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Phosphorylated, Silylated, and Stannylated Derivatives of α-Mercaptocarbonyl Compounds

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Abstract—The authors are summing up their research in the field of phosphorylation, silylation, and stannylation of α-mercaptocarbonyl compounds. Synthetic methods were developed for a series of new saturated and unsaturated organosilicon(tin) reagents that were applied to organophosphorus syntheses. Representatives of new classes of heterocyclic compounds were prepared: 1,3,2-oxathiaphospholenes with four- and five-coordinate phosphorus. A new thiophosphite–thiophosphate rearrangement initiated by molecular oxygen was discovered.

INTRODUCTION

In the last decades the efforts of chemists are to a great extent directed to the synthesis of new types functionally substituted organophosphorus compounds containing unusual sequence of bonds and various combinations of substituents. The attention to this field of chemistry is largely due to the possibility of appearance in this type compounds of interesting intramolecular transformations. In particular, combination in one molecule of a phosphorus atom and a carbonyl group (phosphorylated α-heterocarbonyl compounds) provides a possibility to perform uncommon intramolecular transformations affording new linear and cyclic unsaturated organophosphorus compounds with variously coordinated central atom, and to extend significantly the theoretical understanding of the reactivity of P(III) acids derivatives. Into the study of phosphorylation of hydroxy and α-aminocarbonyl compounds with derivatives of P(III) acids largely contributed Yu.G. Gololobov [1] and F.S. Mukhametov [2] with collaborators. To the beginning of our investigations on elementoylation of α-mercaptocarbonyl compounds appeared only some publications on reactions of α-mercaptoacetic acid and its anilides with P(III) acid halides and amides [3, 4]. Yet the performance of reactions between α-mercaptocarbonyl compounds and derivatives of P(III) acids with the help of silylating and stannylating agents permits revealing of the specific features of the reactivity inherent in α-mercaptocarbonyl compounds due to the presence of the mercapto group, preparation of new types of linear and cyclic compounds containing P, S, Si, Sn, and investigation of their characteristics. A very promising synthesis is that of silylated α-mercaptocarbonyl compounds. Since the energy of O–Si and S–Si bonds are considerably different, in the series of the above compounds may be expected intramolecular transformations including a migration of trimethylsilyl groups. On the other hand, Si,Sn-containing α-mercaptocarbonyl compounds are undoubtedly interesting as starting objects for phosphorylation with P(III) acid chlorides and acyl halides.

1. Silylation and Stannylation of α-Mercaptoketones

The principal approach to the synthesis of organophosphorus compounds with a carbonyl group in the β-position is based on reacting the corresponding α-hydroxy(amino, mercapto)-substituted carbonyl compounds with chlorides and amides of P(III) acids. An alternative to this preparation technique for β-ketophosphites (amidophosphites, thiophosphites) consists in reactions of Si, Sn-organic derivatives of the α-functionally substituted carbonyl compounds with halides of P(III) and P(IV) acids.

The silylated α-mercaptoketones and derivatives thereof are convenient reagents for introducing various structural fragments into organic and organoelemental molecules.

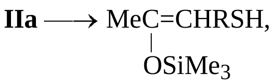
The silylation of the simplest member of the α-mercaptocarbonyl compounds series, mercaptoacetone **Ia**, with trimethylchlorosilane in the presence of an equimolar amount of triethylamine affords ketone **IIa**, thermally unstable compound tarring at fractional distillation [5].

$$\mathrm{MeC(O)CHRSH + Me_3SiCl}$$

Ia, Ib

$$\xrightarrow[-\mathrm{Et_3N\cdot HCl}]{\mathrm{Et_3N}} \mathrm{MeC(O)CHRSSiMe_3},$$

IIa, IIb

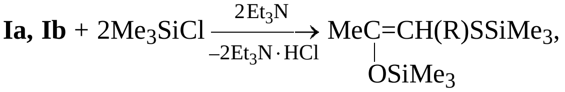


$$\mathbf{IIa} \longrightarrow \mathrm{MeC(OSiMe_3){=}CHRSH},$$

III

R = H (**a**), Me (**b**).

In order to confirm the structure of the compound and to elucidate the factors leading to polymerization we studied the unpurified reaction product by means of IR spectroscopy. In the IR spectrum of the reaction mixture was observed an absorption band at 1710 $\mathrm{cm^{-1}}$ belonging to the stretching vibrations of C=O bond. On storing compound **IIa** at 20°C for 2 h or after short heating the intensity of the 1710 $\mathrm{cm^{-1}}$ (C=O) band in its IR spectrum considerably decreased, and appeared an absorption band in 1610 $\mathrm{cm^{-1}}$ region corresponding to the stretching vibrations of C=C bond, and a band at 2520 $\mathrm{cm^{-1}}$ from S–H bond vibrations. The comparison of the IR absorption bands led to conclusion that compound **IIa** transformed into the corresponding vinylmercaptan **III** that easily polymerized at fractionation. Thus we observed for the first time in such systems an example of S → O 1,4-migration of a trimethylsilyl group from sulfur to oxygen atom. The process apparently can occur either intraor intermolecularly, and its driving force is the formation of an energetically feasible Si–O bond. Since we failed to isolate individual 1-(trimethylsilylthio)-2-propanone **IIa** or vinylmercaptan **III** we attempted to protect the mercapto group of the formed vinylmercaptan with a trimethylsilyl group. The silylation of mercaptoacetone **Ia** with trimethylchlorosilane in the presence of triethylamine at the reagents ratio 1 : 2 : 2 afforded in 34% yield compound **IVa**. The use as silylating agent of *N*,*O*-bis(trimethylsilyl)acetamide raised the yield of the final product to 76%. As showed the ^{1}H NMR spectrum, substituted alkene **IVa** was a mixture of *E* and *Z* isomers [5].



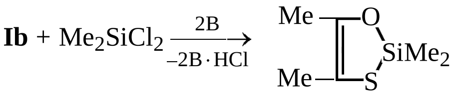
$$\mathbf{Ia, Ib} + \mathrm{2Me_3SiCl} \xrightarrow[-2\mathrm{Et_3N\cdot HCl}]{2\mathrm{Et_3N}} \mathrm{MeC(OSiMe_3){=}CH(R)SSiMe_3},$$

IVa, IVb

R = H (**a**), Me (**b**).

The stability of the S-silylation product is considerably higher if to the α-carbon is introduced a methyl group. In the reaction between 3-mercapto-2-butanone **Ib** and trimethylchlorosilane in the presence of triethylamine was obtained and isolated in an individual state compound **IIb** that was stored unchanged at least for 10 days. The silylation of 3-(trimethylsilylthio)-2-butanone **IIb** with the second molecule of trimethylchlorosilane (in the presence of triethylamine at prolonged heating) afforded compound **IVb** [5].

The presence in α-mercaptoketones of two reactive centers (mercapto and keto groups) suggests a possibility to synthesize silicon-containing heterocycles. The silylation of mercaptobutanone **Ib** with dimethyldichlorosilane in the presence of 2 mol of triethylamine resulted in 2,2,4,5-tetramethyl-1,3,2-oxathiasilolene **V** in 65% yield [6].



V

As already mentioned above the synthesis of compound **IIa** failed due to S → O 1,4-migration of the trimethylsilyl group followed by oligomerization of the arising alkene. We presumed that stable sulfur-containing organoelemental compounds would be obtained with organotin reagents (taking into account the higher strength of Sn–S bond as compared to that of Sn–O bond) [7]. To this end we studied the reactions of mercaptoketones **Ia** and **Ib** with triethylchlorostannane in the presence of sodium isopropylate; as a result we obtained in high yield compounds **VIa** and **VIb** [8].

$$\mathbf{Ia, Ib} + \mathrm{Et_3SnCl} \xrightarrow[-\mathrm{NaCl}]{i\text{-}\mathrm{PrONa}} \mathrm{MeC(O)CH(R)SSnEt_3},$$

VIa, VIb

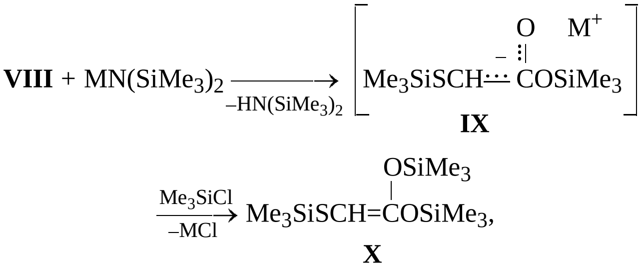
R = H (**a**), Me (**b**).

2. Silylation of Mercaptoacetic acid Esters

In the literature a reaction is described of trimethylchlorosilane with mercaptoacetic acid and its esters [9] resulting in the corresponding silicon and sulfur containing compounds with a carboxy group. We performed an exhaustive silylation of mercaptoacetic acid **VII** and its esters in order to prepare therefrom silicon-containing alkenes. It turned out however that the reaction of acid **VII** with trimethylchlorosilane in the presence of triethylamine (at reagents ratio 1 : 3 : 3) at boiling in benzene stopped at the stage of trimethylsilyl (trimethylsilylthio)acetate **VIII** formation.

$$\underset{\textbf{VII}}{\mathrm{HSCH_2COOH + 3Me_3SiCl}} \xrightarrow[-2\mathrm{B\cdot HCl}]{3\mathrm{B}} \underset{\textbf{VIII}}{\mathrm{Me_3SiSCH_2COOSiMe_3}}.$$

Taking into consideration the weak enolization ability of the carbonyl group in carboxylic acids derivatives we used strong bases, sodium or lithium bis(trimethylsilyl)amides, for cleavage of a proton from the α-carbon. Reaction of compound **VIII** with hexamethyldisilazane salts followed by treating the reaction mixture with trimethylchlorosilane furnished 1-trimethylsilylthio-2,2-bis(trimethylsilyloxy)ethene **X** in over 70% yield [10, 11].

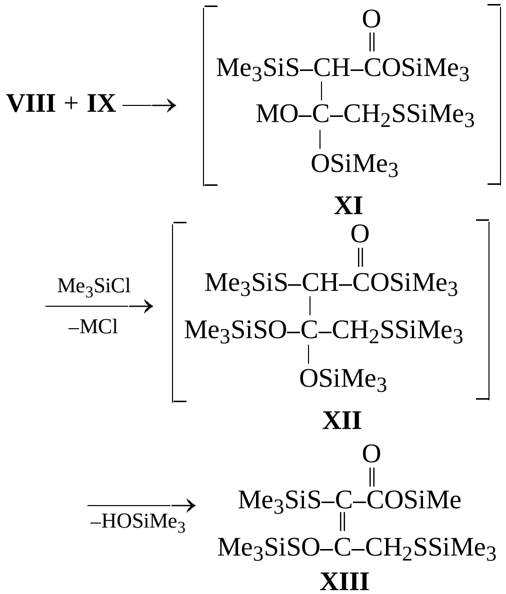


$$\textbf{VIII} + \mathrm{MN(SiMe_3)_2} \xrightarrow[-\mathrm{HN(SiMe_3)_2}]{} \underset{\textbf{IX}}{\left[\mathrm{Me_3SiSCH\overset{-}{\cdots}\overset{\overset{O\quad M^+}{\vdots|}}{C}OSiMe_3}\right]} \xrightarrow[-\mathrm{MCl}]{\mathrm{Me_3SiCl}} \underset{\textbf{X}}{\mathrm{Me_3SiSCH{=}\overset{\overset{OSiMe_3}{|}}{C}OSiMe_3}},$$

M = Li, Na.

The fractionation of the reaction mixture afforded alongside compound **X** a high-boiling reaction product that was according to ^{1}H and ^{13}C NMR and IR spectra 2,4-bis(trimethylsilylthio)-1,3-bis(trimethylsilyloxy)-2-buten-1-one (**XIII**). The latter compound was obtained as a mixture of *Z* and *E* isomers.

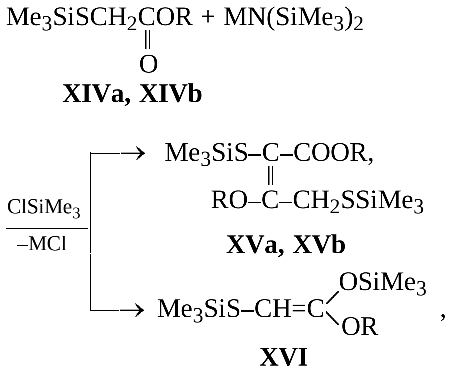
Replacing a hydrogen atom in compound **VIII** by a metal atom forms anion **IX** with delocalized charge.



$$\textbf{VIII} + \textbf{IX} \longrightarrow \underset{\textbf{XI}}{\left[\begin{array}{c} \mathrm{Me_3SiS{-}\underset{|}{C}H{-}\overset{\overset{O}{\|}}{C}OSiMe_3} \\ \mathrm{MO{-}\underset{\underset{OSiMe_3}{|}}{C}{-}CH_2SSiMe_3} \end{array}\right]} \xrightarrow[-\mathrm{MCl}]{\mathrm{Me_3SiCl}} \underset{\textbf{XII}}{\left[\begin{array}{c} \mathrm{Me_3SiS{-}\underset{|}{C}H{-}\overset{\overset{O}{\|}}{C}OSiMe_3} \\ \mathrm{Me_3SiSO{-}\underset{\underset{OSiMe_3}{|}}{C}{-}CH_2SSiMe_3} \end{array}\right]} \xrightarrow[-\mathrm{HOSiMe_3}]{} \underset{\textbf{XIII}}{\begin{array}{c} \mathrm{Me_3SiS{-}\underset{\|}{C}{-}\overset{\overset{O}{\|}}{C}OSiMe} \\ \mathrm{Me_3SiSO{-}C{-}CH_2SSiMe_3} \end{array}}$$

A nucleophilic attack of a carbon atom of this ambident system on a carbon atom of the carbonyl group of acetate **VIII** results in intermediate **XI**. The silylation of the latter with trimethylchlorosilane gives compound **XII** that under conditions of the reaction eliminates a silanol molecule to afford the final reaction product **XII**. The presence in compound **XIII** of readily leaving trimethylsilyl groups makes it a promising reagent for preparation of unsaturated organic and organoelement structures.

Taking into consideration the data obtained we were interested how would affect the silylation pattern the replacement of trimethylsilyl group in compound **VIII** by alkoxy group. The study was carried out on reaction of methyl trimethylsilylthioacetate **XIVa** and ethyl trimethylsilylthioacetate **XIVb** with trimethylchlorosilane in the presence of sodium and lithium bis(trimethylsilyl)amides. It was established that with methyl acetate **XIVa** the reaction resulted completely in condensation product **XVa**.



$$\underset{\textbf{XIVa, XIVb}}{\mathrm{Me_3SiSCH_2\underset{\underset{O}{\|}}{C}OR}} + \mathrm{MN(SiMe_3)_2} \xrightarrow[-\mathrm{MCl}]{\mathrm{ClSiMe_3}} \left\{\begin{array}{l} \underset{\textbf{XVa, XVb}}{\begin{array}{c}\mathrm{Me_3SiS{-}\underset{\|}{C}{-}COOR,} \\ \mathrm{RO{-}C{-}CH_2SSiMe_3}\end{array}} \\ \underset{\textbf{XVI}}{\mathrm{Me_3SiS{-}CH{=}C\begin{array}{l}\diagup OSiMe_3 \\ \diagdown OR\end{array}}}, \end{array}\right.$$

M = Li, Na; R = Me (**XIVa, XVa**), Et (**XIVb, XVb, XVI**).

At the same time at the use of ethyl acetate **XIVb** the main product formed 1-trimethylsilyl-2-trimethylsiloxy-2-ethoxyethene (**XVI**), and compound **XVb** forms in negligible amount. Compound **XVI** on storage or at heating isomerizes into ethyl (1-trimethylsilyl-1-trimethylsilylthio)acetate **XVII** due to O→C 1,3-migration of trimethylsilyl group [12].

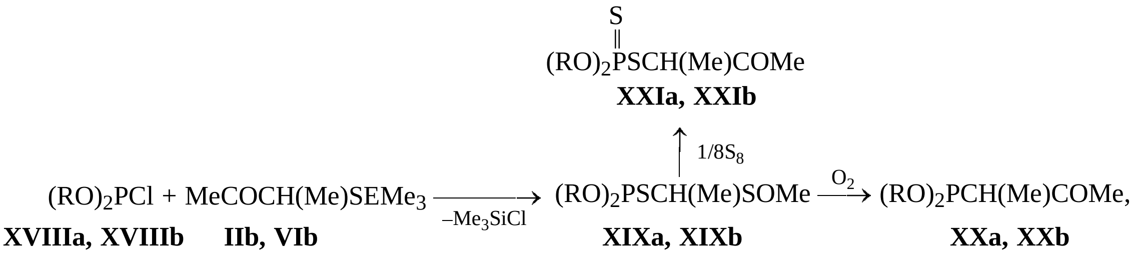
$$\textbf{XVI} \longrightarrow \underset{\textbf{XVII}}{\mathrm{Me_3SiS\overset{\overset{SiMe_3}{|}}{C}HCOOEt}}.$$

Abnormal behavior of compound **XVI** as compared to that of compound **X** consisting in unusual O→C 1,3-migration of trimethylsilyl group is due apparently to a combination of electronic and steric effects of substituents at the oxygen atom of the double bond.

3. *S*-Silylated (Stannylated) α-Mercaptoketones in the Synthesis of Organophosphorus Compounds.

In section 1 we described the preparation of α-mercaptoketones containing S–Si **IIa** and **IIb** and S–Sn **VIa** and **VIb** bonds that should be easily cleaved by phosphorus acids chlorides. We used linear and cyclic chlorides of phosphorus(III) acids as phosphorylating agents.

The reaction of silylated **IIb** and stannylated **VIb** derivatives of α-mercaptobutanone with diethyl and diisopropyl chlorophosphites proceeds at room temperature resulting in each case in a single product of thiophosphite structure **XIXa** and **XIXb** (δ_P 188–189 ppm).



$$(RO)_2PCl + MeCOCH(Me)SEMe_3 \xrightarrow[-Me_3SiCl]{} (RO)_2PSCH(Me)SOMe \xrightarrow{O_2} (RO)_2PCH(Me)COMe,$$

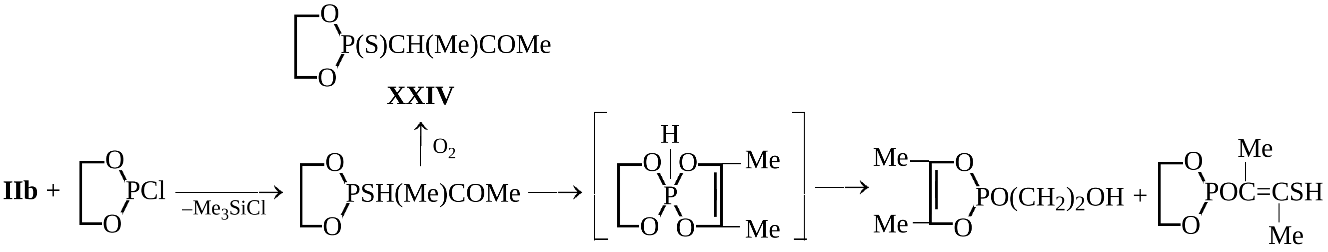
$$(RO)_2PSCH(Me)SOMe \xrightarrow{1/8S_8} (RO)_2\overset{S}{\overset{\|}{P}}SCH(Me)COMe$$

XVIIIa, XVIIIb **IIb, VIb** **XIXa, XIXb** **XXa, XXb** **XXIa, XXIb**

R = Et (**XVIIIa, XIXa**–**XXIa**), *i*-Pr (**XVIIIb, XIXb**–**XXIb**); E = Si (**IIb**), Sn (**VIb**).

The compounds are stable to heating to 150°C; however at contact with the air oxygen they isomerize with strong heat evolution into the corresponding dialkyl thiophosphonates **XXa** and **XXb** (δ_P 88–91 ppm). Compounds **XIXa** and **XIXb** readily take up sulfur to afford dithiophosphates **XXIa** and **XXIb**.

The reaction of silylthiobutanone **IIb** with 2-chloro-1,3,2-dioxaphospholane **XXII** in the first stage gives thiophosphite **XXIII** (δ_P 182 ppm) that even at short exposure to air oxygen immediately isomerizes into thiophosphonate **XXIV** [13]. Unlike that under inert atmosphere in 24 h in the ^{31}P NMR spectrum of the reaction mixture the signal of thiophosphite **XXIII** disappears, and two signals arise with the chemical shifts of 154 and 136 ppm in 5 : 1 ratio. The signal at δ_P 136 ppm completely disappears within 2 days. Basing on ^{31}P NMR data we supposed that in the mixture are present 1,3,2-oxathiaphospholene **XXV** and 1,3,2-dioxaphospholane **XXVI**. We failed to isolate these compounds in the individual state due to tarring of the reaction mixture at heating. Therefore we treated the crude reaction products with acetyl chloride in the presence of triethylamine and then succeeded in isolation of a compound (δ_P 154 ppm) that with the use of ^{1}H NMR and IR spectra and elemental analysis was identified as 1,3,2-oxathiaphospholene **XXVII**.

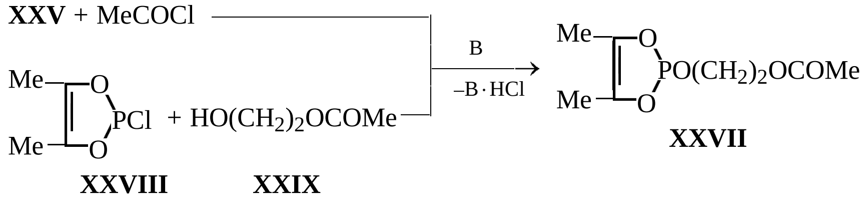


XXIV

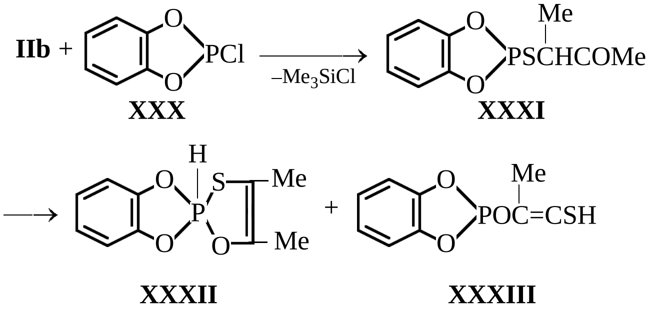
XXII **XXIII** **XXV** **XXVI**

Compound **XXVII** was also prepared by independent synthesis by reaction of 2-chloro-1,3,2-oxathiaphospholene **XXVIII** with ethylene gl-cole acetate **XXIX**.

Thus the intramolecular interaction of trivalent phosphorus and the oxygen of the carbonyl group in the appropriate thiophosphites provides a possibility of new processes affording via an intermediate spiro-

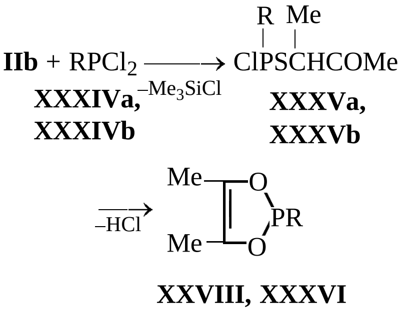


phosphorane the corresponding compounds **XXV** and **XXVI**. Taking into account the published and our proper data we assumed that the stabilization of the intermediate spirophosphorane may be attained by introducing a pyrocatechol fragment to the phosphorus atom. To this end we studied the reaction between silylthiobutanone **IIb** and 2-chloro-1,3,2-benzodioxaphosphole **XXX**. The reaction progress was monitored by ^{31}P NMR spectroscopy.



We established that the reaction proceeded for several hours at room temperature to afford thiophosphite **XXXI** (δ_P 227 ppm). The latter within 2–3 days is converted into a mixture of two phosphorus-containing compounds: the main one is spirophosphorane **XXXII** (δ_P –7 ppm, $^1J_{PH}$ 790 Hz), and the minor product is phosphite **XXXIII** (~5%) (δ_P 130 ppm). On dissolving crystalline spirophosphorane **XXXII** in the ^{31}P NMR spectrum again appear two signals at δ_P 130 and –7 ppm in 1 : 19 ratio. We believe that the signal at δ_P 130 ppm may be ascribed to vinyl phosphite **XXXIII** that in solution occurs in an equilibrium with spirophosphorane **XXX**. The cycle closure in thiophosphite **XXXI** is effected by electrophilic attack of phosphorus atom on the oxygen of the carbonyl group. The existence of spirophosphorane **XXXII** can be regarded as evidence for the scheme suggested earlier for the reaction between silylthiobutanone **IIb** and chlorophospholane **XXII**.

In the course of investigation of silylthiobutanone **IIb** phosphorylation with phosphorus trichloride (at 1 : 1 ratio) by ^{31}P NMR method we fixed a formation of dichlorothiophosphite **XXXVa** (δ_P 203 ppm) [13] which under the reaction conditions underwent cyclization with liberation of hydrogen chloride to furnish oxathiaphospholene **XXVIIIa** (δ_P 210 ppm).



$$\mathbf{IIb} + RPCl_2 \xrightarrow{-Me_3SiCl} Cl\overset{R}{P}SCH\overset{Me}{}COMe$$

XXXIV, R = Cl (**a**), Ph (**b**); **XXXVI**, R = Ph.

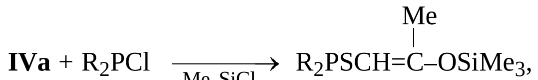
Similar reaction pattern is observed on treating silylthiobutanone **IIb** with phenyl dichlorophosphine **XXXIVb** [13]. The reaction occurs at room temperature and results in 2-phenyl-4,5-dimethyl-1,3,2-oxathiaphospholene **XXXVI** (δ_P 164 ppm).

Summing up the properties of P(III) acids thioesters containing a carbonyl group in the β-position we can state the following. The heterocyclization is favored by enhanced electrophilicity of phosphorus atom, and further transformations are determined by the character of substituent at P(III) atom. A new feature of P(III) acids thioesters with a carbonyl group in β-position is an easily occurring thiophosphite–thiophosphate rearrangement under effect of molecular oxygen.

4. Synthesis of Organophosphorus Compounds Starting with 1-Trimethylsilylthio-2-trimethylsilyloxypropene and 2,2,4,5-Tetramethyl-1,3,2-oxathiasilolene

A special place among organophosphorus compounds belongs to substances with a vinyl fragment attached to phosphorus via heteroatom. The preparation methods are sufficiently well developed and the properties are studied for vinyl phosphites [14] and vinyl amidophosphites [15]. Vinyl thiophosphites are poorly investigated due to the difficulty of their synthesis. The first vinyl thiophosphites were prepared by Yu.G. Gololobov *et al.* [16, 17]; they showed that on heating the compounds can isomerize into thiophosphonates [18].

In silylthiopropane **IVa** synthesized by us two reaction centers are present: sulfur and oxygen atoms linked to a double C=C bond. Also there are readily leaving trimethylsilyl groups. This structure is prone to form new unsaturated linear and cyclic compounds in reaction with P(III) acids halides. As phosphorylating agents was used a series of mono- and dichlorophosphites, and phosphorus trichloride. Reaction of compound **IVa** with diethyl chlorophosphite **XVIIIa**, diisopropyl chlorophosphite **XVIIIb**, acid chloride **XXX**, tetraethyldiamidochlorophosphite **XXXVII** occurred only at sulfur atom and afforded substitution products *O*,*O*-dialkyl-*S*-(2-trimethylsiloxy-1-propen-1-yl)thiophosphites **XXXVIII**–**XLI** [19]. The reaction scheme apparently includes an electrophilic attack of P(III) atom on sulfur followed by elimination of trimethylchlorosilane.



$$\mathbf{IVa} + R_2PCl \xrightarrow[-Me_3SiCl]{} R_2PSCH{=}\overset{Me}{\overset{|}{C}}{-}OSiMe_3,$$

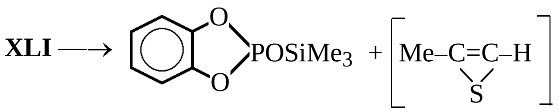
XVIIIa,
XVIIIb,
XXX,
XXXVII

XXXVIII–XLI

R = OEt (**XVIIIa, XXXVIII**), OPr-*i* (**XVIIIb, XXXIX**), NEt_2 (**XXXVII, XL**), *o*-$O_2C_6H_4$ (**XXX, XLI**).

It should be noted that compounds **XXXIX** and **XL** containing isopropyl and diethylamide substituents attached to phosphorus exist as a single stereoisomer. Yet alkene **XLI** is a mixture of *E* and *Z* isomers. The observed distinctions are due apparently to a phenomenon described in the literature: a decrease in the energy barrier to rotation around C=C bond if donor and acceptor groups are bonded at different terminal carbons of the alkene fragment [20]. On introduction to the phosphorus atom of an acceptor pyrocatechol substituent the energy barrier to rotation is reduced and consequently appears a mixture of *E* and *Z* isomers.

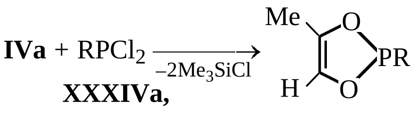
The observed decrease in the yield of thiophosphite **XLI** is caused by partial thermal degradation of the *Z* isomer resulting in 2-trimethylsilyl-1,3,2-benzodioxaphosphole **XLII** and thiirene that polymerizes under the experimental conditions [21].



XLII

The easiest reaction is that between propene **IVa** and chlorophospholane **XXX** (at –10°C); reactions with the other P(III) acids chlorides occur only at heating to 100–120°C. The data obtained are consistent with the suggested reaction pattern including an electrophilic attack of phosphorus on the sulfur atom. The second trimethylsilyl group linked to oxygen interestingly is not replaced by P(III) fragment even at long heating (at reagents ratio 1 : 2).

The possibility of cyclization was demonstrated by the example of reaction between compound **IVa** with P(III) acids dichlorides. The reaction of propene **IVa** with ethyl- **XLIVa** and isopropyl dichlorophosphites **XLIVb**, and also with PCl_3 **XXXIVa** afforded in high yield 1,3,2-oxathiaphospholenes **XLIVa**, **XLIVb**, and **XLV**.

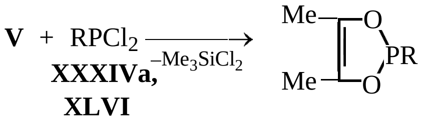


XXXIVa,
XXXIVb

XLIVa, XLV

R = OEt (**XLIIIa, XLIVa**), OPr-*i* (**XLIIIb, XLIVb**), Cl (**XXXIVa, XLV**).

Oxathiaphospholenes were also obtained starting with 2,24,5-tetramethyl-1,3,2-oxathiasilolene **V**. Its reaction with PCl_3 (**XXXIVa**) or Bu_2NPCl_2 (**XLVI**) is carried out at heating to 130–150°C for 1 h and gave rise to 1,3,2-oxathiaphospholenes **XXXVIII** and **XLVII** [6].



XXXIVa,
XLVI

XXVIII, XLVII

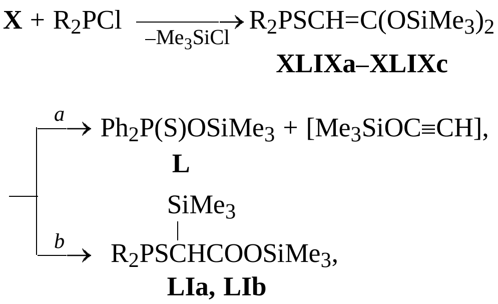
R = Cl (**XXVIII, XXXIVa**), NBu_2 (**XLVI, XLVII**).

The vinyl thiophosphites obtained unlike the earlier prepared alkyl(alkenyl)thiophosphites are not prone to isomerization either on heating or in the presence of the air oxygen [13, 18].

5. Reactions of Silylated Derivatives of α-Mercaptoacetic Acid and its Esters with P(III) Acids Chlorides

Note that 1-trimethylsilylthio-2,2-bis(trimethylsilyloxy)ethene **X** prepared by us is very sensitive to various proton-donor reagents. For instance, the presence in the reaction mixture of hydrogen chloride in even catalytic amounts results in immediate reaction of the latter with ethene **X**, and thus acid catalysis is impossible in reactions of compound **X** with P(III) acids chlorides. This property may be used in more detailed study of reaction mechanism and provides wide possibilities for application of compound **X** to the synthesis of various organic and organophosphorus unsaturated systems. We used as phosphorylating agents diphenylchlorophosphine **XLVIII**, tetraethyldiamidochlorophosphite **XXXVII**, diethyl chlorophosphite **XVIIIa**, dioxaphosphole **XXX**, ethyl dichlorophosphite **XLIIIa**.

Reaction of ethene **X** and chlorophosphine **XLVIII** proceeds at room temperature and yields thiophosphinite **XLIXa** that decomposes at fractionation to afford *O*-trimethylsilyldiphenylthiophosphinate **L** (pathway *a*).



$$\mathbf{X} + R_2PCl \xrightarrow[-Me_3SiCl]{} R_2PSCH{=}C(OSiMe_3)_2$$

XLIXa–XLIXc

$$\xrightarrow{a} Ph_2P(S)OSiMe_3 + [Me_3SiOC{\equiv}CH],$$

L

$$\xrightarrow{b} R_2PS\overset{SiMe_3}{\overset{|}{C}}HCOOSiMe_3,$$

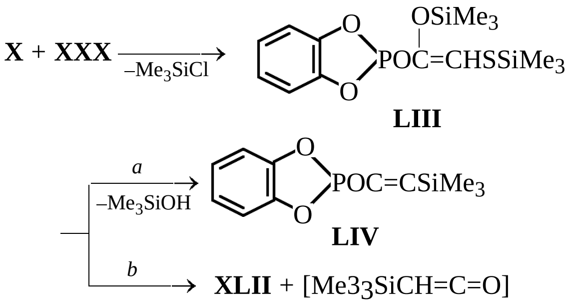
LIa, LIb

R = Ph (**XLIXa**), NEt_2 (**XLIXb, LIa**), OEt (**XLIXc, LIb**).

The reaction of ethene **X** with chlorophosphite **XXXVII** is similar to that with diphenylchlorophosphine and affords thiophosphate **XLIXb** that at fractional distillation in a vacuum converts into compound **LIa** (pathway *b*) due to O→C 1,3-migration of a trimethylsilyl group [22]. Dissimilar paths of transformation occurring with intermediate compounds **XLIXa** and **XLIXb** are due, on the one hand, to stabilization of vinyl thiophosphinate structure **XLIXa** by the presence of the phenyl groups at the central atom, and on the other hand, to the possibility of intramolecular processes resulting in the thermodynamically feasible thiophosphinate **L**.

The reaction of ethene **X** with diethyl chlorophosphite gives rise to a mixture of two isomers, **XLIXb** and **LIb**. As show ^{31}P NMR and IR spectra, at prolonged standing thiophosphite **XLIXb** is completely transformed into isomer **LIb** [23]. Thus the reactions of compound **X** with chlorides **XVIIIa**, **XXXVII**, **XLVIII** proceed exclusively at sulfur atom to afford the corresponding thioesters of P(III) acids that undergo rearrangement with O→C 1,3-migration of a trimethylsilyl group. The driving force of the latter process is apparently the thermodynamical stability of the rearrangement product due to carboxy group formation.

The second group of phosphorylating reagents contains dioxaphosphole **XXX**, ethyl **XLIVa**, and butyl dichlorophosphites **LII**. The main characteristic of these compounds is a significantly increased electrophilicity of P(III) atom. The reaction of compound **X** with acid chloride **XXX** occurs at room temperature and takes several days. As a result arises a thermally unstable vinyl phosphite **LIII** that in the process of isolation transforms into phosphites **LIV** (δ_P 132 ppm) (pathway *a*) and **XLII** (δ_P 122 ppm); cyclophosphite **LIV** polymerizes within 4 days. The structure of compound **LIV** is confirmed by the presence of a molecular ion (M^+ 284) in the electron impact spectrum, and also by the appearance in the IR spectrum of a band at 2150 cm^{-1} corresponding to the C=C bond vibrations.



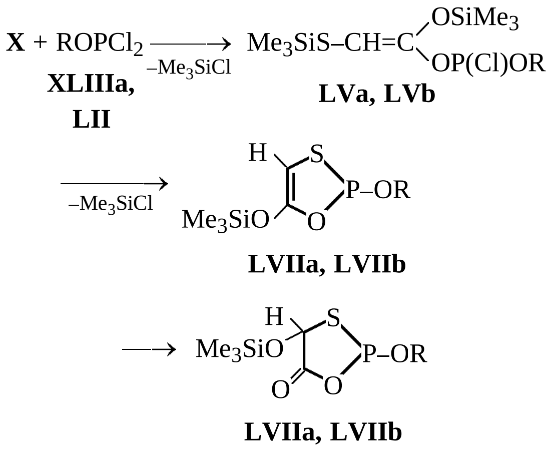
LIII

LIV

The first act of the transformations considered is the replacement of trimethylsilyl group at the oxygen in ethene **X** by benzodioxaphospholene moiety with trimethylchlorosilane elimination. As a result forms compound **LIII** (δ_P 134 ppm). The latter during fractional distillation suffers two type transformations: It loses a trimethylsilanol molecule to afford unsaturated phosphite **LIV** (pathway *a*), and decomposes into silyl phosphite **XLII** and ketene that undergoes polymerization (pathway *b*).

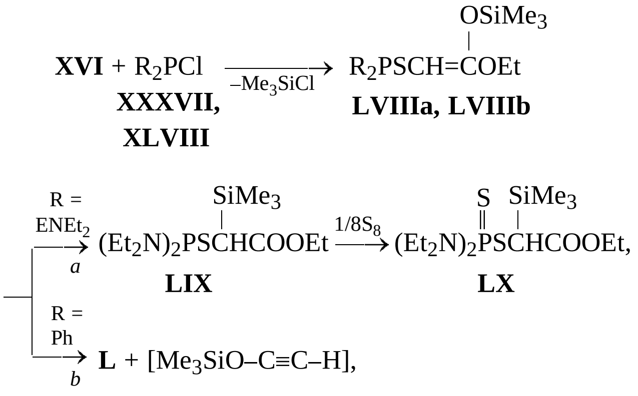
The phosphorylation of ethene **X** with ethyl **XLIVa** and butyl **LII** dichlorophosphites occurs at room temperature within 24 h and affords 2-alkoxy-4-trimethylsilyl-1,3,2-oxathiaphospholan-5-ones (**LVIIa** and **LVIIb**) [23]. Apparently the process includes a nucleophilic attack of the oxygen from the trimethylsilyloxy group on the trivalent phosphorus atom with liberation of trimethylchlorosilane and intermediate formation of vinyl phosphites **LVa** and **LVb** (δ_P 167–169 ppm) that cyclize into unstable phospholenes **LVIb** which through O→C 1,3-migration of a trimethylsilyl group afford the final phospholanones **LVIIa** and **LVIIb** (δ_P 144–148 ppm).

The studies were further extended to phosphorylation of an analog of alkene **X**, compound **XVI**, with acid chlorides **XXXVII** and **XLVIII**. The reaction of compound **XVI** with diamidochlorophosphite **XXXVII** was found to furnish thiophosphite **LVIIIa** (δ_P 121 ppm) that under the reaction conditions re-



XLV–**XLVIII**, R = Et (**a**), Bu (**b**).

arranged into isomeric compound **LIX** (δ_P 124 ppm) (pathway *a*) [12]. The addition of sulfur to the latter provided dithiophosphate **LX** (δ_P 94 ppm).



$$\mathbf{XVI} + R_2PCl \xrightarrow[-Me_3SiCl]{} R_2PSCH{=}\overset{\displaystyle OSiMe_3}{C}OEt$$

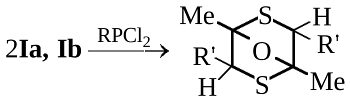
R = Et_2N (**a**), Ph (**b**).

The reaction between ethene **XVI** and diphenyl chlorophosphine **XLVIII** gives thermally unstable thiophosphinate **LIXb** (δ_P 32 ppm) that at fractionation transforms into trimethylsilylthiophosphinate **L** (δ_P 68 ppm) [12]. Thus by an example of reactions between silicon-containing alkenes X, XVI and P(III) acid chlorides was demonstrated that depending on the structure of the latter was affected either sulfur or oxygen atom. These reactions are convenient preparation methods for various cyclic and open-chain P,S,Si-containing compounds.

6. Phosphorylation of α-Mercaptoketones with P(III) Acids Halides and Amides

We described above silylation and stannylation of α-mercaptocarbonyl compounds and the possibility to use the products obtained in the synthesis of functionalized organophosphorus compounds. We presumed that unusual organophosphorus compounds might be obtained by direct phosphorylation of α-mercaptoketones whose molecules contained three reactive sites (mercapto and keto groups, and a labile proton of CH group) dictating the principal pathways of the process. No publications on these reactions existed, and to fill in this gap we studied the reactions of the α-mercaptoketones with some P(III) acids halides and amides.

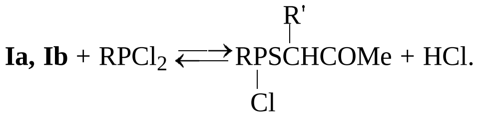
Mercaptoacetone **Ia** at room temperature does not react with P(III) acids chlorides, the reaction occurs only at heating in benzene, and the synthetic result is not affected by the reagents ratio. The main reaction product always is 2,5-dimethyl-2,5-endoxy-1,4-dithione **LXIa** [22].



LXIa, LXIb

R = Cl, OEt, NEt_2; R' = H (**a**), Me (**b**).

In the similar way proceeds the reaction between mercaptobutanone **Ib** with P(III) acids chlorides affording 2,3,5,6-tetramethyl-2,5-endoxy-1,4-dithione **LXIb** [22]. Taking into account some published data we can rationalize this uncommon direction of the reaction. The α-mercaptoketones are known to undergo cyclization easily into sulfur-containing heterocycles in the presence of traces of mineral acids [24]. In the case in question the reaction starts with formation of a phosphorylated derivative **LXII** accompanied with hydrogen chloride liberation. The latter effects the α-mercaptoketone condensation into the corresponding substituted dithione **LXI**. The water liberated in the process of condensation is consumed in reactions with the P(III) acid chloride and with the phosphorylated α-mercaptoketone **LXII**. In both cases arises metaphosphorous acid chloride that eliminating the hydrogen chloride transforms into metaphosphite that further polymerizes [25].

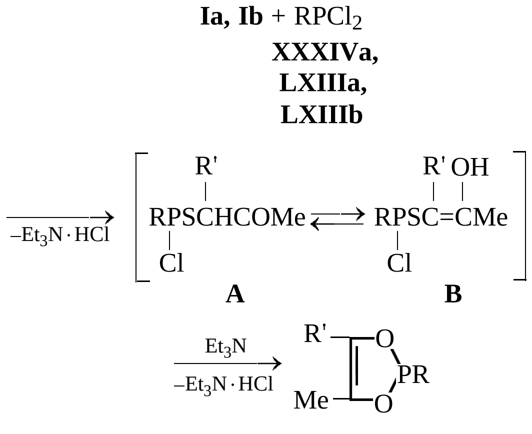


$$\mathbf{Ia, Ib} + RPCl_2 \rightleftarrows R\underset{\displaystyle Cl}{P}S\overset{\displaystyle R'}{C}HCOMe + HCl.$$

LXII

The polymeric derivatives of the metaphosphorous acid are nondistillable viscous fluids of alternating composition that prevents isolation thereof in an individual state. Thus the research we carried out on the reactions of α-mercaptoketones and P(III) acids chlorides revealed the significant dissimilarity of their chemical behavior from that of the oxygen and nitrogen analogs.

To exclude the effect of hydrogen chloride the reaction of α-mercaptoketones **Ia** and **Ib** with phosphorus trichloride **XXXIVa**, ethyl dichlorophosphite **XLIIIa**, and *N*,*N*-diethylamidodichlorophosphite **LXIIIb** was performed in the presence of 2 equiv of base [22, 26, 27].



Ia, Ib + $RPCl_2$ **XXXIVa, LXIIIa, LXIIIb**

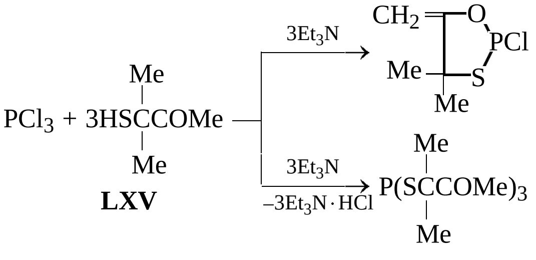
A **B**

LXIVa–LXIVb

LXIV, R = NEt_2, R' = H (**a**); R = OEt, R' = Me (**b**); R = NEt_2, R' = Me (**c**).

The reactions occur at –10–5°C yielding unsaturated P,O,S-containing 5-membered heterocycles, 1,3,2-oxathiaphospholenes **LXVa**–**LXVc** [26, 27]. Note that variation of the initial reagents ratio, reaction temperature, and solvent nature did not helps to detect the intermediate monochlorothiophosphites **A**. This means that the heterocyclization rate in the presence of a base is higher or equal to the rate of formation of the primary phosphorylation product **A**. The results obtained suggest the following pattern of the process [22]. At the first stage occurs phosphorylation of the α-mercaptoketone to yield the intermediate compound **A**. It is known [28] that the CH-acidity of organic compounds containing a thioalkyl group is considerably enhanced due to stabilization of the conjugate carbanion by the sulfur atom. Therefore the enolization of the intermediate compound **A** should be favored and consequently the heterocyclization should occur considerably easier than with the corresponding nitrogen and oxygen analogs. The heterocyclization may be described as a succession of equilibrium transformations including the attack of the oxygen from the carbonyl group on the phosphorus atom in the intermediate **A**, and the intramolecular phosphorylation in the enol form **B** with simultaneous elimination of hydrogen chloride.

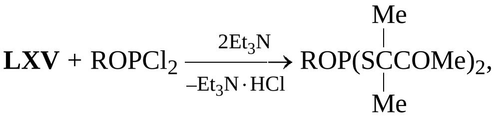
Unlike the reaction of phosphorus trichloride with the tertiary α-hydroxyketones that results in 1,3,2-dioxaphospholenes with an exocyclic C=C bond [29], the similar reaction of 3-mercapto-3-methyl-2-butanone **LXV** in the presence of triethylamine affords tris(1,1-dimethyl-2-oxopropyl)trithiophosphite (δ_P 92 ppm).



LXV

LXVI

The phosphorylation of mercaptobutanone **LXV** with ethyl(butyl) dichlorophosphite in the presence of 2 moles of triethylamine affords dithiophosphites **LXVIIa** and **LXVIIb** [22].



$$\mathbf{LXV} + ROPCl_2 \xrightarrow[-Et_3N\cdot HCl]{2Et_3N} ROP(S\overset{\displaystyle Me}{\underset{\displaystyle Me}{C}}COMe)_2,$$

LXVIIa, LXVIIb

R = Et (**a**), Bu (**b**).

The specific behavior of tertiary α-mercaptoketones in the phosphorylation reveals in the lack of heterocycles among the reaction products. It is known that P(III) acids thioesters more readily disproportionate into thermodynamically stable trithiophosphites than their oxygen analogs [30]. Therefore probably the disproportionation of the corresponding P(III) acid thioesters occurs faster than heterocyclization.

The above described data show that the phosphorylation of various α-mercaptoketones with P(III) acids di- and trihalides depending on the structure of α-mercaptoketones results either in heterocyclization or disproportionation products. There is no published data on reactions between –mercaptoketones and monohalides of P(III) acids. Yet the development of methods for the synthesis of β-ketothiophosphites would have permitted application thereof as starting compounds for creation of new types phosphorus-sulfur-containing structures. In this connection we undertook the study of phosphorylation of α-mercaptoketones with monochlorides of P(III) acids.

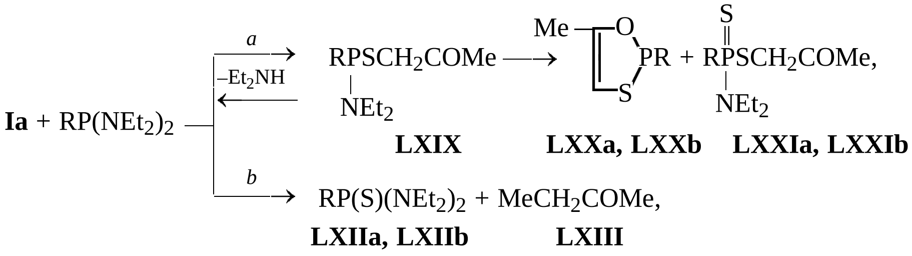
The reaction of mercaptoacetone **Ia** and mercaptobutanone **Ib** with diethyl(diisopropyl) chlorophosphites **XVIIIa** and **XVIIIb** and with chlorophospholane **XX** in the presence of triethylamine gave rise instead of expected thioesters of P(III) acids to dialkyl thiophosphonates **LXVIIIa**–**LXVIIIc** [13].

$$\underset{\textbf{XVIIIa, XVIIIb, XX}}{\textbf{Ia, Ib} + (RO)_2PCl} \xrightarrow[-Et_3N \cdot HCl]{Et_3N} (RO)_2PSCH_2COMe$$

$$\xrightarrow{O_2} \underset{\textbf{LXVIIIa–LXVIIIc}}{(RO)_2P(S)CH_2COMe,}$$

LXX–**LXXII**, R = OMe (**a**), OBu (**b**).

In the reactions of tri- and diamides of P(III) acids we succeeded to fix the formation of intermediate phosphorylation products **LXIX** whose chemical shifts in the ^{31}P NMR spectra were in the range 124–175 ppm depending on the substituents at the phosphorus atom. The process takes the second path *b* when the mixture of an appropriate P(III) amide and α-mercaptoketone is heated to 130°C. Thus in contrast to the behavior of α-hydroxyketones the α-mercaptoketones in reactions with P(III) amides can take a new route resulting in α-mercaptoketones desulfurization and in diamidothiophosphates formation. This property of the α-mercaptoketones is consistent with the published data on P(III) amides sulfurization effected by mercaptans [33].



LXX–LXXII, R = OMe (**a**), OBu (**b**).

It is necessary to note that the pathway *b* resulting in thioamodophosphates formation is irreversible whereas the phosphorylation of α-mercaptoketones (route *a*) is a reversible process. The equilibrium can be shifted to the initial compounds by diethylamine that liberates in the first stage of the process (if the reaction is carried out under rigid conditions without elimination of diethylamine from the reaction sphere), or by the action of diethylamine evolving in the course of heterocyclization (the latter process results in decreased yield of 1,3,2-oxathiaphospholenes). Among the significant results of the investigation on reactions between α-mercaptoketones and P(III) acids amides and chlorides should be mentioned the development of preparation methods for new unsaturated P,S-containing heterocycles, 1,3,2-oxathiaphospholenes, possessing interesting chemical properties.

7. Chemical Properties of 1,3,2-Oxathiaphospholenes

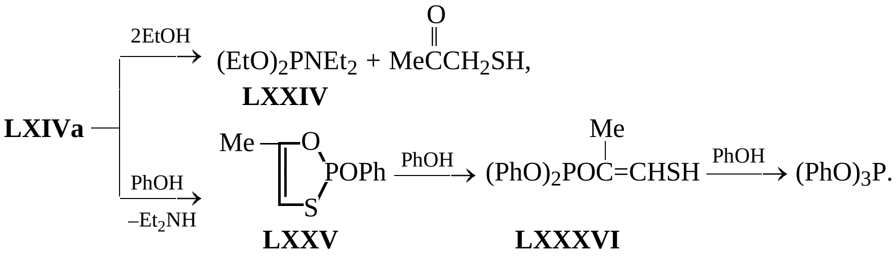
Chemical behavior of 1,3,2-oxathiaphospholenes is determined by the presence in the molecule of several reactive sites (trivalent phosphorus atom, thiol sulfur, C=C bond), and also by mutual influence of the unsaturated cyclic fragment and the phosphorus atom. To establish more complete understanding of the spatial arrangement and electron density distribution in the 1,3,2-oxathiaphospholenes we investigated the molecular structure of 2-chloro-5-methyl-1,3,2-oxathiaphospholene by means of gas phase electronography [34], and measured photoelectronic spectra of some 1,3,2-oxathiaphospholenes [35]. The data of gas phase electronography [34] indicated that the molecular structure of 2-chloro-5-methyl-1,3,2-oxathiaphospholene corresponded to P-envelope with an axial P–Cl bond. From the photoelectronic spectra (ionization potentials, eV) of some oxathiaphosphacyclanes-(cyclenes) [35] was established that the unsaturated oxathiaphospholene ring was more electron-withdrawing (9.36 eV for 2-chloro-5-methyl-1,3,2-oxathiaphospholene) than the saturated oxathiaphospholane one (9.16 eV for 2-chloro-5-methyl-1,3,2-oxathiaphospholane). Note that the ionization potential of 2-chloro-1,3,2-dioxaphospholane (10.2 eV) is considerably higher than that of the sulfur analog. Therefore the ionization potential of 1,3,2-dioxaphospholenes should be significantly higher than that of 1,3,2-oxathiaphospholenes. The ionization potential values characterize the nucleophilic nature of the phosphorus atom in these systems: The increase in the ionization potential evidences the reduced nucleophilicity of the phosphorus atom. Therefore 1,3,2-oxathiaphospholenes should easier react with electrophilic reagents than 1,3,2-dioxaphospholenes. This fact provides a possibility to synthesize 1,3,2-oxathiaphospholenes with tetra- and pentacoordinate phosphorus. On the other hand, the strength of the oxathiaphospholene ring can be evaluated by reactions with proton-donor reagents.

7.1. Reaction of 2-Substituted 1,3,2-Oxathiaphospholenes with Proton–Donor Reagents and P(III) Acids Dichlorides

The high stability of 1,3,2-oxazaphospholines and 1,3,2-dioxaphospholenes against the proton-donor reagents is well known: The hydrolysis thereof requires fairly rigid conditions [36]. In order to compare the chemical properties in the series of 1,3,2-diheterophosphacyclenes we studied reactions of 2-substituted 1,3,2-oxathiaphospholenes with alcohols, phenols, and carboxylic acids under previously applied conditions [36, 37].

2-Diethylamino-5-methyl-1,3,2-oxathiaphospholene (**LXIVa**) reacts with ethanol at 70–80°C with cleavage of the endocyclic P–O and P–S bonds, with conservation of the P–N fragment yielding diethylamidophosphite **LXXIV** and mercaptoacetone. The highest yield of these products is attained at the use of 2 equiv of ethanol.

Yet in reaction of oxathiaphospholene **LXIVa** with phenol as show by ^{31}P NMR spectra the first bond to rupture is P–N to afford phospholene **LXXV** (δ_P 166 ppm) that in the course of further phenolysis first gives phosphite **LXXVI** (δ_P 132 ppm), and then triphenylphosphite (δ_P 128 ppm).

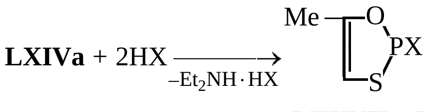


LXXIV

LXXV

LXXXVI

The different way of reacting showed by oxathiaphospholene **LXIVa** with alcohols and phenols is apparently due to decrease in nucleophilicity and increase in acidity in going from ethanol to phenol. In the first case occurs the nucleophilic attack of the ethanol molecule on the electrophilic phosphorus atom of compound **LXIVa** with the rupture of an endocyclic P–O or P–S bond, whereas in the second case the exocyclic nitrogen atom is initially protonated, and the diethylamino group is then replaced by phenoxy group. Similarly occurs the reaction between oxathiaphospholene **LXIVa** with the acetic and trifluoroacetic acids resulting in the corresponding phosphacyclanes **LXXVIIa** and **LXXVIIb** [37].



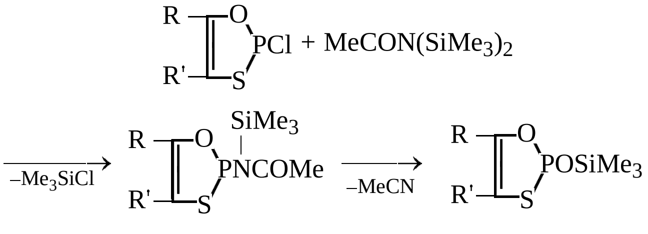
LXXVIIa, LXXVIIb

LXXVII, X = OCOMe (**a**), OCOCF$_3$ (**b**).

The replacement of the exocyclic diethylamino or ethoxy group was observed in reactions of oxathiaphospholenes **XLIVa** and **XLIVb** with ethyl dichlorophosphite and diethylaminodichlorophosphite [37].

7.2. Reaction of 2-Chloro-1,3,2-oxathiaphospholenes with N,O-Bis(trimethylsilyl)acetamide and Hexamethyldisilazane

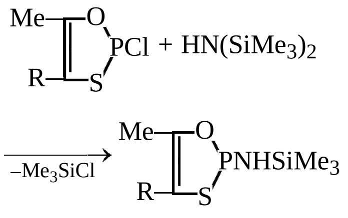
The phosphorylation of *N*,*O*-bis(trimethylsilyl)acetamide with 2-chloro-1,3,2-oxathiaphospholenes at heating provides 2-trimethylsiloxy-1,3,2-oxathiaphospholenes **LXXIXa**–**LXXIXc** in 75–80% yield [38].



LXXVIIIa–LXXVIIIc **LXXIXa–LXXIXc**

LXXVIII, LXXIX, R = Me, R' = H (**a**); R = R' = Me (**b**); R = R' = (CH$_2$)$_4$ (**c**).

Note that at performing these reactions under mild conditions we succeeded in observing the formation of intermediate compounds **LXXVIII** with chemical shifts δ_P 139–142 ppm. Aiming at functionalization of 2-chloro-1,3,2-oxathiaphospholenes we applied another well-known silylating reagent, hexamethyldisilazane. The reaction of 2-chloro-1,3,2-oxathiaphospholenes with the hexamethyldisilazane was carried out at 150°C with distilling off the liberated trimethylchlorosilane, and it gave rise to 2-trimethylsilylamino-1,3,2-oxathiaphospholenes **LXXXa** and **LXXXab**.

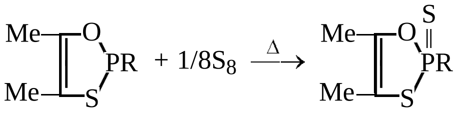


LXXXa, LXXXb

R = H (**a**), Me (**b**).

7.3. Reactions of 2-Substituted 1,3,2-Oxathiaphospholenes with Sulfur, Thiophosphoryl Chloride, Alkyl Iodides, and Diketones

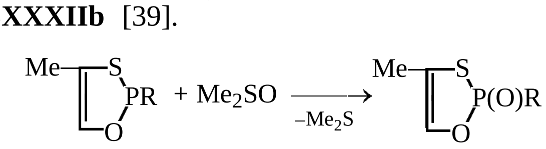
2-Dialkylamino(alkoxy)-1,3,2-oxathiaphospholenes add sulfur only at heating (120°C, 0.5 h) to afford in high yield 2-substituted 2-thioxo-1,3,2-oxathiaphospholenes LXXXIa–LXXXIac [39].



LXXXa–LXXXc

R = NEt$_2$ (**a**), NBu$_2$ (**b**), OEt (**c**).

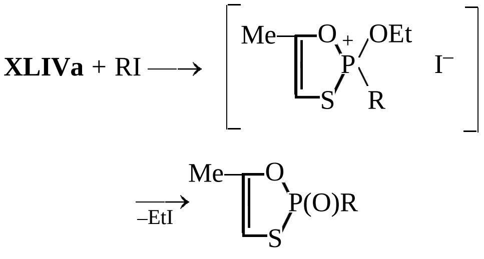
Oxidation of 2-substituted 1,3,2-oxathiaphospholenes with dimethyl sulfoxide (4 h, 100°C) furnished the corresponding phospholenes **LXXXIIa** and **LXXXIIb** [39].



LXXXIIa, LXXXIIb

R = NEt$_2$ (**a**), OEt (**b**).

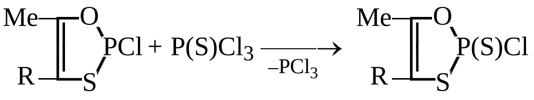
The reaction of 2-ethoxy-5-methyl-1,3,2-oxathiaphospholene **XLIVa** with methyl iodide occurs at heating (2 h, 100–120°C) and provides 2,5-dimethyl-2-oxo-1,3,2-oxathiaphospholenes **LXXXIIIa** and **LXXXIIIb** [39]. Under more rigid conditions proceeds the reaction between 2-ethoxy-5-methyl-1,3,2-oxathiaphospholene and benzyl iodide [40].



LXXXIIIa, LXXXIIIb

LXXXIII, R = Me (**a**), CH$_2$Ph (**b**).

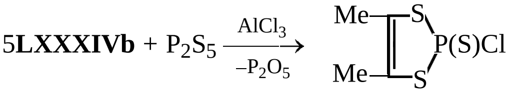
2-Thioxo-2-chloro-1,3,2-oxathiaphospholenes **LXXXIVa** and **LXXXIVb** were prepared by heating (0.5 h, 150°C) of a mixture of 2-chloro-1,3,2-oxathiaphospholenes with thiophosphoryl chloride [39].



LXXXIVa, LXXXIVb

R = H (**a**), Me (**b**).

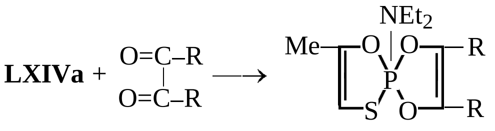
The heating of oxathiaphospholene **LXXXIVb** with phosphorus pentasulfide in the presence of catalytic amount of AlCl$_3$ (2 h, 170–180°C) provided 2-thioxo-2-chloro-4,5-dimethyl-1,3,2-dithiaphospholene **LXXXV** (δ_P 99 ppm) [39].



LXXXV

Compound **LXXXV** apparently arises in keeping with the scheme suggested for the reaction of 2-thioxo-2-chloro-Δ^4-1,3,2-oxaazaphospholene with the phosphorus pentasulfide in the presence of AlCl$_3$, and the reaction includes several stages with the initial one consisting in cleavage of the cyclic fragment under the action of AlCl$_3$ [41].

Compounds containing pentacoordinate phosphorus and P–S bond are virtually unknown. The reactions of 2-diethylamino-5-methyl-1,3,2-oxathiaphospholene **LXIVa** with diacetyl and dibenzoyl afford new bicyclic spirophosphoranes **LXXXVIa** and **LXXXVIb**, light yellow viscous fluids with specific odor [39].



LXXXVIa, LXXXVIb

LXXXVI, R = Me (**a**), Ph (**b**).

7.4. Reactions of 2-substituted 1,3,2-Oxathiaphospholenes with Acyl Halides

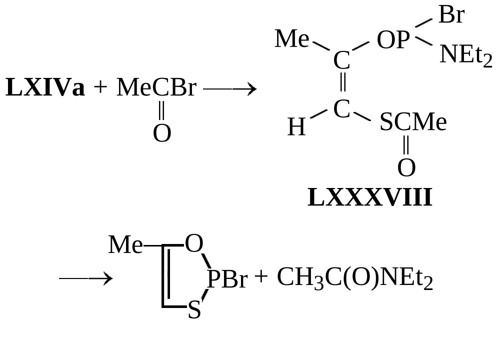
The reactions of trivalent phosphorus acids thioesters with carboxylic acids halides are known to afford P(III) acids halides and thiol esters of the carboxylic acids [42]. In this connection it was interesting to investigate the reactions of 2-substituted 1,3,2-oxathiaphospholenes with various acyl halides and to look for reactions with ring opening.

Oxathiaphospholene **LXIVa** reacts with acetyl and benzoyl chlorides in benzene at 0°C affording chlorothiophosphite **XLV** [43].

$$\textbf{LXIVa} + RC(O)Cl \longrightarrow \textbf{XLV} + RC(O)NEt_2.$$

The physical constants of oxathiaphospholene **XLV** are in agreement with those of an analogous compound obtained earlier [26].

Oxathiaphospholene **LXIVa** with acetyl bromide provides cyclic bromothiophosphite **LXXXVII**. By means of dynamic ^{31}P NMR spectroscopy were observed the following variations with time after mixing the reaction mixture of oxathiaphospholene **LXIVa** and acetyl bromide at –10°C: The signal of the original phospholene **LXIVa** at δ_P 147 ppm rapidly decreased, and a peak appeared at δ_P 180 ppm corresponding to the intermediate *S*-(1-acetylthio-1-propene-2-yl)-*N*,*N*-diethylamidobromophosphite **LXXXVIII** that in 5–10 min became the principal signal, and then it decreased with simultaneous appearance of a resonance at δ_P 237 ppm belonging to bromophospholene **LXXXVII**.

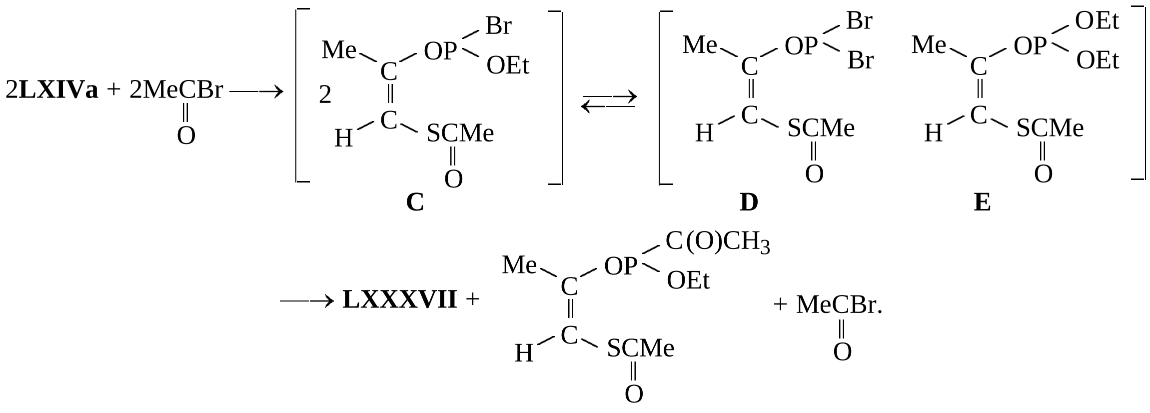


LXXXVIII

LXXXVII

Thus at lower reaction temperature we were able to observe the formation of intermediate compound **LXXXVIII** and to describe the reaction of phospholene **LXIVa** with acetyl bromide including primary rupture of the endocyclic P–S bond.

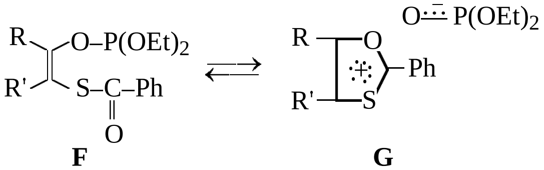
The reaction of ethoxyphospholene **XLIVa** with acetyl bromide occurs at room temperature to yield bromophospholene **LXXXVII** (δ_P 237 ppm) and *O*-ethyl-*O*-(1-acetylthio-1-propen-2-yl)acetylphosphonate **LXXXIX** (δ_P –8 ppm) as a mixture of *Z* and *E* isomers [43]. In keeping with the data obtained in the study of the reaction between phospholene **LXIVa** and acetyl bromide by ^{31}P NMR spectroscopy the following reaction scheme may be assumed for the reaction of phospholene **XLIVa** with acetyl bromide [43]. At the first stage of the reaction occurs cleavage of the P–S bond of the oxathiaphospholene ring under the action of acetyl bromide affording an intermediate **C** that undergoes disproportionation into vinyl phosphites **D** and **E**. The heterocyclization of intermediate **D** provides reaction product **LXXXVII**, and reaction of the liberated acetyl bromide with phosphite **E** finally results in ketophosphonate **LXXXIX**.



C **D** **E**

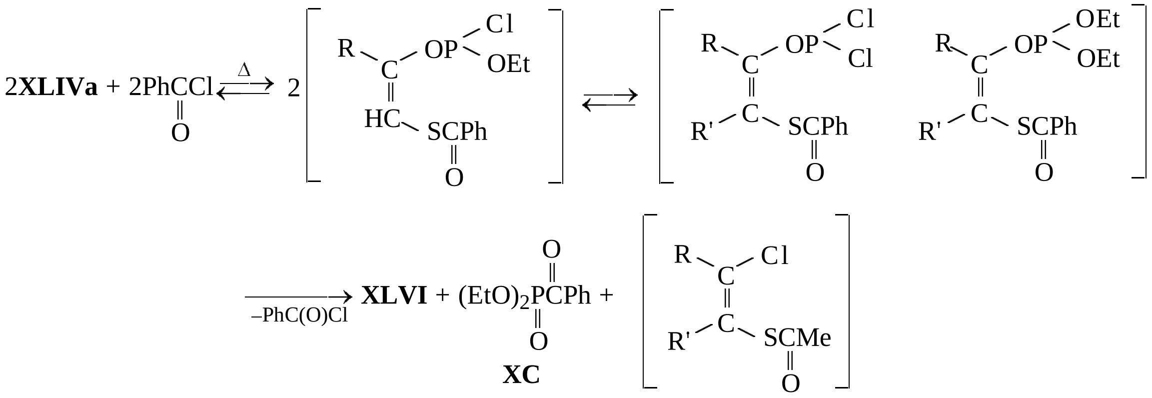
LXXXIX

Unlike acetyl bromide, benzoyl chloride reacts with oxathiaphospholene **XLIVa** only at heating (3 h, 100–110°C) yielding chlorophospholene **XLV** and *O*,*O*-diethyl benzoylphosphonate **XC** (δ_P –2 ppm) [43]. The formation of the final reaction products may be described by a series of successive transformation: opening of the heterocycle at P–S bond; disproportionation of compound **C**, heterocyclization of dichlorophosphite **D**, and reaction of benzoyl chloride with vinyl phosphite **E**. It is known that vinyl phosphites react with acetyl halides conserving the unsaturated fragment of the molecule [44]. Abnormal behavior of compound **E** in the reaction with benzoyl chloride is due to the following reasons. According to the published data, in the aromatic sulfur-containing heterocycles (1,3-dithiolium salts) [45] the cation is stabilized by a phenyl substituent and destabilized by an alkyl one. In keeping with these findings we can presume that at elevated temperature apparently occurs an equilibrium between structures **F** and **G**, and the positive charge in cation **G** is delocalized and stabilized by the phenyl group.



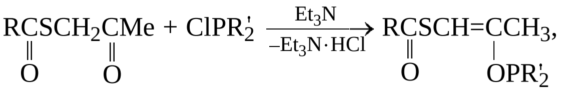
F **G**

Although the concentration of the **G** form is low it is the most reactive one and it reacts with the benzoyl chloride to yield ketophosphonate **XC** and vinyl chloride.



Thus during the study of reactions between 2-ethoxy-1,3,2-oxathiaphosphonates with acyl halides was found a new reaction route including ring opening followed by transformation of the intermediately formed vinyl phosphates. The above reaction schemes were supported by simulation of the intermediate stages.

By reaction of *S*-acetyl(benzoyl)mercaptoacetones with diethyl and pyrocatechol chlorophosphites in the presence of triethylamine were obtained vinyl phosphites **XCIa**–**XCIc** [46].



$$\underset{\substack{\parallel\\ O}}{RC}SCH_2\underset{\substack{\parallel\\ O}}{C}Me + ClPR'_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} \underset{\substack{\parallel\\ O}}{RC}SCH{=}\underset{\substack{|\\ OPR'_2}}{C}CH_3,$$

XCIa–XCIc

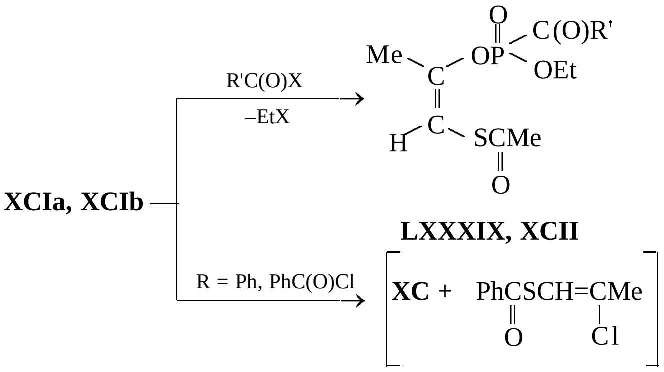
R = Me, R' = OEt (**a**); R = Ph, R' = OEt (**b**); R = Me, R' = *o*-OC_6H_4O (**c**).

The reactions of vinyl phosphites **XCIa**–**XCIc** with acetyl bromide and benzoyl chloride were carried out at the same temperature as used in the simulated processes.

It was established that although the reaction of compound **XCIa** with acetyl bromide occurred at room temperature, yet the reaction with benzoyl chloride required prolonged heating to 100–110°C. In both cases were isolated the corresponding ketophosphonates **LXXXIX**, **XCII**. Their structure was confirmed by ^1H, ^{31}P, and IR spectra, and also by comparison of the physical constants of compound **LXXXIX** with those of a model compound.

The reaction of vinyl phosphite **XCb** with benzoyl chloride was carried out at 100–110°C for 2–3 h. The main product was benzoylphosphonate **LXXXIX**.

Thus the simulation of separate stages of the reaction between oxathiaphospholene **XLIVa** with acyl halides confirmed the validity of the assumed schemes,

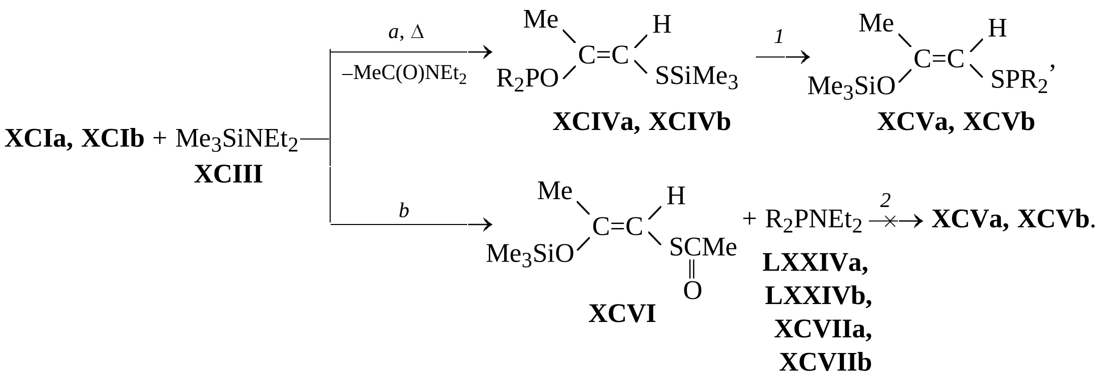


R' = Me (**LXXXIX**), Ph (**XCII**).

and the β-functionally substituted vinyl phosphites turned out to be interesting objects for heterocyclization process study.

The capability to transformations of vinyl phosphites with a functional group in the β-position was also observed in the reactions of compounds **XCIa** and **XCIb** with trimethylsilyldiethylamine **XCIII**. This reaction occurred at 120–130°C and yielded *O,O*-diethyl-*S*-(2-trimethylsiloxy-1-propen-1-yl)-4,5-benzo-1,3,2-dioxaphospholane **XCVb**. Alongside this compound were isolated *O,O*-diethyl-*N,N*-diethylamidophosphite **XCVIIa** or 2-diethylamino-1,3,2-benzodioxaphosphole **XCVIIb** [46].

The monitoring of the reaction progress by ^{31}P NMR spectroscopy demonstrated that after heating of the reaction mixture for 30 min to 120–130°C in the spectrum was observed a signal at δ_P 136–138 ppm corresponding to intermediate compounds **XCIVa** and **XCIVb**; as the heating was continued appeared the signals of the reaction products **LXXXIVa** and **LXXXIVb** (δ_P 184 and 187 ppm). Taking into account the data in the literature on the reaction of silylated amines with thioacetic acid esters [47] the following scheme of reaction may be presumed.



XCIV, XCV, XCVII, R = OEt (**a**), *o*-OC_6H_4O (**b**).

The presence in compounds **XCIa** and **XCIb** of two reactive sites (a phosphorus atom and a carbon atom of carbonyl group) provides a possibility of two reaction pathways. At greater electrophilicity of the phosphorus in compound **XCIb** the prevailing route is *b*, and in vinyl phosphite **XCIa** it is the pathway *a*. The forming intermediate **XCIV** is unstable and under the experimental conditions it provides thiophosphites **XCVa** and **XCVb** via S→O 1,4-exchange migration of trimethylsilyl and phosphorus-containing groups. The experimental data show that no compound **XCVa** and **XCVb** arises in reactions of 1-acetylthio-2-trimethylsiloxy-1-propene **XCVI** with amidophosphites **XCVIIa** and **XCVIIb**. This unusual synthetic outcome, the occurrence of the S→O 1,4-exchange migration of trimethylsilyl and phosphorus-containing groups, demonstrates the great synthetic potential of vinyl phosphites with a sulfur atom linked to various moieties located in β-position.

Thus the investigations of the reactions between *S*-acetylated α-mercaptoketones with P(III) acids halides revealed the curious transformations of vinyl phosphites (intramolecular rearrangement including an S→O 1,4-exchange migration of trimethylsilyl and phosphorus-containing groups; heterocyclization into 1,3,2-oxathiaphospholenes). Into the range of reactions under study are included the disproportionation processes leading to 1,3,2-oxathiaphospholenes, and also to ketophosphonates and to the other compounds. These transformations on the one hand support the assumed schemes of reactions between 1,3,2-oxathiaphospholenes, and on the other hand possess independent value permitting preparation of compounds with vinylthiol moiety.

As a whole the investigation of reactions between α-mercaptoketones and P(III) acids chlorides and amides revealed the specific features of the chemical behavior of the α-mercaptoketones that was distinct from their heteroanalogs (α-amino-, α-hydroxyketones). Besides as a result of the investigations performed were developed synthetic procedures for preparation of oxathiaphospholenes and P(III) acids thioesters containing in the α-position a keto group. The compounds obtained are unquestionably interesting for the synthesis of new functionalized derivatives of organic, and in particular organoelement, compounds.

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