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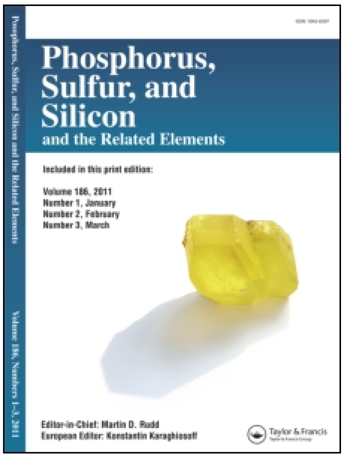

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A NEW STRATEGY FOR THE STEREOSELECTIVE SYNTHESIS OF OLEFINS. RECENT DEVELOPMENTS

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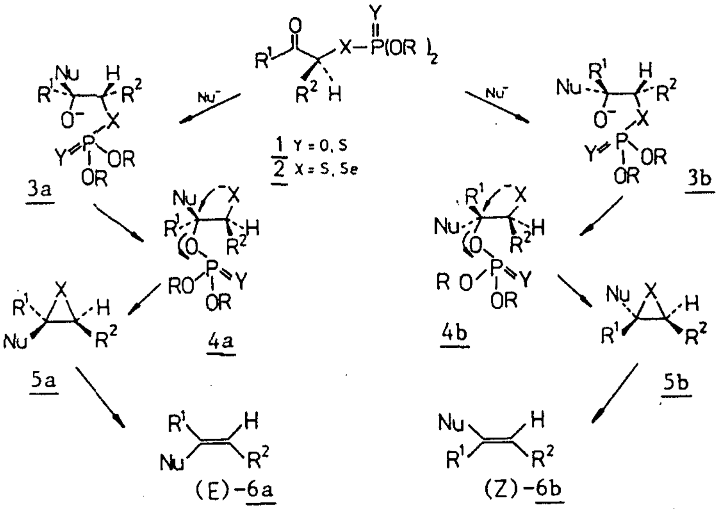
Abstract Stereoselective synthesis of a number of various olefins including functionalized unsaturated compounds based on the S-(β-oxoalkyl) thiophosphates and Se-(β-oxoalkyl) selenophosphates is described.

We have recently reported a new strategy for highly stereoselective conversion of ketones into Z-olefins via S-(β-oxoalkyl) thiophosphates 1 and Se-(β-oxoalkyl) selenophosphates 2.[1] The reaction sequence illustrating this strategy is outlined in Scheme 1.

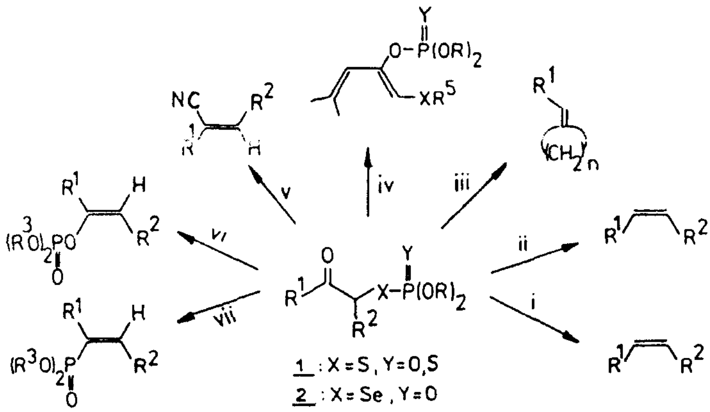


Scheme 1

Silyl enol ethers are routinely generated from appropriate ketones.[2] Their thiophosphorylation and selenophosphorylation giving 1 and 2 is achieved by using readily available oxophosphoranesulphenyl chlorides $(RO)_2P(O)SCl$ and phosphonium salt $(EtO)_3\overset{+}{P}SeCl\ \overset{-}{S}O_2Cl$, respectively.[3,4]

The consecutive reaction of 1 and 2 with selected nucleophiles results in the formation of the diastereoisomeric oxyanions 3a and 3b. The intermediates 3a and 3b undergo rearrangement involving migration of a phosphoryl group from sulphur or selenium to oxygen affording thiolate or selenolate anions 4a and 4b. Subsequent cyclization of 4a and 4b with elimination of phosphate anion gives episulphides or episelenides 5a and 5b. Desulphurization of 5a and 5b by the action of P^{III} compound, or spontaneous deselenylation of 5a and 5b (X=Se) completes the sequence.

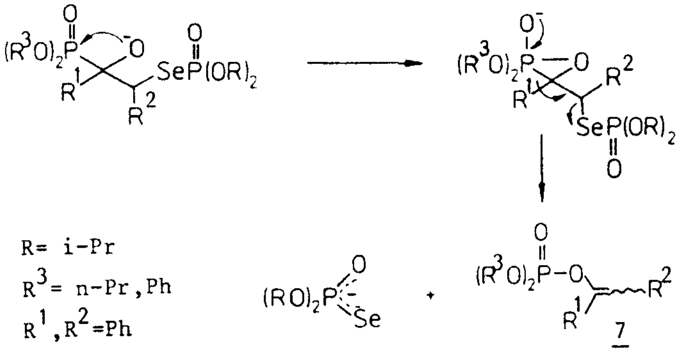
We wish to demonstrate here some representative examples of our methodology. As shown in Scheme 2, a number of various olefins including functionalized unsaturated compounds can be stereoselectively synthesized from thiophosphates 1 and selenophosphates 2.



Scheme 2

i: $NaBH_4$,ROH,r.t.; ii: bakers' yeast,r.t.80 hrs; iii: n=4 or 5,$NaBH_4$, ROH,0°C; iv: R^1=alkyl(aryl)-CH=CH-,a-NaH,Et_2O,r.t. b-R^5Hal,Et_2O,r.t.; v: KCN/18-crown-6,DME,r.t.; vi: R^1,R^2=Ph,X=Se,Y=O,$(R^3O)_2PONa$,benzene, r.t.; vii: X,Y=S,X=Se,Y=O,$(R^3O)_2PONa$,benzene,r.t.

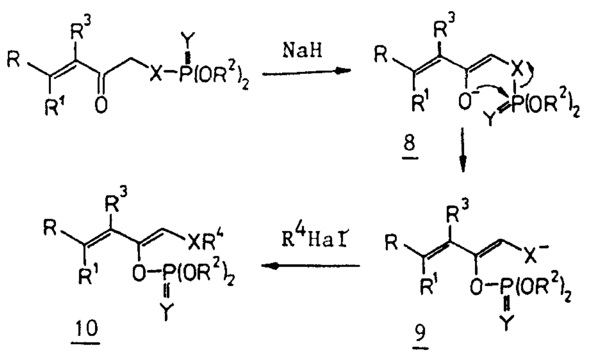
Reactions of hydride anion ($NaBH_4$) with 1 and 2 provide the corresponding Z-olefins with a great facility and efficiency.[1] In the same way, 2 derived from formyl- or acylalkanes are converted to the corresponding exocyclic olefins. Bakers' yeast also reduces 1 in a stereoselective manner but in moderate yield. The phosphates 1 and 2 react with CN^- anion (KCN/18-crown ether) giving Z-vinyl cyanates in excellent yield. Reactions of 1 and 2 with $(R^3O)_2P(O)^-$ can be successfully used as a general route to Z-vinyl phosphonates.[5] However, when the same anions react with selenophosphates 2 bearing two phenyl ligands vinyl phosphates 7 are produced in almost quantitative yield. The most plausible mechanistic explanation for the latter reaction is presented in Scheme 3. This mechanistic pathway is reminiscent of that proposed by Borowitz for Perkow reaction[6] and is fully consistent with the results of our cross experiments. When 2 (R=i-Pr) was treated with $(R^3O)_2P(O)^-$ (R^3= n-Pr,Ph), the resulting vinyl phosphates 7 contained exclusively R^3O ligands.



R= i-Pr
R^3= n-Pr,Ph
R^1,R^2=Ph

Scheme 3

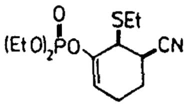
Extending our synthetic studies, we have recently elaborated an efficient approach to thio- and selenophosphates with an α,β-unsaturated carbonyl moiety. These compounds have been applied as convenient substrates in the synthesis of novel heterofunctionalized 1,3-dienes 10.[7]



R,R^1,R^3=H; R,R^3=H,R^1=Ph; R,R^1=Me,R^3=H; R^1=H,R,R^3=$-(CH_2)_4-$; R^2=Et; R^4=alkyl,MeC(O),t-BuC(O),$(EtO)_2P(O)$,$(PhO)_2P(O)$,$(PhO)_2P(Se)$ X=S,Se; Y=O,S; Hal=I,Br,Cl.

A crucial step of the synthesis involves interconversion of the enolate anion 8 into anion 9 via migration of phosphoryl group from sulphur or selenium to oxygen.

Diels-Alder reactions of dienes-10 with selected dienophiles provide rapid access to diversely functionalized cyclohexenones. E.g.: cycloaddition of vinyl cyanate and methyl vinyl ketone to 10 in the presence of EtAlCl$_2$ catalyst, gives the cyclohexenes 11, 12 and 13 with complete regio- and stereo(endo)selectivity. Further useful transformations are possible since these new adducts have both sulphide and phosphate substituents.



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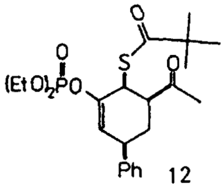

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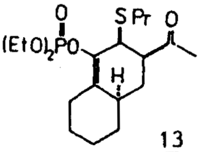

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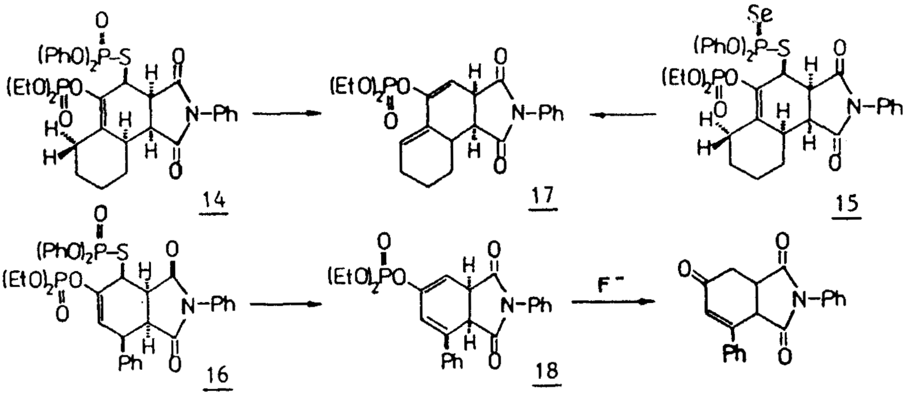
The cycloaddition of dienes 10 with a thiophosphate group affords the adducts 14, 15 and 16, which undergo spontaneous elimination under the reaction conditions (100°C, 3-5 hrs, toluene) to produce cyclohexadienes 17 and 18.



Further investigations are in progress.

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