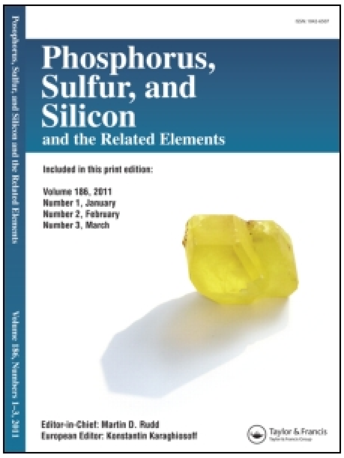

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[2,3]-WITTIG SIGMATROPIC REARRANGEMENT OF α-PHOSPHONYLATED SULFONIUM AND AMMONIUM YLIDES

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Abstract A study of the reactivity of ylides of α-allylamino and α-allylthio-methylphosphonates and a comparison with the reactivity of the corresponding carbanions demonstrate the complementarity of these intermediates for the preparation of α-heteroatom-substituted alkenylphosphonates via [2,3]-sigmatropic rearrangements.

INTRODUCTION

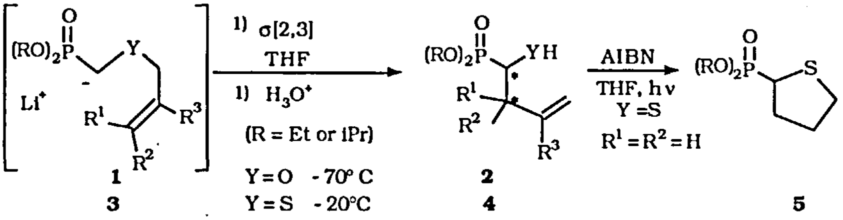
The [2,3]-sigmatropic rearrangement of α-(allyloxy), -(allylamino) or -(allylthio) carbanions and ylides (also called Wittig, thia- or aza-Wittig rearrangement) is a well known process which has been widely used for regio and stereocontrolled formation of carbon-carbon bonds.[1] This rearrangement is also observed with propargylic and benzylic derivatives. More often, these carbanions and ylides were generated by a deprotonation which was made easier by an α-electron withdrawing group. However, no-example of a phosphonate group used for these purpose has been published. Owing to the need for efficient and stereocontrolled methods for the synthesis of α-heteroatom substituted phosphonates (compounds of potential biological interest [2] which can be obtained via these Wittig rearrangements), we have initiated a systematic study of the reactivity of [(allyloxy)-, (allylamino)- or (allylthio)-methyl]phosphonates carbanions and ylides.

This communication summarises briefly the recent results we have obtained concerning the reactivity of the carbanions of α-allylic heterosubstituted phosphonates and then demonstrates that the use of the corresponding ylides (prepared from ammonium or sulfonium salts) complement that of the carbanions as far as the syntheses of [(dialkylamino)- or (alkylthio)-methyl]phosphonates are concerned. Moreover, although a more extensive investigation is still needed concerning the stereochemistry of these rearrangements and its rationalisation, the diastereoselectivity (very high in some cases) can be very different according to the use of a carbanion or an ylide as intermediate. Some results related to the bis-phosphonate series are also presented.

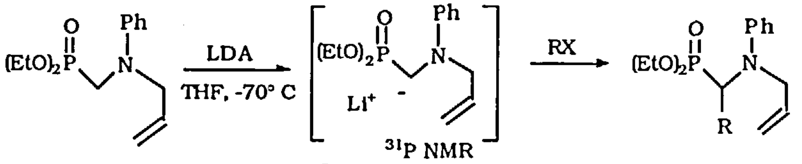
REACTIVITY OF THE CARBANIONS OF [(ALLYLOXY)-, (ALLYLAMINO)- OR (ALLYLTHIO)-METHYL]PHOSPHONATES

The reactivity of the carbanions of [(allyloxy)- and (allylthio)-methyl]phosphonates were first studied [3]. The O-allylic carbanions **1** (with allyl, cinnamyl, crotyl and prenyl groups) resulting from a deprotonation by lithium di-isopropyl amide (LDA) undergoes at -70° C the expected [2,3]-sigmatropic rearrangement. Yields of the resulting α-hydroxyphosphonates **2** are satisfying (60 to 72%) except for the prenyl substituent (28%). A good diastereoselectivity was observed with the cinnamyl but not with the crotyl substituent.

With the corresponding S-allylic carbanions **3**, obtained by allylation of the sodium salt of the mercaptomethylphosphonate,[4] a deprotonation by BuLi, led to α-mercaptobutenylphosphonate derivatives **4** in good yields (66 to 97%) via the thia-Wittig rearrangement. Low diastereoselectivity was observed with the crotyl and cinnamyl group. A synthetic application of compound **4** was the easy synthesis of the phosphorus and sulfur analogue of the proline ester **5**, not described previously, via a radical cyclisation of the (1-mercaptobut-3-enyl)phosphonate.



We then examined the reactivity of the carbanion of allylamino-methylphosphonates. The deprotonation leading to carbanion **6** was observed by addition of 2 equivalents of LDA at -70° to an (N-phenyl N-allyl aminomethyl)phosphonate (deprotonation did not occur from an N-alkyl N-allyl analogue). However carbanion **6**, the formation of which being evidenced by its reaction with various electrophiles, did not undergo any sigmatropic rearrangement, even at higher temperatures.

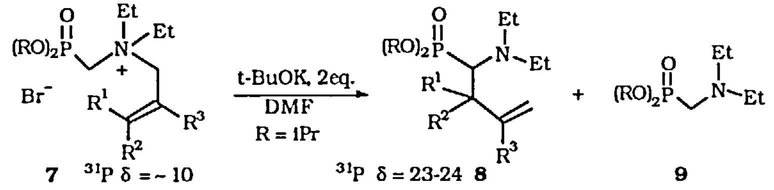


R =	SiMe$_3$	SnBu$_3$	SPh	Me
^{31}P NMR (δ)	25.1	28.2	16.2	24.5

50 to 80 % yields

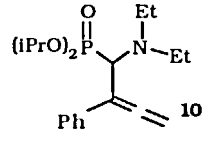
REACTIVITY OF THE YLIDES OF [(ALLYLAMINO)- OR (ALLYLTHIO)- METHYL]PHOSPHONATES

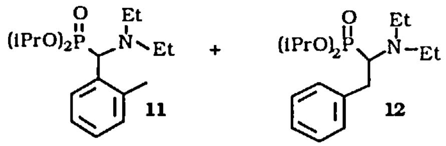
This failure to observe the sigmatropic rearrangement with carbanion **6** was an incitation to examine the reactivity of the corresponding ylide formed by deprotonation of the ammonium salt. However, we did not succeed in the quaternarisation of the N-phenyl substituted amine. Such a quaternarisation leading to salts of type **7** was obtained by addition of allyl, methallyl, crotyl, cinnamyl, or prenyl-bromides to the O,O'-diisopropyl (N,N-diethyl-aminomethyl)phosphonate (the use of isopropyl substituents appeared necessary to avoid partial phosphonate dealkylation encountered with ethyl group). The deprotonation of **7** at - 40°C by t-BuOK in DMF generated the corresponding ylides which spontaneously rearranged into α-aminobutenyl phosphonate derivatives **8** in about 75 % yields exept for the more crowded prenyl derivative (51%). The de-allylation of the ammonium salts usually < to 10% occurs more extensively (40% of **9**) in the last case .



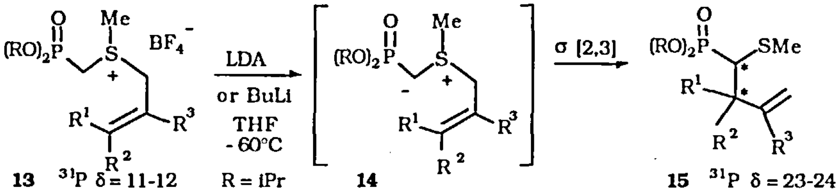
Very good diastereoselectivities were observed in the formation of **8** via the N-crotyl (de = 82%) and N-cinnamyl (de = 100%) ammonium ylide rearrangements.

Starting from the N- propargylic ammonium salts, the expected allenic derivative **10** was obtained and, from the N-benzylic ammonium salts, both [2,3]- and [1,2] sigmatropic rearrangements occured in the ratio 2/1 to give α-amino phosphonates **11** and **12** respectively.





Then, in order to investigate the reactivity of ylides in the sulfur series, we prepared the precursor allylic sulfonium salts **13** in nearly quantitative yields by methylation of the corresponding allylthio, crotylthio and methallylthiomethylphosphonates, in acetonitrile in the presence of $AgBF_4$. These salts, treated with one equivalent of Buli in THF at -60°C, led readily to α-alkylthio butenylphosphonate derivatives **15** in 80 to 90% yields via the non isolated ylides **14**. A good diastereoselectivity (de = 80%) was observed for the rearrangement of the S-crotyl ylide. This was not the case for the rearrangement of the corresponding carbanion (*vide supra*). We did not observed any rearrangement of the corresponding S-benzylic ylide, although the formation of which was confirmed by trapping with PhNCO.[5]

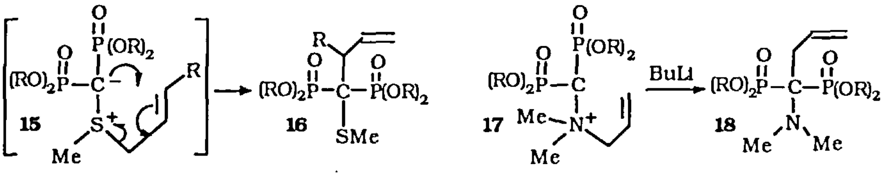


13 ^{31}P δ = 11-12 R = iPr 14 15 ^{31}P δ = 23-24

As far as the potential uses of this rearrangements for stereocontrolled formation of α-heteroatom-substituted phosphonates are concerned, first experiments using the O,O'-dimenthyl substituent on the phosphonate function (prepared from l-menthol) as a chiral auxiliary gave the following results : an excellent asymmetric induction (de = 92%) was obtained for the rearrangement of the carbanion of the (allyloxy methyl)phosphonate **1** (R=menthyl) but a low diastereoselectivity (de=8%) was observed via the sigmatropy of the S-allyl ammonium ylide generated from **7** (R=menthyl, $R^1=R^2=R^3=H$). In the sulfur series, the diastereoselectivity of the rearrangement of the carbanion **3** and ylide **14** with the same optically active phosphonate group will be also examined.

REARRANGEMENT OF SULFONIUM AND AMMONIUM YLIDES IN THE BIS-PHOSPHONATES SERIES

Preceeding work has shown that a [2,3]-sigmatropic rearrangement of an intermediate S-allylic or propargylic sulfonium ylides **15** can be assumed in the reaction of allylic or propargylic bromide with a [(methylthio)-phosphoranylidene-methyl]phosphonate to give the methylene bis-phosphonate derivative **16**.[6] We have now shown that the deprotonation of the S-allylic ammonium salt **17** led to the (N,N-dimethylamino-allyl-methylene)bis-phosphonate **18**. These rearrangements are thus convenient methods for the preparation of new functionalised methylene bis-phosphonates.



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