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New Sulfur, Silicon and Phosphorus Containing Reagents

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The problems of synthesis and transformations of new organoelement reagents containing sulfur, silicon and phosphorus (S-P-O-Si, P(S)-S-Si) are discussed.

INTRODUCTION

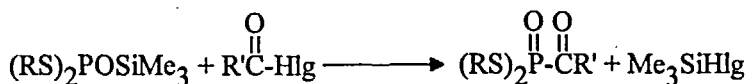
Silyl derivatives of phosphorus (III) and (IV) thioacids with S-P-O-Si and P(S)SSi fragments are important intermediates for synthesizing useful organoelement compounds. However, there are no facile methods of their synthesis. In this communication new convenient methods are presented for synthesis of O-silyldithiophosphites and S-silyldithio- and tetrathio phosphates. Their reactions with various compounds are studied.

RESULTS AND DISCUSSION

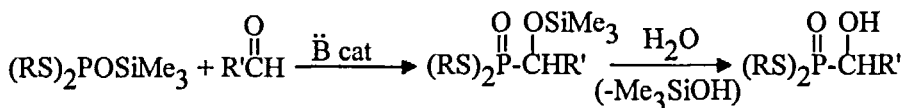
We used bis(silyl)acetamide and have developed an efficient method for the synthesis of O-silyldithiophosphites directly from chlorodithiophosphites.



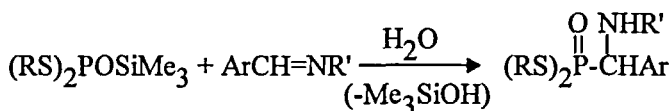
O-Silyldithiophosphites possess a labile Me_3Si group and revealed high reactivity to a large series of nucleophilic and electrophilic reagents to form numerous organothiophosphorus compounds. They react with oxygen, sulfur, water, alcohols, alkyl and acyl halides, and phosphorus (III) chlorides.



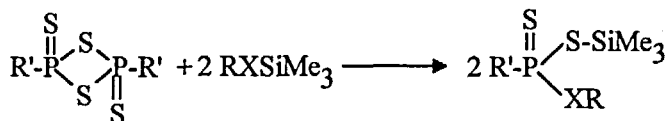
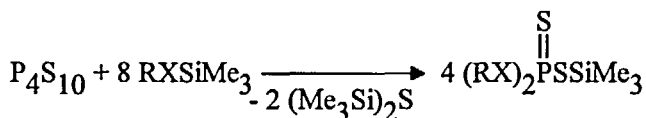
O-Silyldithiophosphites add to C=O group of aldehydes and ketones to give (1-siloxy)alkyl dithiophosphonates.



The reactions of O-silyldithiophosphites with azomethines and alcoxyacetylenes result in adducts of dithiophosphate structure.

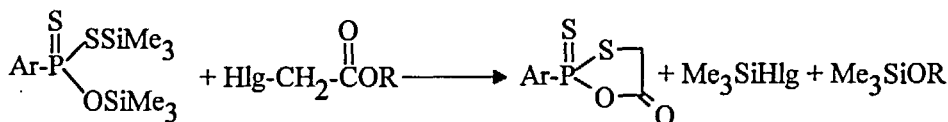
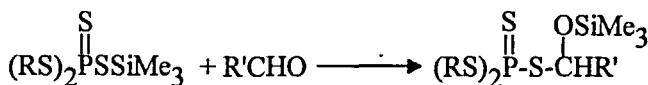


We have recently developed facile methods of synthesizing S-silyl esters of dithio- and tetrathiophosphoric acids and aryldithio- and trithiophosphonic acids on the basis of the reactions P_4S_{10} and Lawesson's and Davy's reagents with alkoxy- and alkylthiosilanes.



R = Alk; Alkenyl; cycloalkenyl, R' = Ar, SAlk; X = O, S

The products obtained serve as intermediates for synthesizing linear and heterocyclic organothiophosphorus compounds. Thus, reactions of silyltetrathiophosphates with aldehydes, acetals, ortho ethers, amins, thioacetals, bis(thiocyanato)methane, dialkyl disulfides and alkyl halides resulted in the products of tetrathiophosphate structure.



Hlg = Cl, Br; R = Alk

Thus, silyl esters of phosphorus (III) and (IV) thioacids are used as sulfurizing, silylating and thiophosphorylating agents.