Polish J. Chem., **75**, 1121–1135 (2001)

REVIEW ARTICLE

Thiophosphates and Selenophosphates as Tools in the Construction of Carbon–Carbon Double Bond*

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(Received February 13th, 2001)

Efficient new methodology of regio- and stereoselective synthesis of a variety of functionalized mono- and polycyclic compounds based on thio- and selenophosphates is reported. The representative examples of these compounds are: vinyl thiiranes, conjugated dienes, cycloadducts, α,β-unsaturated carbonyl compounds, allylic alcohols, α-hydroxy ketones and aromatic compounds.

Key words: thiophosphates, selenophosphates, 1,3-dienes, rearrangements, cyclic enones, allylic alcohols, α-hydroxy ketones, aromatic compounds

Introduction

The carbon–carbon double bond is one of the most important functional groups in organic chemistry. Although numerous synthetic routes to alkenes are known, there is still a need to develop further methods of stereoselective synthesis. Contribution of phosphorus reagents, which have been designed to perform the synthesis of simple and complex alkenes, is very significant. The most important role in the conversion of carbonyl compounds into unsaturated ones is played by the Wittig reaction utilizing phosphonium ylides [1] and the Horner-Wadsworth-Emmons modification exploiting phosphonates [2]. Thiophosphates are also useful in organic synthesis, particularly as reagents for the introduction of sulfur atom [3–5]. However, they have been rarely used in synthesis of unsaturated compounds. Like to Wittig-Horner reagents, stabilized phosphorothiolate carboanions derived from thiolophosphates react with carbonyl derivatives to give the corresponding α,β-unsaturated esters [6–8]. Functionalized enol phosphates have been prepared from thiolophosphates *via* a β-hydroxyphosphorothiolate-β-mercaptophosphate rearrangement [9,10].

Some years ago we become interested in chemistry of thio- and selenophosphates of the following general formulae:

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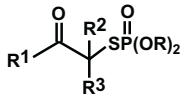
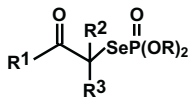
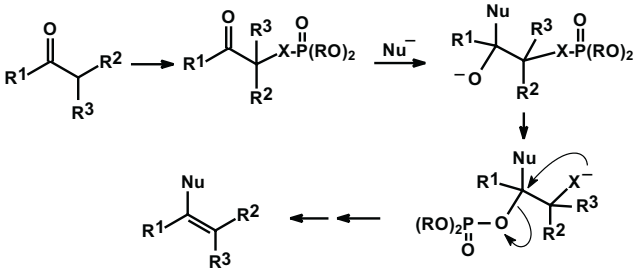
* Dedicated to Prof. Jan Michalski on the occasion of his 80th birthday.
** Author for correspondence.

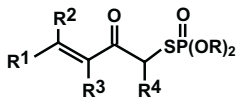
These readily available S-(β-oxoalkyl)thiophosphates [11] and Se-(β-oxoalkyl)-selenophosphates [12] are the key intermediates in our strategy for the stereoselective conversion of carbonyl compounds into alkenes [13] (Scheme 1). Consequently, we began to shift the emphasis of our study to their synthetic applications.

Scheme 1



Our methodology has proven useful in the synthesis of a variety of di- [13,14], tri- and tetrasubstituted [15] olefins, di- [16] and tri- [15] substituted alkenyl cyanides, vinylphosphonates [17], alkenyl phosphonates [18], alkenyl phosphates [19], α-methylene cycloalkanones and α-methylene lactones [20,21], and conjugated enynes [22].

Pushing the scope of our approach further, we look at intermediate thiophosphates **1** and selenophosphates **2** containing an α,β-unsaturated carbonyl moiety [12,23].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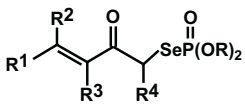
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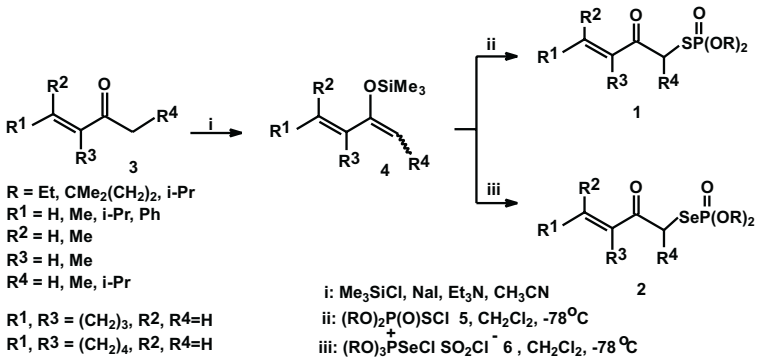
This paper focuses on phosphates **1** and **2** as valuable synthetic intermediates in the preparation of substituted vinyl-thiiranes [24] and diversely substituted conjugated dienes including 2-cyano-1,3-dienes [24] as well as the new (Z)-1,2-heterosubstituted 1,3-dienes containing alkylthio(acylthio, dialkoxyphosphorylthio) substituent in position 1 and a dialkoxyphosphoryl substituent in position 2 [25]. We show that these new dienes are precursors of important organic compounds: new cyclic conjugated dienes, aromatic compounds, cyclic and polycyclic allylic alcohols and α-hydroxy ketones.

Synthesis of thiophosphate and selenophosphate intermediates

We initiated our studies in this field by elaboration of a general synthesis of phosphates **1** and **2**. These compounds were prepared in a two step procedure from appropriate α,β-unsaturated carbonyl compounds in high yield. The corresponding ketones **3** are converted into O-silylated dienolates **4** using trimethylsilyl chloride in the presence of sodium iodide and triethylamine in acetonitrile solution. The stereochemistry of **4** is the same as that of the starting ketones **3**. Then addition of phosphorus S-electrophile diethoxyoxophosphoranesulphenyl chloride $(EtO)_2P(O)SCl$ **5** and Se-electrophile chloroselenotriethoxyphosphonium chlorosulfide $(EtO)_3P^+$–SeCl SO_2Cl^- **6** to **4** afforded compounds **1** and **2** respectively [23] (Scheme 2). Compounds **5** and **6** can be readily prepared from commercial materials and used without isolation [12,26].

Scheme 2



In all cases thiophosphorylation and selenophosphorylation of O-silylated dienolates **4** is fully chemoselective. Dienolates **4** undoubtedly react with electrophiles at C-1 giving the compounds **1** and **2**, in which the thio- and selenophosphate groups are situated β to the carbonyl function. Thiophosphorylation and selenophosphorylation is also stereoselective. In fact, the stereochemistry of dienolates is fully preserved in the final products [23].

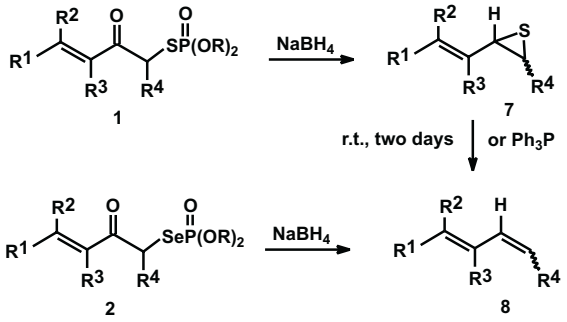
Synthetic applications of intermediate phosphates 1 and 2

1. Synthesis of vinyl thiiranes and conjugated dienes

Thiiranes are an important class of cyclic sulfides from both synthetic and theoretical points of view. Although numerous synthetic routes to thiiranes are known [27–30], only a few examples of the preparation of vinyl thiiranes have been published so far [31–33]. The synthesis of dienes in general, and for application in the Diels-Alder reaction in particular, is still an important synthetic challenge [34–36]. This situation prompted us to develop methodology for a general and efficient synthesis of vinyl-thiiranes and 1,3-dienes.

Selective reduction of thiophosphates **1** using $NaBH_4$ proceeds smoothly at r.t. giving vinyl-thiiranes in almost quantitative yield according to NMR. The configuration of the unsaturated bond of the intermediate thiophosphate **1** is preserved in thiiranes **7** (Scheme 3).

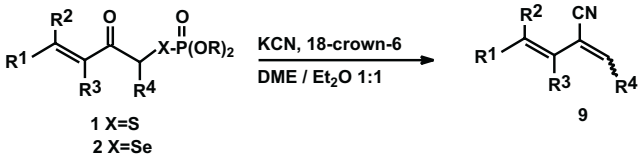
Scheme 3



Thiiranes **7** are readily and efficiently converted into the corresponding substituted conjugated dienes **8** [24] (Scheme 3). They lose sulfur gradually over two days at room temperature to provide conjugated dienes **8**, in which the new unsaturated bond has predominantly, or even exclusively, the E-configuration. However, desulfurization of **7** by the action of triphenylphosphine is stereospecific and proceeds with retention of configuration [37], providing a new unsaturated bond predominantly of Z-configuration. The same dienes **8** were obtained by reduction of selenophosphates **2** using $NaBH_4$ (Scheme 3) [23].

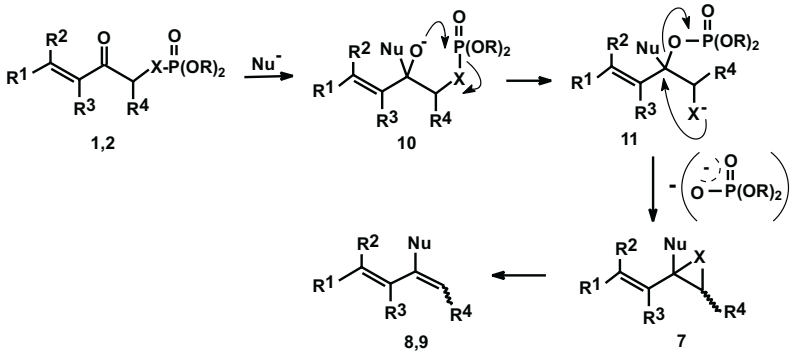
The thiophosphates **1** and selenophosphates **2** also react selectively with cyanide anion (KCN in the presence of 18-crown-6 as catalyst) to give dienes **9** containing a cyanide function (Scheme 4). The yield is good [23].

Scheme 4



Transformation of thiophosphates **1** and selenophosphates **2** into vinyl-thiiranes **7** and dienes **8** and **9** is presented in Scheme 5. The reaction of phosphates **1** and **2** with nucleophiles results in the formation of diastereoisomeric oxyanions **10** in unequal proportions. The intermediate anions rearrange with migration of a phosphoryl group from sulfur (selenium) to oxygen affording thiolate (selenolate) anions **11**. Subsequent cyclization *via* nucleophilic attack at carbon with elimination of phosphate anion gives thiiranes **7** (episelenides), which lose sulfur (selenium) to provide conjugated dienes **8** and **9**. Best results were obtained when conversion of O-silylated

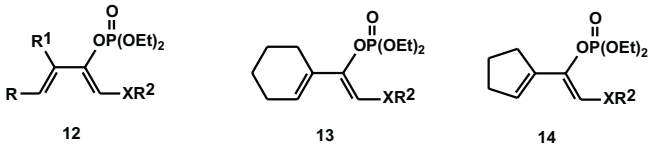
Scheme 5



dienolates into final vinyl-thiiranes **7** and conjugated dienes **8** and **9** was performed as a ''one pot" procedure.

2. Synthesis of 1,2-diheterosubstituted-1,3-butadienes and their Diels-Alder reactions

The introduction of hetero substituents into dienes permits regiocontrolled synthesis of a great variety of highly functionalized cyclohexenones [38]. PhS as a substituent in dienes is even more powerful than RO in determining the orientation of the Diels-Alder reaction [39–42]. On the other hand, 2-dialkoxyphosphoryloxy-1,3-butadiene and its adducts have been found to be unusually stable under the acidic conditions of Lewis acid catalyzed Diels-Alder reactions, when compared with other oxygen substituted dienes containing alkoxy or silyloxy functionalities [43]. Instability of the latter is sometimes a serious problem in these reactions as well as in further transformation of the adducts.

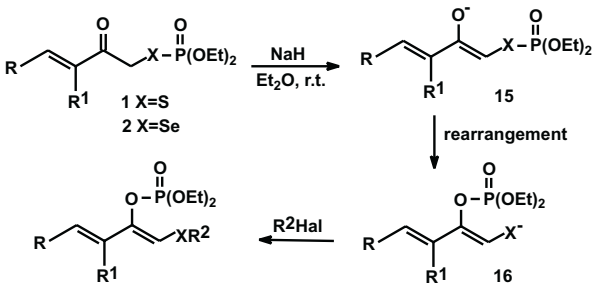


The synthesis of novel dienes **12**, **13** and **14** containing both an alkylthio (acylthio, dialkoxythiophosphoryl- or diphenoxythiophosphoryl-) substituent in position 1 and a diethoxyphosphoryl substituent in position 2 have been elaborated [44] (Scheme 6).

Treatment of readily available thiophosphates **1** or selenophosphates **2** with NaH results in the formation of their enolate anions **15**. The intermediates **15** undergo rearrangement involving migration of a phosphoryl group from sulfur (selenium) to oxygen affording thiolates (selenolates) **16**. The latter react very readily with a number of electrophiles producing desired dienes **12**, **13** and **14** in high yield. All the new enol phosphates have Z-oriented R^2S (R^2Se) and $(EtO)_2P(O)O$ substituents.

Cycloaddition of dienes **12**, **13** and **14** to a variety of dienophiles either in toluene solution at reflux or under Lewis acid catalysis, $EtAlCl_2$, $ZnBr_2$, $LiClO_4$, produce the

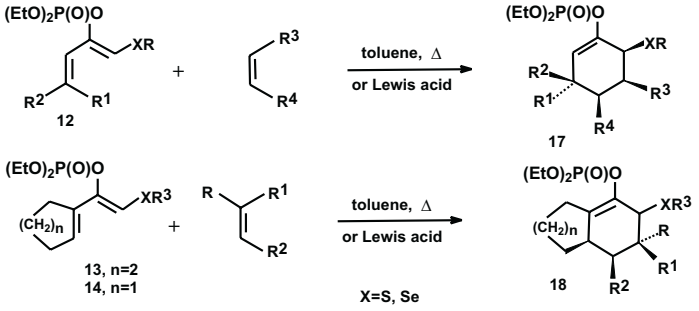
Scheme 6



12 R = H, Ph, Me R^1 = H, Me
R^2 = Me, Et, i-Pr, MeC(O), t-BuC(O), $(PhO)_2P(O)$, $(PhO)_2P(S)$
13 R and R^1 = $(CH_2)_4$
R^2 = Me, Et, i-Pr, MeC(O), $(PhO)_2P(O)$, $(PhO)_2P(S)$
14 R and R^1 = $(CH_2)_3$
R^2 = Me, Et, i-Pr, MeC(O), $(PhO)_2P(O)$

corresponding adducts in good yield [45,46]. All the cycloadditions studied provide adducts with complete regio- and (endo)-stereoselectivity. In every case the functional group of the dienophile is oriented "ortho" to the sulfur (selenium) substituent of the diene. Representative examples of cycloadducts are shown in Scheme 7.

Scheme 7



17a; R=P(O)(OPh)$_2$, R^1=H, R^2=Ph R^3 R^4= 

17b; R=C(O)R' R'=Me, $PhCH_2$, t-Bu, R^1=H, R^2=Ph R^3 R^4= 

17c; R=Me, R^1=Me, R^2=Me R^3 R^4= 

17d; R=Me, R^1=Me, R^2=Me
R^3=C(O)Et R^4=H

18a; R=H, R^1=CN, R^2=H
18b; R=H, R^1=C(O)Me, R^2=H
18c; R=H, R^1=CO_2Et, R^2=H
18d; R=H, R^1=CH_2OH, R^2=H
18e; R=Me, R^1=CH_2OH, R^2=H
18f; R=H, R^1=CN, R^2=CN

18g; R=H, R^1 R^2= 

18h; R=H, R^1 R^2= 

18i; R=H, R^1 R^2=  X=Se n=1

18j; R=H, R^1 R^2=  X=Se n=2

18k; R=H, R^1 R^2= 

18l; R=H, R^1=CO_2Me, R^2=CO_2Me

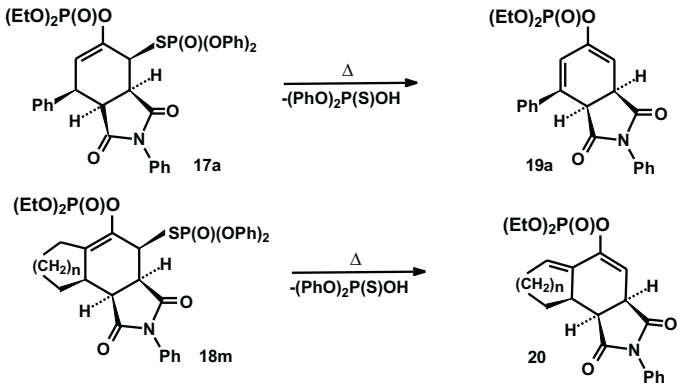
The regiochemistry of the cycloaddition is mainly controlled by the sulfur (selenium) substituent. Regiocontrol by the phenylthio group has been observed in Diels-Alder reactions of several alkoxy- and acyloxyphenylthiobutadienes [40–42]. The structure and configuration of the adducts were determined on the basis of ^{1}H (including COSY experiments), ^{13}C, ^{31}P, IR and high resolution MS data and in some cases by comparison of TNDO/2 simulated and experimental spectra.

The resulting adducts are valuable synthetic intermediates, as the sulfide (selenide) moiety and a phosphoryl group can be eliminated in different ways to afford important new cyclic and bicyclic dienes [47,48], aromatic compounds [47,48], polycyclic allylic alcohols [48] and α-hydroxy ketones [48].

3. Synthesis of novel functionalized cyclic and bicyclic conjugated dienes

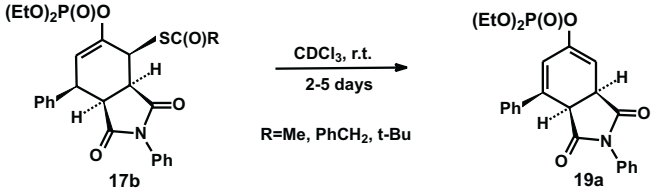
Adducts **17a** and **18m** containing an excellent leaving group like $(PhO)_2P(O)S$ are unstable under conditions of cycloaddition. They undergo spontaneous elimination of diphenylthiophosphoric acid to produce new 1,3-dienes **19a** and **20**:

Scheme 8



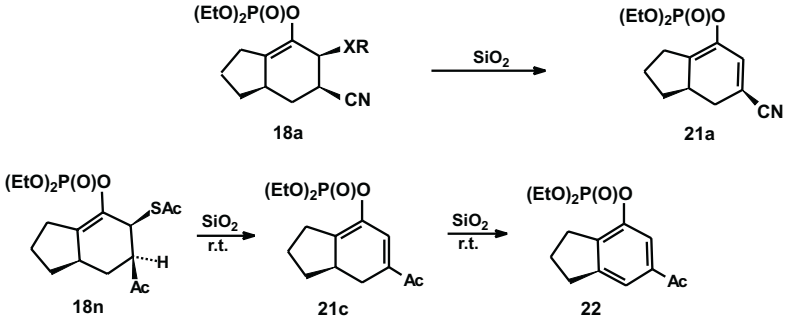
The adducts **17b** containing a thioacyl group are converted in $CDCl_3$ solution into 1,3-diene **19a** at r.t. after a few days.

Scheme 9



An efficient way to catalyze elimination of the sulfur (selenium) substituent is to deposit adducts **18a**, **18n** in CCl_4/AcOEt 5:1 solution on silica gel at r. t. overnight.

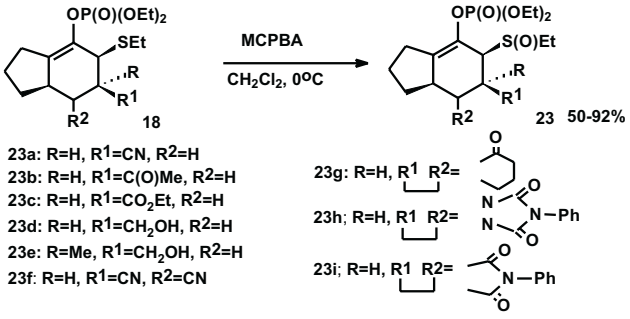
Scheme 10



In the last case after a further 12 hours exposure on silica gel the 1,3-diene **21c** aromatizes to compound **22**.

Oxidation of the cycloadducts with one equivalent of m-chloroperbenzoic acid (MCPBA) at 0°C in dichloromethane affords the sulfoxides **23** in good to high yields. According to ^{1}H NMR data sulfoxides **23a**,**c**,**d**,**f** were formed as mixtures of two diastereoisomers in 1.6:1, 1:1, 1.5:1 and 2.2:1 ratios respectively. It was not possible to separate diastereoisomers using chromatography. However, formation of a single diastereoisomer was observed in the case of sulfoxides **23b**,**c**,**g**,**h**,**i** [48]. The structure of the sulfoxides **23** employed in this study is shown below (Scheme 11).

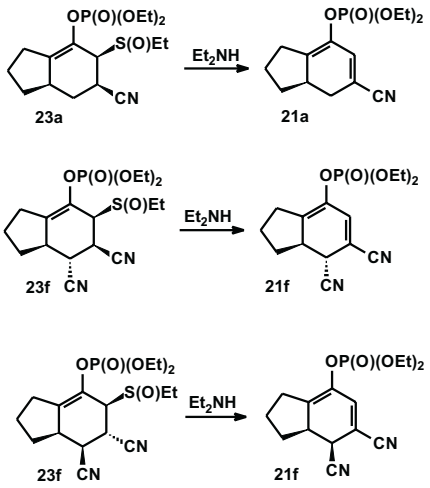
Scheme 11



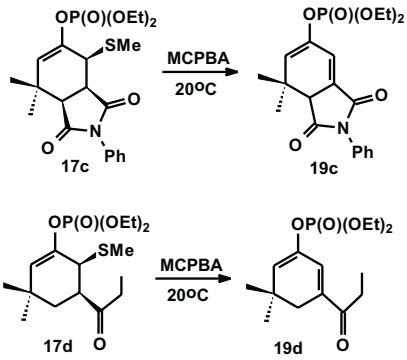
Sulfoxides **23a** and **23f** have a quite acidic hydrogen in the β-position to the sulfoxide leaving group and in the presence of diethylamine provide the new bicyclic conjugated dienes **21a** and **21f** in good yield (Scheme 12).

Oxidation of cycloadducts **17c** and **17d** with MCPBA also provides the cyclic conjugated dienes **19c** and **19d** (Scheme 13).

Scheme 12



Scheme 13

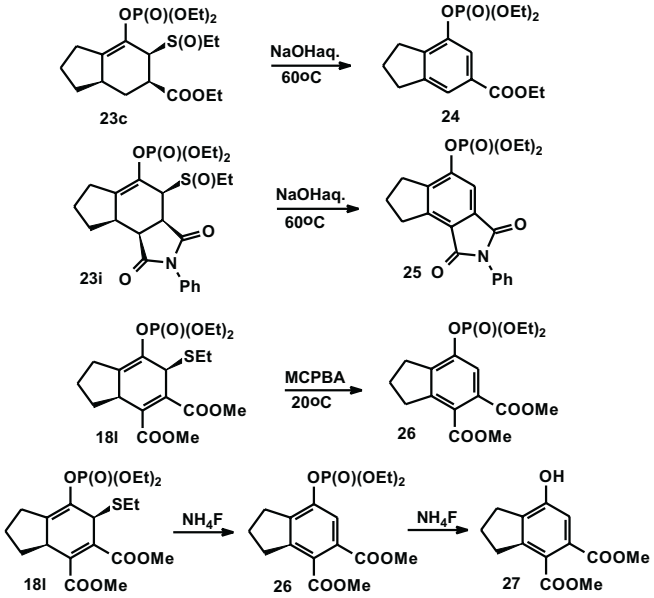


Novel aromatic compounds are obtained in the following manner: from the sulfoxides **23c** and **23i** by their treatment with an aq. solution of NaOH at 60°C; from the adduct **18l** by the action of MCPBA or of ammonium fluoride. Transformation of aromatic compounds **24**, **25** and **26** into their aromatic hydroxy derivatives proceeds very efficiently *via* a dephosphorylation reaction using ammonium fluoride (see Scheme 14).

4. Synthesis of bi- and polycyclic allylic alcohols and α-hydroxyketones

Allylic alcohols and α-hydroxy ketones are key structural "sub-units" of natural products and valuable synthetic intermediates [49,50]. As a consequence many methods have been devised for their preparation [51,52]. Surprisingly, many fewer syntheses of bicyclic and polycyclic allylic alcohols and α-hydroxy ketones have been reported [53–57]. The cycloadducts **17** and **18** are also very attractive reagents, *via* oxidation reaction, in stereospecific synthesis of bicyclic and polycyclic allylic alco-

Scheme 14



hols and α-hydroxy ketones. It is well known that the [2,3] sigmatropic rearrangement of allylic sulfoxides and allylic selenoxides leads to allylic alcohols [58,60].

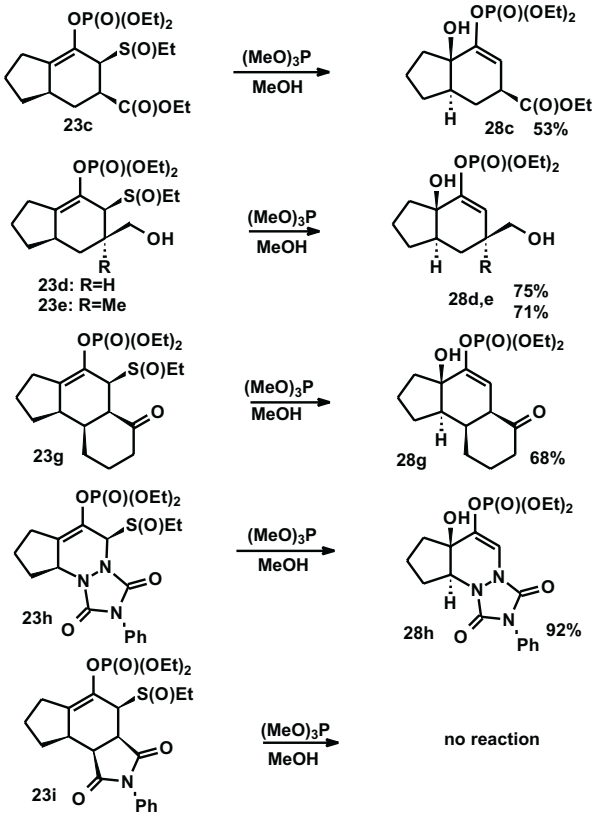
The [2,3] sigmatropic rearrangement of sulfoxides **23c**,**d**,**e**,**g**,**h**,**i** performed in the presence of excess trimethyl phosphite in methanol at r.t. led stereospecifically to the corresponding new functionalized bi- or tricyclic allylic alcohols **28** in good yield [48] (Scheme 15).

However, sulfoxides **23a**,**b** undergo competitive elimination under the same reaction conditions leading to conjugated dienes **21a**,**b**. The ratio of allylic alcohols and dienes is about 2:1. The main factor governing elimination is the high acidity of hydrogen in the β-position to an excellent sulfoxide leaving group. We have found a dramatic solvent effect favoring selective [2,3] sigmatropic rearrangement; the same sulfoxides **23a**,**b** rearranged in benzene instead of methanol, produced much more of the allylic alcohols **28a**,**b** (*via* a [2,3] sigmatropic rearrangement) than of the conjugated dienes **21a**,**b** (ratio 5:1 instead of 2:1) (Scheme 16). The mixture of products can be easily separated using silica gel column chromatography.

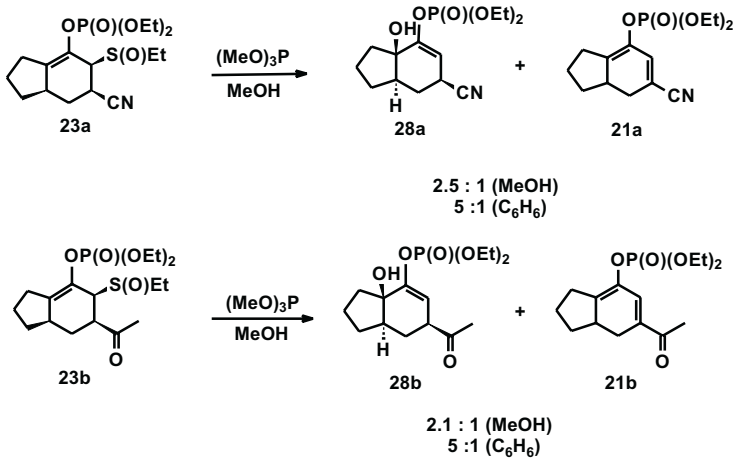
Selenoxides analogues of sulfoxides **23a**,**b** are derived from the corresponding cycloadducts. When treated with excess H_2O_2 in the presence of pyridine at –30°, they afforded nearly the same ratio of allylic alcohols **28a**,**b** and conjugated dienes **21a**,**b** *via* intermediate allylic selenoxides.

In contrast to the sulfoxide **23i** analogues, selenoxides obtained *via* oxidation of cycloadducts **18i** and **18j** easily undergo [2,3] sigmatropic rearrangement giving the tricyclic allylic alcohols **28i** and **28j** stereospecifically (Scheme 17).

Scheme 15

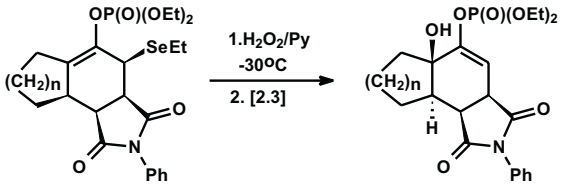


Scheme 16



In all cases presented here [2,3] sigmatropic rearrangement of sulfoxides and selenoxides is stereospecific, giving trans isomers. Trans-fusion of the bicyclic skele-

Scheme 17



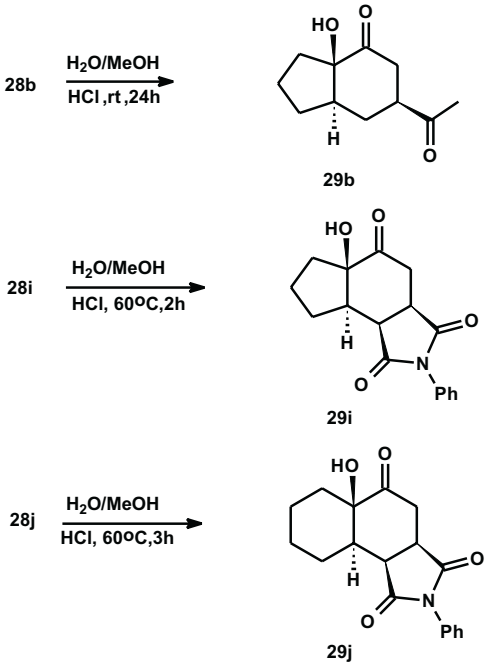
18i: n = 1
18j: n = 2

28i
28j

ton of allylic alcohols is strongly supported by ^{13}C, ^{1}H NMR and X-ray analysis of the alcohols **28i** and **28h** [48].

Allylic alcohols **28** are useful precursors of the sterically defined novel functionalized bi- and tricyclic α-hydroxy ketones. Although a number of different chemical transformations of enol phosphates have been reported [61] there is no efficient method for their dephosphorylation. We have found that dephosphorylation of **28** using acid catalyzed hydrolysis (10% HCl) gave the α-hydroxy ketones **29b**,**i**,**j** in good to moderate yield (Scheme 18).

Scheme 18



29b

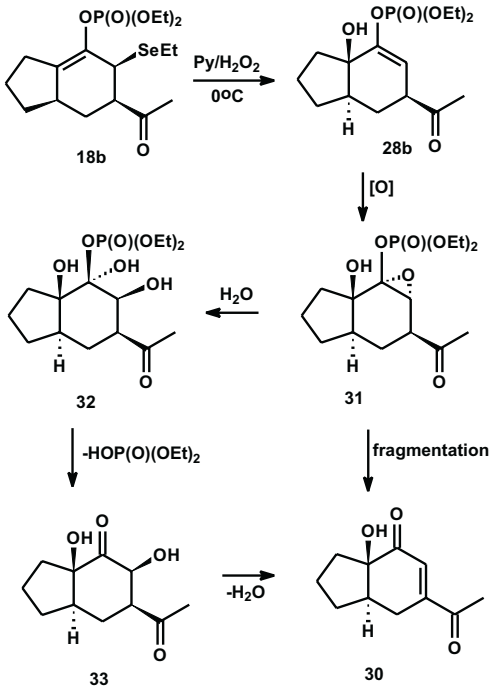
29i

29j

We also found a new route for the conversion of allylic alcohols **28** to α-hydroxy ketones **30** *via* an unusual specific elimination (Scheme 19). For example, oxidation of the selenide **18b** using excess H_2O_2 in the presence of pyridine afforded the epoxy enol phosphate **31** stereospecifically *via* alcohol **28b**. **31** decomposes under reaction conditions to ketone **30**.

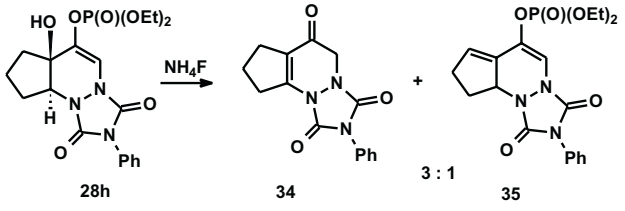
There are two possible ways in which formation of **30** could be accounted for. First, **30** could be formed by fragmentation. Second, epoxide **31** in the presence of traces of water undergoes hydrolysis catalyzed by base giving the intermediate triol **32**. Following elimination of diethyl phosphoric acid from **32** affords dihydroxy ketone **33**. Elimination of water from the latter gives the final product **30** (Scheme 19).

Scheme 19



It is well known that fluoride anion is a strong base but also an excellent nucleophile towards the phosphoryl phosphorus atom. Reaction of allylic alcohols **28h** with ammonium fluoride produces a mixture of **34** and **35** in the ratio 3:1. These compounds were separated using silica gel column chromatography.

Scheme 20



Elimination of water and dephosphorylation gives tricyclic alkenone **34**, whereas elimination of water with participation of another hydrogen atom leads to the formation of the new conjugated diene **35**.

All reactions presented here can be performed as a "one-pot'' procedure starting from O-silylated dienolates **4**.

Conclusions

Thiophosphates **1** and selenophosphates **2** are very useful intermediates in the conversion of carbonyl compounds into different thiiranes and unsaturated compounds. They are also readily available from commercial products. In this review, we have demonstrated that they provide simple routes to novel vinyl thiiranes, cyclic conjugated dienes, aromatic compounds, bi- and polycyclic allylic alcohols and α-hydroxy ketones.

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