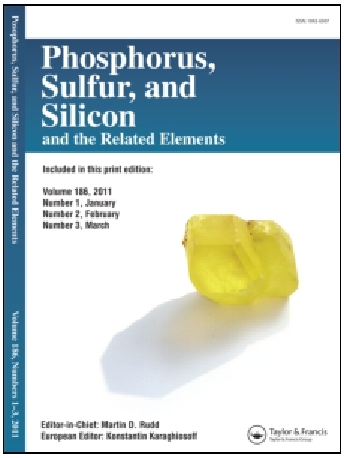

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Synthesis and Properties of Phosphorylated and Silylated α-Mercaptocarbonyl Compounds

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SYNTHESIS AND PROPERTIES OF PHOSPHORYLATED AND SILYLATED α-MERCAPTOCARBONYL COMPOUNDS

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Abstract Phosphorylation and silylation of α-mercaptocarbonyl compounds have been investigated. A novel type of 1.4 S-O migration trimethylsilyl and P(III) groups has been discovered. The thiophosphite-thiophosphonate rearrangement when exposed to oxygen as well as heterocyclization with the formation of 1,3,2-oxathiaphospholenes and 1,3,2-oxathiasilalenes were also found. Some regularities of these processes and the properties of heterocycles synthesized have also been brought out.

INTRODUCTION

The chemical behaviour of phosphorylated α-oxy and α-aminocarbonyl compounds has been investigated in detail. The latter have proved to be convenient semiproducts for the synthesis of new heterocyclic systems, which exhibit high biological activity in a number of cases.[1,2] At the same time α-functionally substituted mercaptans have not been investigated as yet. The investigations of these problems open up new possibilities for the synthesis of unsaturated linear and cyclic P,Si,S-containing substances, for prospecting new rearrangements for obtaining biologically active compounds.

RESULTS AND DISCUSSION

The phosphorylation of some α-mercaptoketones by dialkylchlorophosphites in the presence of a base has been carried out for the preparation of functionally substituted thioesters of the acids of P(III). Though instead of the expected products corresponding thionphosphonates 1 have been isolated.

$$(RO)_2PCl + HSCHR^1C(O)Me \xrightarrow{B} (RO)_2PSCHR^1C(O)Me \longrightarrow$$

$$\longrightarrow (RO)_2P(S)\underset{1}{C}HR^1C(O)Me$$

$$(RO)_2PCl + Me_3Si\text{-}SR^1 \longrightarrow \underset{2}{(RO)_2PSR^1} + Me_3SiCl$$

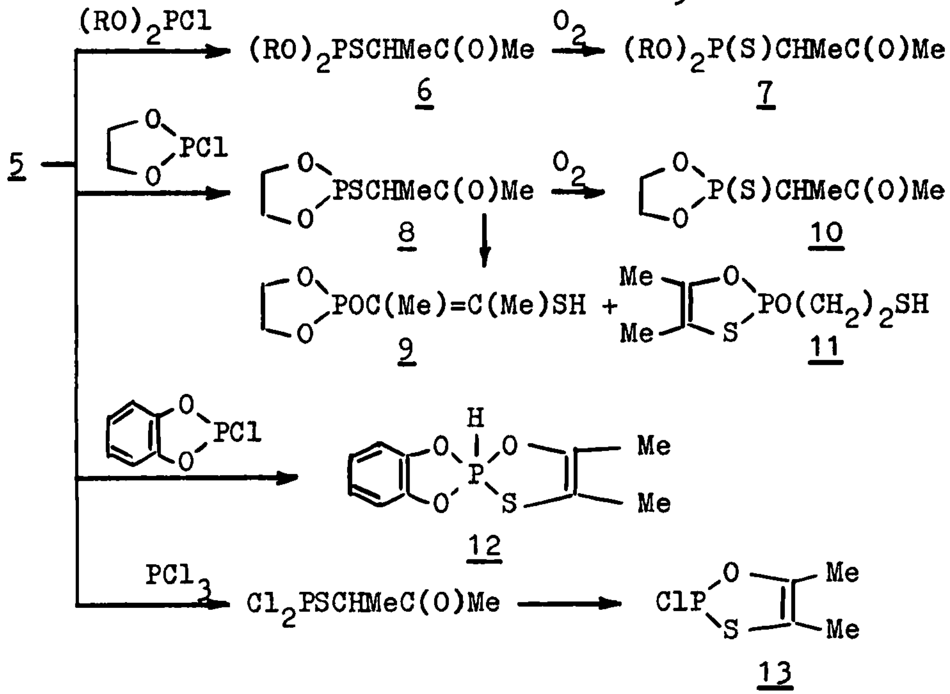
O,O-Dialkyl-S-alkylthiophosphites have also been found to manifest the tendency towards isomerization. Since our attempt to obtain them in the individual form with traditional methods had failed, another route was worked out with silylated mercaptans. Special experiments on the thiophosphite-thiophosphonate rearrangment showed it to be catalized by the oxygen of the air, the simplicity of the reaction depending upon the nature of the substituents attached to sulfur. The above method was extended to the synthesis of functionally substituted thiophosphites. The necessary S-silyl esters of α-mercaptoketones were obtained by silylation mercaptans with various silylating agents. The silylated mercaptoacetone 2 formed proved to be rather unstable and was converted to vinylmercaptan 3 within several hours due to the S→O migration of the trimethylsilyl group. The 3 polymerizes rapidly.

$$MeC(O)CH_2SH + Me_3Si\text{-}X \longrightarrow \underset{2}{Me_3SiSCH_2C(O)Me} \longrightarrow$$

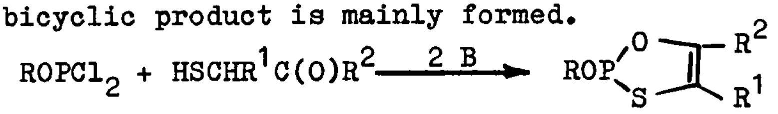
$$\longrightarrow \underset{3}{Me_3SiOC(Me){=}CHSH} \xrightarrow{Me_3SiX} \underset{4}{Me_3SiOC(Me){=}CHSSiMe_3}$$

Trimethylsilyl group, attached to sulfur contributes to the stabilization of unsaturated siloxyvinylmercaptan. The 4 is stable, it represents the mixture of E and Z isomers and is a convenient semiproduct for the insertion of the functionally substituted vinylthiofragment, including the phosphorus atom. The product of silylation of 2-mercaptobutanone-3 5 appeared to be more stable than silylated mercaptoacetone. The phosphorylation of the compound 5 by dialkylchlorophosphites or ethylenglykolechlorophosphite results in the quantitative formation of thiophosphites 6, 8, which rearranges to thiophosphonates 7, 10 even on slight contact with the environment.

$$Me_3SiCl + HSCHMeC(O)Me \xrightarrow{B} \underset{5}{Me_3SiSCHMeC(O)Me}$$



The compound 8 when staied for 2-3 days in the absence of oxygen turns to 9, 11. The phosphorylation of the 5 by pyrochatecholchlorophosphite and phosphorus trichloride gives rise to the 12, 13 - the first representatives of a new class of P,O,S-containing unsaturated heterocycles. Anologous results have been obtained from the investigation of the interaction of phosphorus trichloride and alkyldichlorophosphites with α-mercaptoketones in the presence of a base. Without the latter the O,S-containing bicyclic product is mainly formed.



Some mono-, di- and triamidophosphites were introduced into the reaction with α-mercaptoketones in order to extend the number of phosphorylating reagents. Depending on the temperature conditions two trends can be observed giving rise to oxathiaphospholenes, dithiophosphates and thiophosphonates. We have investigated reactions of 1,3,2-oxathiaphospholenes with various nucleophilic and electrophilic agents, leading to the formation of a new heterocyclic tetra- and pentacoordinated phosphorus atom. The P-S bond in 1,3,2-oxathiaphospholenes has been shown to break easily when exposed to protondonor and halogen-containing agents.

Unlike α-mercaptoketones the ethers of thioglykol acid when heated react with phosphorus trichloride with the formation of dichlorothiophosphite. While passing dry hydrogen chloride through dichlorothiophosphite the latter decomposes exothermally into the initial agents, but at 180-190 °C undergoes heterocyclization with the formation of 2-chloro-5-oxa-1,3,2-oxathiaphospholane. The phosphorylated derivatives of thioglykol acid have been prepared by the interaction of di-, triamides and chloranhydrides of the trivalent phosphorus acids with unsubstituted and silylated ethers of thioglykol acid. When dry oxygen is passed through the synthesized compounds the latter isomerize to corresponding thiophosphonacetic ethers, which are isolated in the good yields. The common regularities of the isomerization of phosphorylated α-mercaptocarbonyl compounds when exposed to oxygen have been investigated.

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