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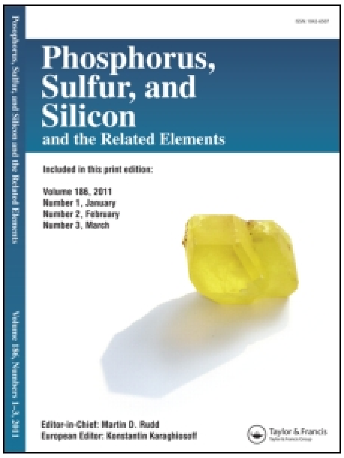

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A New Strategy for the Stereoselective Synthesis of Olefins Based on Selenophosphates

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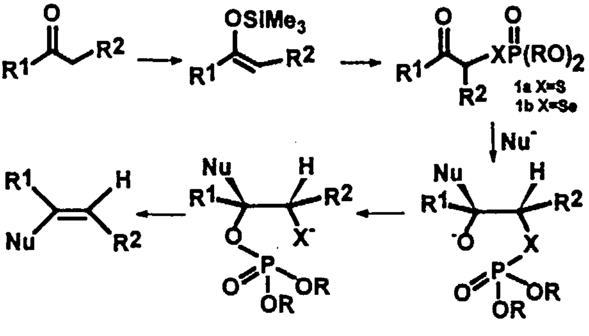
Abstract: New selenophosphates **2** containing the α,β-unsaturated carbonyl moiety have been prepared and applied as intermediates in the synthesis of novel 1,3-dienes **7** with an alkylselenosubstituent in position 1 and the diethoxyphosphoryloxy substituent in position 2. Diels-Alder reactions of dienes **7** with some dienophiles have been investigated; they are fully regio- and endo-stereospecific. The Diels-Alder cycloadducts **8** and **9** have been transformed by oxidation into the corresponding functionalized allylic alcohols **12**

Keywords: selenophosphates, 1,3-dienes, allylic alcohols.

Introduction

We have recently reported a new strategy for stereoselective conversion of ketones into Z-olefins via intermediate S-(β-oxoalkyl)thiophosphates **1a** or Se-(β-oxoalkyl)selenophosphates **1b**. The key steps in this strategy involve the formation of phosphates **1a** or **1b** and their reactions with appropriate nucleophiles.[1,5]



Scheme 1

It is noteworthy that conversion of silyl enol ethers to final products can be performed as a "one- pot reaction" and that the reactions of selenophosphates with nucleophiles in many cases are stereospecific.

It has been demonstrated that this methodology is very useful for the synthesis of Z-olefins[1] and functionalized Z-olefins such as alkenyl phosphonates,[2] vinyl phosphonates,[3] alkenyl phosphates,[3] alk-2-enenitriles[4], α-methylene cycloalkenones and α-methylene-lactones.[5]

This communication deals with further progress in the application of selenophosphates to the synthesis of unsaturated systems. Recently we showed that selenophosphates **2** containing an α,β-unsaturated carbonyl moiety are valuable intermediates because, just like their thio-analogues,[3,6,7] they can be transformed into new cyclic 1,3-dienes or functionalized cyclic allylic alcohols.

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Results and Discussion

New (E)-selenophosphates **2** can be prepared by the following procedure. The appropriate carbonyl compounds **3** are converted into O-silylated dienolates **4** by the action of Me_3SiCl, NaI in the presence of Et_3N. Then fully chemoselective addition of the excellent selenophosphorylating agent chloroselenotriethoxyphosphonium chlorosulfide $(EtO)_3P^+$-SeCl SO_2Cl^- to **4** afforded **2**. Selenophosphates **2** are convenient intermediates in the synthesis of new 1,3-dienes **7** containing an alkylseleno substituent in position 1 and the diethoxyphosphoryloxy substituent in position 2. Treatment of **2** with sodium hydride gives the enolate anion **5**, which undergoes rearrangement involving migration of the phosphoryl group from selenium to oxygen, affording the selenolate anion **6**. Then **6** reacts with alkyl halides producing the 1,3-dienes **7**. This synthesis performed as a "one-flask procedure" is stereospecific giving new enol phosphates **7** having Z-oriented R^2Se and $(EtO)_2P(O)O$ substituents.

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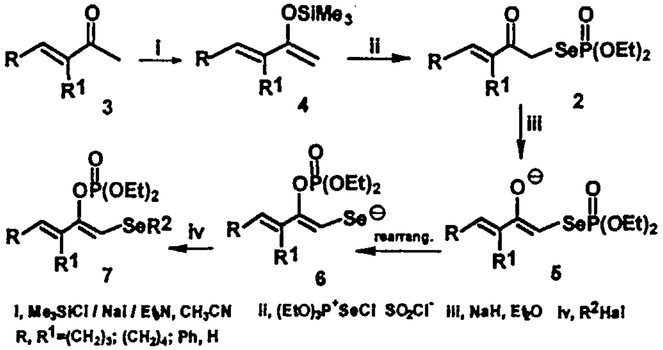
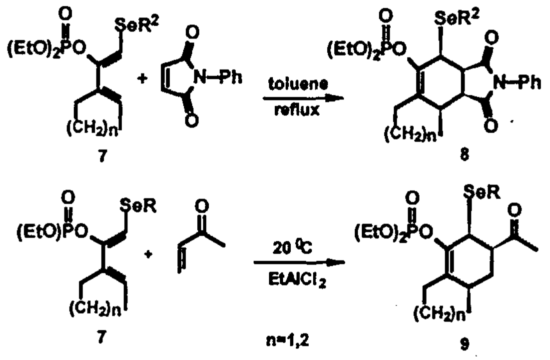


Scheme 2

We have established the Z configuration on the basis of characteristic values (≥ 1 Hz) of the $^4J_{PH}$ coupling constant.

Cycloadditions of the dienes 7 with selected dienophiles occur either in toluene solution under reflux or with Lewis acid catalysis. We have found that these reactions are fully regio- and endo-stereospecific producing the corresponding cycloadducts 8 and 9, in which the functional group of the dienophiles is oriented "ortho" to the selenium substituent of the dienes.

Some representative examples of the Diels-Alder reactions are outlined in Scheme 3.



Scheme 3

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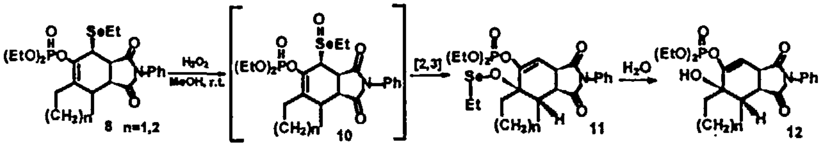
On the basis of our results and others reported in the literature[8] it can be concluded, that the regiochemistry of the Diels-Alder reactions of our dienes 7 is fully controlled by the selenium atom.

Cycloadducts 8 are transformed by oxidation into novel cyclic functionalized allylic alcohols. Treatment of 8 with hydrogen peroxide in methanol at room temperature gives the intermediate allyl selenoxides 10, which display fast [2,3]-sigmatropic rearrangement to the allyl selenates 11. Hydrolysis of the latter afforded only the trans isomer of the corresponding allylic alcohols 12 (Scheme 4).



Scheme 4

In the case of cycloadducts 9, however, sigmatropic rearrangement is accompanied by elimination giving new 1,3-dienes.

The structure and configuration of the new cycloadducts, allylic alcohols and the 1,3-dienes were determined on the basis of ^1H, ^{13}C, ^{31}P NMR, high resolution MS data and in some cases by X-ray data.

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CHIRAL DIFERROCENYL DICHALCOGENIDES IN ASYMMETRIC SYNTHESIS

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Our recent studies on asymmetric synthesis using chiral organochalcogen (S, Se, Te) compounds are presented. A variety of chiral diferrocenyl dichalcogenides have been newly prepared, some of which being employed as reagents for new asymmetric reactions such as selenoxide elimination, [2,3]sigmatropic rearrangement of chiral selenoxides, selenimides and tellurimides, and intramolecular selenenylation of alkenes. These dichalcogenides, as well as several newly prepared chiral ferrocenyl monochalcogenides, also act as chiral ligands in the rhodium- and iridium-catalyzed asymmetric hydrosilylation and transfer hydrogenation of ketones.

KEYWORDS: selenoxide, selenimide, tellurimide, chiral diferrocenyl dichalcogenide, chiral ligand, hydrosilylation

1. INTRODUCTION

A variety of characteristic and useful organic reactions using organochalcogen (S, Se, Te) compounds have been revealed, but their application to asymmetric organic synthesis is still undeveloped especially in the cases of Se and Te. We are interested in the