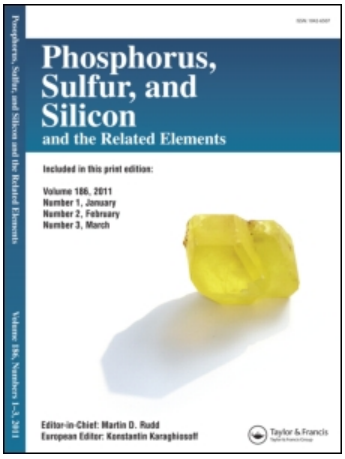

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F. Tardy[a]; M. Moreau[a]; D. Bouchu[a]; A. Skowronska[b]; J. Michalski[b]
[a] Universite LYON 1, Villeurbanne Cedex, France [b] Centre of molecular and monomolecular Studies, Boczna, Lodz, Poland

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Conversion of Cyclic Phosphorothioates into Halophosphates and Neutral Phosphorus Esters and Amides

F. Tardy[a], M. Moreau[a], D. Bouchu*[a], A. Skowronska[b], J. Michalski[b]

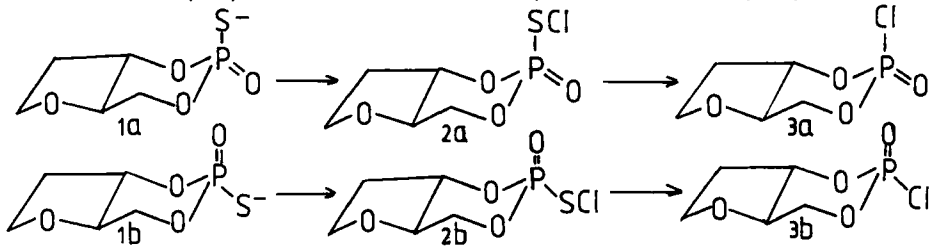
a) Universite´ LYON 1, 43, bd du 11 Novembre 1918,
69622 Villeurbanne Cedex, FRANCE

b) Centre of molecular and monomolecular Studies,
Boczna 5, Lodz, POLAND

Cyclic phosphorus esters and amides in the 1,3,2-dioxaphosphorinane-2-one series are usually obtained by the condensation of a diol with a suitable phosphorus oxyhalide. In the case of dissymetric diols the formation of two diastereoisomeric products, epimeric at phosphorus, can be expected. This procedure failed or proceeded with low yields when applied to the preparation of cyclic phosphates which would lead to the formation of sterically strained dioxaphosphorinane ring.[1]

It has been reported from other laboratories [2] that activation of cyclic phosphates (for example by the Appel reaction) enabled their conversion to the corresponding amidates. When applied to nucleoside cyclic-3',5'- phosphates this led to mixtures of diastereoisomers.

We chose to start from the phosphorothioates in order to have a better selectivity. Thus, in the context of studies about the preparation and reactivity of oxophosphoranesulphenylchlorides (RO)(R'O)P(O)SCl towards tricoordinated phosphorus compounds, we were able to achieve the stereospecific synthesis of ring strained chlorophosphates under mild conditions.[3] For example the reaction of the phosphorothioates **1a** and **1b** with equimolar amount of sulphuryl chloride in



methylene chloride below 0°C led to the corresponding oxophosphoranesulphenylchlorides **2a** and **2b** with full retention of configuration of the phosphorus atom. Treatment of those with phosphorus trichloride at -40°C stereospecifically affords the chlorophophates **3a** and **3b**. The activation of other sterically strained cyclic phosphorothioates and nucleoside cyclic-3',5'-phosphorothioates is currently being investigated.

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