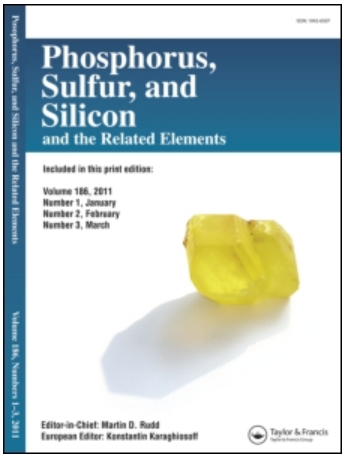

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A New Stereoselective Route to the Unsymmetrical Tetraalkyldithiopyrophosphates

Andrzej Lopusiński[a]; Marek Potrzebowski[a]
[a] Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Łodz, Poland

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A NEW STEREOSELECTIVE ROUTE TO THE UNSYMMETRICAL TETRAALKYLDITHIOPYROPHOSPHATES

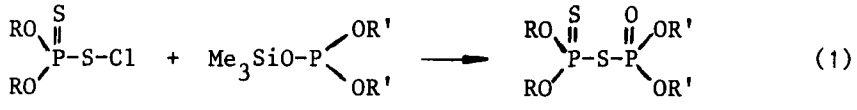
ANDRZEJ ŁOPUSIŃSKI and MAREK POTRZEBOWSKI
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Boczna 5, 90-362 Łodz, Poland

Abstract The unsymmetrical dithiopyrophosphates 9 are formed in reaction of dialkoxythioxaphosphoranesulfenyl chlorides 1 with dialkyltrimethylsilylphosphites. The stereospecificity of this reaction is demonstrated on model derivatives of diastereoisomeric-4-methyl-1,3,2-dioxaphosphorinans ring system. The novel synthesis of 4a and 4b and their structural assignment is also described.

The development of the chemistry of the phosphoroorganic dicoordinate sulfur halogens RR'P(X)YZ X=O,S; Y=S,Se; Z=Cl,Br is due to the utility of this class of compounds in synthetic organophosphorus chemistry.

We have recently discovered a convenient route, to thioxaphosphoranesulfenyl chlorides and bromides.[2] These compounds have been found to behave as ambident electrophiles[3] revealing some new facets of the chemistry of organophosphorus pseudohalogens.

The thioxaphosphoranesulfenyl chlorides 1 are very convenient reagents for the preparation of unsymmetrical tetraalkyldithiopyrophosphates. Eq. (1).

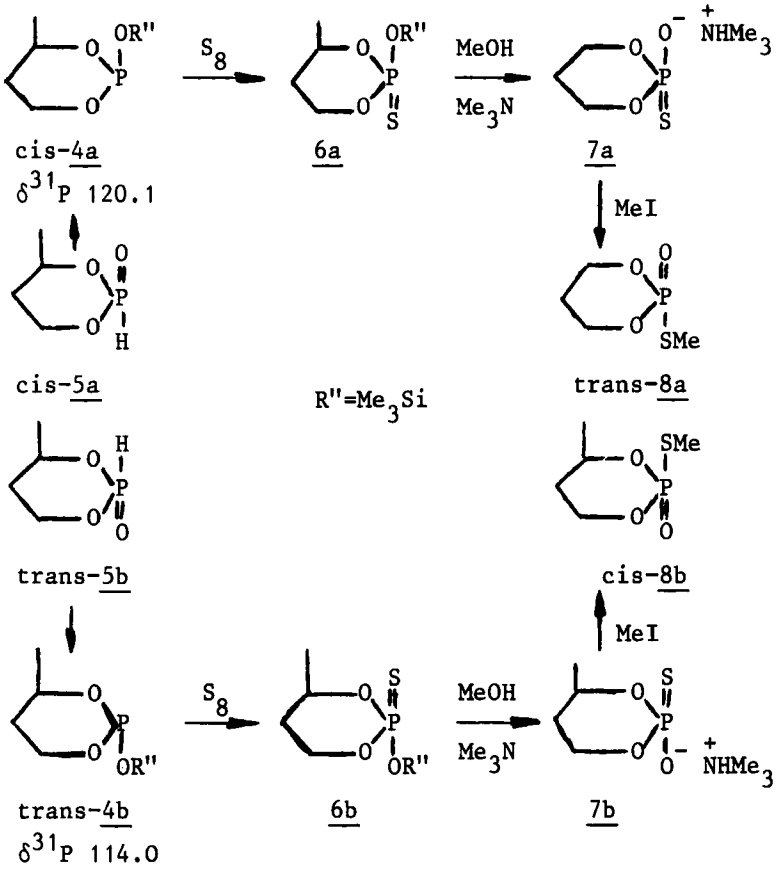


(1)

The reaction between thioxaphosphoranesulfenyl chlorides and silylphosphites proceeds in neutral solvents at low temperature with

almost quantitative yield. The efficacy of the reaction and its stereospecificity follows from the studies performed on model cis- and trans-2-trimethylsilyloxy-4-methyl-1,3,2-dioxaphosphorinans 4a and 4b.

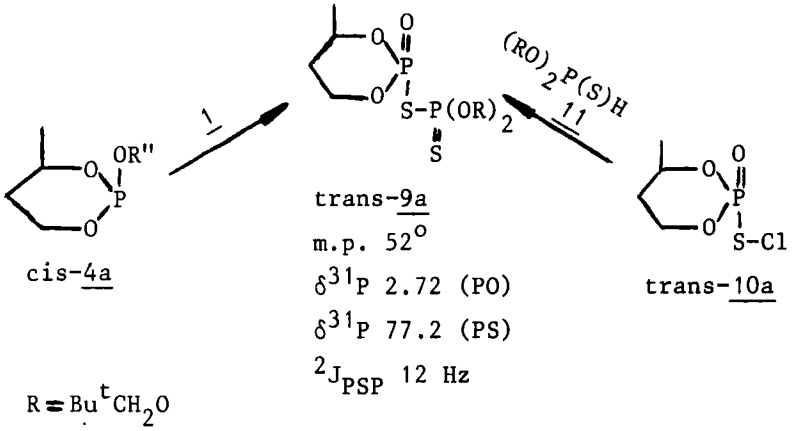
The starting silylphosphites 4a,b are obtained by reaction of phosphites 5a and 5b[4] with trimethylchlorsilane in the presence of triethylamine.



The configuration of the diastereoisomeric silylphosphites 4a and 4b was assigned on the basis of stereoselective addition of the elemental sulfur followed by desilylation of the thionoesters 6a and 6b and finally alkylation of the resulting salts 7a,b to obtain the thioloesters 8a,b of known configurations. This sequence

assigns the cis and trans configurations to 4a and 4b respectively, since their transformation into 8a,b does not involve bond breaking at the phosphorus atom.

The cis-2-trimethylsilyloxy-4-methyl-1,3,2-dioxaphosphorinan 4a reacts in hexane solution smoothly with 1 at -5°C affording the crystalline trans-dithiopyrophosphate 9a. Eq. (2).



cis-4a

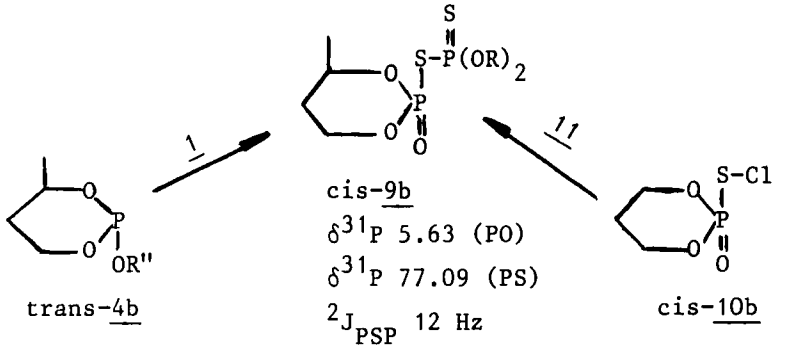
trans-9a
m.p. 52°
$\delta^{31}P$ 2.72 (PO)
$\delta^{31}P$ 77.2 (PS)
$^2J_{PSP}$ 12 Hz

trans-10a

(2)

R = Bu^tCH_2O

Under similar conditions the trans silylphosphite 4b reacts with the sulfenyl chloride 1 to give the cis dithiopyrophosphate 9b as an nondistillable oil (Eq. 3).



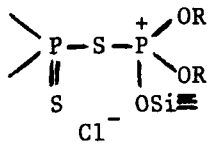
trans-4b

cis-9b
$\delta^{31}P$ 5.63 (PO)
$\delta^{31}P$ 77.09 (PS)
$^2J_{PSP}$ 12 Hz

cis-10b

(3)

The structures of dithiopyrophosphates 9a and 9b were confirmed by an independent synthesis of these compounds starting from sulfenyl chlorides 10a and 10b and thiophosphite 11, which is a synthetic alternative[6] to the method presented.



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It is almost certain that the reaction of 1 with phosphites 4a and 4b involves phosphonium intermediate 12. However, its concentration is too low to be observed by ^{31}P NMR spectroscopy.

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