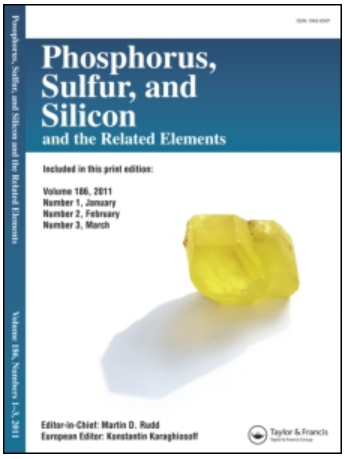

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Chemistry of C-Phosphorylated Thioformic Acid Derivatives

L. W. Kowalenko[a]; N. I. Buwashkina[a]
[a] Moscow Mendeleew Institute of Chemical Engineering, GSP, USSR

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CHEMISTRY OF C-PHOSPHORYLATED THIOFORMIC ACID DERIVATIVES

L.W.KOWALENKO and N.I.BUWASHKINA
Moscow Mendeleew Institute of Chemical Engineering,
Miusskaya pl. 9, Moscow A-47, GSP 125820, USSR

O-Alkylesters of dialkoxyphosphorylthioformic acids were formed in the Arbusov reaction of alkylchlorothionoformates with triesters of phosphorous acid

$$(RO)_3P + Cl\text{-}CS\text{-}OR' \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{-}\overset{S}{\overset{\|}{C}}OR' + RCl$$

Although dialkyl phosphonates do not react with alkylchlorothionoformates in the same conditions the yields of phosphonothionoformates are decreased by some impurities in trialkyl phosphites. One of the side-reactions is thion-thiol-rearrangement at carbon atom. The thiol esters resulting from this rearrangement were previously obtained in the reaction of sodium salts of dialkoxyphosphorylmonothioformic acids with methyliodide.[1] We prepared S-ethylesters of dialkoxyphosphorylthioformic acids from trialkylphosphites and S-ethylchlorothioformate. The reaction of alkylamines with O-alkylesters of dialkoxyphosphorylthioformic acids gave dialkylesters of N-alkylsubstituted thiocarbamoylphosphonic acids in form of yellow solids. These compounds were also prepared in the base-catalyzed reaction of dialkyl phosphonates and alkylisothiocyanates.[2] The mass spectra of dialkoxyphosphorylthionoformates stored without tert-butylcatechol showed cracking patterns with very high m/z values. An important pathway of fragmentations of C--phosphorylated thioformates is represented by the formation of ions with P-S-bonds resulting from cleavage of P-C-bonds.

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