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# Phosphorus, Sulfur, and Silicon and the Related Elements

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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.<sup>1</sup> Changes in the stereochemistry of these alkenes may reduce or completely remove their biological activities, and so many synthetic methodologies have been developed.<sup>2-3</sup>

We recently reported a new strategy for stereoselective conversion of carbonyl compounds into various (Z)-olefins<sup>4</sup> via readily available S- $(\beta$ -oxoalkyl)thiophosphates<sup>5</sup> and Se- $(\beta$ -oxoalkyl)selenophosphates.<sup>6</sup>

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)<sub>2</sub>P(O)SCl 9<sup>7</sup> gives 5 whereas addition of a selenophosphorylation agent (EtO)<sub>3</sub>P<sup>+</sup>-SeClSO<sub>2</sub>Cl 10<sup>6</sup> 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<sub>4</sub> 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).



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 <sup>1</sup>H, <sup>13</sup>C NMR data (and in some cases by TNDO/2 calculated <sup>1</sup>H NMR data) and in some cases by comparison with an authentic sample.

	R <sup>1</sup>	R <sup>2</sup>	R3	Yield of 1° %	Z/E ratio of 1	Yield of 2* %	Z/E ratio of 2
a	Ph	Me	<sup>-</sup> PhCH₂	61	86:14	63	79:21
b	Ph	Et	PhCH <sub>2</sub>	68	82:18	72	50:50
c	Ph	Me	n-C8H15	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 <sub>5</sub> H <sub>11</sub>	53	88:12	63	66:34
g	Me	n-Pr	Ph	57	50:50	-	-
h	Me	Ph	PhCH <sub>2</sub>	55	55:45	53	55:45
i	PhCH=CH	Me	Et	50	62:38	60	50:50

TABLE 1. Olefins 1 and 2 prepared from 6

\* 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)<sub>2</sub>P(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-But, 4-Ph R'=Et, ButCH2

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)<sub>2</sub> 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<sub>4</sub> 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

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