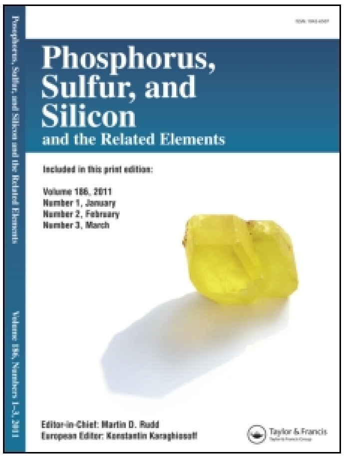

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E. S. Batyeva[a]; O. G. Sinyashin[a]; V. A. Al'fonsov[a]
[a] A.E. Arbuzov Institute of Organic and Physical Chemistry Kaean Branch Academy of Sciences, Kazan, USSR

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THE CHEMISTRY OF THIOLODERIVATIVES OF TRIVALENT PHOSPHORUS ACIDS

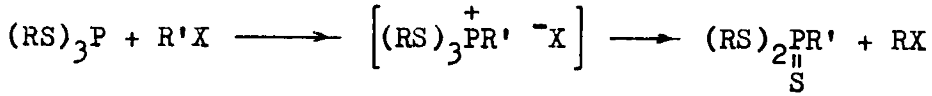
E.S.BATYEVA, O.G.SINYASHIN, V.A.AL'FONSOV

A.E.Arbuzov Institute of Organic and Physical
Chemistry Kazan Branch Academy of Sciences,
Arbuzov str., 8, Kazan, 420083, USSR

Abstract The substitution and addition reactions have been studied in the series of thioloderivatives of P(III) acids. The reactions have been shown to proceed with the rupture of the P-S bond, the phosphorus coordination being preserved.

RESULTS AND DISCUSSION

Among various organophosphorus compounds thioloderivatives of the P(III) acid have been a poorly investigated class of organophosphorus compounds as yet. A systematic study of the chemical behaviour of the thioloderivatives of P(III) acids in the substitution and addition reactions has been carried out. Trialkyltrithiophosphites have been estimated to react with alkylhalides in accordance with the Arbuzov reaction scheme resulting in S,S-dialkyltrithiophosphonates rather than in substitution products as described earlier.



$$(RS)_3P + R'X \longrightarrow \left[(RS)_3\overset{+}{P}R'\ {}^{-}X\right] \longrightarrow (RS)_2\underset{\underset{S}{\|}}{P}R' + RX$$

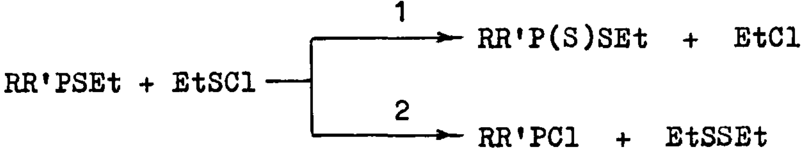
This makes the reactions of thioesters of P(III) acids with alkylhalides unlike those of thiophosphites with acylhalides, involving the substitution reaction.

$$(RS)_3P + R'C(O)X \xrightarrow{HX} (RS)_2PX + R'C(O)SR$$

The reactions of thioesters of P(III) acids with mineral and organic acids take place with the rupture of the P-S bond. In this case as a rule the substitution of the thiol group at the phosphorus atom results in the anhydride derivative of the corresponding P(III) acid and mercaptane.

$$R_2P\text{-}SR + HX \rightleftharpoons R_2P\text{-}X + RSH$$
$$X = Cl,\ RC(O)O,\ R_2P(S)S,\ R_2P(S)\ \text{et.al.}$$

The study of the reactions of thioesters of phosphorous and phosphinous acids with aliphatic and aromatic sulphene chlorides has shown the interaction to the Arbuzov reaction scheme (1) and with the substitution of the alkylthiogroup at trivalent phosphorus by the halogen atom (2).



The interaction of thioesters of P(III) acids with halogens and halogen containing electrophilic reagents is mostly carried out with the substitution of the thiol group at the phosphorus atom with the conservation of its coordination. We consider the reactions to proceed through the intermediate formation of sulphene halides.

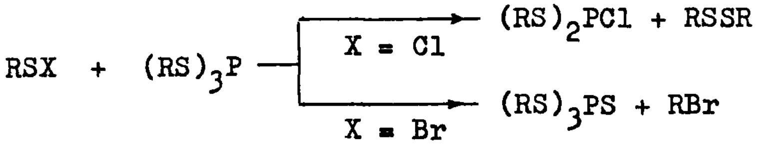
The interaction of trialkyltrithiophosphites with chlorine and bromine with the correlation of reagents 2:1 results in corresponding halodithiophosphites, tetrathiophosphates and alkylhalides.

$$2\ (RS)_3P + X_2 \longrightarrow (RS)_2PX + (RS)_3PS + RX$$

The same trend has been observed in the reaction of trithiophosphites with another chlorinating agent - PCl_5.

The interaction of trithiophosphites with CCl_4 also takes place with the correlation of the reagents 2:1 and results in trichloromethyldithiophosphonite, chlorodithiophosphite and dialkyldisulphide. In similar conditions trichlorobromomethane reacts with trithiophosphite with the formation of tetrathiophosphate and alkylbromide along with trichloromethyldithiophosphonite.

$$(RS)_3P + CCl_3X \rightleftharpoons (RS)_2PCCl_3 + RSX$$

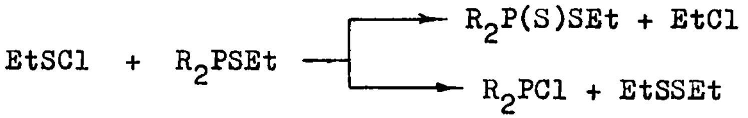


The study of the reactions of the thioesters of phosphinous and phosphorous acids with halogenacetic acids has shown the interaction to take place with the correlation of the initial reagents 2:1, as was the case with the other compounds containing halogens. The products are the halogenanhydrides of corresponding P(III) acids, the oxydation products of initial thioesters and the esters of corresponding thiolcarboxylic acids.

$$R_2P\text{-}SR' + {>}CX\text{-}COOH \longrightarrow R_2P(O)SR' + R_2P\text{-}X + {>}CHC(O)SR$$

The systematic study of the reactivity of thiol derivatives of P(III) acids towards substituted acetylenes has been carried out for the first time. Different directions of interaction both with the conservation and change of phosphorus atom coordination have been shown to occur depending on the chemical environment of the phosphorus atom and the nature of acetylene compounds. Thioesters of P(III) acids and amidothiophosphites react with 1-chloro-2-organoacetylenes not according to the Arbuzov reaction scheme but with the formation of the substitution products of the alkylthio group at P(III) atom with the conservation of its coordination number.

$$R_2PSEt + Cl\text{-}C{\equiv}C\text{-}R' \longrightarrow EtSCl + R_2P\text{-}C{\equiv}C\text{-}R' \longrightarrow \text{oligomer}$$



$$EtSCl + R_2PSEt \longrightarrow \begin{cases} R_2P(S)SEt + EtCl \\ R_2PCl + EtSSEt \end{cases}$$

However the introduction of thioloderivatives of P(III) acids to the phosphorus atom results in another direction of interaction with halogenacetylenes. Previously unknown derivatives of diamidoacetylenthiophosphonous acid have been obtained as a result of the reaction of diamidothiophosphites with 1-chloro-2-organoacetylenes.

$$(R_2N)_2PSR' + Cl\text{-}C{\equiv}C\text{-}R'' \longrightarrow (R_2N)_2P(S)\text{-}C{\equiv}C\text{-}R'' + R'Cl$$

A new trend in the reactions of the thioderivatives of P(III) acids with chloroacetylenes has been found, i.e. the injection of dichloroacetylene with the P-S bond of the thioesters of P(III) acids. An original method of synthesizing a new class of phosphorylated ethylenes has been developed on this basis.

$$\mathrm{RP(SR')_2 + Cl{-}C{\equiv}C{-}Cl \longrightarrow \overset{R'S}{\underset{R}{>}}P{-}C(Cl){=}C(Cl){-}SR'}$$

The addition of thioesters of P(III) acids to etoxyacetylene has been investigated for the first time. The reactions proceed with the cleavage of the P-S bond and provide the formation of hardly accessible phosphorylated-P(III)-monothioacetals of ketene.

$$\mathrm{R_2PSEt + HC{\equiv}C{-}OEt \longrightarrow \overset{R_2P}{\underset{H}{>}}C{=}C\overset{OEt}{\underset{SEt}{<}}}$$

E-isom.

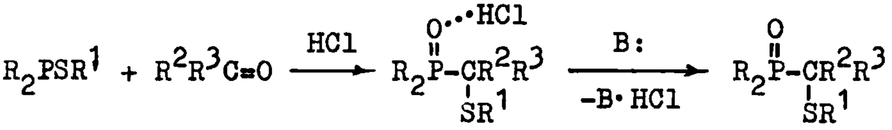
NMR ^1H, ^{13}C, ^{31}P spectroscopy method has established the regio- and stereoselectivity of the process.

New addition reactions in a series of thioesters of P(III) acids proceeding with the rupture of the P-S bond have been found.

The possibility of regioselective injection of oxiranes according to the P-S bond of thioderivatives of P(III) acids has first been demonstrated when studying the reactions of thioesters of P(III) acids with oxiranes.

$$\mathrm{RR'PSEt + \underset{O}{CH_2{-}CHR''} \longrightarrow RR'POCH(R'')CH_2SEt}$$

Reactions of addition of thioesters of P(III) acids to carbonyl compounds by the "injection" of the carbonyl fragment into the P-S bond with the formation of derivatives of α-thioalkylphosphonic acids have been performed for the first time.



$$\mathrm{R_2PSR^1 + R^2R^3C{=}O \xrightarrow{HCl} R_2\overset{O\cdots HCl}{\overset{\|}{P}}{-}\underset{SR^1}{CR^2R^3} \xrightarrow[-B\cdot HCl]{B:} R_2\overset{O}{\overset{\|}{P}}{-}\underset{SR^1}{CR^2R^3}}$$

The process has been estimated to be acid catalyzed. An advantageous method of obtaining α-alkylthioalkylphosphonates has been developed on the basis of the proposed diagram with acidic catalyzers.

Accordingly reactions with the rupture of the P-S bond are characteristic of the thioloderivatives of P(III) acids.