SHORT PAPER

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The stereospecific preparation of (*Z*)-α-stannyl-1-alkenylphosphonates as precursors of stereodefined α-substituted vinylphosphonates†

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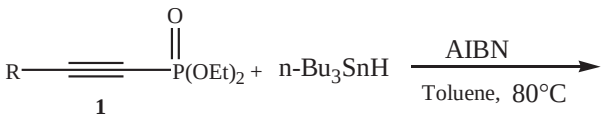
The radical hydrostannation of 1-alkynylphosphonates gives the (*Z*)-α-stannyl-1-alkenylphosphonates **2** stereoselectively; **2** can be transformed into α-iodo-1-alkenylphosphonates and α-substituted vinylphosphonates with retention of configuration.

Keywords: α-substituted vinylphosphonates

1-Alkenylphosphonates are very useful compounds for organic transformations[1] and for the synthesis of biologically active compounds.[2] On the other hand, alkenylstannanes are of particular synthetic interest and have attracted a great deal of attention in recent years.[3-4] We anticipate the α-stannyl-1-alkenylphosphonates, a new class of 1,1-difunctional reagents which combined α-stannyl and phosphonato groups in one molecule will play an important role in organic synthesis. They can be regarded as synthetic equivalents of a vinylphosphonate carbanion which may react with various electrophiles to afford the α-substituted vinylphosphonate. For this purpose, we started to synthesise the α-stannyl 1-alkenylphosphonates and explore their application in organic synthesis.

We first studied the radical hydrostannation of 1-alkynylphosphonates. The results show the reaction between 1-alkynylphosphonates and Bu_3SnH in toluene solution at 80°C in the presence of 10% amounts of AIBN affording *Z*-isomers **2** as major products together with a small amount (5–15%) of the *E*-isomers **3** in moderate to good yield. However, the β-stannyl products have not been detected. The products **2** and **3** were separated easily by column chromatography on silica gel. The stereochemistry of products **2** was assigned according to the $^3J_{HP}$ coupling constant measurement in their ^1H NMR spectra.[5] $^3J_{HP}$ values varied from 58 to 65 Hz for *E*-isomers and from 31 to 34 Hz for *Z*-isomers. (Scheme 1, Table 1).



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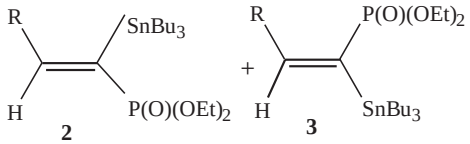
a, R=Ph; b, R= n-C_4H_9;
c, R=C_5H_{11}; d, R=CH_2OMe



Scheme 1

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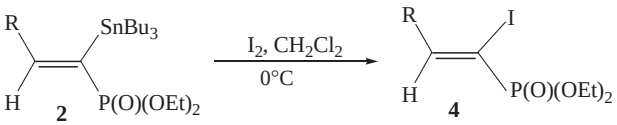
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Hydrostannation of 1-alkynylphosphonates

Entry	Product/%[a]		Yield/%[b]
	R	**2**	**3**	
1	Ph	95%	5%	82
2	C_4H_9	92%	8%	73
3	C_5H_{11}	90%	10%	71
4	CH_2OMe	85%	15%	67

[a]The ratio was determined by ^1H NMR.
[b]Purified yields of **2** after column chromatography.

The (*Z*)-α-stannyl 1-alkenylphosphonates **2** are trisubstituted alkenes in which two synthetically versatile groups are linked to the same sp^2-hydridized carbon atom. These intermediates can be considered as vinylstannanes or vinylphosphonates. Therefore, we first explored the iododestannylation of these difunctionalised reagents for synthesising (E)-α-iodo-1-alkenylphosphonates. Treatment of the **2** with iodine at 0°C for 1 hour afforded the corresponding compounds **4** in excellent yield with retention of configuration (Scheme 2, Table 2).



a, R=Ph; b, R= n-C_4H_9;
c, R=C_5H_{11}; d, R=$MeOCH_2$.

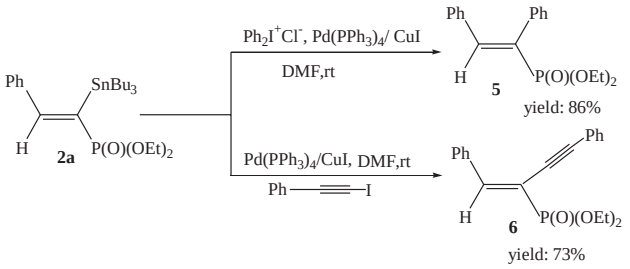
Scheme 2

Table 2 Iododestannylation of α-tri-n-butylstannyl-1-alkenylphosphonates

Starting materials	R	Product	Yield/%[a]
2a	Ph	**4a**	91
2b	C_4H_9	**4b**	90
2c	C_5H_{11}	**4c**	95
2d	$MeOCH_2$	**4d**	87

[a]Purified yield after column chromatography.

The (*E*)-α-stannyl-1-alkenylphosphonates **2** can also undergo palladium-catalysed cross-coupling reactions with various electrophiles to form the C-C bond with the retention of configuration. For example, the coupling of compound **2a** with diphenyliodonium chloride or 1-iodo-2-phenylethyne at room temperature in the presence of $Pd(PPh_3)_4$ and CuI in DMF affords (*E*)-α-phenyl-phenylethenylphosphonate (**5**) and (Z)-1-phenyl-4-phenyl -2-(diethylphosphonato)-but-1-ene-3-yne **6** in 86% and 73% yield respectively (Scheme 3).



Scheme 3

In conclusion, we have developed a facile route to (*Z*)-α-stannyl-1-alkenylphosphonates **2** regio- and stereoselectively. The (*Z*)-α-stannyl-1-alkenylphosphonates **2** can be easily converted into various α-substituted vinylphosphonates. This method has the advantages of accessible material, mild reaction condition and simple procedure.

Experimental

All reactions involving moisture sensitive regents were carried out in anhydrous solvents, oven dried glassware and under nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker AC 400 spectrometer at 400MHz. $CDCl_3$ was used as solvent and TMS as internal standard. Mass spectra were obtained on a HP 5989-B mass spectrometer by electronic impact at 70eV. I R spectra were determined on a Bruker Vector-22 instrument as neat films.

General procedure for the synthesis of **2a–d**: A catalytic amount of AIBN (0.1 mmol) was added to a stirred solution of **1a–d** (1 mmol) in anhydrous and degassed toluene (5ml) and Bu_3SnH (1.3 mmol) was added via syringe. The resulting solution was warmed to 80°C and the reaction was monitored by TLC. After the completion of the reaction, the resulting solution was evaporated to dryness. The column chromatography of the residue on silica gel eluting first with hexane to eliminated tin residue followed by hexane/ ethyl acetate = 50/50 to afford the expected stannylated compounds **2a–d**.

2a[6]**:** A colourless oil. IR (neat): 2955, 1583, 1390, 1239, 1028 cm^{-1}; ^{1}H NMR: δ 0.81–0.88 (m, 15H), 1.20–1.83 (m, 18H), 4.10 (m, 4H), 7.26-7.34 (m, 5H), 8.40 (d, 1H, *J* = 33.6 Hz); MS (EI) (%) 529 (M^+, 2), 473 (M-C_4H_9, 100), 301 (17), 183 (9), 41(63).

2b: A colourless oil. IR (neat): 2956, 1587, 1388, 1235, 1028 cm^{-1}; ^{1}H NMR: δ 0.87–0.92 (m, 16H), 1.25–1.72 (m, 24H), 2.20 (m, 2H), 4.00 (m, 4H), 7.35 (dt, 1H, *J* = 30.1, 7.2 Hz); MS (EI) (%) 510 (M^+, 4), 453 (M-C_4H_9, 38), 281 (8), 81(12), 41 (100); Anal. For $C_{22}H_{47}O_3PSn$: Calcd (Found) C, 51.88 (51.40); H, 9.30 (9.40) %.

2c: A colourless oil. IR (neat): 2956, 1589, 1387, 1232, 1025 cm^{-1}; ^{1}H NMR: δ 0.87–0.95 (m, 18H), 1.28–1.49 (m, 24H), 2.10 (m, 2H), 4.00 (m, 4H), 7.32 (dt, 1H, *J* = 38.9, 7.2 Hz); MS (EI) (%) 524 (M^+, 2), 467 (M-C_4H_9, 100), 295 (17); Anal For $C_{23}H_{49}O_3PSn$: Calcd (Found) C, 52.79 (52.42); H, 9.44 (9.48) %.

2d: A colourless oil. IR (neat): 2954, 1588,1236, 1028; ^{1}H NMR: 0.89 (t, 9H, *J* = 7.3 Hz), 0.99 (t, 6H, *J* = 8.3 Hz), 1.29–1.48 (m, 18H), 3.37 (s, 3H), 3.09–4.14 (m, 6H), 7.50(dt, 1H, *J* = 37, 7.3 Hz); MS (EI) (%) 497 (M^+, 2), 441 (M-C_4H_9, 76), 119 (14) 41 (100); Anal For $C_{20}H_{43}O_4PSn$: Calcd (Found) C, 48.31 (48.60); H, 8.72 (8.61) %.

General procedure for the synthesis of **4a–d**: A solution of iodine (1 mmol) in dry CH_2Cl_2 (5 mL) was added to a solution of compound **2a–d** (1 mmol) in dry CH_2Cl_2 (5 ml) which was stirred at 0°C. The reaction mixture was stirred for 1 hour at room temperature, and then washed with a dilute aqueous $Na_2S_2O_3$ solution and water, dried over $MgSO_4$ and then concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with ethyl acetate/hexane = 50/50 to afford the compounds **4a–d.**

4a: A yellow oil. IR (neat): 2983, 1591, 1244, 1021 cm^{-1}; ^{1}H NMR: δ 1.41 (t, 6H, *J* = 7.0 Hz), 4.18 (m, 4H), 7.33–7.77 (m, 5H) 8.13 (d, 1H, *J* = 18.1 Hz); MS (EI) (%) 366 (M^+, 8), 239 (M-I, 70), 183 (85), 102 (100); Anal For $C_{12}H_{16}IO_3P$: Calcd (Found) C, 39.37 (39.08); H, 4.40 (4.45); I 34.66 (34.60) %.

4b: A yellow oil. IR (neat): 2956, 1602, 1252, 1025 cm^{-1}; ^{1}H NMR: δ 0.90 (t, 3H, *J* = 7.0 Hz), 1.30–1.46 (m, 10H), 2.30 (m, 2H), 4.14 (m, 4H), 7.05 (dt, 1H, *J* = 23, 6.8 Hz); MS (EI) (%) 346 (M^+, 100), 219 (M-I, 40), 163 (26), 81 (36); Anal. For $C_{10}H_2IO_3P$: Calcd (Found) C, 34.70 (34.30); H, 5.82 (5.88); I, 36.66 (36.85) %.

4c: A yellow oil. IR (neat): 2957, 1602, 1254, 1024 cm^{-1}; ^{1}H NMR: 0.90 (t, 3H, *J* = 7.2 Hz), 1.28–1.51 (m, 12H), 2.30 (m, 2H), 4.12 (m, 4H), 7.05(dt, 1H, *J* = 18.3, 7.1 Hz); MS (EI) (%) 360 (M^+, 100), 233 (M-I, 98), 95 (73); Anal For $C_{11}H_{22}IO_3P$: Calcd (Found) C, 36.68 (36.90); H, 6.16 (6.05); I, 35.23 (35.45) %.

4d: A yellow oil. IR (neat): 2957, 1600, 1253, 1025; ^{1}H NMR: 1.37(t, 6H, *J* = 7.8 Hz), 3.35 (s, 3H), 4.15 (m, 4H), 4.40 (dd, 2H, *J* = 3.16, 5.8 Hz), 7.54 (dt, 1H, *J* = 18.5, 5.8 Hz); MS (EI) (%) 334 (M^+, 47), 207 (M-I, 13), 119 (42) 45 (100); Anal For $C_8H_{16}IO_4P$: Calcd (Found) C, 28.76 (28.30); H, 4.83 (4.75); I, 37.99 (38.10) %.

General procedure for the synthesis of **5** *or* **6***:* **2a** (1.0 mmol) and diphenyliodonium chloride[7] or 1-iodo-2-phenylethyne (1.0 mmol) were dissolved in DMF (5 ml) under nitrogen at room temperature. $Pd(PPh_3)_4$ (0.05 mmol) and CuI (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 hexane / ethyl acetate = 50/50 to afford **5** and **6** in 86% and 73% yield, respectively.

5: oil.^{1}H NMR: δ = 1.25–1.28 (t, 6H, *J* = 6.8 Hz), 4.05–4.14 (m, 4H), 7.05–7.46 (m, 10H) 7.60 (d, 1H, *J* = 24 Hz); IR (film): 2978, 1584, 1492, 1250; MS: *m/z* 316 (M^+, 71%), 206 (52), 178 (100), 77 (12); Anal For $C_{18}H_{21}O_3P$: Calcd (Found) C, 68.34 (68.25); H, 6.69 (6.71).

6: oil .^{1}H NMR: δ = 1.12–1.17 (t, 6H, *J* = 6.8 Hz), 4.09–4.18 (m, 4H), 7.09–7.44 (m, 10) 7.63 (d, 1H, *J* = 21 Hz); IR (film): 2993, 2230,1613, 1250; MS: *m/z* 340 (M^+, 57), 231 (49), 203 (100), 77 (9); Anal For $C_{20}H_{21}O_3P$: Calcd (Found) C, 70.58 (70.47); H, 6.22 (6.29).

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