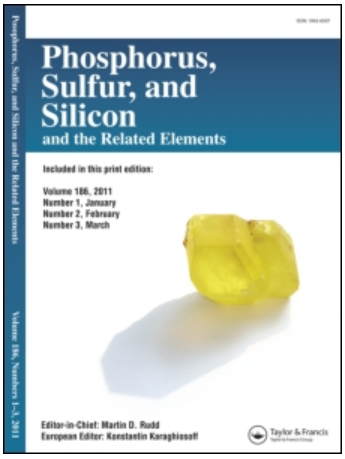


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Phosphonates Containing Sulfur and Silicon: New Stereochemical and Mechanistic Aspects

M. Mikołajczyk[a]; Piotr Bałczewski[a]; P. Graczyk[a]
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland

To cite this Article Mikołajczyk, M. , Bałczewski, Piotr and Graczyk, P.(1987) 'Phosphonates Containing Sulfur and Silicon: New Stereochemical and Mechanistic Aspects', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 225 — 228

To link to this Article: DOI: 10.1080/03086648708080563

URL: http://dx.doi.org/10.1080/03086648708080563

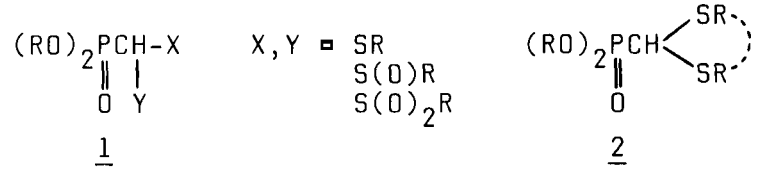
Phosphorus and Sulfur, 1987, Vol. 30, pp. 225–228
Photocopying permitted by license only

PHOSPHONATES CONTAINING SULFUR AND SILICON: NEW STEREOCHEMICAL AND MECHANISTIC ASPECTS

M.MIKOŁAJCZYK*, PIOTR BAŁCZEWSKI and P.GRACZYK
Centre of Molecular and Macromolecular Studies,
Polish Academy of Sciences, 90-362 Łódź, Poland

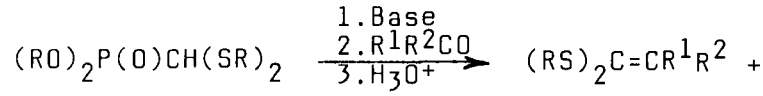
Abstract - Synthesis, reactivity and conformation of cyclic S,S-thioacetals of formylphosphonates are described. The chemistry of α-trimethylsilyl-α-methylthiometanephosphonate is briefly discussed.

For the past few years, work in this Laboratory has centered on the preparations and reactions of the phosphonates containing α-organosulfur substituents of general formula (1). Among them S,S-thioacetals of formylphosphonates (2) are of special interest because they



1 2

are reagents of choice for the synthesis of ketene S,S-thioacetals via the Wittig-Horner reaction with carbonyl compounds[1].



The present communication describes the results of our further studies on this class of compounds.

SYNTHESIS OF 2

As far as the synthesis of 2 is concerned[2], it was found now that they may conveniently be prepared by the reaction of diazomethanephosphonates with organic disulfides in the presence of the proper catalysts.

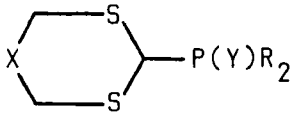
$$(RO)_2P(O)CHN_2 + (RS)_2 \xrightarrow{Et_2O\cdot BF_3} 2$$

The best results in terms of the yield and purity of products were obtained with $Et_2O\cdot BF_3$. The use of $Rh_2(OAc)_4$ as a catalyst was found to give α-phosphoryl sulfides.

CONFORMATION OF 2-PHOSPHORYL 1,3-DITHIANES

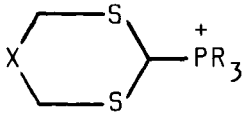
2-Substituted 1,3-dithianes in solution have eiter dynamic or rigid chair structure with substituents occupying axial or equatorial position. Therefore, it was of interest to investigate conformation of 1,3-dithiane with the phosphorus containing groups at the anomeric carbon atom.

To this end the model compounds 3 and 4 were synthesized and their structures were elucidated by means ^1H, ^{31}P and ^{13}C-NMR spectroscopy and X-ray analysis.



3

X = CH_2, tBuCH, Me_2C, S
Y = O, S
R = MeO, Ph



4

X = CH_2, Me_2C, S
R = Ph, Me_2N

All the data obtained so far point to a rigid chair conformation of the six-membered ring with the axial

phosphoryl group[3,4]. Conformation of 4 will be briefly discussed.

REACTION OF 2 WITH α,β-UNSATURATED CARBONYL COMPOUNDS

In an extension of our earlier work[1], the reaction of 2 with α,β-unsaturated aldehydes and ketones was investigated. It was found that aldehydes give the corresponding Wittig-Horner reaction products in high yields (65-80%) via the hydroxy-adduct (1,2-addition) as detected by ^{31}P-NMR spectroscopy.

$$(RO)_2P(O)\overset{Li}{C}H(SR)_2 \xrightarrow[-(RO)_2PO_2Li]{R^1R^2C=C(R^3)CHO} R^1R^2C=C(R^3)CH=C(SR)_2$$

However, the reaction with α,β-unsaturated ketones proceeds in a different way. All the experimental results lead to formulation of the following general reaction course.

$$(RO)_2P(O)\overset{Li}{C}(SR)_2 \xrightarrow[-78^oC]{R^1CH=CHC(O)R^2} [1,4\text{-adduct}]Li$$

$$\xrightarrow[25^oC]{} [1,2\text{-adduct}]Li \longrightarrow \text{the Wittig-Horner reaction products}$$

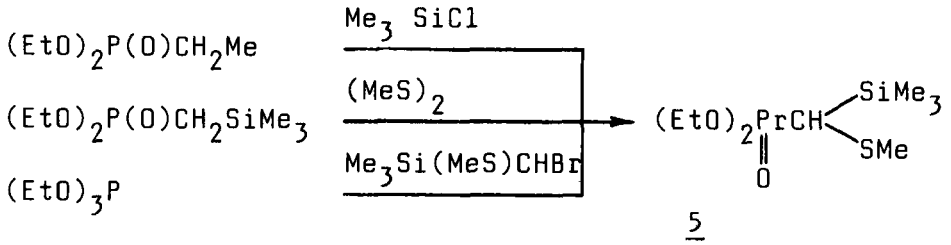
In this context, it is of interest that the reaction of the lithium salts of α-phosphoryl sulfides with α,β-unsaturated ketones gives 1,4-adducts as the final reaction products and was found to proceed as follows:

$$(RO)_2P(O)\overset{Li}{C}HSMe \xrightarrow[-78^oC]{R^1CH=CHC(O)R^2} [1,2\text{-adduct}]Li$$

$$\xrightarrow[25^oC]{} [1,4\text{-adduct}]Li \xrightarrow{H^+} 1,4\text{-adduct}$$

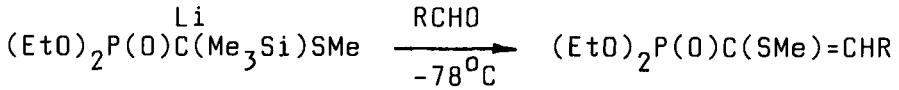
SYNTHESIS AND REACTIVITY OF α-TRIMETHYLSILYL-α-METHYL-THIOMETHANEPHOSPHONATE (5)

The title compound was prepared in three different ways: (a) by silylation of α-phosphoryl sulfide, (b) by sulfenylation of α-trimethylsilyl methanephosphonate and (c) by the Arbusov reaction of triethyl phosphite with the appropriate bromide.



5

The lithium salt of 5 on treatment with aliphatic, aromatic and α,β-unsaturated aldehydes gives the Peterson reaction products in high yields (60-85%).



The reaction with ketones is more complicated, the Peterson reaction product is formed in 5% yield only. In summary, the phosphonates 2 and 5 are useful synthetic intermediates and their chemistry is connected with interesting stereochemical and mechanistic aspects.

REFERENCES

1. M.Mikołajczyk, et.al., Tetrahedron, 34, 3801 (1978).
2. H.Gross, et.al., Phosphorus and Sulfur, 16, 257 (1983).
3. M.Mikołajczyk, et.al., Tetrahedron, 40, 4886 (1984).
4. M.Engelhardt, et.al., Magnetic Resonance in Chem., 25, 18 (1985).