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STEREOSELECTIVE AND CONVENIENT SYNTHESIS OF DIETHYL (E)-α-TRIPHENYLSTANNYL OR (Z)-α-TRIBUTYLSTANNYL α-ALKENYLPHOSPHONATES

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ABSTRACT : Diethyl (*E*)-α-triphenylstannyl or (*Z*)-α-tri-*n*-butylstannyl α-alkenylphosphonates are conveniently and stereoselectively prepared using a "tin-Peterson-like" reaction. Protonolysis of the carbon-tin bond of α-tributylstannyl derivatives proved to be easy and stereospecific.

Functional vinyltin compounds are versatile reagents in organic synthesis[1]. Their transmetallation and metal-catalyzed cross-coupling reactions are of considerable value for the generation of vinyllithium and other potential vinyl carbanions, leading to stereoselective formation of carbon-carbon bonds[1,2]. In connection with the synthetic applications of these reactions, the search of conceptually new routes to olefinic stannanes continues to attract the attention of numerous research groups[3].

As part of a program directed towards the development of new Horner and Peterson reagents, we recently reported an efficient and stereoselective synthesis of (*E*)- or (*Z*)-α-alkenyl- phosphonates obtained by reaction of α-triorganostannyl-α-lithioalkylphosphonates with aldehydes[4].

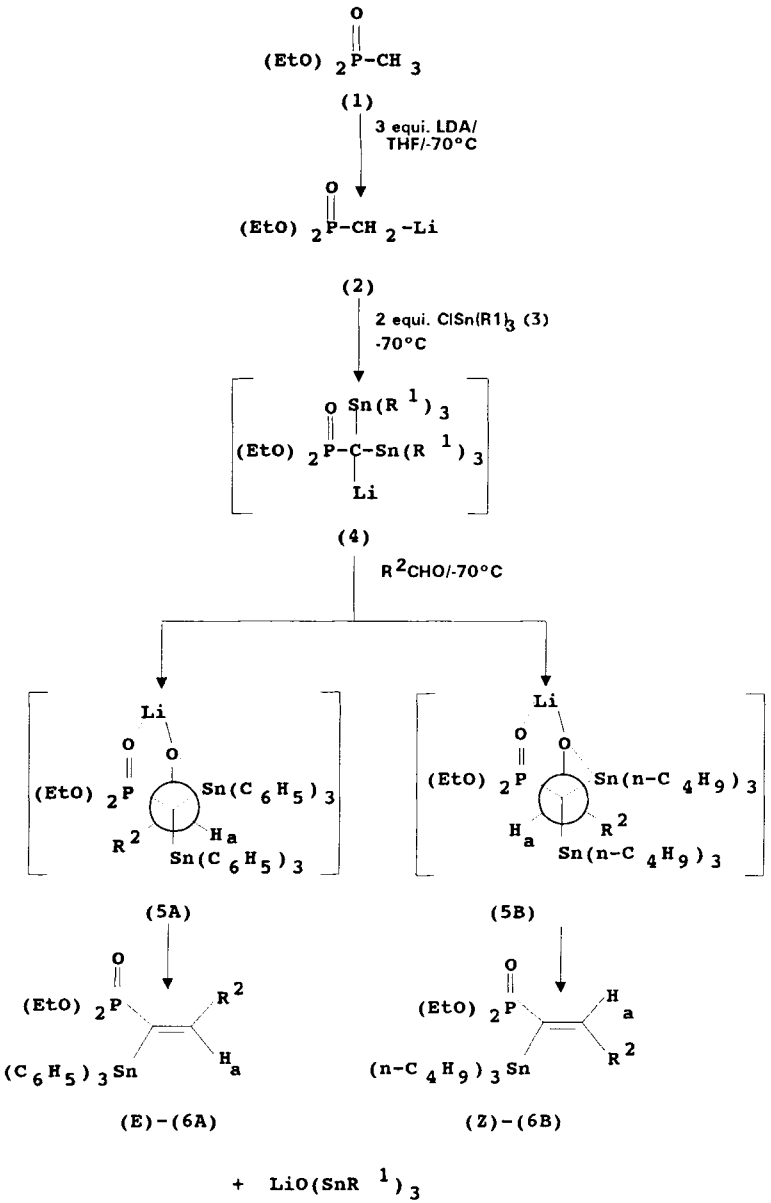
We describe here a practical one-pot synthesis of diethyl (*E*)-α-triphenylstannyl- or (*Z*)-α-tri-*n*-butylstannyl-α-alkenylphosphonates **(6)** from corresponding diethyl α-*bis*-triorganostannyl- α-lithiomethylphosphonates **(4)**, *in-situ* generated from the diethyl methylphosphonate **(1)**. Our strategy takes advantage of the presence of two *gem*-triorganostannyl moieties in **(4)** : one is used as functional group carrier in the "tin-Peterson-like" reaction, while the second one is retained and stereoselectively positioned on the double bond in **(6)** (Scheme 1).

Lithiated carbanions **(4)**, stable at low temperature, were generated as follows : diethyl methylphosphonate **(1)** was first reacted with 3 equivalents of LDA in tetrahydrofuran (THF) at -70°C, leading to the diethyl α-lithiomethyl phosphonate **(2)**; conversion of **(2)** into **(4)** was then achieved at -70°C, over a period of about 1 hour, after addition of 2 equivalents of tri-*n*-butyl- **(3A)** or triphenyl **(3B)**-tin chloride. The use of 3 equivalents of LDA is essential for the quantitative formation of **(4)**[5].

Subsequent reaction of **(4)** with aromatic or aliphatic aldehydes, at -70°C, led to diethyl α-triorganostannyl-α-alkenylphosphonates **(6)**, in high yields, by complete elimination,at 0°C, of the triorganotin oxide moiety, according to a "tin-Peterson-like" reaction (Scheme 1). The reaction was monitored by ^{31}P NMR spectroscopy.

We found that the stereochemistry of **(6)** selectively depends on the substituent $\mathbf{R^1}$ in the stannyl group $\mathbf{Sn(R^1)_3}$. Actually, with aromatic aldehydes, triphenylstannyl group led predominantly to the (*E*)-**(6A)** isomer (Table 1). In contrast, tri-*n*-butylstannyl group favoured the formation of the (*Z*)-**(6B)** isomer (Table 2).

These results are in good accordance with the previously observed stereoselectivity in the "tin-Peterson-like" synthesis of α-alkenylphosphonates and could be rationalized by a fast *syn*-elimination of the electropositive and relatively less hindered triphenylstannyl group from the kinetic adduct **(5A)**, giving the (*E*)-



Scheme 1

Table 1

Diethyl α-triphenylstannyl-α-alcenylphosphonates (6A)

Product	R^2	^{31}P NMR ($CDCl_3$) δ (ppm) (*E*)/(*Z*)	Ratio[a] (*E*):(*Z*)	$^3J_{PHa}$[b] (Hz) (*E*)/(*Z*)	$^2J_{P-117Sn}$[c] (Hz) (*E*)/(*Z*)	$^2J_{P-117Sn}$[c] (Hz) (*E*)/(*Z*)	Pure isomer isolated[d]- (Yield %)	M.p. (°C)
6Aa	C_6H_5	20.2/23.8	92:8	58/33	148/132	154/137	*E* - (80)	89
6Ab	4-Me-C_6H_4	19.9/23.4	91:9	59/33	150/134	157/140	*E* - (84)	91
6Ac	4-MeO-C_6H_4	19.4/23.3	94:6	59/33	150/134	157/139	*E* - (82)	125
6Ad	C_6H_5-CH=CH	20.2/23.4	93:7	(e)/(e)	143/130	150/138	*E* - (78)	70
6Ae	CH_3-CH=CH	20.3/23.9	91:9	62/(e)	149/135	156/140	*E* - (83)	95
6Af	3,4-OCH_2O-C_6H_3	19.9/23.3	82:18	(e)/32	148/132	155/139	*E* - (80)	105
6Ag	$CH_3CH_2CH(CH_3)$	20.1/22.6	47:53	61.5/(e)	173/156	181/163	*E* - (30) *Z* - (35)	60 68
6Ah	$CH_3CH(CH_3)$	20.3/22.5	51:49	62/(e)	170/154	177/161	*E* - (38) *Z* - (35)	84 90

(a) Ratio determined on the crude products, by GC and ^{31}P NMR spectroscopy.
(b) Determined on the ^1H NMR spectra of the crude products.
(c) Determined on the ^{31}P NMR spectra of the crude products.
(d) Purification by flash chromatography and crystallization (hexane/ether). All purified products exhibited ^1H NMR spectra and microanalyses (C : ± 0.3%, H : ±0.2%), in accordance with their molecular structure.
(e) $^3J_{HaP}$ was not determined because overlapping of Ha and aromatic protons signals.

(6A).isomer. Conversely, the more hindered and less reactive tri-*n*-butylstannyl group should allow the equilibration to take place, leading to the less hindered and more stable conformation **(5B)**, which should give the (*Z*)-**(6B)** isomer, after *syn*-elimination of the tri-*n*-butyltin oxide moiety[4,6]. With aliphatic aldehydes, results were less homogeneous than in aromatic series : whereas triphenyltin was not a

Table 2

Diethyl α-tributylstannyl-α-alcenylphosphonates (6B)

Product	R^2	^{31}P NMR ($CDCl_3$) δ (ppm) (*E*)/(*Z*)	Ratio[a] (*E*):(*Z*)	$^3J_{PHa}$[b] (Hz) (*E*)/(*Z*)	$^2J_{P-117Sn}$[c] (Hz) (*E*)/(*Z*)	$^2J_{P-119Sn}$[c] (Hz) (*E*)/(*Z*)	Pure isomer isolated[d] - (Yield %)
6Ba	C_6H_5	24.1/24.6	10:90	58/33.5	109/100	112/103	*Z* - (85)
6Bb	4-Me-C_6H_4	21.0/25.3	8:92	61/33	111/103	116/107	*Z* - (84)
6Bc	4-MeO-C_6H_4	21.4/25.6	6:94	63.5/33.5	111/103	115/107	*Z* - (86)
6Bd	C_6H_5-CH=CH	21.4/25.0	8:92	63/33	104/100	108/103	*Z* - (84)
6Be	CH_3-CH=CH	21.8/26.0	57:43	63/31.5	110/103	114/107	*Z* - (40) *E* - (30)
6Bf	3,4-OCH_2O-C_6H_3	21.0/25.4	10:90	62/33.5	110/101	114/104	*Z* - (82)
6Bg	$CH_3CH_2CH(CH_3)$	21.7/24.9	88:12	64/32.5	129/120	134/125	*E* - (52)
6Bh	$CH_3CH(CH_3)$	21.6/24.8	83:17	64.5/32	126/118	131/123	*E* - (54)

(a) Ratio determined on the crude product, by GC and ^{31}P NMR spectroscopy.
(b) Determined on the ^1H NMR spectra of the crude products.
(c) Determined on the ^{31}P NMR spectra of the crude products.
(d) Purification by column chromatography over silicagel, eluent : ether/hexane (50/50). All purified products exhibited ^1H NMR spectra in accordance with their molecular structures, and were isolated as oils.

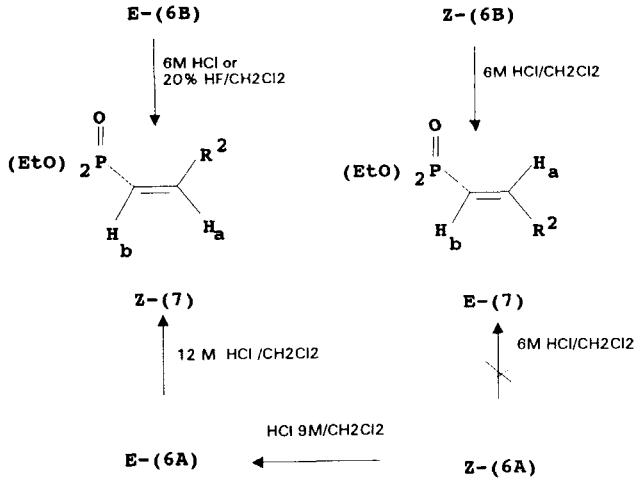
stereoselective group (Table 1, products **6Ag**, **6Ah**), tributylstannyl group, on the other hand, induced a good (*Z*)-stereoselectivity (Table 2, products **6Bg**, **6Bh**), except with crotonaldehyde (Table 2, product **6Be**). Pure stereoisomers were isolated, in good yields, after crystallization **(6A)** or column chromatography **(6B)** (Tables 1 & 2).

The stereochemistry of compounds **(6)** was assigned according to the $^{3}J_{HaP}$ coupling constant measurements in their ^{1}H NMR spectra[7]. $^{3}J_{HaP}$ values varied from 58 to 65 Hz for (*E*)-isomers and from 31 to 34 Hz for (*Z*)-isomers. In ^{31}P NMR spectra of compounds **(6)**, the signal of (*Z*)-isomer appeared 2.5 to 4.3 ppm down field from the one of (*E*)-isomer. Moreover, in addition to their main singlet, each stereoisomer exhibited two symmetrical doublets resulting from coupling between the ^{31}P nucleus and the two non-zero-spin tin isotopes, namely ^{117}Sn (7.6 % of natural abondance) and ^{119}Sn (8.6 % of natural abondance)[1]. The resulting coupling constants are in agreement with the following sequences : $^{2}J^{E}_{P\text{-}117Sn} > {}^{2}J^{Z}_{P\text{-}117Sn}$ and $^{2}J^{E}_{P\text{-}119Sn} > {}^{2}J^{Z}_{P\text{-}119Sn}$, whatever the $\mathbf{R^1}$ substituent in the triorganostannyl group (Tables 1 and 2).

An important application of α-triorganostannyl alkenylphosphonates in organic synthesis lies in electrophilic cleavage of the tin-carbon bond. In order to investigate this reaction, we decided to study the acidic hydrolysis of some phosphonates **6**. Stereospecific substitution of a trimethylstannyl by a proton generally occurs during protonolysis of vinyltrimethyltin derivatives[9]. We observed the same stereospecific cleavage when pure (*E*)- or (*Z*)-α-tri-*n*-butylstannyl alkenylphosphonates **6B** were treated with 6M hydrochloric acid (or 20% hydrofluoric acid), in a biphasic system, at room temperature : they were completely transformed into the corresponding phosphonates 7 having the (*Z*)- or the (*E*)-configuration, respectively (Scheme 2 and Table 3).

The (*E*)- or (*Z*)-geometry of the C=C double bond in phosphonates **7** was assigned by $^{3}J_{HaP}$ and $^{3}J_{HaHb}$ coupling constants measurements, in ^{1}H NMR spectra[7].

As expected, the behavior of α-triphenylstannyl alkenylphosphonates **6A** towards acidic hydrolysis was noticeably different. Under previous conditions (6M HCl or 20% HF), (*E*)- or (*Z*)-**6A** remained unchanged. Under forcing conditions (9M



Scheme 2

Table 3

Diethyl α-alkenyphosphonates (7)

Product	R^2	^{31}P NMR ($CDCl_3$) δ (ppm)	$^3J_{HaP}$ (Hz)	$^3J_{HaHb}$ (Hz)	Pure yield[a]	Hydrolysis conditions[b]	Starting phosphonate (6)
(*E*)-(7c)	4-MeO-C_6H_4	17.7	23	18	90	6M HCl	(*Z*)-(6Bc)
					83	12M HCl	(*E*)-(6Ac)
(*Z*)-(7g)	$C_2H_5CHCH_3$	14.6	53	13	88	6M HCl	(*E*)-(6Bg)
					78	20% HF	(*E*)-6Ag)
(*Z*)-(7h)	CH_3CHCH_3	15.0	52.5	12.5	86	6M HCl	(*E*)-(6Bh)

(a) Purification by flash chromatography over silica gel, eluent : hexane/ether (50/50). All purified products exhibited ^1H NMR spectra in accordance with their molecular structures, and were isolated as liquids.
(b) At room temperature and in biphasic system, not any hydrolysis of the phosphonic ester functions was observed.

HCl), complete isomerization of (*Z*)-**6A** into (*E*)-**6A** was observed. Finally, under more drastic conditions (12M HCl), the (*E*)-isomer was cleaved to give the corresponding phosphonate (*Z*)-7 (Scheme 2 and Table 3).

In spite of difficult cleavage of triphenylstannyl derivatives, α-triorganostannyl alkenylphosphonates seem to represent interesting precursors of various alkenylphosphonates, especially those with (*Z*)-geometry, not easily prepared by other ways[10].

In conclusion, we describe here an efficient and mild methodology for stereoselective synthesis of new (*E*)- or (*Z*)-α-triorganostannyl α-alkenylphosphonates, based on the stereochemical control by the substituent on the tin, in a Peterson-like process. Having already tested the feasibility of electrophilic protonolysis of the carbon-tin bond, we are now investigating the use of these attractive reagents in organic synthesis.

EXPERIMENTAL

Materials : Diethyl methylphosphonate **(1)** was prepared by Arbuzov reaction[5,11]; all other reagents are commercially available (Aldrich chemical Co.). THF was dried and distilled from the Na/benzophenone complex before use. ^{1}H NMR spectra were recorded on a Varian T-60 or on a Bruker AC 200 spectrometers, in reference to TMS as internal standard. Following abbreviations are used : s, d, t, qui, m, dd... for singlet, doublet, triplet, quintuplet, multiplet, double doublet... respectively. ^{31}P NMR spectra were recorded at 81.01 MHz, on a Bruker AC 200 spectrometer, in reference to 85% H_3PO_4 as external standard. Gas chromatography (GC) was performed on a Delsi IGC 121 FL chromatograph equipped with a 2 m OV 17 column. Elemental microanalyses were realized on a Carlo Erba 1106 analyser. Melting points were determined with a Kofler apparatus and were uncorrected.

Preparation of the Diethyl (*E*)-1-(triphenylstannyl)-2-phenyl-1-ethenylphosphonate (6Aa, Table 1). **Typical Procedure :**A 1.5 molar solution of *n*-butyllithium in hexane (44 mL, 0.066 mol) was placed in a three-necked flask equipped with stirrer, addition funnel, low temperature thermometer, and nitrogen-inlet tube. A solution of diisopropylamine (6.68 g, 0.066 mol) and diethyl methylphosphonate (3.05 g, 0.02 mol) in THF (60 mL) was added dropwise to the stirred, cooled (-70°C) solution of *n*-BuLi and stirring was continued at -70°C for 15 min. A solution of triphenyltin chloride (15.4 g, 0.04 mol) in THF (25 mL) was then added quickly. The solution was kept at low temperature for 1 h, and benzaldehyde (2.12 g, 0.02 mol), in THF (15 mL), was added. The resulting mixture was gradually warmed to 0°C, kept at this temperature for 1 h, hydrolyzed (H_2O, 50 mL) then extracted (Et_2O, 3×30 mL then CH_2Cl_2, 2×30 mL). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure giving the crude product (11.3 g), which was analyzed by ^{31}P NMR spectroscopy (*E*/*Z* ratio = 92/8). The crude product was flash chromatographed on silica gel using ether/hexane (50/50) as eluent and crystallized from ether/hexane mixture giving white spangles (9.4 g, 80% yield). ^1H NMR ($CDCl_3$), δ (ppm) = 1.0 (t, $^3J_{HH}$ = 7Hz, 6H : 2×C<u>H</u>$_3$CH$_2$O); 3.8 (qui, $^3J_{HH} = {}^3J_{HH}$ = 7Hz, 4H : 2×CH$_3$C<u>H</u>$_2$O); 7.6 (d, $^2J_{HaP}$ = 58Hz, 1H : <u>H</u>a); 7.2 - 7.9 (m, 20H : <u>H</u>arom.). Anal. for $C_{30}H_{31}PO_3Sn$ (588.7), calc.% C 61.15, H 5.26, found C 60.9, H 5.1.

Preparation of the Diethyl (*Z*)-1-(tri-*n*-butylstannyl)-2-(4-methoxyphenyl)-1-ethenylphosphonate (6Bc, Table 2). **Typical Procedure :** To a stirred solution of diethyl α-lithio-methylphosphonate (0.02 mol) prepared as above, was added quickly, at -70°C, a solution of tri-*n*-butyltin chloride (13.0 g, 0.04 mol) in THF (15 mL) and stirring was continued for 1h at this temperature. *p*-Anisaldehyde

(2.72 g, 0.02 mol) in THF (15 mL) was added at -70°C and the resulting mixture was gradually warmed to 0°C and kept at this temperature for 1h. Subsequent work-up was the same as above giving the crude product (10.9 g, *E/Z* ratio = 6/94). The crude product was purified on silica gel using ether/hexane (50/50) as eluent to get a colourless liquid (9.6 g, 86% yield). ^{1}H NMR ($CDCl_3$), δ (ppm) = 0.6 - 1.5 (m, 33H : 2×C$\underline{H}_3$CH$_2$O & 3×*n*-C$_4$H$\underline{9}$); 3.8 (s, 3H : C$\underline{H}_3$O); 3.9 (qui, $^3J_{HH} = {}^3J_{PH}$ = 7Hz, 4H : 2×CH$_3$C$\underline{H}_2$O); 6.6 - 7.2 (AB system, $^3J_{HH}$ = 9Hz, 4H : $\underline{H}$arom.); 8.15 (d, $^3J_{HaP}$= 33.5Hz, 1H : $\underline{H}$a).

Preparation of Diethyl (*Z*)-3-methyl-1-pentenylphosphonate [(*Z*)-**7g**, Table 3] **from Diethyl (*E*)-1-tri-*n*-butylstannyl-3-methyl-1-pentenylphosphonate** [(*E*)-**6Bg**, Table 1] **. Typical procedure :** Diethyl (*E*)-1-tri-*n*-butylstannyl-3-methyl)-1-pentenylphosphonate (2.03 g, 0.004 mol) in CH_2Cl_2 (10 mL) was poured in 6M aqueous HCl (25 mL) and the mixture was stirred at room temperature for about 1h, then extracted with CH_2Cl_2 (2×10 mL). Organic layer was dried ($MgSO_4$); the solvent was removed under reduced pressure to give the crude product, which was analyzed by GC, ^{31}P and ^{1}H NMR spectroscopy (no trace of (*E*)-isomer was detected) and then purified by flash chromatography over silica gel (eluent hexane/ether : 50/50) giving the pure product (0.77 g, 88% yield). ^{1}H NMR ($CDCl_3$), δ (ppm) = 0.9 (t, $^3J_{HH}$=7Hz, 3H, C$\underline{H}_3$CH$_2$CH); 1.0 (d, $^3J_{HH}$=7Hz, 3H, C$\underline{H}_3$CH); 1.1-1.5 (m, 8H, CH$_3$C$\underline{H}_2$CH & 2xC$\underline{H}_3$CH$_2$O); 3.0 (m, 1H, C$\underline{H}$CH$_3$); 4.1 (qui, $^3J_{HP}$=$^3J_{HH}$=7HZ, 4H, 2xCH$_3$C$\underline{H}_2$O); 5.5 (dd, $^2J_{HbP}$=19.8Hz & $^3J_{HaHb}$=13Hz, 1H, $\underline{H}$b); 6.2 (ddd, $^3J_{HaP}$=53Hz, $^3J_{HaHb}$=13Hz & $^3J_{HH}$=11Hz, 1H, $\underline{H}$a).

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