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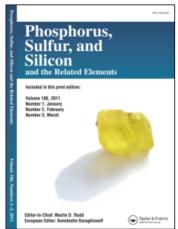
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Synthesis and Tautomerism of 1,3,2-Azathiaphosphacyclanes

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OR & FR A Z CI S

SYNTHESIS AND TAUTOMERISM OF 1,3,2-AZATHIAPHOSPHACYCLANES

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1,3,2-Azathiaphosphacyclanes were prepared by intramolecular alkylation of N- $(\omega$ -haloalkyl)amidophosphates and phosphonates.

Keywords: 1,3,2-Azatiaphosphacyclanes; ring-chain tautomerism

The facile synthetic route to 6- and 7-membered 1,3,2-azatiaphosphacyclanes $\bf 1$ was elaborated on the base of intramolecular S-alkylation in N-(ω -haloalkyl)amidophosphates and phosphonates $\bf 2$ under heating with NaI in MeCN solution. The compounds $\bf 1$ were prepared with 90–95% yields.

$$\begin{array}{c|c}
R \\
P \\
N-(CH_2)_n X \\
R''
\end{array}$$

$$\begin{array}{c|c}
NaI,MeCN \\
\Delta, -R'I
\end{array}$$

$$\begin{array}{c|c}
R \\
P \\
N \\
R''
\end{array}$$

$$\begin{array}{c|c}
I \\
R''
\end{array}$$

$$\begin{array}{c|c}
I \\
R''
\end{array}$$

R=Alkyl, AlkylO; n=3,4; X=Cl,Br; R"= Bu,Ph

SCHEME 1

In the case of diphenylthiophosphoryl derivate 3 (n=3) the cyclic phosphonium salt 4 was obtained. The tautomeric equilibrium between cyclic salt 4 and acyclic form 3 was found.

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SCHEME 2

The equilibrium position depends both on the solvent nature and temperature.