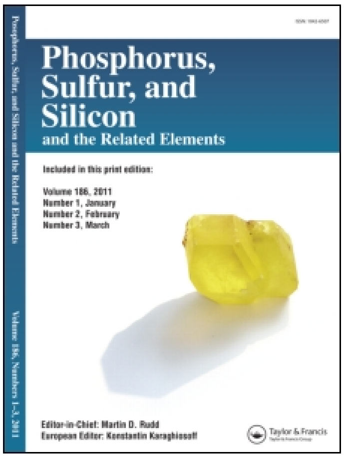

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SYNTHESIS AND PROPERTIES OF MIXED ORGANIC DERIVATIVES OF ELEMENTS OF III, IV and V GROUPS AND PHOSPHORUS (IV) THIOACIDS

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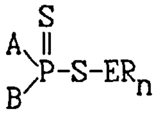
Abstract New convenient methods of synthesizing useful mixed organic derivatives of B, Si, Ge, Sn, Pb, As and phosphorus (IV) thioacids with a P(S)S-E fragment were developed. Their spectral, structural and chemical properties were studied.

INTRODUCTION

Organoelement derivatives of phosphorus (IV) thioacids with the general formula



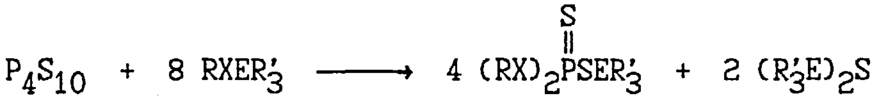
$$\begin{matrix} A \\ B \end{matrix}\!\!>\overset{S}{\overset{\|}{P}}\text{-S-ER}_n$$

A, B = AlkO, ArO, AlkS, Alk_2N, Alk, Ar; R = Alk, Ar;
E = B, Si, Ge, Sn, Pb, As; n = 2, 3

with a P(S)S-E fragment serve as intermediates for synthesizing numerous linear and heterocyclic organothiophosphorus compounds. In this case a series of fundamental problems of phosphorus chemistry could be solved. However there no convenient methods of their synthesis. They were obtained by the interactions of dithiophosphoric acids or their salts with organoelement halides. These techniques are multistep procedures, as the initial dithiophosphoric acids had to be synthesized by treatment of organic hydroxy compounds with P_4S_{10} with the evolution of gaseous H_2S.

RESULTS AND DISCUSSION

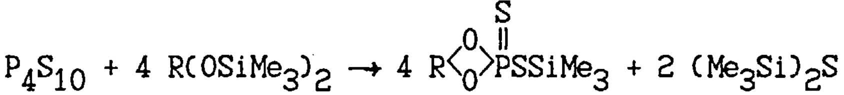
The reactions of P_4S_{10} with trimethylsilyldialkylamines and bis(trimethylsilyl)sulfide were reported to yield S-trimethylsilyl N,N'-bis(dialkylamido)dithiophosphates and tris(trimethylsilyl) tetrathiophosphates.[1] We have tried to extend these degradation reactions of P_4S_{10} to other organosilicon compounds. We used the trimethylsilyl protecting group in protonodonating reagents such as saturated and unsaturated alcohols, enols, thiols and diols and have developed facile methods of synthesizing S-trimethylsilyl dithio- and tetrathiophosphates directly from P_4S_{10} and thus avoided the formation of H_2S. Similar results were obtained in the reactions of P_4S_{10} with alkoxy- and alkylthiogermanes, stannanes and plumbanes at 20-40°C.



$$P_4S_{10} + 8\ RXER'_3 \longrightarrow 4\ (RX)_2\overset{\overset{S}{\|}}{P}SER'_3 + 2\ (R'_3E)_2S$$

R = Alk, $H_2C{=}CHCH_2$-, $HC{\equiv}C\text{-}CH_2$-; R'= Alk, Ar; X= O, S;

E = Si, Ge, Sn, Pb

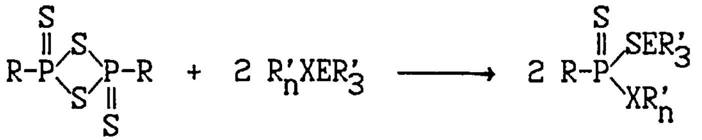


$$P_4S_{10} + 4\ R(OSiMe_3)_2 \rightarrow 4\ R{<}^{O}_{O}{>}\overset{\overset{S}{\|}}{P}SSiMe_3 + 2\ (Me_3Si)_2S$$

R = alkylene

These preparative methods are characterized by minimum steps, simple operations, mild conditions, high yields of products and no by-products. Alkoxysilanes have proven to be less reactive toward P_4S_{10} than alkylthiosilanes. The reactivity of alkoxides of main IV group elements increases in the following series: Si < Ge < Sn < Pb.

The mechanism of the reaction of P_4S_{10} with silylamines has been discussed by Roesky and Remmers[1] when the nucleophilic nitrogen atom attacks the phosphorus atom of P_4S_{10}. We assumed that during the destruction process of P_4S_{10} some intermediates can be formed in which a structural fragment may be similar to that of 2,4-bis(alkylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes (homologues of Davy's reagent) in their trimer form. Consequently the interaction of 1,3,2,4-dithiadiphosphetane-2,4-disulfides with organoelement derivatives can be used as a model reaction of some intermediate processes of degragation of P_4S_{10}. We varied the 1,3,2,4-dithiadiphosphetane-2,4-disulfides on the one hand and the silicon, germanium, tin and lead derivatives on the other hand.

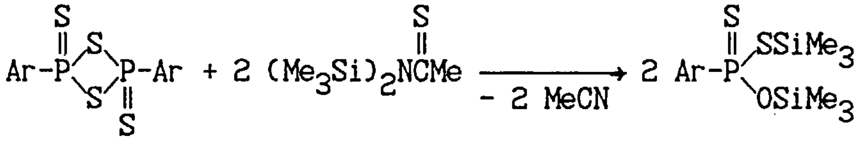


R = SAlk, $NAlk_2$, $4\text{-}MeOC_6H_4$; R' = Alk; R'' = Alk, Ph;

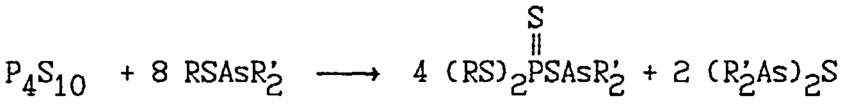
X = O, S, N; E = Si, Ge, Sn, Pb; n = 1, 2

The reactivity of alkoxides of main IV group elements towards 1,3,2,4-dithiadiphosphetane-2,4-disulfides increases in the series: Si < Ge < Sn < Pb. Ultrasonic irradiation leads to the increased reaction rate and the reduction in reaction temperature and time in the reactions of P_4S_{10} and Lawesson's reagent with bis(trialkylstannyl)sulfide and alkylthiostannanes and to the increased yields of stannyl tetrathiophosphates and aryltrithiophosphonates.

Bis(trimethylsilyl)acetamide reacts with 2,4-bis-(aryl)-1,3,2,4-dithiadiphosphetane-2,4-disulfides to form O,S-bis(trimethylsilyl)aryl dithiophosphonates.

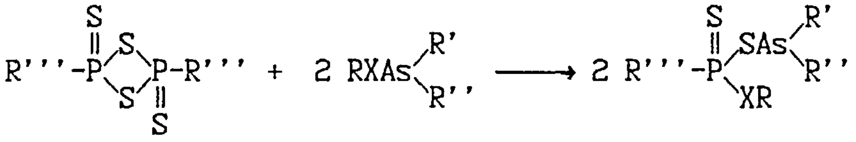


We extended this approach to the organic derivatives of main III and IV group elements. New preparative methods of synthesizing S-organoarsenic derivatives of tetrathiophosphoric and aryldithio- and trithiophosphonic acids were developed on the basis of the reactions of P_4S_{10}, Davy's and Lawesson's reagents with alkoxides and alkylmercaptides of arsenic (III) at 20°C.



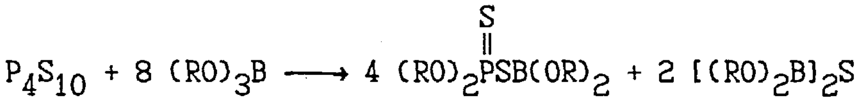
$$P_4S_{10} + 8\ RSAsR'_2 \longrightarrow 4\ (RS)_2\overset{S}{\overset{\|}{P}}SAsR'_2 + 2\ (R'_2As)_2S$$

R = Alk; R' = Alk, Ph

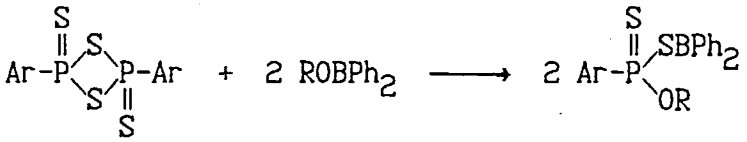


R = Alk; R' = Alk, Ph, OAlk; R'' = Alk, Ph, OAlk;
R''' = SAlk, 4-$MeOC_6H_4$; X = O, S

However reactions of P_4S_{10} and Lawesson's reagent with alkoxides of boron take place under severe conditions (130-150°C, 2-3 h) with the formation of boron derivatives of dithiophosphoric and aryldithiophosphonic acids. These reactions were also facilitated when ultrasound was employed (60-90°C, 20-50 min).



$$P_4S_{10} + 8\ (RO)_3B \longrightarrow 4\ (RO)_2\overset{S}{\overset{\|}{P}}SB(OR)_2 + 2\ [(RO)_2B]_2S$$



R = Alk; Ar = 4-$MeOC_6H_4$

The products obtained serve as intermediates for synthesizing linear and heterocyclic organothiophosphorus compounds. Reactions of trimethylsilyl tetrathiophosphates with aldehydes, acetals, ortho ethers, aminals, thioacetals, bis(thiocyanato)methane, disulfides and alkyl halides resulted in the products of tetrathiophosphate structure. Heterocyclic compounds were obtained in the reactions of O,S-bis(trimethylsilyl)aryl dithiophosphonates with α-halogen carboxylic esters.

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