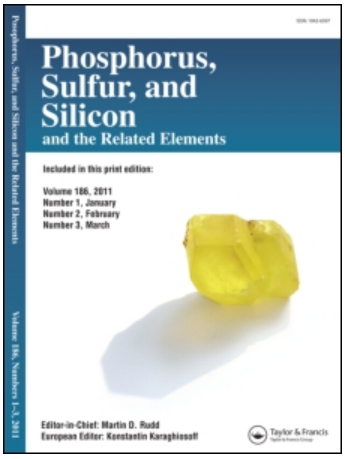

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Ketothiolo- and Ketoselenolophosphates as Efficient Reagents in Organic Synthesis

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KETOTHIOLO- AND KETOSELENOLOPHOSPHATES AS EFFICIENT REAGENTS IN ORGANIC SYNTHESIS

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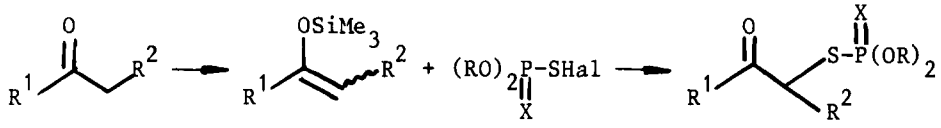
Abstract Novel general routes to thiolophosphates 1 and selenophosphates 2 and their application to regio- and stereoselective synthesis of olefins, functionalized olefins and heterofunctionalized dienes-1,3 is described.

Although ketothiolophosphates were described a long time ago,[1] little information is available about their use in organic synthesis.[2]

In an extention of our work on the application of organophosphorus compounds in organic synthesis, we have recently been looking at the chemistry of aldehydo- and ketothiolophosphates 1, as well as ketoselenolophosphates 2.

Here are the results of our studies on the preparation and synthetic utility of compounds 1 and 2.

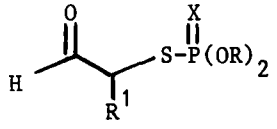
First we prepared a variety of compounds 1 and 2 in order that we might later investigate fully their synthetic possibilities. We elaborated a novel general synthesis of acyclic and cyclic thiolophosphates 1 based on the reaction of silyl enol ethers 3 with oxo-(thioxo)phosphorane sulphenyl halides $(RO)_2P(X)SHal$ 4. The choice of 3 and 4 is quite significant; there are several simple methods by which different kinds of silyl enol ethers 3 may be prepared, and 4 are both readily accessible and among the best reagents for introduction of the thiophosphoryl function into organic compounds.



3 4 1 + Me_3SiHal

X = O,S; Hal = Cl,Br

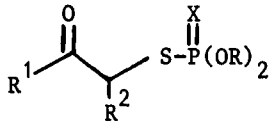
The reaction of 3 and 4 is regioselective, and stereoselective in the case of a cyclic rigid structure; it leads to 1 in excellent yields. The reaction is also broad in its application; using it we prepared thiolophosphates 1a-d.



1a

R = alkyl X = O,S

R^1= H, alkyl

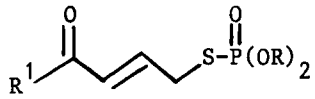


1b

R = alkyl X = O,S

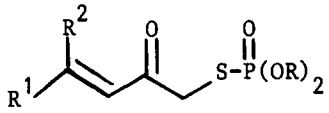
R^1= alkyl, aryl R^2= H, alkyl, aryl

R^1,R^2= $-(CH_2)_n-$ n = 3,4



1c

R = alkyl R^1= H



1d

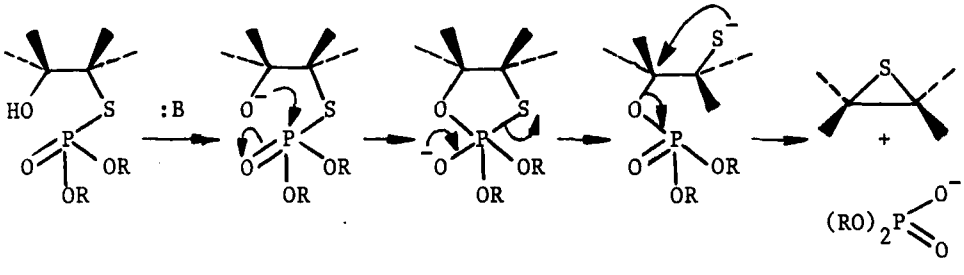
R = alkyl R^1= H, alkyl, aryl

R^2= H, alkyl

In a similar manner we have synthesized ketoselenophosphates 2, the seleno analogues of 1b.

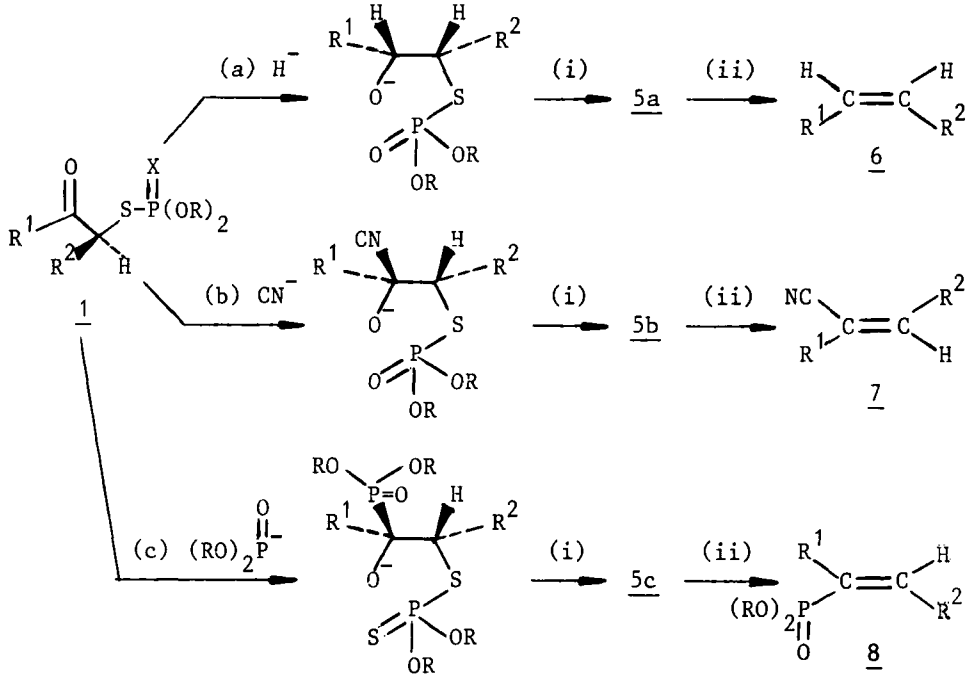
Having succesfully prepared thiolophosphates 1a-d and selenolophosphates 2, we turned to their synthetic application.

Our general synthetic strategy was based on three important features of 1 and 2: a) the presence of an excellent leaving group; b) the presence of a carbonyl function in the α-position to a chiral centre; c) an ability to undergo rearrangement involving migration of a phosphoryl group from sulphur to oxygen.[2] The mechanism of a similar rearrangement of alcohols having a thiolophosphoryl group in the vic-position has been recently elucidated[3] (Scheme I).



Scheme I

We have shown that reactions of 1 with nucleophilic reagents such as $NaBH_4$, Me_3SiCN, KCN (in the presence of 18-crown ether) and R_2PONa $(RO)_2PONa$ are regio- and stereoselective, and proceed at ambient temperature to episulphides 5 in excellent yield. 5 have been readily converted into the corresponding olefins 6 and functionalized olefins 7 and 8 (Scheme II). Z-olefins 6, 7 and 8 are formed predominantly (75-95%). The transformations (a), (b) and (c) shown in Scheme II can be one-pot reactions.

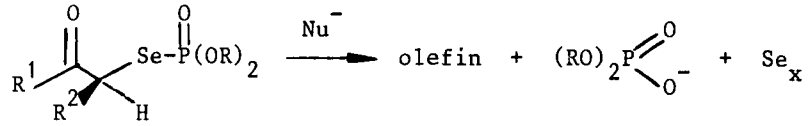


(i) rearrangement (see Scheme I)

(ii) Ph_3P or $(EtO)_3P$

Scheme II

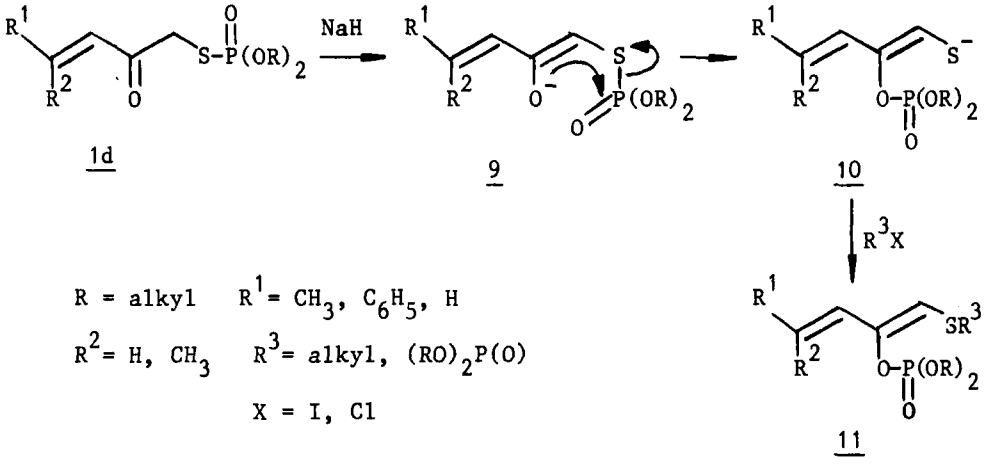
The reactions of ketoselenolophosphates 2 with the same nucleophiles proceed under very mild conditions giving almost exclusively (90-100%) Z-olefins 6 and functionalized Z-olefins 7 and 8, both cleanly and quantitatively.



Nu = H, CN, $(RO)_2P(O)$

The formation of episulphides 5a,b,c and the configurations of the final olefins have been established on the basis of ^{31}P, ^{1}H, ^{13}C NMR data.

Reaction of ketothiolophosphates 1d with sodium hydride produces an enolate anion 9, which rearranges to anion 10. Alkylation or phosphorylation of 10 gives new heterofunctionalized dienes-1,3 11 (Scheme III). From 11 [4+2] adducts with diethyl fumarate are obtained.



1d 9 10 11

Scheme III

The transformations of Scheme III constitute a novel, simple and efficient route to new heterosubstituted dienes-1,3.

In conclusion, we have presented a new strategy for regio- and stereoselective conversion of ketones into olefins and functionalized olefins, via intermediate ketothiolophosphates 1 and ketoselenolophosphates 2 and into heterofunctionalized dienes-1,3 via intermediates 1.

Our main aim as we continue this work is to determine the scope of application of this strategy in organic synthesis.

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