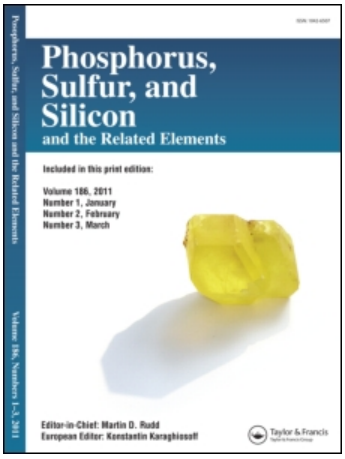

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Leszek Łuczak[a]; Jana Vereshchagina[ab]; Andrzej Łopusinski[a]; Jan Michalski[a]
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland [b] Kazań Institute of Technology, Russia

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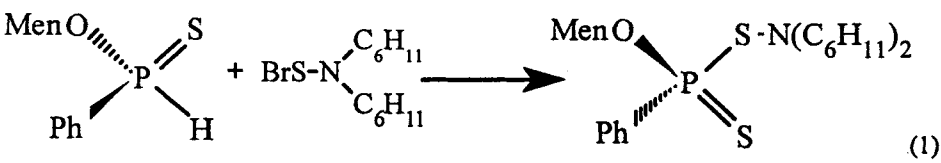
STEREOCHEMISTRY OF P-CHIRAL THIOXOPHOSPHORANE-SULFENYL HALIDES RR'P(S)SX

LESZEK ŁUCZAK, JANA VERESHCHAGINA,# ANDRZEJ ŁOPUSINSKI and JAN MICHALSKI
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Łódź, Sienkiewicza 112, Poland

Abstract: Stereoselective synthesis of the P-chiral thioxaphosphoranesulfenyl (dicyclohexyl)amide (l-menthyl-O)PhP(S)SN(C_6H_{11})$_2$ and its conversion into the P-chiral thioxaphosphoranesulfenyl chloride (l-menthyl-O)PhP(S)SCl is described. First synthesis of P-chiral thioxaphosphoranesulfenyl bromides (l-menthyl-O)PhP(S)SBr *via* the bromolysis of the bis-thiophosphoryl disulfide [(l-menthyl-O)PhP(S)S-)]$_2$ is presented. Transformations of P-chiral thioxaphosphoranesulfenyl chlorides and bromides into the corresponding sulfenamides proceed with the preservation of stereochemical integrity at the chiral P-center.

Our primary idea of these studies was to use P-chiral thioxaphosphoranesulfenyl halides RR'P(S)SX **1** (X=Br,Cl) as a stereochemical probe to follow mechanisms of nucleophilic displacements at the sulfenyl functionality. In our earlier work the sulfenyl chlorides **1a** (R=EtO, R'=l-menthoxy, X=Cl) has been synthesized as pure diastereoizomers containing P-chiral centers of opposite configuration.[1] Our present objective was to synthesize the pure diastereoizomer $(R)_P$ **1b** (R=Ph, R'=l-menthoxy, X=Cl) via a crystalline sulfenamide RR'P(S)SNR"$_2$ **2** suitable for X-ray analysis. With this in mind we succeeded in obtaining the pure sulfenamide $(R)_P$ **2a** (R=Ph, R'=l-menthyl, R"=C_6H_{11}) by the condensation of the (l-menthylphenylhydrogen phosphonothionate $(S)_P$ **3** with dicyclohexylaminosulfenyl bromide **4**.



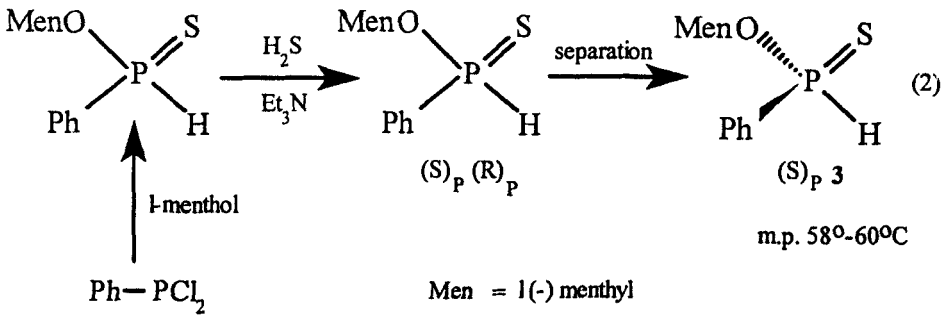
(1)

$(S)_P$ **3** **4** $(R)_P$ **2a**

m.p. 88°-90°C

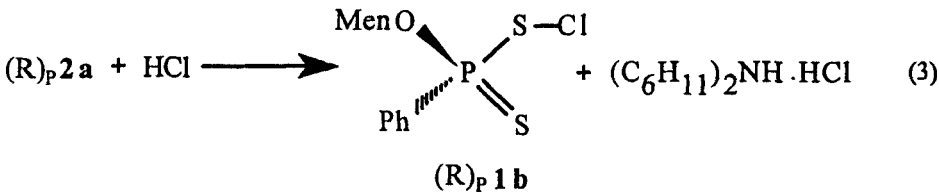
Post-doctoral Fellow, on leave of absence from Kazań Institute of Technology (Russia).

The hydrogen phosphonothionate $(S)_P$ **3** is readily available by the following sequence of reactions and the final separation by crystallization. Attempts to prepare pure **3** $(R)_P$ failed. This diastereoisomer is present as the major component after separation of **3** $(S)_P$.



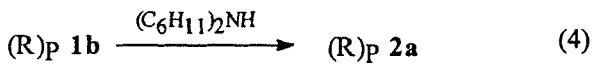
(2)

The sulfenamide $(R)_P$ **2a** was transformed into the sulfenyl chloride $(R)_P$ **1b** in the fully stereoselective way by hydrogen chloride produced in situ from Me_3SiCl and EtOH.



(3)

The sulfenyl chloride $(R)_P$ **1b** when allowed to react with dicyclohexylamine gives the pure sulfenylamide $(R)_P$ **2a**.

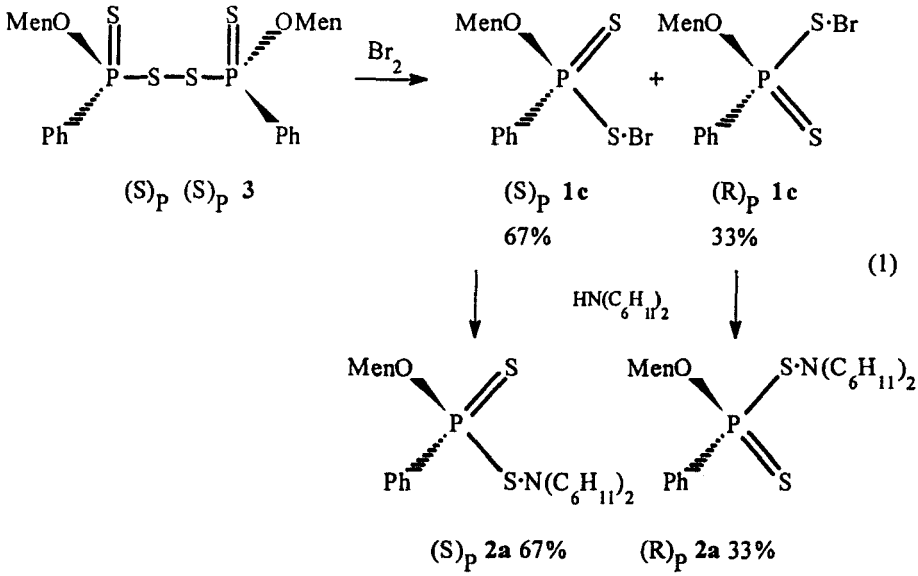


(4)

Stereochemical integrity of the chiral phosphorus center is preserved in the reaction (4). This corroborates with the $S_N2(S)$ or A-E type mechanisms of nucleophilic substitution at the dicoordinate sulfur atom.

The methodology applied for the synthesis of P-chiral sulfenyl chlorides **1** (X=Cl) failed to give the corresponding bromides **1** (X=Br) in a pure individual diastereoizomers. Therefore another strategy allowing stereoselective preparation of P-chiral sulfenyl bromides **1c** (R=Ph, R'=l-menthoxy) had to be employed. We took advantage of the fact that the pure

diastereoisomeric bis-thiophosphoryl disulfide $(S)_P(S)_P$ **3** have been prepared in our earlier studies.[3] The reaction of this disulfide with elemental bromine gave a mixture of the diastereoisomeric bromides $(S)_P$ **1c** (X=Br) and $(R)_P$ **1c** in the proportion 33/67.

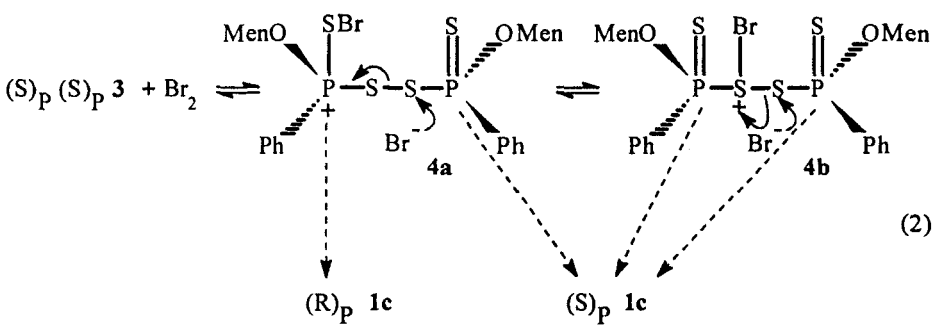


$(S)_P$ $(S)_P$ **3** $(S)_P$ **1c** 67% $(R)_P$ **1c** 33% (1)

$(S)_P$ **2a** 67% $(R)_P$ **2a** 33%

The bromides were converted into the sulfenamides **2a** $(S)_P$ and **2a** $(R)_P$ in exactly the same proportions.

A plausible mechanistic explanation of this stereochemical outcome involves equilibrium between sulfonium and phosphonium reactive intermediates.

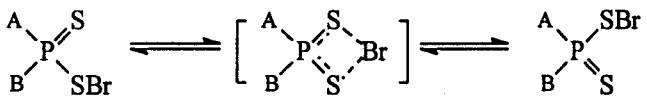


(2)

The sulfonium bromide **4b** should be a source of the sulfenyl bromide $(S)_P$ **1b**. The bromides **1b** derived from the phosphonium structure **4a** are likely to be a 1:1 mixture of diastereoisomers $(S)_P$ **1c** and $(R)_P$ **1c**. The bromide **1c** derived from the phosphonium centre is formed with a methathesis of ligands[4] and should have the configuration **1b** $(R)_P$.

In the presence of hydrogen bromide each of the diastereoisomeric bromides **1c** undergoes very fast isomerization to give 1:1 mixture of both diastereoisomers **1c** $(S)_P$ and **1c** $(R)_P$. This explains our failure to prepare bromides **1c** in stereoselective way via the reaction of hydrogen bromide with the diastereoisomeric sulfenamides **2a**.[2]

Relative stereochemical stability of the bromides **1c**, at least at ambient temperature in solution, excludes the halotropy shown in scheme (7).



(7)

The fully stereoselective transformations of the sulfenyl bromides **1c** $(S)_P$ and **1c** $(R)_P$ into the corresponding sulfenamides **2a** $(S)_P$ and **2a** $(R)_P$, shown in scheme (1), proceeds with preservation of stereochemical integrity at the chiral P-centre. This result speaks against dissociative mechanisms in the nucleophilic displacement at the dicoordinate sulfur centre both ionic or radical.[5]

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