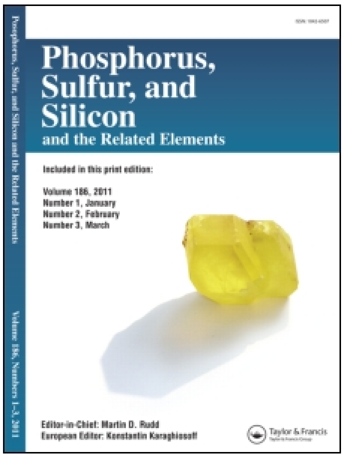

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Synthesis of Organophosphorus Compounds in Terms of Elemental Phosphorus, Sulfur and their Derivatives

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We have developed new facile methods for synthesizing various organophosphorus compouds on the basis of elemental phosphorus and sulfur, phosphorus sulfides and esters of thiophosphorous acids.

Keywords: elemental phosphorus; sulfur; organophosphorus compouds

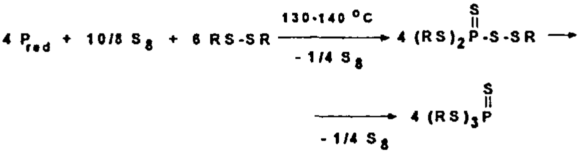
INTRODUCTION

One of the timely problems of phosphorus chemistry is the development of ecologically pure methods for their preparation. The traditional techniques for their synthesis are based on phosphorus chlorides. We have developed new facile methods for synthesizing various organophosphorus compouds on the basis of elemental phosphorus and sulfur, phosphorus sulfides and esters of thiophosphorous acids.

RESULTS AND DISCUSSION

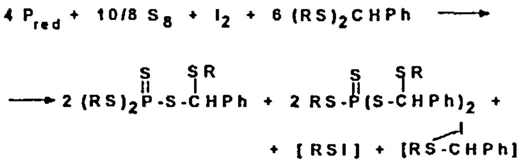
Most of the reactions of elemental phosphorus (white or red) with organic substances studied have been carried out under basic and phase transfer catalyst conditions[1-2]. Proton donating substances such as alcohols were used in the reactions of a mixture of elemental phosphorus and sulfur. However, these reactions are accompanied by the evolution of hydrogen sulfide and result in the mixture of products which hamper their isolation and purification[3]. In this connection we investigated the reaction of elemental phosphorus and sulfur with non-containing proton reagents such as dialkyl disulfides, thioacetals, disilylated diols and stannylated alcohols[4, 5].

We have observed that the reaction of red phosphorus and elemental sulfur with dialkyl disulfides leads to trialkyl pentathiophosphates with the S-S bond at 130-140°C[4]. These pentathiophosphates decompose during distillation to form trialkyl tetrathiophosphates with elimination of sulfur.



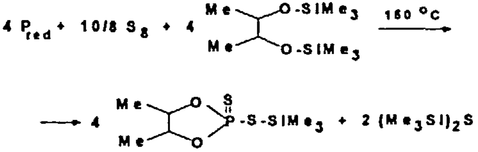
$$4\,P_{red} + 10/8\,S_8 + 6\,RS\text{-}SR \xrightarrow[-1/4\,S_8]{130\text{-}140\,^{\circ}C} 4\,(RS)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}SR \xrightarrow[-1/4\,S_8]{} 4\,(RS)_3\overset{S}{\overset{\|}{P}}$$

The formation of tetrathiophosphates and trithiophosphites occurs already at room temperature in the presence of elemental iodine in dry benzene. Similar results were obtained when white phosphorus was used. We have also found that the interaction of red phosphorus with thioacetals in the presence of elemental sulfur and iodine results in products of a (1-alkylthio)alkyl tetrathiophosphate structure.



$$4\,P_{red} + 10/8\,S_8 + I_2 + 6\,(RS)_2CHPh \longrightarrow 2\,(RS)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\overset{SR}{\overset{|}{C}}HPh + 2\,RS\text{-}\overset{S}{\overset{\|}{P}}(S\text{-}\overset{SR}{\overset{|}{C}}HPh)_2 + [RSI] + [RS\text{-}CHPh]$$

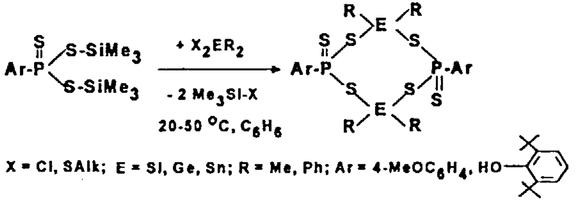
Cyclic silyldithiophosphates were synthesized by treating disilylated diols with a mixture of red phosphorus and elemental sulfur.



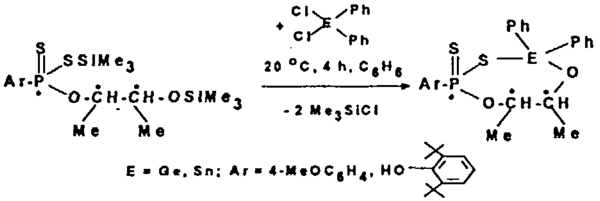
Similarly stannyldithiophosphates were formed in the reaction of mixture of red phosphorus and sulfur with stannylated alcohols.

We consider that the reactions of elemental phosphorus and sulfur with organic substances may proceed through the intermediate formation of phosphorus sulfides. We decided to confirm this assumption and studied the reactions of phosphorus sulfides with dialkyl disulfides and thioacetals. These reactions resulted in the same final products that were found in the case of the reactions of mixtures of elemental phosphorus and sulfur as well. In the case of the reactions of dialkyl disulfides we observed the formation of the same intermediate pentathiophosphates with the S-S bond. Use of nucleophilic reagents such as potassium carbonate, sodium sulfide and sodium alkylthiolates results in the reactivity enhancement of phosphorus sulfides with dialkyl disulfides. Iodine leads to an increased reaction rate and yields of products formed in both types of reactions.

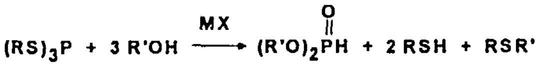
It was known that the reaction of the mixture of red phosphorus and sulfur with anisole results in the formation of Lawesson's reagent [3]. Lawesson's reagent and its analogues have proved to be effective initial substances for the synthesis of new types of cyclic organothiophosphorus compounds through their silyl derivatives. For this purpose we have obtained a series of disilyl esters of dithiophosphonic and trithiophosphonic acids on the basis of the reactions of 1,3,2,4-dithiadiphosphetane-2,4-disulfides with disilylated sulfides and diols. We have also shown the prospects of these disilyldithiophosphonates and trithiophosphonates in the reactions with dimethylsilane and diphenylstannane dichlorides which resulted in new eight membered silicon and germanium-containing heterocycles.



We have managed to synthesize a new type of seven membered phosphocyclanes on the basis of disilyldithiophosphonates in their reactions with diphenylgermanium and tin dichlorides.



When the reaction of disulfides and white phosphorus and later on with thiols involving the formation of trialkyltrithiophosphite in good yields was discovered it has become possible to use the latter as initial material for synthesizing various organophosphorus compounds[1]. We used the reaction based on the trialkylphosphites for obtaining organophosphorus compounds without any sulfur atoms.



$$(RS)_3P + 3\,R'OH \xrightarrow{MX} (R'O)_2\overset{\overset{O}{\|}}{P}H + 2\,RSH + RSR'$$

M = Cu, Zn, Cd, Hg; X = Cl, Br, I

We have studied the reactions of triethyl and triphenyl trithiophosphites with excess alcohols (EtOH, MeOH) in the presence of metal halides.

Thus, novel methods for synthesizing organophosphorus compounds were developed in terms of elemental phosphorus and sufur and their derivatives.

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