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Chemistry of C-Phosphorylated Thioformic Acid Derivatives

L. W. Kowalenko^a; N. I. Buwashkina^a

^a Moscow Mendeleev Institute of Chemical Engineering, GSP, USSR

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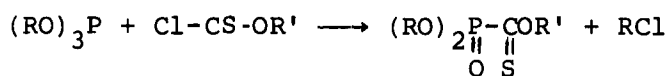
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CHEMISTRY OF C-PHOSPHORYLATED THIOFORMIC ACID DERIVATIVES

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

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



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 thionthiol-rearrangement at carbon atom. The thiol esters resulting from this rearrangement were previously obtained in the reaction of sodium salts of dialkoxylphosphorylmonothioformic acids with methyl iodide.¹ We prepared S-ethylesters of dialkoxylphosphorylthioformic acids from trialkyl phosphites and S-ethylchlorothioformate. The reaction of alkylamines with O-alkylesters of dialkoxylphosphorylthioformic 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 dialkoxylphosphorylthionoformates 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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