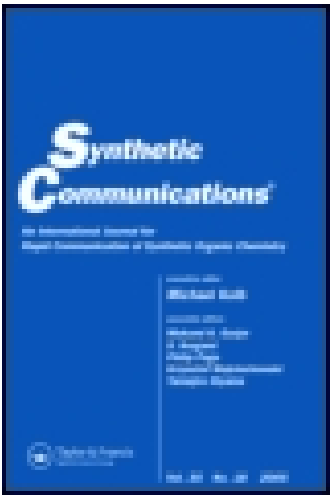

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Stereoselective Synthesis of (E) or (Z) α-Alkenylphosphonates via α-Stannylated Phosphonates

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STEREOSELECTIVE SYNTHESIS OF (E) OR (Z) α-ALKENYLPHOSPHONATES VIA α-STANNYLATED PHOSPHONATES

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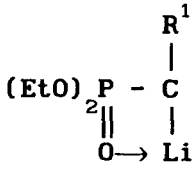
Abstract: α-lithiostannylalkylphosphonates react with aldehydes with the complete elimination of the organotin moiety. The stereoselective formation of the (E) or (Z) α-alkenylphosphonates is closely dependent on the tin substituent.

In connection with our studies on the behaviour of the α-stabilized alkylphosphonate carbanions **(2)** in olefination reaction with aldehydes, we have generated and used **(2a)** and **(2b)** in Wittig-Horner[1] and Peterson[2] reactions respectively . We have observed that the

α-phosphonyl carbanions **(2a)** give the thermodynamic alkenes **(4E)** only. By contrast the α-silyl carbanions **(2b)** give predominantly the kinetic alkenes **(4Z)** with little stereoselectivity. This is explained by the more oxophilic silyl group.



(2)

(a) E= $PO(OR)_2$

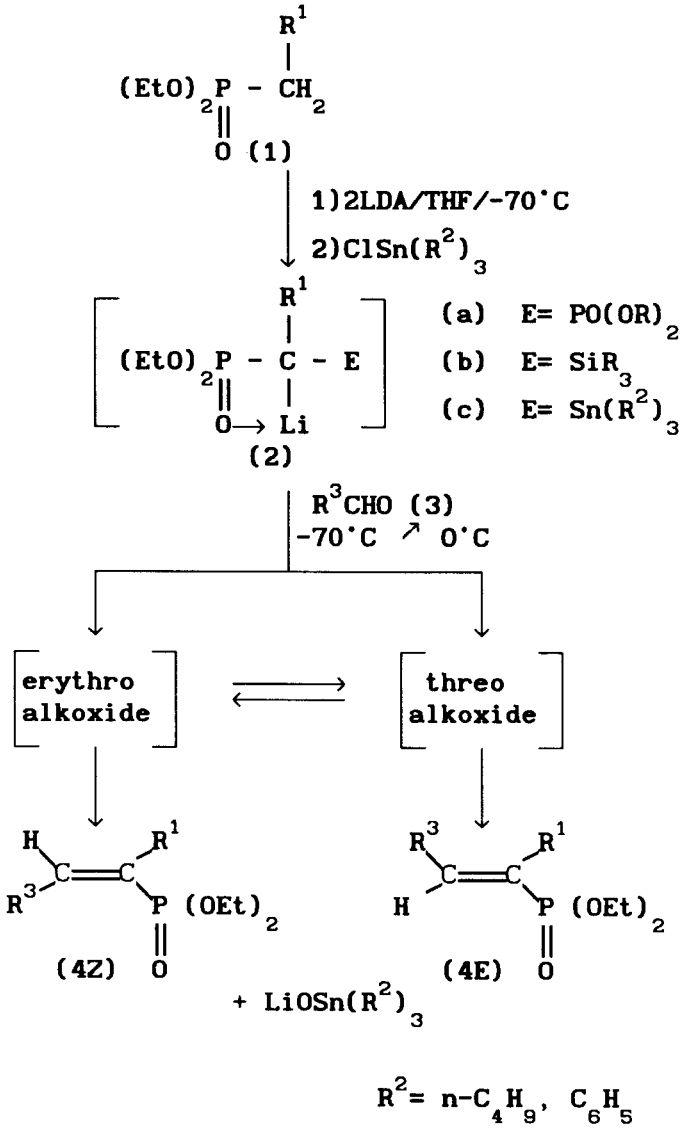
(b) E= SiR_3

(c) E= $Sn(R^2)_3$

It was of interest to extend the reaction to the α-lithiostannylalkylphosphonates **(2c)** recently prepared in high yields[3]. In this paper we report the behaviour of these carbanions towards aldehydes and the surprising effect of the stannyl substituent $Sn(R^2)_3$ on the stereochemistry of the olefination reaction.

In light of this program we have investigated the reactivity of aldehydes (**3**) with the readily accessible and stable carbanions (**2c**) generated "in situ" from alkylphosphonates (**1**) and triorganotin chloride[3] (Scheme). The reaction was monitored by ^{31}P-NMR spectroscopy and GC.

We have found that all the α-lithiostannylalkylphosphonates **(2c)** used yield on reaction with aldehydes the alkenylphosphonate (**4**) by complete elimination of the triorganotin oxide moiety. There is



a precedent for this tin-phosphorus competition in the diphenylphosphine oxide series[4].

Moreover when R^1= H and R^3= C_6H_5 and in the case of the very crowded tin substituent R^2= n-C_4H_9, the reaction invariably yields the thermodynamic isomer **(4E)** in 97% isomeric purity (Table 1, entry 1). By contrast the less crowded tin substituent R^2= C_6H_5, yields a 40/60 mixture of the (E) and (Z) isomers (**4**) (Table 1, entry 4) similar to Peterson-like reactions using no stabilized organostannyl carbanions[5].

To better investigate the stereoselectivity induced by the stannyl group we have chosen to extend the reaction to α-substituted carbanions (**2c**) (R^1= CH_3, C_2H_5, n-C_3H_7)[3], and aliphatic or aromatic aldehydes (**3**) (Table 1). Under the same experimental conditions as above the formation of α-alkenyl-phosphonates (**4**) is complete after 6 hours at 0°C with high stereoselectivity depending on the nature of the stannyl group $Sn(R^2)_3$.

Actually the butylstannyl group (R^2= n-C_4H_9) favorises the formation of the thermodynamic isomer **(4E)** (Table 1, entries 2 and 3) and by contrast the kinetic isomer **(4Z)** is obtained when R^2= C_6H_5 (Table 1, entries 4 to 9). It is conceivable that the erythro β-oxidophosphonate intermediate being generated, in predominant form, the elimination step is affected by the stannyl group depending on the nature of R^2 substituent. The triphenylstannyl group being more

Table 1

Entry	R^1	R^2	R^3	Yield[a] (%)	^{31}P-NMR δ(ppm) (E)[b]	(Z)[c]	E/Z[d]
1	H	n-C_4H_9	C_6H_5	74	18.2	16.2	97/3
2	CH_3	n-C_4H_9	i-C_3H_7	76	21.6	19.1	80/20
3	CH_3	n-C_4H_9	4-MeO-C_6H_4	82	22.3	18.0	84/16
4	H	C_6H_5	C_6H_5	78	18.2	16.2	40/60
5	CH_3	C_6H_5	4-MeO-C_6H_4	80	22.3	18.0	8 /92
6	CH_3	C_6H_5	i-C_3H_7	75	21.6	19.1	5 /95
7	C_2H_5	C_6H_5	4-MeO-C_6H_4	68	22.6	18.3	3 /97
8	C_2H_5	C_6H_5	C_6H_5	63	21.8	17.7	5/95
9	n-C_3H_7	C_6H_5	n-C_3H_7	65	21.9	19.5	10/90

a) after purification

b) $^3J_{H-P}$ vary between 24 and 40 Hz.

c) $^3J_{H-P}$ vary between 12 and 20 Hz.

d) The ratio is determined, on the crude product, by GC and ^{31}P-NMR spectroscopy.

electropositive and less hindered than tributylstannyl group, promotes a faster decomposition of the erythro intermediate to give the (Z) isomer[5]. On the other hand, the less reactive tributylstannyl group induced a conformational change prior to elimination and gives predominantly the (E) isomer.

All the alkenylphosphonates (**4**) are compared to authentic samples (^{31}P and ^{1}H-NMR spectra)[1,2,6]. In ^{31}P-NMR spectroscopy, the (E) isomer is found at a higher field that the (Z) isomer and ($\delta^{31}P_{(E)}$ - $\delta^{31}P_{(Z)}$) is approximately 3 ppm (Table 1).

This synthesis being based on the stereochemical control of the substituent on the tin [R^2 in (**2c**)], we are now investigating the effect of various factors such as the nature of the heteroatom (Si, Ge, Sn), degree of aggregation and solvation, in order to generalize the scheme.

Experimental

Materials: alkylphosphonates (**1**) were prepared according to literature procedures[3]; all the other reagents are commercially available (Aldrich chemical Co.). THF was dried and distilled on Na/benzophenone before use. ^{1}H-NMR spectra were recorded on a Varian T-60 spectrometer. ^{31}P-NMR spectra were obtained, in $CDCl_3$, using BRUKER AC 200 spectrometer and 85% H_3PO_4 as external reference.

Preparation of diethyl α-alkenylphosphonates (4) (General Procedure)

A 1.5 molar solution of butyllithium in hexane (28 mL, 0.042 mol) is placed in a three-necked flask equipped with stirrer, addition funnel, low temperature thermometer, and nitrogen-inlet tube. A solution of diisopropylamine (2.20g, 0.022 mol) and diethyl alkylphosphonate (0.02 mol) in THF (80 mL) is added dropwise to the stirred, cooled (-60°C) solution and stirring is continued at -60°C for 10 min. A solution of triorganotin chloride (0.02 mol) in THF (15 mL) is then added quickly. The solution is kept at low temperature for 3 h, and the aldehyde (0.02 mol), in THF (15 mL), is added. The resulting mixture is gradually warmed to 0°C, kept at this temperature for 6 hours, hydrolyzed (H_2O, 30 mL) and extracted (Et_2O, 3x30 mL and CH_2Cl_2 2 x 30 mL). The combined organic layers are dried ($MgSO_4$), the solvent is removed under reduced pressure, the stereochemistry of the mixture is controlled by ^{31}P-NMR and GC (Table 1) and the crude product is chromatographed on a silica gel column (20cmx4cm;230-400 mesh) using Et_2O/hexane 50/50 as eluent.

References

1. (a) Elia Aboujaoude, E.; Lietge, S.; Collignon, N.; Teulade, M. P.; Savignac, P. Tetrahedron lett., 1985, 4435.

(b) Savignac, P.; Teulade, M. P.; Elia Aboujaoude, E.; Collignon, N.; Synthetic comm. 1987, 1557.

2. (a) Elia Aboujaoude, E.; Lietge, S.; Collignon, N.; Teulade, M. P.; Savignac, P. Synthesis, 1986, 934.
(b) Savignac, P.; Elia Aboujaoude, E.; Collignon, N.; Teulade, M.P.; Phosphorus Sulfur 1987, 30, 491.
3. Mimouni, N.; About-Jaudet, E.; Collignon, N. Synthesis 1991, 31.
4. Tilhard, H.J.; Ahlers, H.; Kauffmann, Th. Tetrahedron Lett., 1980, 2803
5. (a) Kauffmann, Th.; Kriegesmann, R.; Hamsen, A. Chem. Ber., 1982, 115, 1818.
(b) Kauffmann, Th. Angew. Chem. Int. Ed., 1982, 21, 410
6. Teulade, M. P.; Savignac, P.; Elia Aboujaoude, E.; Lietge, S.; Collignon, N. J. Organomet. Chem., 1986, 304, 283.

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