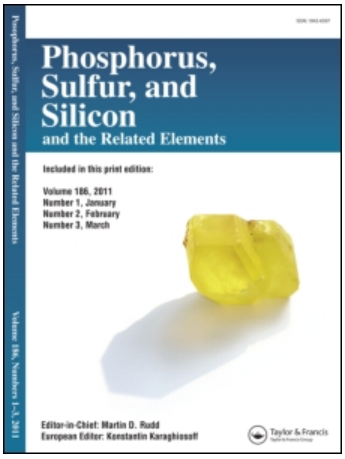

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Skowrońska, A. , Maciagiewicz, I. , Dybowski, P. , Krawczyk, E. and Owsianik, K.(1999) 'A New Synthesis of Tri- and Tetrasubstituted Olefins Based on Thio- and Selenophosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 409 — 412
To link to this Article: DOI: 10.1080/10426509908546268
URL: http://dx.doi.org/10.1080/10426509908546268

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 409-412
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A New Synthesis of Tri- and Tetrasubstituted Olefins Based on Thio- and Selenophosphates

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Stereoselective synthesis of tri- and tetrasubstituted functionalized olefins and new phosphates bearing functionalized cyclic substituent has been developed using thiophosphates and selenophosphates as key intermediates.

Keywords: trisubstituted olefins; tetrasubstituted olefins; tio- and selenophosphates

INTRODUCTION

The stereoselective synthesis of trisubstituted and tetrasubstituted alkenes is of great interest because of the wide occurrence of such compounds in natural products.[1] Changes in the stereochemistry of these alkenes may reduce or completely remove their biological activities, and so many synthetic methodologies have been developed.[2-3]

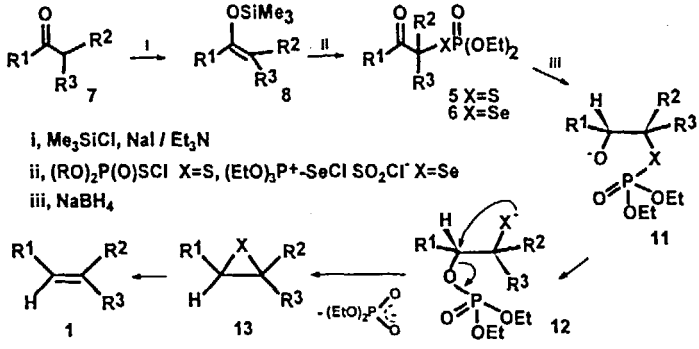
We recently reported a new strategy for stereoselective conversion of carbonyl compounds into various (Z)-olefins[4] via readily available S-(β-oxoalkyl)thiophosphates[5] and Se-(β-oxoalkyl)selenophosphates.[6]

We now report (an extension of our methodology) a stereoselective synthesis of trisubstituted alkenes **1** and functionalized tetrasubstituted alkenes **2** as well as novel phosphates **3** and **4** bearing a cyclic substituent functionalized by C(O)OEt, SH or C(O)OEt, CN and SH groups.

RESULTS AND DISCUSSION

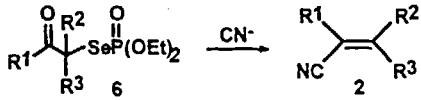
New thiophosphates **5** and selenophosphates **6** are prepared by the following procedure (Scheme 1). The appropriate ketones **7** are converted into silyl enol ethers **8**. Then addition of an excellent thiophosphorylation reagent $(RO)_2P(O)SCl$ **9**[7] gives **5** whereas addition of a selenophosphorylation agent $(EtO)_3P^+$-$SeClSO_2Cl^-$ **10**[6] gives **6**.

Compounds **9** and **10** can be readily obtained from commercially available materials and used without isolation. Treatment of **5** and **6** with $NaBH_4$ results in the formation of oxyanions **11**. The intermediate **11** undergoes rearrangement involving migration of a phosphoryl group from sulfur or selenium to oxygen, affording thiolate or selenolate anions **12**. Subsequent cyclization of **12** with elimination of phosphate anion provides episulfides or episelenides **13**. Desulfurization by triethyl phosphite or spontaneous deselenylation gives **1** in good yield (Scheme 1). The best results are obtained when the olefination reaction is performed as a "one-pot" procedure. The reaction is stereoselective when R^1 and R^2 (or R^3) are bulky substituents. But when R^1 is rather small group, the ratio of (Z)- to (E)-alkenes is 1:1 (Table 1).



Scheme 1

An analogous reaction occurs between **6** and cyanide anion (KCN / 18-6 crown ether) and provides the nitriles **2** in good yield.



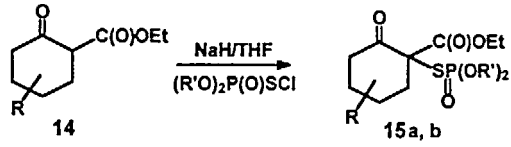
The configuration of all compounds **1** and **2** was established from ^1H, ^{13}C NMR data (and in some cases by TNDO/2 calculated ^1H NMR data) and in some cases by comparison with an authentic sample.

TABLE 1. Olefins 1 and 2 prepared from 6

	R^1	R^2	R^3	Yield of 1[a] %	Z/E ratio of 1	Yield of 2[a] %	Z/E ratio of 2
a	Ph	Me	$PhCH_2$	61	86:14	63	79:21
b	Ph	Et	$PhCH_2$	68	82:18	72	50:50
c	Ph	Me	n-C_8H_{15}	52	72:28	52	50:50
d	Ph	Me	Ph	51	76:24	-	-
e	Ph	Et	Ph	46	100:0	71	90:10
f	t-Bu	Me	n-C_5H_{11}	53	88:12	63	66:34
g	Me	n-Pr	Ph	57	50:50	-	-
h	Me	Ph	$PhCH_2$	55	55:45	53	55:45
i	PhCH=CH	Me	Et	50	62:38	60	50:50

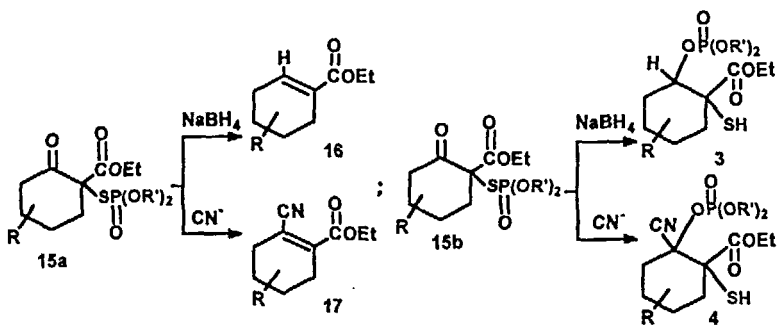
[a] No attempts were made to optimize the yields; all yields refer to pure isolated products

We have also elaborated a protocol for the synthesis of novel cyclic thiophosphates **15**. Enol anion generated from the corresponding dicarbonyl compounds **14**, and subjected to phosphorylation with $(RO)_2P(O)SCl$ at -70°C, provided **15ab** as a mixture of two diastereoisomers in a ratio (depending on substituent) between 4:1 and 3:1. The isomers can be separated by column chromatography.



R=6-Me, 5-Me, 4-Bu^t, 4-Ph R'=Et, Bu^tCH_2

The configuration of the dominating diastereoisomers of **15b** (when R=6-Me, 4-Ph) was established by X-ray analysis. In both cases the S-$P(O)(OR)_2$ substituent is situated in an axial position and the C(O)OEt substituent in an equatorial position. As we expected both selective reduction of the ketone function using $NaBH_4$ and the reaction of CN^- anion with the minor diastereoisomers **15a** proceeds smoothly giving the corresponding cyclic olefins **16** and **17**. However the same reactions with major diastereoisomers **15b** lead to the cyclic phosphates **3** and **4**.



Phosphates **3** and **4** are attractive precursors of other important functionalized cyclic systems.

In summary, we have developed a general protocol for the stereoselective synthesis of trisubstituted alkenes and functionalized tetrasubstituted alkenes as well as phosphates bearing functionalized cyclic substituent. Current activities include further refinement of this methodology.

ACKNOWLEDGMENT

This project was financially assisted by the Polish State Committee for Scientific Research (grants 3TO9A03709 and 3TO9A02915).

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