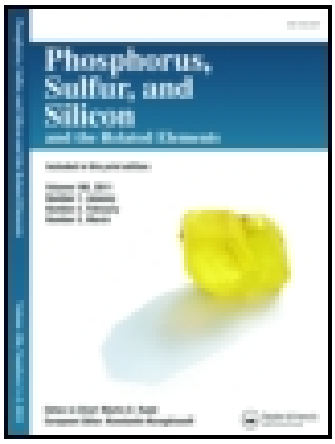

Phosphorus, Sulfur, and Silicon and the Related Elements

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# Novel 3-Cyanosubstituted 1,2-Thiaphosphacyclanes: Synthesis and Stereochemistry

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# NOVEL 3-CYANOSUBSTITUTED 1,2-THIAPHOSPHACYCLANES: SYNTHESIS AND STEREOCHEMISTRY

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*The facile synthetic route to 5- and 6-membered 3-cyano-2-oxo-1,2-thiaphosphacyclanes and 6-cyano-2-oxa-10-oxa(thia)-phosphabicyclo [4.4.0]-decane-1-oxides was elaborated via intramolecular S-alkylation in a series of ω-haloalkylsubstituted thiophosphorylacetonitriles. The compounds were used to prepare novel P(III)-containing bidentate ligands with definite stereochemistry. Diastereomeric transformations among 2-oxo-1,2-thiaphosphinanes were found and the mechanism of such transformations is suggested.*

*Keywords:* Intramolecular S-alkylation; 1,2-thiaphosphinanes; 1,2-thiaphospholanes; thiophosphorylacetonitriles

In spite of the fact, that functionalized 1,2-oxaphosphacyclanes are rather well investigated and some of them have already found numerous industrial applications, their nearest analogues having ring sulfur atom were still unknown. Recently, one of us, with coworkers,[1] demonstrated that nonfunctionalized omega-haloalkyl-substituted thiophosphoryl compounds undergo intramolecular S-alkylation easily, yielding either phosphacyclanium salts or 2-oxo-1,2-thiaphosphacyclanes (thiolphostones). Unfortunately, the subsequent functionalization of these compounds with the introduction of a substituent in the ring was a rather problematic task. Nevertheless, it was evident that this above reaction must be the general principle of 1,2- thiaphosphacyclane structure formation. In other words, using different functionalized

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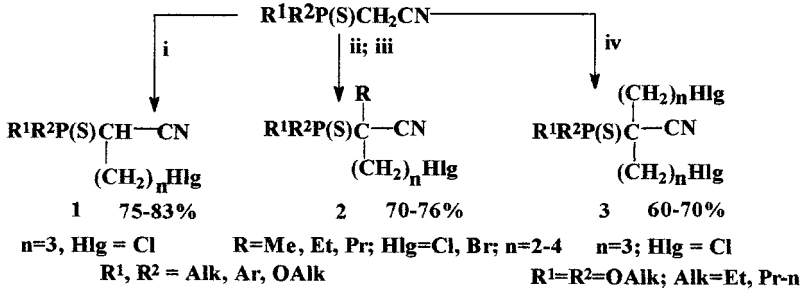


**FIGURE 1** i: $Br(CH_2)_3Cl$, 50% aq. $NaOH/CH_2Cl_2$/cat. TEBA; ii: RHlg, 50% aq. $NaOH/CH_2Cl_2$/cat. TEBA; iii: $Hlg^1(CH_2)_nHlg^2$, $KOH/CH_3CN$/cat. TEBA; iv: $Br(CH_2)_3Cl$, 50% aq. NaOH/without solvent/cat. TEBA.

thiophosphoryl compounds bearing omega-haloalkyl moiety as a starting material, one could obtain a wide range of thiaphosphacyclanes of interest. We realized this very simple and attractive idea with the example of intramolecular S-alkylation in a series of $\omega$-haloalkylsubstituted thiophosphorylacetonitriles, wherein dual reactivity was practically excluded during intramolecular cyclization.

## RESULTS AND DISCUSSION

The starting compounds **1–3** were obtained via alkylation of thiophosphorylacetonitriles under phase-transfer catalysis (PTC) conditions, wherein usage of different PTC systems allows facile preparing of different haloalkylsubstituted derivatives with high selectivity and good yields[2,3] (Figure 1).

Naturally , an introduction of strong electron-withdrawing cyano group decreases the tione sulfur nucleophilicity. That is why in some cases we exchange Cl for I to increase the electrophilicity of a halogen atom. Regardless of that, the compounds **1′** with the diphenythiophosphoryl group transform to the corresponding phosphacyclanium salts in $CH_3CN$ solution very slowly in comparison with their nonfunctionalized analogues (Figure 2). The equlibrium position is achived in about 6 months, but the amount of cyclic salt does not exceed 15%.

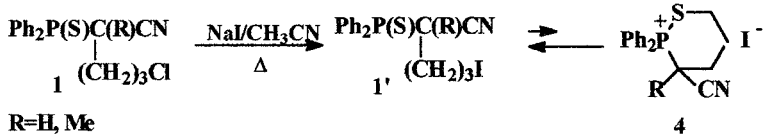


**FIGURE 2** R=H, Me.

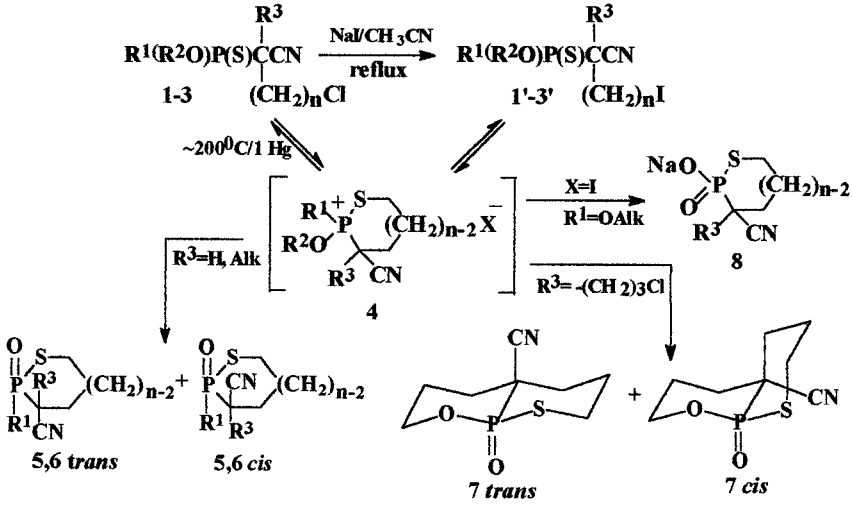


**FIGURE 3** $R^1 = Me$, OEt, OPr; Ph; $R^3 = H$, Me, Et, Pr; **5**, $n = 2$; **6**, $n = 3$.

At the same time, in the case of at least one alkoxy group at the phosphorus atom, the cyano group appears to facilitate the subsequent dealkylation shifting and therefore the equlibrium position. So even thiophosphorylacetonitrile derivatives **1–3** bearing a terminal chlorine atom are thermally unstable and transform to the corresponding five- and six-membered mono- and bicyclic thiolphostones **5–7** under distillation in vacuo[3–6] (Figure 3). Note that seven-membered cycles are not formed by such a procedure. Naturally, for the corresponding iodine derivatives **1′–3′**, S-alkylation proceeds under much more mild conditions and often with higher yields. Such modification could not be used only in the case of thiophosphonate structure in the starting compounds. The yields of the compounds obtained depend on the cyclization method in use, cyclic size, and the nature of alkyl group in the alkoxy group at the phosphorus atom, which undergoes dealkylation as well.

Compounds **5–7** were obtained as mixtures of cis and trans isomers and were resolved into individual ones by fractional crystallization and column chromatography. The structure of the starting compound and the methods of cyclization specify the ratio of the isomers formed during the cyclization. In $^{31}$P-NMR spectra the isomers have two closely located signals where mutual disposition is constant in a variety of solvents in use. This fact enables one to use $^{31}$P-NMR spectroscopy as a simple and convenient method for monitoring the stereochemical composition of the reaction mixtures and final products.

Detailed x-ray investigation[3] carried out for a variety of 3-cyano-substituted 1,2-thiaphosphacyclanes **5–7** shows that in all compounds under investigation the cyano group occupies the axial position. For 2-oxo-1,2- thiaphospholanes **5** the isomer having a downfield chemical shift in $^{31}$P-NMR spectra is characterized by cis disposition of P=O and CN groups with identical configuration of chiral centers ($R^*_P$,$R^*_C$), while the second isomer is the trans one with the opposite configuration of asymmetric atoms ($R^*_P$,$S^*_C$). On the contrary, for 2-oxo-1,2-thiaphosphinanes the diastereomer with a downfield shift in its $^{31}$P-NMR spectra is characterized by antiperiplanar disposition of cyano group and phosphoryl oxygen atom (trans, $R^*_P$,$S^*_C$), while synclinal arrangement of above mentioned groups (cis, $R^*_P$,$R^*_C$) corresponds to diastereomer with the smaller value $\delta_P$. And phosphabicyclodecane **7** fits this dependence as well.

Diastereomeric transformations were found in a series of 2-oxo-1,2-thiaphosphinanes **6**. The crude products consisting of both isomers transformed slowly to a preferred individual one, with substituent $R^1$ at the phosphorus atom occuping the most advantageous position in the view of general anomeric effect. Thus, there was obtained a cis isomer with an axial OAlk group when $R^1 = OAlk$ and a trans isomer with an axial phosphoryl oxygen when $R^1 = Alk$. In benzene solutions the slow opposite conversion of the preferred diastereomer to the equilibrium mixture with initial statistical ratio of isomers was observed. Since such transformations were not observed for the individual diastereomers of 3-alkyl-substituted 1,2-thiaphosphinanes **6** and 1,2-thiaphospholanes **5**, we believe that the carbanion mechanism of such transformations is realized.[4,5] That is to say, diastereomer conversions proceed via the dissociation of the 3-hydrogen atom, formation of a flat carbanion, and subsequent hydrogen attachment, with the configuration inversion of the asymmetric 3-carbon atom.

It was also shown that both isomers of 2-oxa-10-thia-phosphabicyclodecane present conglomerates that undergo crystal-induced spontaneous resolution (recrystallyzation from benzene). Thus, we obtained optically active crystals with rather high enantiomeric excess (*ee* 70% for cis isomer and 40% for the trans one). The ratio of enantiomers was estimated by $^{31}$P-NMR spectra using l-phenylethylamine as the shift reagent.

The reduction of 3-cyano-2-oxo-1,2-thiaphosphacyclanes **5**,**6** by $HSiCl_3$ was used to prepare novel P(III)-containing bidentate ligands with definite stereochemical configuration. The reaction proceeds under mild conditions while retaining the cyano group, cyclic structure, and configuration of the starting 2-oxoderivative. The complexes with Co(II), Rh(III), Re(I), and Pd(II) were obtained and investigated.

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