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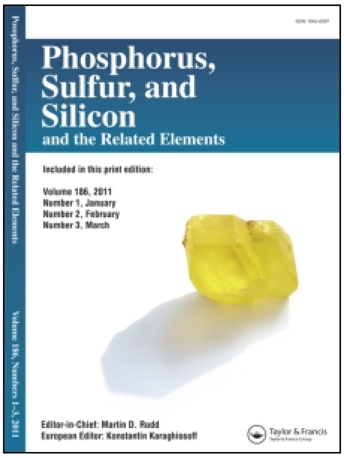

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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α-Triorganostannylalkyl and Alkenylphosphonates: Synthesis and Perspectives

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To cite this Article Mimounl, N. , About-jaudet, E. , Collignon, N. and Savignac, Ph.(1993) 'α-Triorganostannylalkyl and Alkenylphosphonates: Synthesis and Perspectives', Phosphorus, Sulfur, and Silicon and the Related Elements, 75: 1, 99 — 102

To link to this Article: DOI: 10.1080/10426509308037374

URL: http://dx.doi.org/10.1080/10426509308037374

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 75, pp. 99–102
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α-TRIORGANOSTANNYLALKYL AND ALKENYLPHOSPHONATES: SYNTHESIS AND PERSPECTIVES

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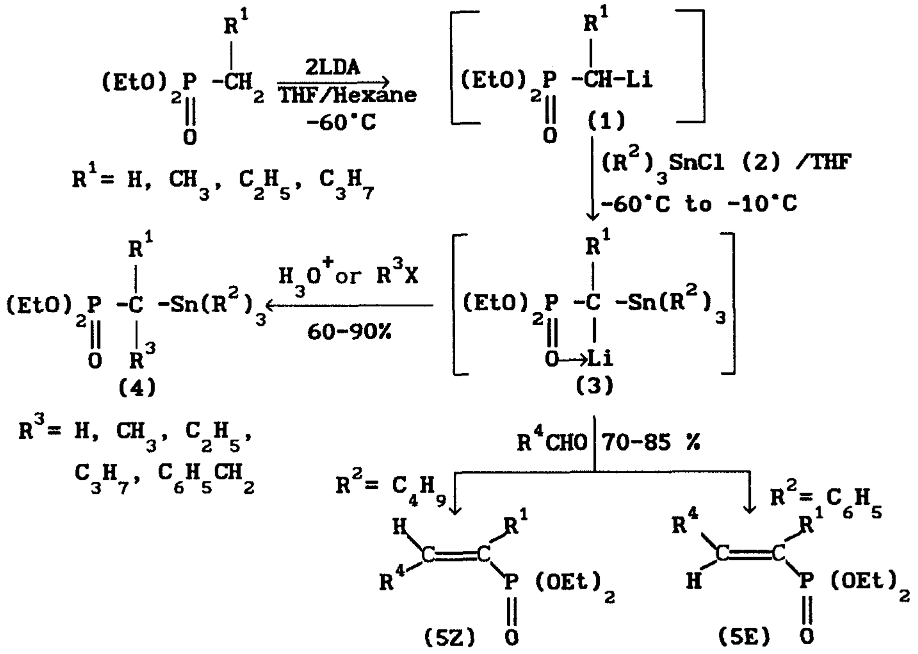
In this work we were interested to investigate the reactivity and behavior of triorganostannyl groups α-linked to an alkylphosphonate moiety. The well known properties of triorganostannyl groups: steric hindrance, oxophilic and pseudohalogen character[1] allow us to promote new valuable reagents giving rise to high stereo- and chemoselective transformations.

As part of a program aimed at developing new functional reagents, we recently reported the synthesis of α-triorganostannylalkylphosphonates **(4)** by stannylation of α-lithioalkanephosphonates **(1)** with a triorganostannyl chloride **(2)**, in the presence of one equivalent of lithium diisopropylamide (LDA), followed by hydrolysis or alkylation of the stabilized carbanionic intermediates **(3)** (Scheme 1)[2].

In light of these experiments we investigated the reactivity of aldehydes with **(3)**. We observed that all the α-lithiostannylalkylphosphonates **(3)** put on reaction yield the alkenylphosphonate **(5)**, with high stereoselectivity depending on the nature of the stannyl group $Sn(R^2)_3$, with complete elimination of the triorganotin oxide moiety.

Actually the tributylstannyl group (R^2= n-C_4H_9) favorises the formation of the thermodynamic isomer **(5E)** and by contrast the kinetic isomer **(5Z)** is obtained when R^2= C_6H_5. The triphenylstannyl group being more electropositive and less hindered than tributylstannyl group, promotes a faster decomposition of the erythro β-oxidophosphonate intermediate to give the (Z) isomer. On the other hand, the less reactive tributylstannyl group induced a conformational change and gives predominantly the (E) isomer by decomposition of the threo intermediate (scheme 1)



SCHEME 1

During the preparation of compounds **(4)** we remarked that the direct stannylation of the diethyl α-lithiomethylphosphonate **(1**, R^1= H), generated from diethyl methanephosphonate, with two equivalents of tributyltin **(2a)** or triphenyltin chloride **(2b)** leads to the direct formation of distannylated carbanion **(6)**, stable at low temperature.

Subsequent reaction of **(6)** with aldehydes leads to the pure (E) or (Z) triorganostannylalkenylphosphonates **(7)**, with high stereoselectivity and in excellent yields. We found that the stereochemistry of **(7)** depends, as previously, on the nature of the stannyl group $Sn(R^2)_3$ (scheme 2).

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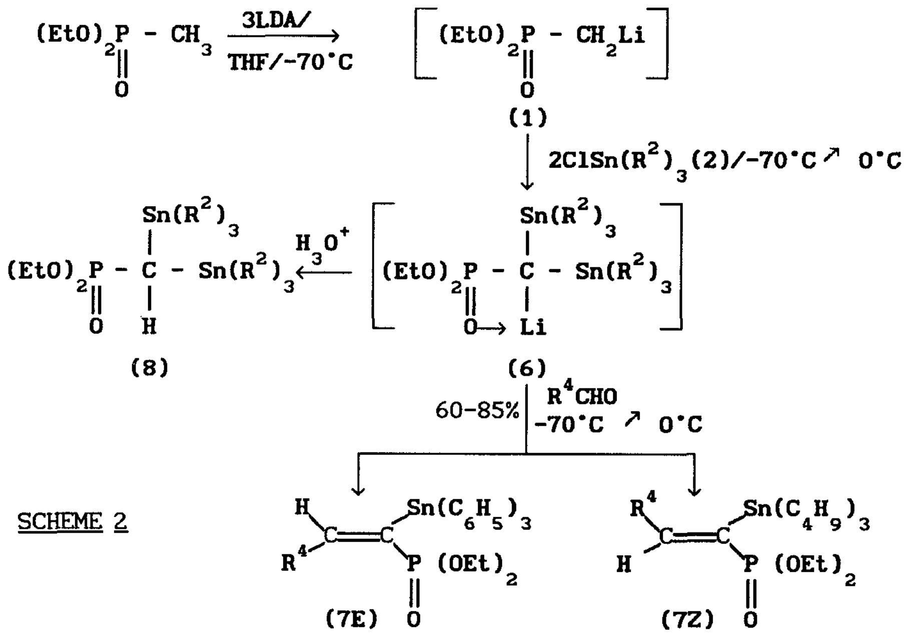
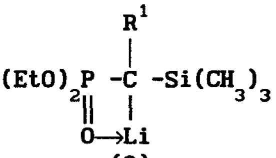


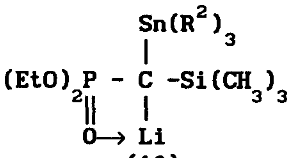
SCHEME 2

In the second step of our work we compared the carbanions **(3)** and **(6)** with the silylated derivatives **(9)** and **(10)**, prepared in the same way.



$(EtO)_2P(=O\rightarrow Li)-C(R^1)-Si(CH_3)_3$

(9)



$(EtO)_2P(=O\rightarrow Li)-C(Sn(R^2)_3)-Si(CH_3)_3$

(10)

The more oxophilic silyl group is eliminated completily at very low temperature (-70°C), to give with small stereoselectivity a mixture of (E) and (Z) isomers (**5Z/5E** < 80/20 and **7E/7Z** < 78/22)^3.

Finally we were interested in the reactivity of the stannylated compounds **(7)** and **(8)** towards electrophilic or nucleophilic reagents. The transmetalation of **(7Z)** with BuLi, at -70°C, gives the lithiated vinyl intermediate **(11)**. The reaction of **(11)** with many reagents leads stereospecifically to **(12E)**. These compounds can be easily prepared by reaction of **(7Z)** with electrophilic reagents, in carbon tetrachloride (CCl_4) at room

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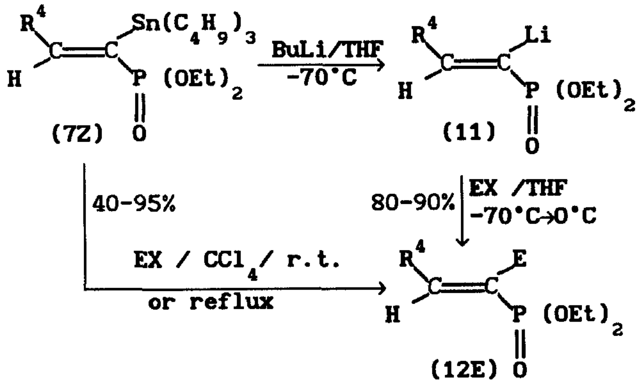
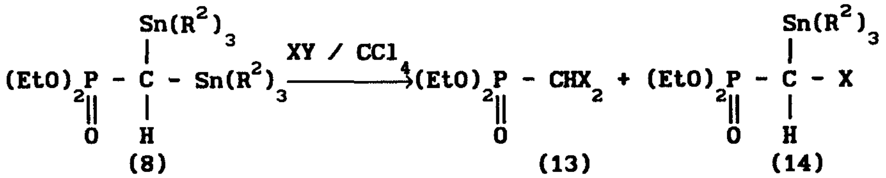
temperature or at reflux (scheme 3).

SCHEME 3



The reaction of **(8)** with many halogenated compounds in CCl_4, at room temperature, leads to the dihalogenated compounds **(13)** accompanied sometimes of small quantities of **(14)**. The formation of compounds **(14)** demonstrates that the reaction is performed in two steps (scheme 4).



$$\underset{\textbf{(8)}}{(EtO)_2\underset{O}{\underset{\|}{P}} - \overset{Sn(R^2)_3}{\overset{|}{\underset{H}{\underset{|}{C}}}} - Sn(R^2)_3} \xrightarrow{XY\ /\ CCl_4} \underset{\textbf{(13)}}{(EtO)_2\underset{O}{\underset{\|}{P}} - CHX_2} + \underset{\textbf{(14)}}{(EtO)_2\underset{O}{\underset{\|}{P}} - \overset{Sn(R^2)_3}{\overset{|}{\underset{H}{\underset{|}{C}}}} - X}$$

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