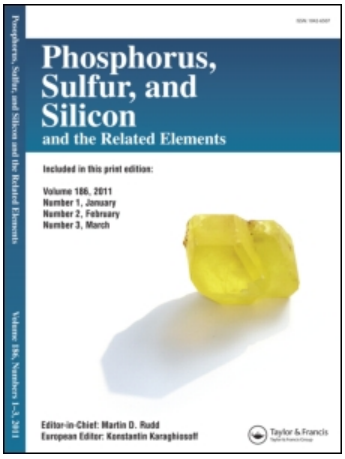

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PHOSPHORYLATED AND SILYLATED DERIVATIVES OF ALFA-MERCAPTOCARBONYL COMPOUNDS

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Abstract The phosphorylation and silylation of α-mercaptocarbonyl compounds have been investigated. Novel different cyclic and linear silicon(phosphorus) containing derivatives have been obtained.

Key words: α-Mercaptocarbonyl compounds, trimethylchlorosilane, chlorophosphites, phosphorylation, silylation, 1,3,2-oxathiaphospholenes, thiophosphites, siloxyalkenes.

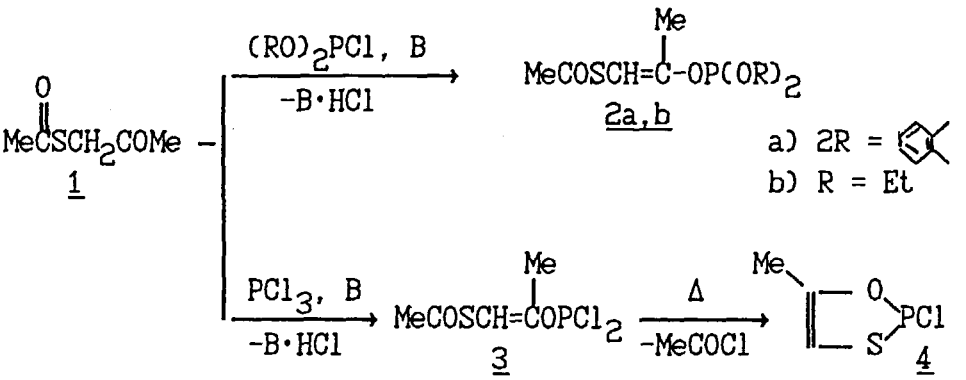
INTRODUCTION

The chemical behaviour of phosphorylated α-oxy- and α-aminocarbonyl compounds has been described in detail [1,2]. Meanwhile, the phosphorylation and silylation of α-functionally substituted mercaptanes has not been adequately investigated [3]. In this paper we would like to report on phosphorylated and silylated products of α-mercaptocarbonyl compounds and their use in elementoorganic synthesis.

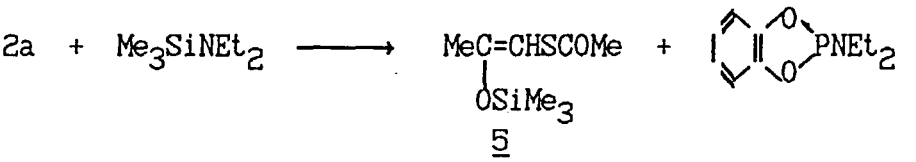
RESULTS AND DISCUSSION

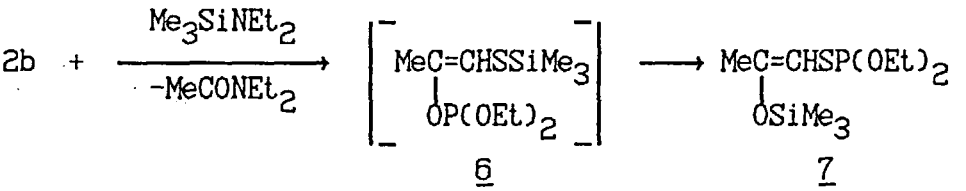
By the interaction of α-mercaptoacetone with acetylchloride ketone 1 was obtained. The interaction of 2-chloro-1,3,2-dioxabenzophospholene or diethylchlorophosphite with ketone 1 results in the formation of functionally substituted vinylphosphites 2a,b. When phosphorus trichloride is used in this reaction vinyldichlorophosphite 3 is formed,

which when heated is converted into 1,3,2-oxathiaphospholene 4 with the elimination of acetylchloride.



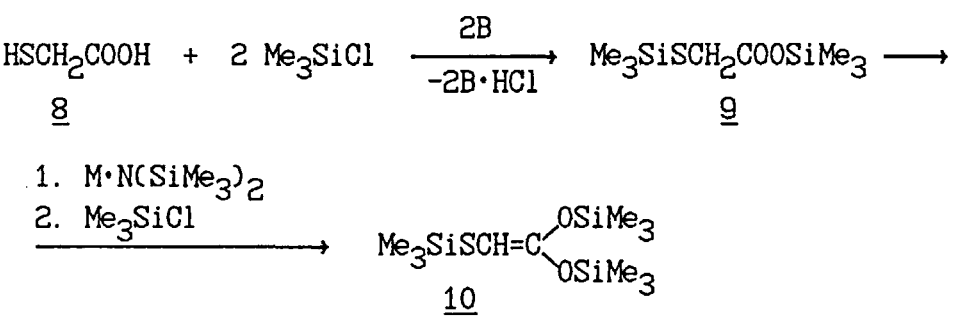
In the reaction of phosphite 2a with trimethylsilyldiethylamine the nucleophilic attack is directed to a highly electrophilic phosphorus atom with the elimination of 2-diethylamino-1,3,2-dioxabenzophospholene and formation of siloxyalkene 5. Meanwhile, when the electrophility of phosphorus atom is rather low, as in molecule 2b, the interaction with trimethylsilyldiethylamine is accompanied by elimination of N,N-diethylacetamide and formation of vinylphosphite 7.



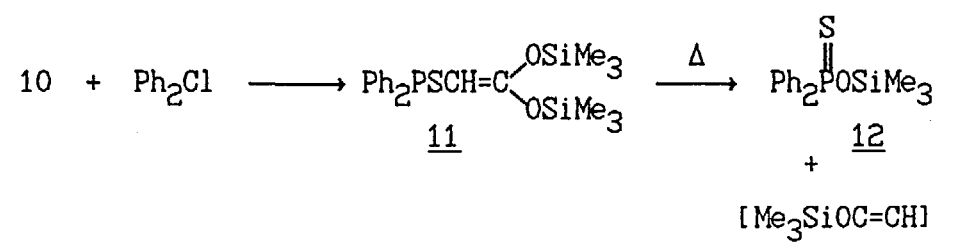


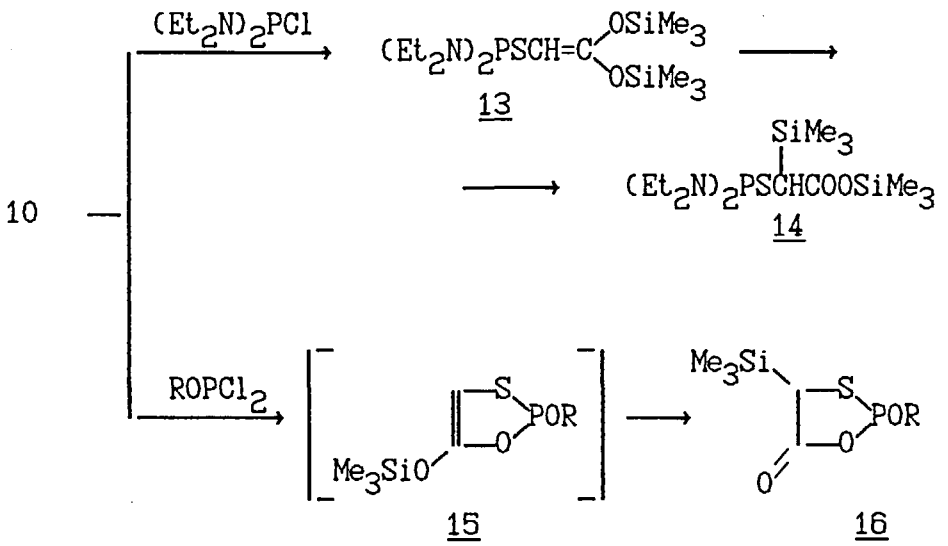
This result is the consequence of the formation of vinylphosphite 6, which is converted into a final product 7 due to the internal 1,4 O-S exchange process.

We also conducted the silylation of α-mercaptoacetic acid 8. At first trimethylsilyl(trimethylsilylthio)acetate 9 was obtained, which when acted upon by sodium or lithium bis(trimethylsilyl)amide and trimethylchlorosilane was converted into 1-trimethylsilylthio-2,2-bis(trimethylsiloxy)ethylene 10. As is known, the carbonyl group of carbonic acids is not subgect to enolization and therefore the strong base must be used for the rupture of C-H bond and introduction of trimethylsilyl group.



The compound 10 is a novel organosilicon synton, which may be used for obtaining different organophosphorus compounds. Its interaction with diphenylchlorophosphine proceeds at room temperature and gives rise to thiophosphinite 11 which when distilled is converted into siloxythiophosphinate 12.





The interaction of siloxyethene 10 with tetraethyldiaminochlorophosphine is accomplished with the formation of thioamidophosphite 13, which when distilled or stored for a long time is rearranged into compound 14. The reaction of alkene 10 with alkyldichlorophosphites is unexpected. In this case the products of reaction are 2-alkoxy-4-trimethylsilyl-1,3,2-oxathiaphospholane-5-one 16. Apparently, reaction proceeds with the internal formation of oxathiaphospholenes 15, which under reaction conditions are isomerized into the final products 16.

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