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Phosphorus, Sulfur, and Silicon and the Related Elements

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

Mihaela Gulea , Patrice Marchand , Monique Saquet , Serge Masson & Noël Collignon

^a Laboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université de Caen, 14050 Caen

^b Laboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université de Caen, 14050 Caen

^c Laboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université de Caen, 14050 Caen

^d Laboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université de Caen, 14050 Caen

^e Laboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université de Caen, 14050 Caen To cite this article: Mihaela Gulea , Patrice Marchand , Monique Saquet , Serge Masson & Noël Collignon (1999) Generation and Reactivity of α -Phosphorylated Sulfur Stabilised Carbanions and Ylides; Selective Syntheses of α -Thiosubstituted Phosphonates, Phosphorus, Sulfur, and Silicon and the Related Elements, 153:1, 327-328, DOI: <u>10.1080/10426509908546454</u>

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

MIHAELA GULEA^a, PATRICE MARCHAND^a, MONIQUE SAQUET^a, SERGE MASSON^a and NOËL COLLIGNON^b

^aLaboratoire de Chimie Moléculaire et Thio-organique, UMR CNRS 6507, ISMRA-Université de Caen, 14050 Caen and ^bLaboratoire d'Hétérochimie Organique, UPRESA CNRS 6014, INSA-Rouen, IRCOF, Rue Tesnière, 76821 Mont-Saint-Aignan, France

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 reagents¹.

We have previously described² 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*)-menthylphosphite³, we easily obtained the phosphonodithioformiate 1 which was readily reduced and allylated to give sulfide 2². 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 C₁ of **5** and **6** was determined from the α -hydroxyphosphonate **7**, of known absolute configuration³ (C₁-R), *via* a Mitsunobu⁵ acetylthiolation with full inversion of configuration. Thiolacetate **8**₈ (C₁-R) was found to be epimer of **8**₉ 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 signatropy, a direct access (in neutral medium) to sulfonium ylide 9, by reaction of the carbene derived from a diazomethylphosphonate with allylic sulfides⁶, was investigated. The diazo compounds 10 (R'= *l*-menthyl) and 10' (R'= iPr) were converted into metallocarbenes by addition of copper acetylacetonate or modium 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' ($R'\approx iPr$) 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 compound⁷). Moreover, this method, which does not require any base, allowed to carry out the signatropic rearrangement of a dipropargyl sulfonium ylide into the phosphonate 13.



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