pyruvates (**3c,d**) were prepared both as the ethyl and (-)-menthyl derivatives. Simple *trans*-vinylstannanes exhibited no significant stereochemical drift, with the isomerically pure **1f** producing the pure *trans*- β -silylacrylate ester **3g**. However, with the (*Z*)-1-methoxy-1,3-butadienylstannane **1d**, partial loss of stereochemistry occurs (**3e** *E/Z* = 70:30) in the coupling process, a common phenomenon for less thermodynamically stable dienes [MMX calculations suggest that either *Z*-diene or *E*-**3e** isomerization is energetically favorable].^{5,12} Despite this limitation, the Stille protocol is a highly effective tool for the carboalkoxylation of organostannanes which has been further demonstrated in the present study. Of particular significance is the fact that it has been shown for the first time that α -methoxylated unsaturated esters can be efficiently assembled from α -methoxyvinylstannanes and chloroformates through the Stille protocol.

Table 1. Esters from organostannanes and chloroformates *via* Stille coupling

1	R	R'	2	R''	3	Yield (%) ^a
a	<i>n</i> -Bu	Ph	a	Et	a	85
b	Me	<i>n</i> -C ₅ H ₁₁ C≡C	a	Et	b	77
c	Me	CH ₂ =C(OMe)	a	Et	c	78
c	Me	CH ₂ =C(OMe)	b	(-)-Men	d	76
d	<i>n</i> -Bu	<i>t</i> -CH ₂ =CHCH=C(OMe)	a	Et	e	63 ^b
e	<i>n</i> -Bu	<i>t</i> (<i>n</i> -C ₅ H ₁₁)CH=CH	a	Et	f	85 ^c
f	<i>n</i> -Bu	<i>t</i> -(TMS)CH=CH	a	Et	g	83 ^d

^a Isolated yields of analytically pure product. ^b A 70:30 *E/Z* mixture was obtained. ^c A 90:10 *t/c* mixture was obtained from 90:10 *t/c* **1e**. ^d Only the *trans* isomer was obtained from **1f**.

Experimental Section

General Procedures. All experiments were conducted employing pre-dried glassware (1 h, 150 °C) under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study. ¹³C NMR spectra were obtained on a General Electric QE-300, a General Electric GN-300, a Bruker Advance DPX-300 and / or a Bruker Advance DRX-500 spectrometers. ¹H, ¹³C, ¹¹B and ²⁹Si NMR were recorded in CDCl₃ or C₆D₆, unless otherwise used, and the chemical shifts were expressed in relative to CDCl₃ (7.26 and 77.0 ppm in ¹H and ¹³C NMR, respectively) or C₆D₆ (7.15 and 128.0 ppm in ¹H and ¹³C NMR, respectively) as the internal standard. Multiplicity assignments and sequence in ¹³C NMR were made with the aid of DEPT and HETCOR experiments. The ¹H-¹³C chemical shift correlation experiment was obtained using standard sequence.¹⁴ The spectra were acquired with 4K X 256 data points [*S* (*t*₁, *t*₂)] and a data acquisition of 16 scans X 128 increments of *t*₁ and zero filling in both dimensions. ¹H NMR assignments were carried out with the aid of ¹H-¹H COSY experiment. COSY-90 was collected as 1024 X 256 blocks of data, and was processed using sinusoidal multiplication in each dimension followed by symmetrization of the final data matrix. Infrared spectra were obtained on a Nicolet Magna IR-750, a Perkin-Elmer 281 or a Nicolet Series 6000 FT-IR spectrophotometers. Mass spectral data was obtained with a Hewlett-Packard 5995A GC/MS spectrometer (70 eV). Gas chromatographic analyses were performed with a Perkin-Elmer 8320 capillary or a Perkin-Elmer Autosystem XL gas chromatographs using 30 m X 0.25 mm I.D. 20% SE-30 vitreous silica open tubular columns. Optical rotation data were obtained using a Perkin-Elmer 243B Polarimeter. Elemental analyses were performed by Atlantic Microlab, Norcross, Georgia. Organostannanes were prepared by standard methods.^{6,11}

Palladium-catalyzed cross-coupling reactions

Ethyl benzoate (3a). To a solution of benzyl(chloro)bis(triphenylphosphine) palladium (II) ($\text{BnPdCl}(\text{PPh}_3)_2$, 0.04 g, 0.005) and benzene (25 mL), were added *via* syringe ethyl chloroformate (**2a**, 0.782 g, 7 mmol) and **1a** (1.46 g, 2 mmol). After refluxing for 10 h, an additional 0.02 g of catalyst and 0.35 g of **2a** were added to the mixture. After refluxing for 2 h, the mixture was extracted with either a saturated solution of KF/NaHCO_3 or 5 % NaCHO_3 , dried (Na_2SO_4), filtered over Al_2O_3 , concentrated and distilled to give 0.51 g (85 %) of **3a** bp 75-77 °C (1.5 Torr). All physical and spectroscopic data were identical to those of an authentic sample of **3a**.^{15a} ^1H NMR (CDCl_3 300 MHz) δ 1.38 (t, $J = 7.1$ Hz, 2H), 7.39-7.55 (m, 3H), 8.04 (m, 2H) ppm. ^{13}C NMR (CDCl_3 75 MHz) δ 14.2, 60.7, 128.2, 129.4, 130.4, 132.6, 166.4 ppm. IR (TF) 3060, 3030, 2980, 2935, 2900, 1720, 1600, 1580, 1450, 1370, 1310, 1275, 1120, 1105, 1070, 1025, 785, 710 cm^{-1} . GCMS m/z (relative intensity) 150 (24), 122 (34), 106 (11), 105 (100), 77 (4), 74 (11), 51 (55).

Ethyl 2-octynoate (3b). To a solution of $\text{BnPdCl}(\text{PPh}_3)_2$ (0.065 g, 0.009 mmol) in benzene (25 mL) were added *via* syringe **2a** (0.19 g, 1.77 mmol) and **1b** (0.334 g, 1.3 mmol). After cooling to room temperature, pentane (50 mL) was added. The mixture was extracted with either a saturated solution of KF/NaHCO_3 or 5 % NaCHO_3 , dried (Na_2SO_4), filtered over Al_2O_3 , concentrated and distilled to give 0.20 g (77 %) of **3b** bp 127 °C, Kugelrohr (8.5 Torr). All physical and spectroscopic data were identical to those of an authentic sample of **3a**.^{15b} ^1H NMR (CDCl_3 300 MHz) δ 0.81 (t, $J = 6.8$ Hz, 3 H), 1.18-1.32 (m, 9 H), 1.47 (qt, $J = 7.0$ Hz, 2 H), 2.23 (t, $J = 7.0$ Hz, 2 H), 4.12 (q, $J = 7.0$ Hz, 2 H) ppm. ^{13}C NMR (CDCl_3 75 MHz) δ 13.6, 13.8, 18.3, 21.9, 27.0, 30.7, 61.4, 73.0, 89.0, 153.5 ppm. IR (TF) 2960, 2945, 2880, 2230, 1710, 1470, 1360, 1250, 1070, 1050, 880, 750 cm^{-1} . GCMS m/z (relative intensity) 168 (4), 164 (17), 139 (15), 125 (17), 123 (77), 111 (24), 97 (20), 95 (79), 94 (27), 93 (46), 91 (23), 84 (28), 81 (27), 80 (16), 79 (58), 77 (23), 88 (16), 87 (90), 86 (100), 85 (24), 55 (43), 53 (35), 51 (22).

Ethyl 2-methoxypropenoate (3c). As for **3b**, using $\text{BnPdCl}(\text{PPh}_3)_2$ (0.35 g, 0.05 mmol), benzene (200 mL), **2a** (3.92 g, 35 mmol) and **1c** (7.33 g, 35.0 mmol) after 16 h at reflux, 3.56 g (78 %) of **3c** was obtained, bp 108-110 °C (85 Torr). All physical and spectroscopic data were identical to reported values.¹⁶ ^1H NMR (CDCl_3 300 MHz) δ 1.32 (t, $J = 7.0$ Hz, 3H), 3.65 (s, 3H), 4.27 (q, $J = 7.0$ Hz, 2H), 4.60 (d, $J = 2.7$ Hz, 1H), 5.44 (d, $J = 2.7$ Hz, 1H) ppm. ^{13}C NMR (CDCl_3 75 MHz) δ 14.0, 55.5, 61.3, 93.1, 152.3, 162.9 ppm. IR (TF) 2990, 2920, 2860, 1745, 1630, 1450, 1360, 1325, 1205, 1050, 1020, 850, 790 cm^{-1} . GCMS m/z (relative intensity) 130 (M^+ , 46), 101 (34), 5 (31), 84 (31), 73 (48), 58 (34), 57 (100), 56 (28), 55 (57), 53 (7).

(-)-Menthyl 2-methoxypropenoate (3d). As for **3b**, using $\text{BnPdCl}(\text{PPh}_3)_2$ (0.33 g, 0.045 mmol), benzene (200 mL), (-)-menthyl chloroformate (**2b**, 6.56 g, 30 mmol) and **1c** (6.62 g, 30.0 mmol) afforded after refluxing for 16 h, 5.16 g (76 %) of **3d** bp 132 °C (0.8 2Torr) $[\alpha]_D^{25} = -84^\circ$ ($c = 0.112$, CHCl_3). Anal. Calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_3$: C, 69.95, H, 10.07. Found: C, 70.01, H, 10.03. ^1H NMR (CDCl_3 300 MHz) δ 0.72 (d, $J = 7.0$ Hz, 3H), 0.84-0.87 (m, 6H), 0.89-1.07 (m, 4H), 1.39-1.52 (m, 1H), 1.62-1.66 (m, 4H), 1.79-1.89 (m, 1H), 1.96-2.02 (m, 2H), 3.60 (s, 3H), 4.56 (d, $J = 2.6$ Hz, 1H), 4.77 (dt, $J = 10.9, 4.4$ Hz, 1H), 5.27 (d, $J = 2.6$ Hz, 1H) ppm. ^{13}C NMR (CDCl_3

75 MHz) δ 16.1, 20.3, 21.7, 23.2, 26.0, 31.1, 33.9, 40.3, 46.7, 74.9, 92.6, 152.1, 162.2 ppm. IR (TF) 3010, 2950, 2870, 1760, 1650, 1460, 1200, 1180, 1030, 990, 840, 750 cm^{-1} . GCMS m/z (relative intensity) 138 (36), 104(17), 95 (61), 83 (52), 81 (52), 69 (29), 67 (21), 57 (100), 55 (58).

Ethyl 2-methoxy-(2E,4)-pentadienoate (3e). As for **3b**, using $\text{BnPdCl}(\text{PPh}_3)_2$ (0.65 g, 0.09 mmol), benzene (100 mL), **2a** (0.45 g, 4.2 mmol) and **1d** ((Z)-1-tributylstannyl-1-methoxy-1,3-butadiene, 1.35 g, 3.6 mmol) afforded 0.35 g (61 %), of **3e** as a 70:30 *E/Z* mixture bp 115-118 °C (2 Torr). ^{18}H NMR (CDCl_3 300 MHz) (major isomer) δ 1.34 (t, $J = 7.0$ Hz, 3H), 3.66 (s, 3H), 4.30 (q, $J = 7.0$ Hz, 2H), 5.85 (d, $J = 10.9$ Hz, 1H), 5.14-5.32 (m, 2H), 7.18-7.31 (m, 1H) ppm, (minor isomer) 1.29 (t, $J = 7.0$ Hz, 3H), 3.71 (s, 3H), 4.28 (q, $J = 7.0$ Hz, 2H), 5.33-5.51 (m, 2H), 6.65-6.71 (m, 1H), 6.75-6.77 (m, 1H) ppm. ^{13}C NMR (CDCl_3 75 MHz) (major isomer) δ 14.2, 55.6, 61.2, 113.7, 119.1, 131.7, 146.0, 163.0 ppm, (minor isomer) 14.1, 60.4, 60.9, 122.5, 125.5, 129.7, 145.6 ppm. IR (TF) 3095, 2980, 2880, 1720, 1630, 1590, 1450, 1370, 1345, 1240, 1180, 1140, 1100, 1030, 1100, 1000, 920, 780, 730 cm^{-1} . GCMS m/z (relative intensity) 156 (72), 128 (34), 127 (40), 117 (70), 98 (33), 83 (34), 78 (280, 69(43), 68 (100).

Ethyl trans-2-octenoate (3f). As for **3b**, using $\text{BnPdCl}(\text{PPh}_3)_2$ (0.08 g, 0.01 mmol), benzene (25 mL), **2a** (1.09 g, 10 mmol) and **1e** (90:10 *t/c*-1-heptenyltri-*n*-butylstannane, 3.10 g, 8 mmol). After 6 h, 0.03 g of catalyst and 1.5 g of **2a** were added. After refluxing for 3 h, 1.16 g (85 %) of **3f** were obtained as a *trans-cis* mixture (90:10) bp 70-72 °C (1.5 Torr). All physical and spectroscopic data were identical to those of an authentic sample of **3a**. ^{15b}H NMR (CDCl_3 300 MHz) (major isomer) δ 0.88 (m, 6H), 1.28 (m, 4H), 1.44 (m, 2H), 2.18 (m, 2H), 4.15 (q, $J = 6.6$ Hz, 2H), 5.79 (d, $J = 15.4$ Hz, 1H), 6.94 (dt, $J = 15.4, 6.6$ Hz, 1H) ppm. ^{13}C NMR (CDCl_3 75 MHz) (major isomer) δ 13.7, 14.0, 22.2, 27.6, 31.2, 32.0, 59.9 121.1, 149.2, 165.5 ppm, (minor isomer) δ 13.8, 14.0, 22.0, 27.7, 31.5, 59.5, 119.4, 150.3, 166.3 ppm. IR (TF) 2950, 2900, 2850, 1730, 1655, 1460, 1365, 1305, 1260, 1200, 1170, 1125, 1040, 985, 860 cm^{-1} . GCMS m/z (relative intensity) 170 (2), 125 (42), 124 (20), 101 (31), 99 (31), 96 (23), 88 (17), 82 (22), 73 (44), 68 (25), 55 (100).

Ethyl trans-3-trimethylsilyl-2-propenoate (3g). As for **3f**, using $\text{BnPdCl}(\text{PPh}_3)_2$ (0.08 g, 0.01 mmol), benzene (25 mL), **2a** (1.04 g, 9.6 mmol) and **1f** (3.73 g, 9.6 mmol). After refluxing for 6 h, 1.14 g (83 %) of **3g** were obtained, bp 90-92 °C (1.5 Torr). All physical and spectroscopic data were identical to reported values. ^{17}H NMR (CDCl_3 300 MHz) δ 0.12 (s, 9H), 1.30 (t, $J = 7.1$ Hz, 3H), 4.20 (q, $J = 7.1$ Hz, 2H), 6.23 (d, $J = 19.0$ Hz, 1H), 7.25 (d, $J = 19.0$ Hz, 1H) ppm. ^{13}C NMR (CDCl_3 75 MHz) δ -2.3, 13.9, 60.0, 133.9, 148.7, 165.2 ppm. IR (TF) 3010, 2980, 2880, 2670, 1720, 1600, 1430, 1360, 1300, 1250, 1230, 1160, 1030, 990, 840, 750, 685 cm^{-1} . GCMS m/z (relative intensity) 171 (0.9), 158 (12), 157 (100), 121 (31), 103 (25), 99 (12), 83 (35), 75 (66), 73 (63), 59 (20), 58 (25), 53 (17).

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References and Notes

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18. Our attempts to obtain an acceptable elemental analysis for this unstable isomeric mixture were unsuccessful. Our NMR data is consistent with those reported for the corresponding

isomeric methyl esters (Stevenart-De Mesmaeker, N.; Merenyi, R.; Viehe, H. G. *Tetrahedron Lett.* **1987**, 28, 2591). This problem is evidently common for such dienoates with the reported isomeric methyl esters also being analyzed only spectroscopically.