SHORT PAPER

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(*E*)-α-Iodovinylstannanes as convenient precursors for stereoselective synthesis of trisubstituted alkenes[†]

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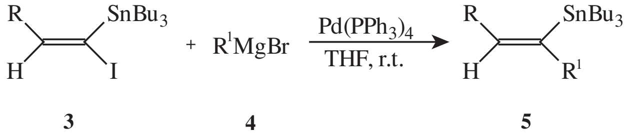
Based on the different reactivities of iodo-groups and tributylstannyl groups, (*E*)-α-iodovinylstannanes can undergo sequential cross-coupling reactions in the presence of a palladium(0) catalyst to form two carbon-carbon bonds to the same olefinic carbon leading to trisubstituted alkenes stereoselectively.

Keywords: (E)-α-iodovinylstannane, palladium, cross-coupling reaction, stereoselective synthesis

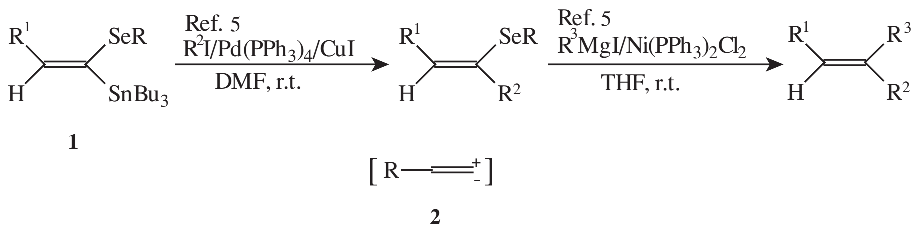
Selectivity provides a formidable challenge for synthetic chemists. In this area, the highly stereoselective synthesis of trisubstituted alkenes is of high interest because many biologically active compounds occurring in nature possess the structural skeleton of trisubstituted alkenes.[1-3] Difunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, Sn–Si, Sn–Al, Sn–Cu, Sn–Mg, and Sn–Zr combinations, play an important role in organic synthesis, especially in developing many convenient methods for the stereoselective synthesis of substituted alkenes. These reagents and their synthetic applications have been reported.[4] Recently, Huang and Ma.[5] reported that alkynylselenides underwent palladium-catalysed hydrostannation with tributylstannane hydride to give stereoselectively (*E*)-α-selenylvinylstannanes **1**. On the basis of the different reactivity of the selanyl group and the tributylstannyl group, compounds **1** can undergo sequential transition metal catalysed cross-coupling reactions, providing a convenient method for the stereoselective synthesis of trisubstituted alkenes[5](Scheme 1). These reactions show that (*E*)-α-selenylvinylstannanes **1** represent the synthetic equivalent of the cation-anion synthon **2**.

Vinyl iodides are important intermediates, but the difunctional group reagent containing tin has rarely roused extensive attention. (*E*)-α-Iodovinylstannanes **3** can be easily prepared in good yields with high stereoselectivity by the hydrozirconation of alkynylstannanes and successive reaction with iodine.[6] (*E*)-α-Iodovinylstannanes **3** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and vinyl iodides. Vinyl iodides have been employed to effect palladium-catalyzed cross-coupling reactions with Grignard reagents.[7] Besides, the trialkylstannyl groups in vinylstannanes can be easily substituted by transition metal catalysed coupling reactions.[8] Based on the different reactivities of iodo-groups and tributylstannyl groups, they should be substituted by nucleophiles and electrophiles, respectively, in the presence of transition metal complexes. Therefore, we carried out the palladium(0) catalysed cross-coupling reaction of (*E*)-α-iodovinylstannanes **3** with Grignard reagents **4**. The experimental results showed that the cross coupling reaction of compounds **3** with Grignard reagents in the presence of $Pd(PPh_3)_4$ at room temperature afforded the corresponding (*Z*)-1,2-disubstituted vinylstannanes **5** in which the iodo-group was selectively substituted by an alkyl or aryl group with retention of configuration in good yields (Scheme 2). The typical results are summarised in Table 1. The configuration of (*Z*)-1,2-disubstituted vinylstannane **5c** could be confirmed by treatment of **5c** with *n*-butyllithium in THF at –78°C followed by hydrolysis, a reaction which occurs stereoselectively, to form (*E*)-1-phenyl-1-hexene. The stereochemistry of (*E*)-1-phenyl-1-hexene was easily established, since its ^1H NMR spectrum gives rise to a doublet at δ 6.38 with a coupling constant of 16 Hz, typical of *trans* protons.



Scheme 2

Vinylstannanes are important synthetic intermediates owing to the versatile reactivity of the stannyl group and the carbon–carbon double bond.[9] (*Z*)-1,2-Disubstituted vinylstannanes **5** are also effective precursors for preparing stereodefined trisubstituted alkenes. In the presence of $Pd(PPh_3)_4$ and CuI they can easily undergo a cross-coupling reaction with aryl halides providing an effective method to synthesise



Scheme 1

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

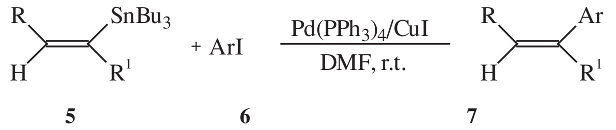
Table 1 Synthesis of (*Z*)-1,2-disubstituted vinylstannanes **5a–f**

Product[a]	R	R^1	Yield[b]/%
5a	*n*-C_4H_9	*n*-C_4H_9	88
5b	*n*-C_4H_9	Ph	83
5c	Ph	*n*-C_4H_9	76
5d	Ph	Ph	83
5e	CH_3OCH_2	*n*-C_4H_9	67
5f	CH_3OCH_2	Ph	86

[a]All products were characterised by IR, ^1H NMR and elemental analyses.
[b]Isolated yield based on **3** used.

trisubstituted alkenes. We observed that when compounds **5** were allowed to react with aryl iodides **6** in the presence of catalytic amounts of $Pd(PPh_3)_4$ and CuI in DMF at room temperature, the tin free trisubstituted alkenes **7** were obtained in good yields (Scheme 3). Typical results are summarised in Table 2.

As (*E*)-α-iodovinylstannanes **3** undergo a two-step cross-coupling reaction to form two carbon-carbon bonds to the same olefinic carbon and allow the synthesis of trisubstituted alkenes stereoselectively, **3** can also be regarded as the equivalent of the cation–anion synthon **2**.



Scheme 3

Table 2 Stereoselective synthesis of trisubstituted alkenes **7a–e**

Product[a]	R	R^1	Ar	Yield[b]/%
7a	*n*-C_4H_9	Ph	Ph	67
7b	*n*-C_4H_9	*n*-C_4H_9	4-ClC_6H_4	70
7c	Ph	*n*-C_4H_9	4-$CH_3OC_6H_4$	65
7d	CH_3OCH_2	Ph	Ph	74
7e	CH_3OCH_2	*n*-C_4H_9	Ph	72

[a]All products were characterised by IR, ^1H NMR and elemental analyses.
[b]Isolated yield based on **5** used.

In summary, compared to the reported methods,[5,10] the present method for the synthesis of stereodefined trisubstituted alkenes has some attractive advantages such as readily available starting materials, a straightforward and simple procedure, mild reaction conditions and good yields

Experimental

(*E*)-α-Iodovinylstannanes **3** were synthesised according to established procedures.[6] ^1H NMR spectra were recorded on a Bruker AC-P200 (200MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. IR spectra were obtained by use of neat capillary cells on a Shimadzu IR-435 instrument. Microanalyses were performed on Vario EL and Perkin-Elmer CHN 2400 instruments. All solvents were dried, deoxygenated and freshly distilled before use.

General procedure for the synthesis of (Z)-1,2-disubstituted vinylstannanes **5a–f:** To a stirred solution of butyl or phenylmagnesium bromide **4** (2.0 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in THF (5 ml) was added dropwise a solution of (E)-α-iodovinylstannane **3** (1.0 mmol) in THF (1 ml) under Ar over 1h at room temperature. The reaction mixture was stirred at room temperature for another 2 h, treated with sat. aq NH_4Cl (10 ml) and extracted with diethyl ether (2×20 ml). The ethereal solution was washed with water (3×20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with light petroleum (30–60°C) to give **5a–f** as oils.

(Z)-5-tributylstannyl-5-decene(**5a**): ν_{max}(film)/cm^{-1} 2957, 2926, 2872, 1598, 1464, 1376; $\delta_H(CDCl_3)$ 0.65–1.71(m, 41H), 2.08(m, 4H), 6.28(t, 1H, *J*=7.0Hz); Anal. Calcd for $C_{22}H_{46}Sn$: C, 61.54; H, 10.72. Found: C, 61.43; H, 10.65.

(Z)-1-Phenyl-1-tributylstannyl-1-hexene(**5b**): ν_{max}(film)/cm^{-1} 3073, 3013, 2926, 2854, 1595, 1486, 1463, 699; $\delta_H(CDCl_3)$ 0.64–1.65(m, 34H), 2.04(m, 2H), 6.04(t, 1H, *J*=7.0Hz), 6.89–7.25(m, 5H); Anal. Calcd for $C_{24}H_{42}Sn$: C, 64.14; H, 9.35. Found: C, 64.27; H, 9.41.

(Z)-1-Phenyl-2-tributylstannyl-1-hexene(**5c**): ν_{max}(film)/cm^{-1} 3058, 3023, 2955, 2871, 1593, 1492, 1463, 1376, 770, 700; $\delta_H(CDCl_3)$ 0.66–1.70(m, 34H), 2.09(m, 2H), 7.04–7.35(m, 6H); Anal. Calcd for $C_{24}H_{42}Sn$: C, 64.14; H, 9.35. Found: C, 64.03; H, 9.25.

(Z)-1,2-Diphenyl-1-tributylstannylethene(**5d**): ν_{max}(film)/cm^{-1} 3057, 3021, 2954, 2870, 1597, 1492, 1463, 1376, 763, 699; $\delta_H(CDCl_3)$ 0.63–1.55(m, 27H), 6.96–7.50(m, 11H); Anal. Calcd for $C_{26}H_{38}Sn$: C, 66.52; H, 8.10. Found: C, 66.30; H, 8.02.

(Z)-1-Methoxy-3-tributylstannyl-2-heptene(**5e**): ν_{max}(film)/cm^{-1} 2957, 2871, 1602, 1463, 1115, 998; $\delta_H(CDCl_3)$ 0.68–1.68(m, 34H), 2.06(m, 2H), 3.23(s, 3H), 3.85(d, 2H, *J*=5.8Hz), 6.41(t, 1H, *J*=7.0Hz); Anal. Calcd for $C_{20}H_{42}OSn$: C, 57.55; H, 10.07. Found: C, 57.41; H, 10.11.

(Z)-1-Phenyl-3-methoxy-1-tributylstannyl-1-propene(**5f**): ν_{max} (film)/cm^{-1} 3057, 3015, 2922, 2871, 1618, 1596, 1485, 1463, 1122, 754, 699; $\delta_H(CDCl_3)$ 0.65–1.58(m, 27H), 3.28(s, 3H), 3.92(d, 2H, *J*=5.8Hz), 6.20(t, 1H, *J*=7.0Hz), 6.87–7.32(m, 5H); Anal. Calcd for $C_{22}H_{38}OSn$: C, 60.41; H, 8.70. Found: C, 60.32; H, 8.65.

General procedure for the synthesis of trisubstituted alkenes **7a–e:** To a solution of (Z)-1,2-disubstituted vinylstannane **5** (1.0 mmol), aryl iodide **6** (1.1 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in DMF (4 ml) was added CuI (19 mg, 0.1mmol) under Ar. The reaction mixture was stirred at room temperature for 48 h, treated with sat. aq NH_4Cl (10 ml) and extracted with CH_2Cl_2 (2×15 ml). The organic layer was washed with sat. aq NH_4Cl (2×10 ml), water (3×20 ml) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography on silica gel eluting with light petroleum (30–60°C).

1,1-Diphenyl-1-hexene(**7a**): ν_{max}(film)/cm^{-1} 3079, 3056, 3022, 2956, 2871, 1598, 1494, 1443, 699; $\delta_H(CDCl_3)$ 0.89(t, 3H, *J*=5.4Hz), 1.21–1.77(m, 4H), 1.87–2.36(m, 2H), 5.91(t, 1H, *J*=7.0Hz), 6.81–7.45(m, 10H); Anal. Calcd for $C_{18}H_{20}$: C, 91.53; H, 8.47. Found: C, 91.41; H, 8.33.

(Z)-5-(4-Chlorophenyl)-5-decene(**7b**): ν_{max}(film)/cm^{-1} 3080, 3010, 2957, 2871, 1637, 1593, 1490, 1470, 841, 800; $\delta_H(CDCl_3)$ 0.68–1.63(m, 14H), 1.96-2.32(m, 4H), 5.83(t, 1H, *J*=7.0Hz), 6.81 (d, 2H, *J*=9.0Hz), 7.12(d, 2H, *J*=9.0Hz); Anal. Calcd for $C_{16}H_{23}Cl$: C, 76.65; H, 9.18. Found: C, 76.49; H, 9.09.

(Z)-1-Phenyl-2-(4-methoxyphenyl)-1-hexene(**7c**): ν_{max}(film)/cm^{-1} 3056, 3023, 2956, 2835, 1606, 1574, 1493, 1445, 1033, 830, 696; $\delta_H(CDCl_3)$ 0.90(t, 3H, *J*=6.8Hz), 1.11-1.65(m, 4H), 2.08–2.34 (m, 2H), 3.75(s, 3H), 6.89–7.43(m, 10H); Anal. Calcd for $C_{19}H_{22}O$: C, 85.71; H, 8.27. Found: C, 85.59; H, 8.21.

1,1-Diphenyl-3-methoxy-1-propene(**7d**): ν_{max}(film)/cm^{-1} 3056, 3026, 2923, 1630, 1598, 1493, 1445, 1116, 760, 701; $\delta_H(CDCl_3)$ 3.24(s, 3H), 3.85(d, 2H, *J*=5.8Hz), 6.23(t, 1H, *J*=7.0Hz), 7.08–7.45(m, 10H); Anal. Calcd for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.83; H, 7.20.

(Z)-1-Methoxy-3-phenyl-2-heptene(**7e**): ν_{max}(film)/cm^{-1} 3058, 3026, 2922, 1645, 1600, 1495, 1463, 1096, 700; $\delta_H(CDCl_3)$ 0.89 (t, 3H, *J*=6.8Hz), 1.12–1.66(m, 4H), 2.06–2.36(m, 2H), 3.25(s, 3H), 3.86(d, 2H, *J*=5.8Hz), 6.18(t, 1H, *J*=7.0Hz), 7.09–7.34(m, 5H); Anal. Calcd for $C_{14}H_{20}O$: C, 82.35; H, 9.80. Found: C, 82.16; H, 9.71.

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