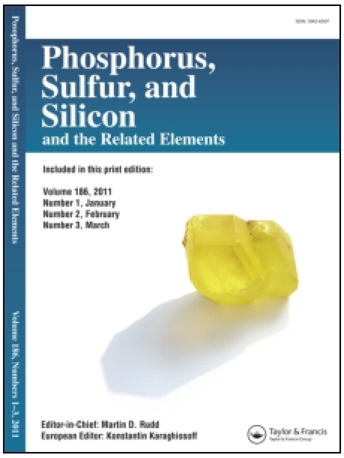

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Generation and Reactivity of α-Phosphorylated Sulfur Stabilised Carbanions and Ylides ; Selective Syntheses of α-Thiosubstituted Phosphonates

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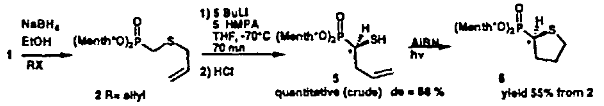
An asymmetric synthesis of an α-mercapto-but-3-enyl phosphonate and the preparation of various α-phosphorylated unsaturated sulfides were respectively achieved *via* carbanion and ylide [2,3]-sigmatropic rearrangements.

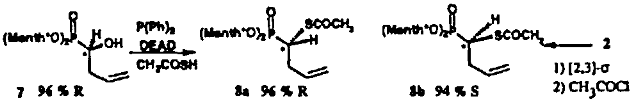
α-Mercapto substituted phosphonates are much less described than their α-hydroxy or α-amino analogues which are well known for their biological activities. Moreover, α-phosphorylated sulfides, sulfoxydes and sulfones can find synthetic uses as functionalised olefination reagents[1].

We have previously described[2] the use of a [2,3]-Wittig rearrangement of carbanions or ylides to generate α-thio substituted alk-3-enylphosphonates. In connexion with this work we report herein an asymmetric version of the synthesis of an α-mercaptobut-3-enyl phosphonate together with a study of the use of diazomethylphosphonates to generate ylides from various allylic sulfides.

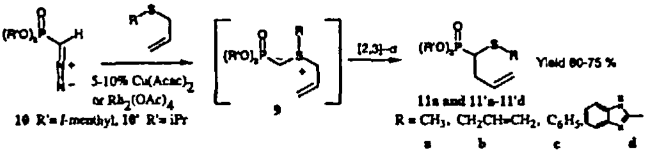
Only two examples of asymmetric Wittig rearrangements for the synthesis of α-hydroxyphosphonates have been recently published[3,4] but, to our knowledge, no enantioselective way to α-mercaptophosphonates have been described. Starting from the di-(*l*)-menthylphosphite[3], we easily obtained the phosphonodithioformiate **1** which was readily reduced and allylated to give sulfide **2**[2]. The carbanion of **2** generated with an excess of base at low temperature undergoes [2,3]-sigmatropic rearrangement leading to the thiol **5** with a diastereoisomeric excess of 88%. The crude thiol was then cyclised without epimerisation into the 2-phosphono-thiolane **6** (isoster of L-proline).



The configuration at C_1 of **5** and **6** was determined from the α-hydroxyphosphonate **7**, of known absolute configuration[3] (C_1-R), *via* a Mitsunobu[5] acetylthiolation with full inversion of configuration. Thiolacetate **8a** (C_1-R) was found to be epimer of **8b** obtained from lithiated **5**. An S configuration can thus be attributed to thiol **5** and sulfide **6**.

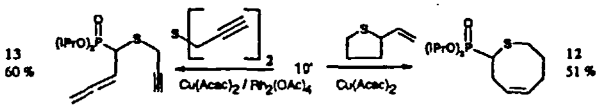


In contrast with this selective [2,3]-σ shift, no diastereoselectivity was observed from the rearrangement of the ylide **9** obtained from the corresponding sulfonium salt and BuLi at -70°C. Since the use of an excess of base could have been responsible of a racemisation after sigmatropy, a direct access (in neutral medium) to sulfonium ylide **9**, by reaction of the carbene derived from a diazomethylphosphonate with allylic sulfides[6], was investigated. The diazo compounds **10** (R'= *l*-menthyl) and **10'** (R'= iPr) were converted into metallocarbenes by addition of copper acetylacetonate or rhodium acetate in the presence of allyl methyl sulfide. Phosphorylated sulfides **11a** and **11'a** were isolated in good yield but again, in the case of **11a**, no diastereoselectivity was observed.



The reaction was then tested with **10'** (R'= iPr) and various allylic sulfides (**b-d**) and, in each case, was optimised by choosing the catalyst (or a mixture of catalysts) to minimize the competitive dimerisation of the intermediate phosphonometallocarbene.

The potential of this reaction was also illustrated by a ring expansion reaction of an α-phosphorylated cyclic sulfonium ylide leading to the new eight membered ring **12** (analogue of the described carboxylic compound[7]). Moreover, this method, which does not require any base, allowed to carry out the sigmatropic rearrangement of a dipropargyl sulfonium ylide into the phosphonate **13**.



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