SHORT PAPER

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Stereoselective synthesis of 1,3-enynylstannanes via a palladium catalysed cross-coupling reaction of (*E*)-α-iodovinylstannanes†

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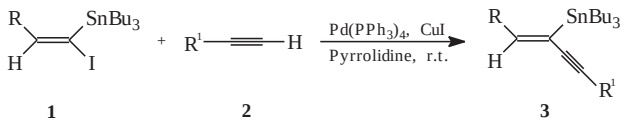
(*E*)-α-Iodovinylstannanes undergo a direct coupling reaction with terminal alkynes in the presence of $Pd(PPh_3)_4$ and CuI in pyrrolidine at room temperature to give 1,3-enynylstannanes in good yields.

Keywords: 1,3-enynylstannane, (*E*)-α-iodovinylstannane, stereoselective synthesis, cross-coupling reaction

The conjugated enyne moiety is incorporated in a number of natural products and it can be readily converted in a stereospecific manner into the corresponding diene system.[1-3] Recently, the discovery of strong antifungal agents[4] and new powerful antitumor antibiotics[5] has stimulated intense interest in the chemistry of enynes, which is at the origin of the biological properties of these substances. The metal or heteroatom-containing enynes will also be useful as building blocks for this purpose, since many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. Many methods can be used for the synthesis of chalcogenoenynes, such as the addition of organotellurolates[6] or thiols[7] to diynes, the coupling reactions of halovinylic chalcogenides with alkynyl Grignard reagents[8] or ethynyltributylstannane,[9] the coupling reactions of bromovinylic chalcogenides with terminal alkynes[10] and the cross-coupling of (*E*)-α-selenylvinylstannanes with 1-haloalkynes.[11] However, so far, the stereoselective synthesis of 1,3-enynylstannanes has received less attention.[12] In this paper, we wish to report a novel stereoselective synthesis of 1,3-enynylstannanes via a cross-coupling reaction of (*E*)-α-iodovinylstannanes with terminal alkynes in the presence of $Pd(PPh_3)_4$ and CuI (Scheme 1).

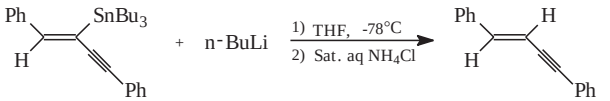


1 **2** **3**

Scheme 1

The required starting (*E*)-α-iodovinylstannanes **1** were prepared in good yields with high stereoselectivity by the hydrozirconation of alkynylstannanes and successive reaction with iodine.[13] We observed that when (*E*)-α-iodovinylstannanes **1** were allowed to react directly with terminal alkynes **2** in the presence of catalytic amounts of tetrakis (triphenylphosphine)palladium(0) and CuI in pyrrolidine at room temperature for 2h, 1,3-enynylstannanes **3** were obtained in good yields. The typical results are summarised in Table 1.

The products were identified by ^{1}H NMR, IR spectra and elemental analyses. The double bond geometries of the products **3** were determined by the treatment of (*Z*)-1-phenyl-2-tributylstannyl-4-phenyl-1-buten-3-yne at –78°C with butyllithium in THF followed by hydrolysis with sat. aq NH_4Cl to produce (*E*)-1,4-diphenyl-1-buten-3-yne **4** (Scheme 2).[14] The stereochemistry of product **4** was easily established, since the ^{1}H NMR spectrum of product **4** gives rise to two doublets at δ6.30 and δ7.01 with coupling constant of 16Hz, typical of *trans* positioned protons. The experimental results showed that the palladium-catalysed cross-coupling reaction of (*E*)-α-iodovinylstannanes with terminal alkynes occurred with total retention of configuration.



3 **4**

Scheme 2

In conclusion, we have developed a novel approach to the stereoselective synthesis of 1,3-enynylstannanes by the cross-coupling reaction of (*E*)-α-iodovinylstannanes with terminal alkynes in the presence of $Pd(PPh_3)_4$ and CuI. The reactions have the advantages of mild conditions, short reaction times, simple manipulation and good yields.

Experimental

$Cp_2Zr(H)Cl$ and alkynylstannanes were prepared according to the literature, respectively[15,16]. ^{1}H NMR spectra were recorded on an AZ-300MHz spectrometer with TMS as an internal standard. IR spectra were obtained on a Perkin-Elmer 683 instrument as neat films. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. Pyrrolidine was dried, deoxygenated and freshly distilled before use.

General procedure for the synthesis of (E)-α-iodovinylstannanes: A mixture of $Cp_2Zr(H)Cl$ (5 mmol) and alkynylstannane (5 mmol) in THF (25 ml) was stirred under nitrogen at room temperature for 40 min to yield a clear solution. Iodine (5 mmol) was added to the resulting solution at 0°C and the mixture was stirred for 30min and then at room temperature for 30min. The mixture was diluted with diethyl ether (90 ml), filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by column chromatography on silica gel eluting with hexane or hexane/ether (20:1).

(E)-1-Iodo-1-tributylstannyl-1-hexene: yield 81%; ν_{max}(film)/cm^{-1} 2954, 2871, 1581, 1463, 1377; $\delta_H(CDCl_3)$ 0.66–1.78(m, 34H), 1.91–2.23(m, 2H), 7.22(t, 1H, *J*=7.0Hz); Anal. Calcd for $C_{18}H_{37}SnI$: C, 43.29; H, 7.41. Found: C, 43.12; H, 7.26.

(E)-1-Iodo-1-tributylstannyl-2-phenylethene: yield 78%; ν_{max} (film)/cm^{-1} 3057, 3022, 2955, 2871, 1598, 1488, 1463, 1377; $\delta_H(CDCl_3)$ 0.67–1.80(m, 27H), 7.08-7.41(m, 5H), 8.47(s, 1H); Anal. Calcd for $C_{20}H_{33}SnI$: C, 46.24; H, 6.36. Found: C, 46.03; H, 6.27.

(E)-1-Iodo-1-tributylstannyl-3-methoxy-1-propene: yield 69%; ν_{max}(film)/cm^{-1} 2956, 2871, 1590, 1463, 1376, 1106; $\delta_H(CDCl_3)$ 0.68–1.74(m, 27H), 3.29(s, 3H), 3.69(d, 2H, *J*=6.5Hz), 7.42(t, 1H,

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

Table 1 1,3-Enynylstannanes prepared according to Scheme 1

Entry	R	R^1	Yield[a]/%	IR(neat)/cm^{-1}	^1H NMR($CDCl_3$),δ(J/Hz)	Elemental analysis(calcd.) C%	H%
1	*n*-C_4H_9	*n*-C_4H_9	91	2958, 2929, 2194, 1464	6.38 (t, 1H, *J*=7.0), 2.50–2.06 (m, 4H), 1.81–0.66 (m, 41H)	63.82 (63.58)	10.31 (10.15)
2	*n*-C_4H_9	Ph	85	3031, 2927, 2178, 1583, 1488, 1463	7.51–6.93 (m, 5H), 6.55 (t, 1H, *J*=7.0), 2.48–2.05 (m, 2H), 1.83–0.68 (m, 34H)	65.73 (65.96)	8.68 (8.88)
3	*n*-C_4H_9	CH_3OCH_2	68	2957, 2927, 2175, 1463	6.49 (t, 1H, *J*=7.0), 4.27 (s, 2H), 3.23 (s, 3H), 2.48–2.10 (m, 2H), 1.80–0.66 (m, 34H)	59.98 (59.86)	9.71 (9.52)
4	Ph	*n*-C_4H_9	93	3023, 2927, 2307, 1597, 1488, 1463	7.53–7.03 (m, 6H), 2.40–0.65 (m, 36H)	66.13 (65.96)	8.97 (8.88)
5	Ph	Ph	82	3022, 2924, 2175, 1596, 1487, 1463	7.52–7.02 (m, 11H), 1.65–0.66 (m, 27H)	68.31 (68.15)	7.86 (7.71)
6	Ph	CH_3OCH_2	74	3023, 2925, 2183, 1598, 1488, 1463	7.49–7.01 (m, 6H), 4.13 (s, 2H), 3.26 (s, 3H), 1.70–0.64 (m, 27H)	62.71 (62.47)	8.40 (8.24)
7	CH_3OCH_2	*n*-C_4H_9	87	2928, 2872, 2195, 1463, 1122	6.43 (t, 1H, *J*=7.0), 3.81 (d, 2H, *J*=6.4), 3.20 (s, 3H), 2.41-0.68 (m, 36H)	59.77 (59.86)	9.50 (9.52)
8	CH_3OCH_2	Ph	81	2922, 2359, 1596, 1488, 1463, 1122	7.44–7.02 (m, 5H), 6.01 (t, 1H, *J*=7.0), 3.93 (d, 2H, *J*=6.2), 3.30 (s, 3H), 1.80–0.63 (m, 27H)	62.66 (62.47)	8.35 (8.24)
9	CH_3OCH_2	CH_3OCH_2	82	2924, 2872, 2189, 1463, 1122	6.58 (t, 1H, *J*=7.0), 4.11 (s, 2H), 3.85 (d, 2H, J=6.4), 3.29 (s, 3H), 3.25 (s, 3H), 1.73–0.65 (m, 27H)	56.12 (55.94)	8.93 (8.86)
10	Ph	$HOCH_2$	79	3350, 3024, 2925, 2186, 1598, 1488	7.48–7.01 (m, 6H), 4.29 (s, 2H), 1.79 (s, 1H), 1.71–0.68 (m, 27H)	61.95 (61.74)	8.17 (8.05)

[a]Isolated yield based on **1** used.

J=7.0Hz); Anal. Calcd for $C_{16}H_{33}OSnI$: C, 39.43; H, 6.78. Found: C, 39.21; H, 6.62.

General procedure for the cross-coupling reaction of (E)-α-iodovinylstannanes with terminal alkynes: To a solution of $Pd(PPh_3)_4$ (0.05mmol, 0.058g) and CuI (0.1mmol, 0.019g) in pyrrolidine (2ml) at 0°C under Ar, was added the terminal alkyne (2.0mmol) and after stirring at r.t. for 10min, a solution of (*E*)-α-iodovinylstannane (1.0mmol) in pyrrolidine (1ml) was added dropwise over 30min with stirring. The reaction mixture was stirred at r.t. for another 1.5h, hydrolysed with sat. aq NH_4Cl (10ml) and extracted with CH_2Cl_2 (2×15ml). The organic layer was washed with sat. aq NH_4Cl (15ml) and water (2×15ml) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil, which was purified by column chromatography on silica gel using hexane (for entry 1, 2, 4, 5), hexane/ether (20:1)(for entry 3, 6, 7, 8, 9) or hexane/EtOAc (7:1) (for entry 10) as eluent.

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