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Progress in the chemistry of thio derivatives of trivalent phosphorus acids

O G Sinyashin, E S Batyeva, A N Pudovik
Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch of the USSR Academy of Sciences, Kazan'

ABSTRACT. The methods for synthesising thio derivatives of P(III) acids and their chemical behaviour in substitution and addition reactions are examined.

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I. Introduction

Thio derivatives of trivalent phosphorus acid (TTPA) have until recently remained one of the least studied classes of organophosphorus compounds. Although the first examples of this class of compounds were obtained more than 100 years ago, there were virtually no systematic studies of the chemical behaviour in their class for a long time. Only at the end of the 1950's and the beginning of the 1960's did TTPA start to attract more attention from research workers. This occurred because several TTPA were found to have practical application and continue to be of use as additives for lubricating oils,[1,2] stabilisers of polymeric materials,[3–6] heat-stable additives for organic products,[7,8] vulcanisation accelerators of rubbers,[9] etc. Moreover, with the discovery in the 1950's of the reaction between elemental phosphorus and disulphides,[10,11] the industrial synthesis of trialkyl phosphorotrithioites became a possibility. At the same time, the problem of finding ecologically preferable, 'chlorine-free' methods for synthesising various organophosphorus compounds based on phosphorotrithioites became important. Evidently the solution to these practical problems was not possible without a detailed study of the reactivity of TTPA.

By the mid-1970's investigations had been carried out on the synthesis and some chemical properties of esters and acid halides of P(III) thioacids had been studied, so that it was possible to find the first examples of the difference in chemical behaviour between TTPA and their oxygen analogues. These specific aspects of the chemistry of TTPA were partially covered in monographs[12,13] and a review[14] of that period and received the most attention in the review of Krasil'nikova,[15] which dealt with problems on the dual reaction of esters of P(III) thioacids with alkyl and acyl halides.

However, about 10 years has passed since it was published and during this time the chemistry of TTPA has undergone a new stage of development. Previously unknown classes and types of TTPA have been discovered, and an abundance of synthetic material has been collected on essentially new reactions involving TTPA, so it has been possible to establish the general mechanisms of these reactions. A wide range of physicochemical methods has been involved in structural and stereochemical studies of this class of compounds, which have recently been reviewed in a monograph.[16] Also at the present time it has become necessary to correlate and, as far as possible, classify the abundant and interesting material collected during the last few years in the world chemical literature.

In the review presented here, the findings of the last ten years, concerned with synthetic methods and properties of TTPA, have mainly been used.

II. Synthesis

By analysing the considerable flow of literature on the synthesis of TTPA, we have considered it practicable to limit ourselves to an examination of preparative methods based on those chemical conversions which lead to the formation of a P(III)–S bond in the molecule. The reactions which use trivalent phosphorus compounds that already contain a P(III)–S bond as starting materials will be examined when problems of the reactivity of the latter are discussed.

1. Synthesis based on elemental phosphorus

The direct synthesis of trialkyl phosphorotrithioites from elemental phosphorus and disulphides was developed back in the early 1950's:[10,11]

$$P_4+6RSSR\rightarrow 4(RS)_3P\,.$$

It was later shown[17,18] that phosphorotrithioites can be obtained in high yield by reaction of white phosphorus with thiols in the presence of sodium thiolate in CCl_4.

$$P_4+6RSH+6RSNa+6CCl_4\rightarrow 4(RS)_3P+6CHCl_3+6NaCl\,.$$

By using perfluorochloromethylsulphenyl chlorides in a reaction with elemental phosphorus it was possible to achieve the direct synthesis of perfluorochloromethyl phosphoromono- and phosphorodi-chloridothioites:[19]

$$P_4+CF_nCl_{3-n}SCl\rightarrow(CF_nCl_{3-n}S)_xPCl_{3-x}+(CF_nCl_{3-n}S)_2$$
$x=1, 2$ when $n=1, 2$; $x=1-3$ when $n=3$.

However, up to the present time phosphorylation of sulphur-containing compounds has continued to remain the most common method for obtaining TTPA.

2. Phosphorylation of sulphur-containing compounds

In recent years this method has been developed on the one hand by improving the reactions of this type that were already known and on the other hand by modifying them through expanding the range of both phosphorylating agents and reactants being phosphorylated.

The most widely used process is the phosphorylation of metal thiolates[20,21] and thiols[21–26] with P(III) acid halides.

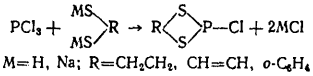
$$R_{3-n}PX_n + nR'SM \rightarrow R_{3-n}P(SR')_n + nMX$$

R = alkyl, aryl, RO, RS, Me_2N; X = Cl, Br, M = H, Na, Pb.

In the latter case a base is generally used, and in order to avoid an induction period in the reaction of P(III) halides with thiols it was proposed that the phosphorylation should be carried out in the presence of formamide[23] or other nitrogen-containing catalysts.[24]

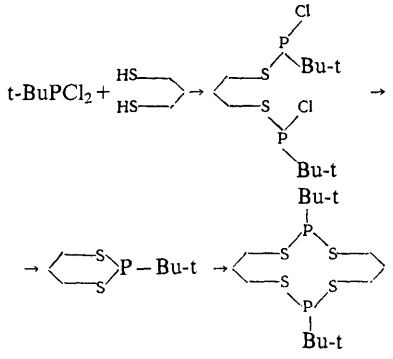
By using this reaction it was possible to obtain new types of bis-phosphorylated methylamines[27,28] and functionally substituted TTPA, including silicon-containing P(III) thioesters,[5,29,30] of γ- and ω-chloro-substituted phenylphosphonochloridothioites,[31] phosphorus(III)-containing dithiolothiadiazoles,[32] and *S*-phosphorylated derivatives of thioglycolic acid esters[33,34] and amides.[33]

By introducing *o*-dithiolobenzene, ethane- and *cis*-ethylene-dithiols, or their metal derivatives into a reaction with PCl_3, it was possible to synthesise a number of 1,3,2-dithiaphospholanes[35] and 1,3,2-dithiaphospholenes[36] containing an exocyclic P–Cl bond:



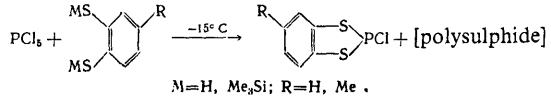
M = H, Na; R = CH_2CH_2, CH=CH, *o*-C_6H_4

At the same time, it is necessary to use a base in order to obtain 1,3,2-dithiaphospholanes with a P–C bond.[37] In the absence of the former the reaction of t-butyldichlorophosphine with 1,3-propanedithiol results in the formation of a twelve-membered ring containing phosphorus and sulphur atoms together with 2-t-butyl-1,3,2-dithiaphosphorinane.[38] The process takes place via an intermediate acyclic product:



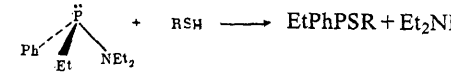
Recently[35,39] PCl_5 has also been used successfully as a phosphorylating agent for the synthesis of acyclic and cyclic TTPA:

$$PCl_5 + (C_6F_5S)_2Pb \rightarrow [(C_6F_5S)_5P] \rightarrow (C_6F_5S)_3P + (C_6F_5S)_2$$



M = H, Me_3Si; R = H, Me.

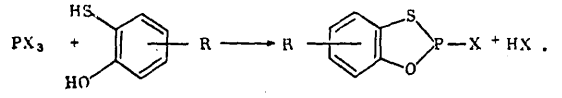
An attempt was made to utilise the phosphorylation of thiols with P(III) acid amides[40] in order to obtain optically active phosphinothioites.[40] However, when the optically active ethylphenylphosphinous diethylamide was treated with thiols, only the racemic thioester of this acid was formed:



When this reaction was extended to bis(trimethylsilyl) aminophosphine it was possible to synthesise the first example of a new class of TTPA—ethylthiophosphine:[41]

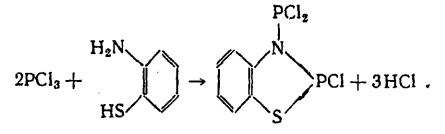
$$(Me_3Si)_2NPH_2 + EtSH \rightarrow EtSPH_2 + (Me_3Si)_2NH.$$

During the last ten years there has been a development of the phosphorylation of bifunctional reactants that have other proton-containing substituents in the molecule in addition to the thiol group; this is due to the growing interest of research workers in the chemistry of heterocycles. The reaction of phosphorus trihalides with certain 2-thiolophenols on heating gives the corresponding 2-halo-4,5-benzo-1,3,2-oxathiaphospholanes:[42,43]

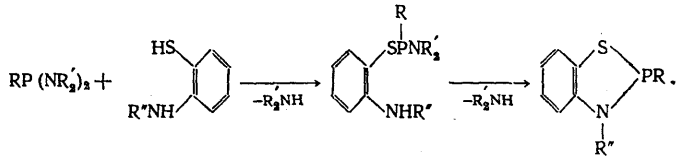


X = Cl, Br; R = H, alkyl, t-alkyl, OMe

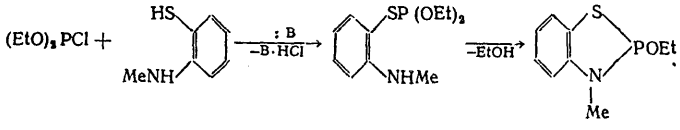
At the same time, attempts to synthesise 2-chloro-4,5-benzo-1,3,2-thiazaphospholane by phosphorylation of *o*-aminothiophenol with PCl_3 proved unsuccessful. In the presence of a base only a four-coordinate phosphorus derivative was isolated,[44] while in the absence of a base a halogenated *N*-phosphorylated 4,5-benzo-1,3,2-thiazaphospholane was formed:[45]



More successful was the use of alkyl- and aryl-phosphono-diamidites[46] and diethyl phosphorochloridite,[47] which made it possible to obtain a number of 1,3,2-thiazaphospholanes by reaction with *o*-aminothiophenol and its *N*-methyl derivative:



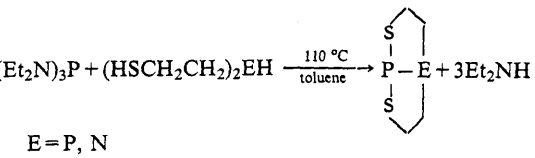
R = Me, Et, Ph; R′ = Me, Et; R″ = H, Me



It should be noted that in most cases the process takes place via the formation of linear products which are phosphorylated on the thiol group. In this case the factors (structure of reactants, temperature, presence of acidic catalysts, etc.) that affect the formation of products with a linear structure as well as cyclisation products have been determined.[46,47]

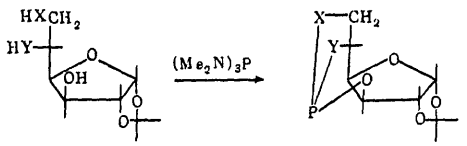
The temperature conditions of the reaction also govern the ratio of *S*- and *N*-phosphorylation products formed by reaction of indole-3-thiols with P(III) acid amides and chlorides,[48,49] the thiol group of indole-3-thiols being more active in reactions with chlorides.[49]

By using the reactions of polyfunctional compounds, in particular bis(β-thioloethyl)phosphine or bis(β-thioloethyl)amine, with triaminophosphine, a method has been developed for the preparation of bicyclic eight-membered heterocycles—2,8-dithia-1,5-diphospha- or 2,8-dithia-1-phospha-5-aza-bicyclo[3.3.0]octanes[50]



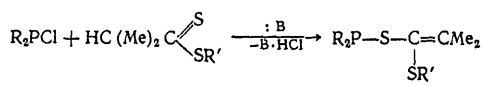
E = P, N

The reaction of thiolodeoxy-1,2-alkadiene-α-*D*-glucofuranose with PCl_3 [51] or hexamethyltriaminophosphine[52] was used for the synthesis of sugar bicyclophosphorothioites:



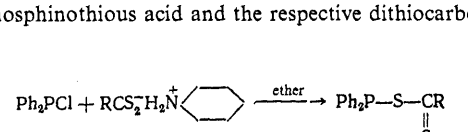
X = S, Y = O
X = O, Y = S .

Phosphorylation has also been widely used to obtain TTPA that contain electron-withdrawing substituents on the sulphur atom. Thus, because the high mobility of the α-hydrogen atoms in dithiocarboxylic acid esters makes it possible to phosphorylate the latter on the sulphur atom of the thiocarbonyl group, a method based on the reaction of P(III) acid chlorides with dithioisobutyrate esters in the presence of a base could be developed for the synthesi of the previously unknown vinyl phosphorothioites:[53,54]



R = Cl, Et, EtO, Et_2N; R′ = Me, Et .

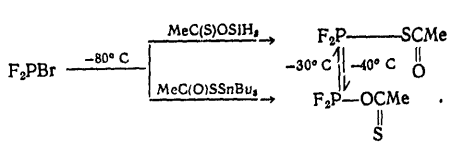
Piperidine salts of dithiocarboxylic acids proved to be convenient for the synthesis of the first examples of mixed anhydrides of diphenylphosphinothious acid and the respective dithiocarboxylic acid:[55]



R = Et, *p*-R′C_6H_4; R′ = Cl, Me, MeO.

These reactions were subsequently extended to dialkyl phosphorochloridites.[56]

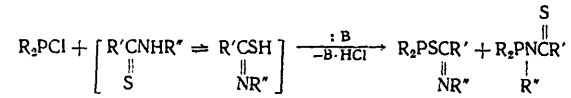
In a study of the phosphorylation of metal derivatives of thioacetic acid it was found[57] that *S*-acetyl phosphorodifluoridothioite is only formed when phosphorus difluorobromide reacts with the silyl ester of thioacetic acid at −80 °C:



At the same time, the reaction of phosphorus difluorobromide with tributylstannyl thioacetate gives the *O*-phosphorylation product—*O*-thioacetyl phosphorodifluoridite—which on heating to −30 °C is partially isomerised to *S*-acetyl phosphorodifluoridothioite.[57]

Phosphorylation of free thioacetic acid with PCl_5 only occurs on the sulphur atom and triacetyl phosphorotrithioite is formed.[58] The reaction of thioacetic acid with chlorophosphines in the presence of a base takes place in a similar manner.[58,59]

Taking into account the tendency of thiocarboxamides to form thiolimidoyl structures, studies were made of their phosphorylation with P(III) acid chlorides in the presence of a base.[60,61] While dialkyl phosphorochloridites react smoothly with thioacetamide to give only the *S*-phosphorylation product,[60] the reaction of diethyl phosphorochloridite with thiobenzoic acid *N*-methylamide gives *S*- and *N*-phosphorylation products in approximately equal proportions.[61] The phosphorylation of *N,N′*-diphenylthiourea occurs in a similar manner to that for the latter:[61]

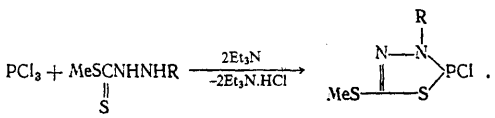


R = EtO, PrO, Et_2N; R′ = Me, Ph, NHPh; R″ = H, Me, Ph .

Reaction of phosphorodiamidochloridite with thiobenzoic acid *N*-methylamide again gives an imidoyl phosphorothioite as the sole product.[61]

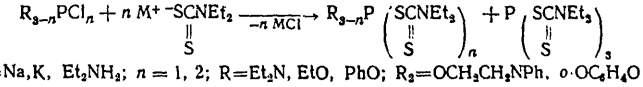
The products of *S*-phosphorylation-2-benzthiazolyl phosphorothioites—are also the only ones when Captax is reacted with trivalent phosphorus acid amides.[62]

Examples of new types of phosphorus-containing heterocycles—2-phenyl- and 2-acetyl-1-chloro-4-methylthio-1,5,2,3-phosphathiadiazoles—were synthesised by phosphorylation of the methyl esters of 3-substituted dithiocarbazic acids in the presence of triethylamine:[63]



R = Ph, MeCO

Treatment of alkali metal[64–66] or diethylammonium[66] *N*-diethyldithiocarbamates with P(III) acid chlorides gives phosphorylated derivatives of *N*-diethyldithiocarbamic acid:

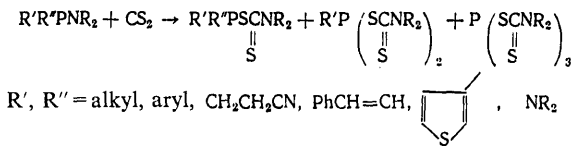


M = Na, K, Et_2NH_2; *n* = 1, 2; R = Et_2N, EtO, PhO; R_2 = OCH_2CH_2NPh, *o*-OC_6H_4O

It should be noted that compounds with a single dithiocarbamate group were only obtained in the case of 2-chloro-3-phenyl-1,3,2-oxaphospholane.[65,66]

Phosphorylated derivatives of dithiocarbamic acid can also be synthesised by reaction of P(III) acid amides with carbon disulphide, as was reported in detail back in 1963.[67] At the beginning of the 1980's this reaction once again drew the attention of research workers because a number of phosphorylated dithiocarbamates obtained from it proved to be effective vulcanisation accelerators for rubbers with polyfunctional action.[68–71] By studying new types of acyclic P(III) acid amides in reactions with carbon disulphide it was possible on the one hand to extend considerably the range of organophosphorus compounds containing one, two, or three dithiocarbamate groups[65,66,69,70] and on the other hand to determine the factors (nature of substituents, ratio of initial reactants, presence of acidic catalysts, etc.)[66,72] affecting the rate and direction of

reaction as well as the structure of the products formed and the composition of the reaction mixture:



R′, R″ = alkyl, aryl, CH_2CH_2CN, PhCH=CH, , NR_2

R = alkyl, $R_2=(CH_2)_n$, $(CH_2CH_2)_2O$; $n = 4,5$.

In the case of cyclic phosphoramidites containing both an exo- and endo-cyclic P–N bond, carbon disulphide is inserted selectively into the exocyclic phosphorus–nitrogen bond.[64,65]

In the last ten years a whole series of studies has been published on the synthesis of TTPA containing the heterosystem P–S–E (E = Si, Ge, P), information about which was previously restricted to individual studies.[73,74]

The possibility of forming *S*-silyl esters of P(III) thioacids was shown[75] when the reactions of different silylphosphines with elemental sulphur dissolved in hydrocarbons were studied:

$$RR'PSiMe_3 \xrightarrow{[S]} RR'PSSiMe_3$$

R=R′=Me, Me_3Si; R=Me_3Si, R′=Me, $P(SiMe_3)_2$.

In a study of the reaction of *bis*(difluorophosphine) sulphide with chlorogermane, *S*′-germyl phosphorodifluoridothioite was obtained for the first time:[76]

$$(F_2P)_2S + ClGeH_3 \xrightarrow{20^\circ C} F_2P{-}S{-}GeH_3 + F_2PCl\ .$$

However, it is not possible to synthesise the *S*-silyl or *S*-stannyl analogues of the latter by phosphorylation of disilathiane or bis(tributylstannyl) sulphide with difluorohalophosphines due to the high rate of the second stage of the reaction, resulting in the formation of bis(difluorophosphine) sulphide:[77]

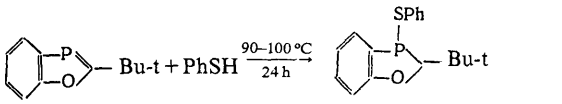
$$F_2PX + S(ER_3)_2 \xrightarrow[-XER_3]{} [F_2PSER_3] \xrightarrow[-XER_3]{F_2PX} F_2P{-}S{-}PF_2$$

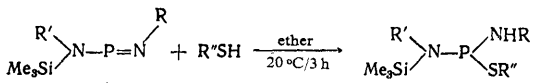
X = Cl, Br; E = Si, Sn; R = H, Bu.

Reaction of disilathiane with tetramethylphosphorodiamidochloridite also takes place in a similar manner.[78]

3. Synthesis of TTPA from bicoordinated phosphorus compounds

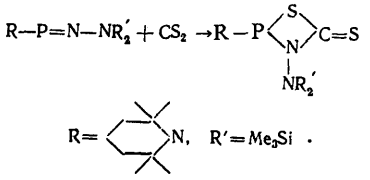
A new approach to the synthesis of previously unknown types of TTPA is opened up by the addition reactions of thiols to phosphaalkenes[79,80] and imidophosphenous acid amides:[81]





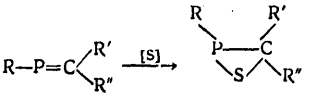
R = R′ = Me_3Si, t-Bu; R = t-Bu, R′ = Me_3Si; R″ = Pr, t-Bu, Ph.

It was possible to obtain a four-membered phosphorus-containing heterocycle by [2+2]-cycloaddition of carbon disulphide to 1-aminodiazaphosphene.[82]



R= , R′ = Me_3Si .

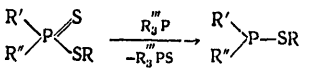
Certain phosphaalkenes reacted smoothly with sulphur by a [2+1]-cycloaddition to give the previously unknown 1,2-λ^3-thiaphosphiranes.[83,84]



R = $Me_3Si-C\equiv C$, R′ = R″ = Me_3Si; R = R″ = Bu-t, R′ = H.

4. Other methods for obtaining TTPA

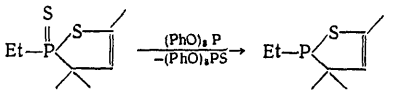
During the last ten years processes involving desulphurisation of four-coordinated phosphorus derivatives by treatment with tertiary phosphines and other P(III) derivatives have been used to an increasing extent for the synthesis of TTPA. Thus, the elimination of sulphur from phosphinodithioate esters,[85] including those that were optically active, with trialkylphosphines was successfully carried out, resulting in the isolation of the corresponding phosphinothioite esters:



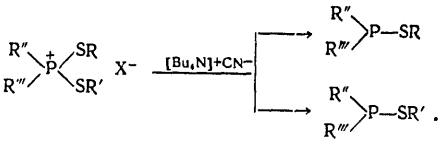
R = Me, R′ = R″ = Ph; R = *p*.$MeOC_6H_4$, R′ = Me, R″ = Ph; R‴ = Me, Bu .

However, optical activity cannot be retained in the reaction products due to the low pyramidal inversion barrier of phosphinothioites.[85]

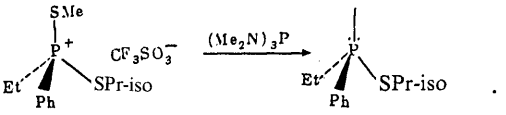
By using triphenyl phosphite to reduce 3,3,5-trimethyl-2-thione-2-ethyl-1,2-thiaphosphol-4-ene it was possible to synthesise the corresponding phospholene with a tricoordinated phosphorus atom:[86]



Phosphinothioite esters were obtained by P–S cyanolysis of quasiphosphonium salts containing an alkylthio group on the phosphorus atom:[87]

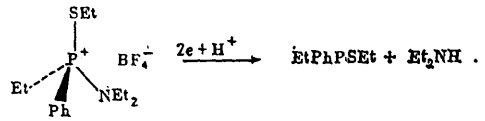


When this method was modified using hexamethyltriaminophosphine as the nucleophilic reagent it was possible to carry out the stereoselective synthesis of optically active phosphinothioites:[88]



For this reaction it was established in two studies[87,88] that, depending on the nature of the RS group, both its selective elimination giving only one phosphinothioite and the formation of a mixture of phosphinothioite esters were possible.

At the same time, electrochemical reduction of optically active ethylphenyl(diethylamino)ethythiophosphonium tetrafluoroborate in acetonitrile at 20 °C gives ethyl ethylphenylphosphinothioite that is optically inactive:[85]



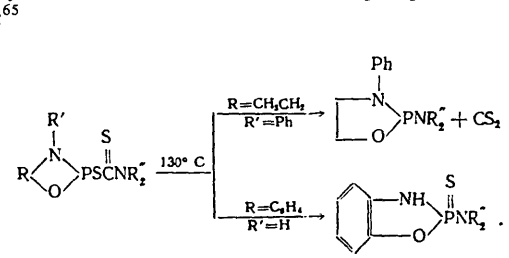
The formation of alkyl phosphorodichloridothioite occurred[89] on decomposition of certain diazadiphosphetidines, and a number of diphenylphosphinothioite esters were obtained by thermal decomposition of phosphorylated semimercaptals,[90] being accelerated in the presence of acidic catalysts.

III. Chemical properties

At the beginning of the 1970's the chemical conversions of TTPA were studied in the greatest detail in the case of reactions with alkyl and acyl halides, and in the course of these studies dual reactivity of P(III) acid thioesters was found.[15] In the last ten years the range of both electrophilic and nucleophilic reagents has been considerably extended, so it has been possible to determine the general mechanisms governing the chemical behaviour of TTPA in substitution and addition reactions and to establish the differences between the reactivity of the system $\geq\ddot{P}-\ddot{S}$ and that of other ambident systems with a heteroatom (N, O) on trivalent phosphorus.

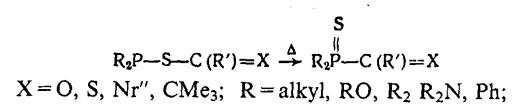
1. Thermal stability and isomerisation of TTPA

Studies on the thermal stability of P(III) acid thioesters using differential thermal analysis[20] indicate that the latter have quite a high stability when exposed to heat. In contrast to this, dialkyl phosphoranilidodithioites undergo thermal disproportionation even on distillation under vacuum or on heating in a sealed tube.[91] Products obtained from insertion of carbon disulphide into the exocyclic P–N bond of 2-dialkylamino-1,3,2-oxaphospholanes are also thermally unstable; on heating under vacuum they decompose to the original oxaphospholane with elimination of carbon disulphide.[65] At the same time, when 2-(*N*-dimethylthiocarbamoylthio)-4,5-benzo-1,3,2-oxaphospholane is exposed to heat, only 2-dimethylamino-2-thione-4,5-benzo-1,3,2-oxaphospholane is isolated:[65]



The change in the course of decomposition in this case is due to the presence of the condensed phenyl ring system.

The thermal thiol-thione isomerisation, due to *S,C*-migration of the phosphorus atom is of the greatest interest. Thus, phenyl diphenylphosphinothioite isomerises to triphenylphosphine sulphide only at 350 °C.[92] This type of rearrangement takes place much more readily in the case of ethyl phosphinothioites in the presence of iodosilane[93] and in a number of TTPA that contain electron-acceptor groups on the sulphur atom in the molecule, including those such as P(III) thioacid vinyl esters,[94] mixed thioanhydrides of P(III) acids and thioacetic[58,59] or dithiocarboxylic acids,[56] imidoyl phosphorothioites,[61] etc.



X = O, S, Nr'', CMe_3; R = alkyl, RO, R_2 R_2N, Ph;
R' = Me, iso-Pr, Ph, NHPh.

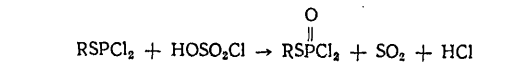
In the latter case it is necessary to isolate separately *S*-acetimidoyl phosphorothioites, which do not undergo thermal isomerisation but decompose to dialkyl phosphorothioites and acetonitrile, which is apparently due to the presence of a mobile proton on the imine nitrogen atom:[60]



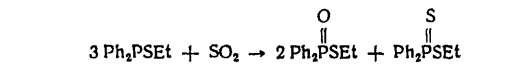
Thiol-thione isomerisation takes place on gentle heating of *S*-phosphorylated thioglycolic ester derivatives.[34]

2. Oxidation, addition of sulphur, and imination

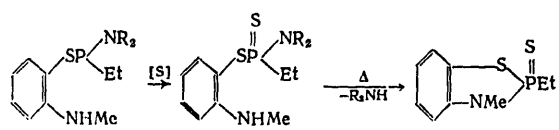
A characteristic feature of P(III) derivatives, including TTPA, is their tendency to undergo oxidation, addition of sulphur, and imination, which result in the formation of the corresponding P(V) derivatives. Thus, 2-benzthiazolyl phosphorothioites,[62] vinyl dialkyl phosphorothioite,[54] and *S*-thioacyl phosphorothioites[56] are readily oxidised with atmospheric oxygen to the corresponding phosphorothioates. Chlorosulphonic acid proved to be a convenient oxidising agent of TTPA such as alkyl phosphorodichloridothioite:[95]



The oxidation of diphenylphosphinothioite with sulphur dioxide[96] is accompanied by the formation of diphenylphosphinodithioate.

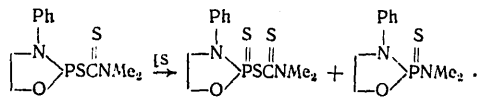


Reactions of elemental sulphur with TTPA have been studied quite extensively in recent years with the object of synthesising new types of P(V) acid derivatives, in particular, 3-thiophosphorylthioindoles,[49] 2-thiolobenzthiazolyl phosphorodithioates,[62] and optically active, *O,S*-dialkyl alkylphosphonodithioates.[97] The addition of sulphur to *S*-(*o*-methylaminophenyl) ethylphosphonamidothioite takes place in a similar manner.[46] However, in this case, the addition product cyclises during distillation to form 2-ethyl-2-thione-3-methyl-4,5-benzo-1,3,2-thiazaphospholane:

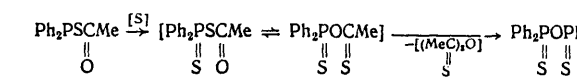


TTPA that contain electron-acceptor substituents react with sulphur in a more complex manner. Thus, as a result of the reaction of elemental sulphur with 2-dithiocarbamoyl-3-phenyl-1,3,2-oxazaphospholane, together with an addition product, 2-dimethylamino-2-thione-3-phenyl-1,3,2-oxaphospholane is also

formed by elimination of carbon disulphide from the dithiocarbamoyl derivative:[65]



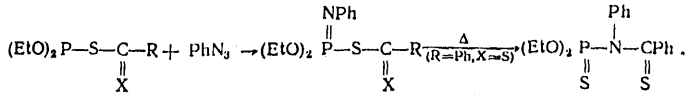
A dithionepyrophosphinate is obtained from *S*-acetyl diphenylphosphinothioite:[59]



It has been suggested[59] that at the first stage *S*-acetyl diphenylphosphinodithioate is formed, being converted to thioacetyl diphenylphosphinothioate as a result of phosphorotropic rearrangement; disproportionation of the latter gives the final product.

Trichlorophosphorus sulphide has been used in separate cases to introduce thione sulphur into TTPA molecules.[63]

Imination reactions of TTPA have in recent years only been studied in the case of the reaction of phenyl azide with vinyl phosphorothioites[54] and *S*-thioacyl phosphorothioites,[56] the corresponding phosphazo compounds being obtained:



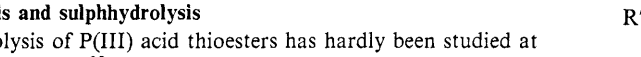
In the latter case[56] an imide-amide rearrangement can take place during distillation, which is due to migration of the thiocarbonyl group in the trio of atoms S–P–N.

3. Reactions of TTPA with proton-containing compounds

Substitution reactions on the trivalent phosphorus atom in a number of TTPA have been most effectively studied for reactions of the latter with compounds containing a mobile hydrogen atom. With these studies it was possible on the one hand to extend the methods for obtaining those TTPA already known in addition to new types and on the other hand to detect unusual pathways of particular reactions caused by the presence of alkylthio groups in the molecule.

(a) Hydrolysis and sulphhydrolysis

The hydrolysis of P(III) acid thioesters has hardly been studied at all. There are results[98] indicating that trialkyl phosphorotrithioites under normal conditions are stable to the action of water. At the same time, dialkyl phosphoramidodithioites are hydrolysed to ammonium salts of phosphorous acid and the corresponding phosphorotrithioites:[91,99]

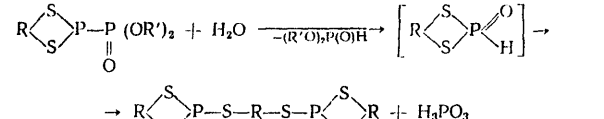


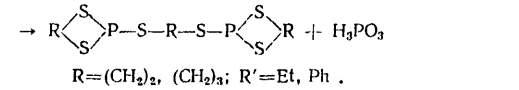
R=Et, Pr; R′=H, R″=Ph; R′=R″=Me .

It has been established that the rate of hydrolysis is dependent on the nature of the amide substituent on the trivalent phosphorus atom.[91,99]

In contrast to this, 2-benzthioazolyl phosphorodiamidothioites react with water and carbon disulphide with cleavage of the P–S bond and retention of the P–N bond[62] as a result of the pseudohalogen nature of the benzthiazolyl group.

The nature of the substituents also governs the rate of hydrolysis of 2-dialkoxyphosphoryl-1,3,2-dithiaphospholanes and the analogous dithiaphosphorinanes;[100] this takes place with an initial cleavage of the P–P bond followed by disproportionation of the phosphorodithioic acid formed:

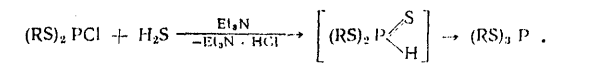




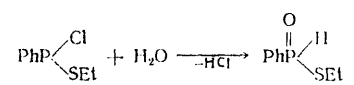
R=$(CH_2)_2$, $(CH_2)_3$; R′=Et, Ph .

It was shown[100] that hydrolysis can be accelerated by the action of acids and alkalis.

A similar disproportionation of intermediate dialkyl phosphorotrithioites has been suggested[101] in the sulphhydrolysis of cyclic and acyclic phosphorochloridodithioites.



Only when the reaction of *S*-ethyl phenylphosphonochloridothioite with water was studied by ^{31}P NMR spectroscopy was the formation of *S*-ethyl hydrogen phenylphosphonothioite detected for the first time:[102]

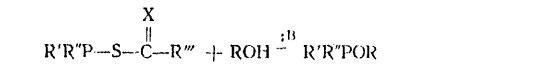


The latter decomposes during the reaction in a similar manner to other derivatives of this class of products.[103]

1-Chloro-1,5,2,3-phosphathiadiazole is readily hydrolysed by atmospheric moisture to give the initial dithiacarbazates.[63]

(b) Alcoholysis and thiolysis

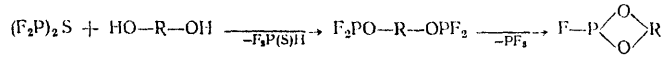
Alcoholysis reactions have been studied in a fairly detailed manner for a number of TTPA. The ready cleavage of the P–S bond by treatment with alcohols occurs in those TTPA containing benzthiazolyl,[62] dithioacyl,[55] thioacetimidoyl,[60] dithiocarbamate,[65] and other[86] groups with electron-withdrawing substituents on the sulphur atom.



R′, R″=RO, R_2N, Ph; R′R″=OCH_2CH_2NPh; R‴=alkyl, aryl, R_2N; X=S, NH.

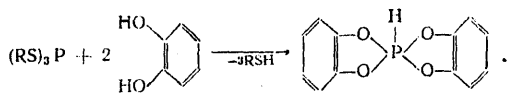
At the same time, alcoholysis of *tris*(*N*,*N*-dialkylaminothiocarbamoyl) phosphorotrithioite takes place under more severe conditions to give a complex mixture of products;[66] this is apparently due to the presence of intramolecular coordinate bonds in this type of TTPA.[72,104]

There has been extensive study of the reactions of bis(difluorophosphine) sulphide with alcohols, phenols, and diols, which give different types of phosphoromono- and phosphorodi-fluoridites:[105]



Cleavage of the P–S bond in trialkyl phosphorotrithioites is effected by sodium ethoxide[106] and also pyrocatechol.[107] In the latter case only *bis*(*o*-phenylenedioxy)phosphorane is formed,

whatever the ratio of the initial reactants.

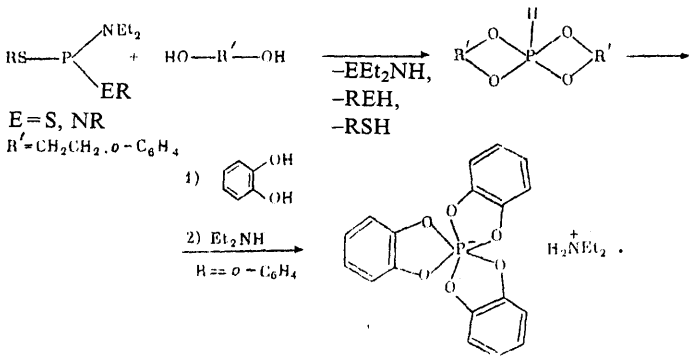


The reaction of dialkyl phosphoramidodithioites with alcohols takes place under severe conditions to give trialkyl phosphite and phosphorotrithioites:[99]

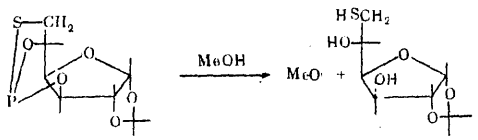
$$(RS)_2PNEt_2 + R'OH \xrightarrow{-Et_2NH} (RS)_2POR' \xrightarrow[-2RSH]{2R'OH} (R'O)_3P\,.$$
$$(RS)_2PNEt_2 + RSH \xrightarrow{-Et_2NH} (RS)_3P,\ R=R'=Et,\ Bu$$

Alcoholysis and phenolysis of bis(*N,N*-diethylcarbamoyl)diethylphosphoramidodithioite gives similar products.[66] It was established[99] that the amine generated at the first stage of the reaction catalyses the subsequent replacement of the alkylthio groups on the trivalent phosphorus atom by alkoxyl groups. When alcoholysis and phenolysis is carried out with removal of the amine, it is possible to stop the process at the stage where mixed *O,S,S*-phosphorodithioites are formed.[99] In this case the reaction is accelerated in the presence of acidic catalysts.

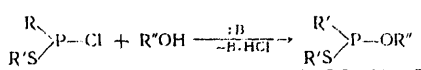
The reaction of phosphoromono- and phosphorodi-amidothioites with aliphatic and aromatic diols takes place with substitution of amide and alkylthio groups on the phosphorus atom, giving either a spirophosphorane with a P–H bond or compounds with a hexacoordinated phosphorus atom,[99] depending on the nature of the diol:



In a series of P(III) acid *O,S*-thioesters alcoholysis was only studied in the case of bicyclophosphorothioites of sugars:[51]



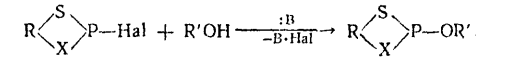
Anhydride derivatives of P(III) thioacids are widely used for the phosphorylation of alcohols and phenols. Thus, by alcoholysis of *S*-alkyl phosphonochloridothioites in the presence of the natural alkaloid, brucine, it was possible to obtain readily racemising optically active *O,S*-dialkyl phosphonothioites:[97]



R = Et, Bu; R′ = iso-Pr, iso-Bu, C_6H_{13}; R″ = Me, Et; B – brucine.

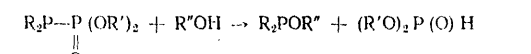
In the absence of a base, this type of reaction with phenylphosphonous acid derivatives does not stop at the stage where mixed *O,S*-thioesters are formed but gives partial *O*-alkyl phenylphosphonites by further phosphorylation of alcohol.[102]

A number of alkoxy derivatives of phosphorus-containing heterocycles have been obtained by phosphorylation of aliphatic alcohols and phenols with 2-halo-1,3-2-oxathiaphospholanes[42,43,108] and the analogous oxathiaphosphorinanes,[109] and also with 1-chloro-1,5,2,3-phosphathiadiazoles:[63]



R = $CH_2CH_2CH_2$, *o*-C_6H_4, RS–C=N, Hal = Cl, Br;
X = O, S, NR″; R′ = alkyl, Ph, *o*-FC_6H_4 etc.

Dialkyl acetyl phosphorodithioites,[110] 2-dialkyloxyphosphoryl-substituted 1,3,2-dithiaphospholanes or 1,3,2-dithiaphosphorinanes, and also their acyclic analogues can be used for the mild phosphorylation of aliphatic alcohols.[100] Alcoholysis of the latter takes place with cleavage of the P–P bond:

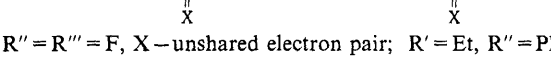


R_2 = S $(CH_2)_n$ S, $(BuS)_2$; *n* = 2, 3; R′ = Et, Ph; R″ = Me, Et .

For cyclic compounds the process is complicated by scission of the P–S bond in the ring, and the result depends on the structure of the compound, ratio of reactants, temperature, and reaction time.[100]

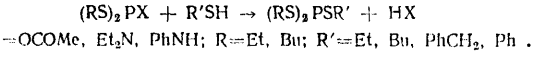
Phosphorylation of thiols with TTPA has not been studied very much. It was shown that the exocyclic P–Hal bond in 2-halo-1,3,2-dithia-[35,109] and 2-halo-1,3,2-oxathia-phospholanes[42,43] readily undergoes thiolysis in the presence of a base in a similar manner to the reactions with alcohols.

Information is also available on the thiolysis of P–S–P bonds:[105,111]



R′ = R″ = R‴ = F, X – unshared electron pair; R′ = Et, R″ = Ph, R‴ = EtO; X = S

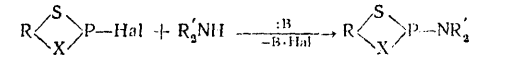
In recent years it has been established that acyclic acyl phosphorodithioites[110,112] and phosphoramidodithioites,[99,113] in contrast to their oxygen analogues which when treated with thiols are converted in most cases to thiophosphoryl compounds, can be successfully used to phosphorylate thiols:



X = OCOMe, Et_2N, PhNH; R = Et, Bu; R′ = Et, Bu, $PhCH_2$, Ph .

(c) Aminolysis

The synthesis of various P(III) thioacid amides is usually carried out by phosphorylation of primary and secondary amines with suitable P(III) halides. In recent years this method has been widely used to obtain 2-amino derivatives of 1,3,2-diheterophospholanes and 1-amido-1,5,2,3-phosphathiadiazoles.[63]



R = C_6H_4, RS–C=N; X = O, NR″; R′ = H, alkyl, Ph.

Together with dialkyl phosphorochloridodithioite,[113] acyl phosphorodithioites[112] and also mixed anhydrides of phosphorodithious and phosphorodithioic acids[114] have been proposed as

phosphorylating agents for the synthesis of acyclic phosphoramidodithioites:

$$(RS)_2PX + 2\,R'R''NH \rightarrow (RS)_2PNR'R'' + R'R''NH\cdot HX$$
X=Cl, OCOMe, (RO)$_2$P (S) S; R'=R''=Et; R'=H, R''=Ph .

The difficult-to-prepare aminodifluorophosphines can readily be obtained by reaction of primary and secondary amines with bis(difluorophosphine) sulphide.[105] The P–S bond also readily undergoes aminolysis in those TTPA containing benzthiazolyl,[62] dithioacyl,[55] thioacetimidoyl,[60] and dithiocarbamate[65] groups which have a pseudohalogen nature.

(d) Reactions with acids

Up to the end of the 1970's there was virtually no information in the literature about the reactions of TTPA with acids. At the beginning of the 1980's, as a result of a systematic study of the chemical behaviour of P(III) acid thioesters reacting with acids it was established[98] that in contrast to the oxygen analogues—phosphites—the pathway of the Arbuzov reaction is not followed but cleavage of the P–S bond occurs. Thus, the reactions of HCl with trialkyl phosphorotrithioite,[115] *S*-phosphorylated thioglycolates,[34] and *O,O*-dialkyl *S*-acetimidoyl phosphorothioites[60] occur with replacement of the alkylthio group on the trivalent phosphorus atom:

$$R'_2P-SR + HCl \rightleftharpoons R'_2P-Cl + RSH$$
R=Et, CH_2COOEt, C(Me)=NH; R'=EtS, RO, Cl .

Diphenylphosphinothioite esters react with HI in a similar manner,[116] but in this case the reaction is complicated by secondary processes.

Only in the case of *S*-germyl phosphorodifluoridothioite does cleavage of the S–Ge bond with hydrogen halides occur;[76] this is probably due to the greater electrophilicity of the germanium atom:

$$F_2PSGeH_3 + HX \rightarrow F_2P(S)H + XGeH_3$$
X=Cl, Br .

Studies of the reactions between P(III) acid thioesters and carboxylic acids showed[103,115] that they occur under severe conditions with cleavage of the P–S bond and formation of carboxylic acid thiol esters and *O*-containing phosphorus acids:

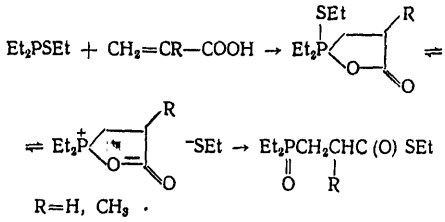
$$R'R''PSR + R'''COOH \xrightarrow{100-140^\circ C} R'R''POCOR''' + RSH$$
$$R'R''POCOR''' + R'''COOH \rightarrow R'R''P(O)H + (R'''CO)_2O$$
$$(R'''CO)_2O + RSH \rightarrow R'''C(O)SR + R'''COOH$$
R'=R''=SR; R=Et, Pr; R'''=Ph; R=R'=Et, R''=Ph, R'''=Me
R'=Et, Ph; R''=SR; R'''=Ph .

If there are alkylthio groups present on the phosphorus atom in the *O*-containing acids, they are unstable during the reaction and decompose with elimination of mercaptan to give P(III) acid anhydrides.[103]

Introduction of chlorine atoms into the acetic acid molecule has a substantial effect on the course of the reaction between the latter and P(III) acid thioesters.[117,118] In this case, instead of acidolysis, replacement of the alkylthio group on the trivalent phosphorus atoms by a chlorine atom takes place, giving the corresponding P(III) acid chlorides as well as oxidation products from the initial thioesters and products from dechlorination of carboxylic acids as the corresponding thiol esters:[118]

$$2\,\begin{matrix}R'\\R''\end{matrix}\!\!>\!PSR + CCl_nH_{3-n}COOH \rightarrow \begin{matrix}R'\\R''\end{matrix}\!\!>\!PCl + \begin{matrix}R'\\R''\end{matrix}\!\!>\!P(O)SR + CCl_{n-1}H_{4-n}C(O)SR$$
R'=R''=SR; R=Et, Pr; n=3; R'=Ph, R''=Et; n=3;
R'=Et, R''=Ph; R=Et, n=1–3 .

In studies on the reactions of phosphinothioites with α,β-unsaturated carboxylic acids, the previously unknown 1:1 addition products—diethyl-β-ethylthiocarbonylalkylphosphine oxides—were obtained:[119,120]

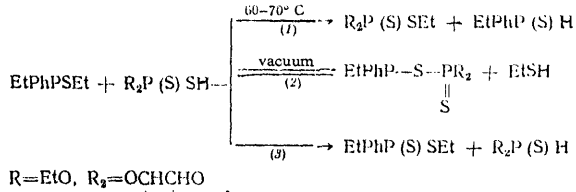


R=H, CH_3 .

When the reaction was monitored using IR and ^{31}P NMR spectroscopy[120] it was possible to detect an initially formed monocyclic phosphorane with a P–S bond, which probably then decomposes via an intermediate quasiphosphonium compound to the final phosphine oxide.

In contrast to phosphinothioites, phosphorotrithioites and phenylphosphonodithioites cause α,β-unsaturated carboxylic acids to polymerise.[120]

The reaction conditions have a significant effect on the course of the reaction between P(III) acid thioesters and organic acids. While ethylphenylphosphinothioite reacts with phosphorodithioic acids at 60–70 °C to form diethyl phosphorodithioate and ethylphenylphosphinothious acid [route (1)], at room temperature under vacuum a mixed anhydride of ethylphenylphosphinothious acid and the corresponding phosphorodithioic acid is obtained [route (2)]:[111]



R=EtO, R_2=OCHCHO (Me Me) .

It should be noted that whatever the method used to carry out the reaction it is accompanied by a subsidiary process involving desulphurisation of the phosphorodithioic acid by the initial phosphinothioite [route (3)].[111]

In a study of these reactions an unusual cleavage of the P–S bond in ethylphenylphosphinothioite on treatment with phosphorothious acid under vacuum was identified for the first time:[111]

$$EtPhPSEt + R_2P(S)H \xrightarrow[-EtSH]{vacuum} EtPhP(=S)-PR_2 .$$

A similar route also occurs in the reaction of dialkyl phosphites with Schrader's anhydride[121] and related compounds[122] in the presence of a base:

$$R_2P(=S)-S-P(OEt)_2 + (EtO)_2P(O)H \xrightarrow{Et_3N} R_2P(=O)-P(OEt)_2 + (EtO)_2PSH\cdot NEt_3$$
R= (EtO)$_2$P (S) S; R_2=SCHMeCH$_2$S .

At the same time, dialkyl phosphoramidodithioites react with mineral[113] and organic[112,114] acids, retaining the P–S bond and replacing the amide group on the trivalent phosphorus atom to form

the corresponding P(III) thioacid anhydride derivatives:

$$(RS)_2PNR'R'' + 2HX \rightarrow (RS)_2PX + R'R''NH \cdot HX$$
R=Et, Pr; R'=R''=Et; R'=H, R''=Ph; X=Cl, OCOMe, $(RO)_2P(S)S$.

Acyclic[114,123,124] and cyclic[122] phosphorochloridodithioites in the presence of triethylamine react in a similar manner with organic acids:

$$(RS)_2PCl + HX \xrightarrow{Et_3N} (RS)_2PX + Et_3N \cdot HCl$$
R=Et, Pr; X=OCOMe, $(RO)_2P(S)S$, $(EtO)_2P(O)$.

In the absence of base, acidolysis of ethyl phosphorodichloridothioite takes place only on heating with removal of an alkylthio group and formation of ethyl thioacetate, acetyl chloride, and metaphosphorous anhydride:[125]

$$EtSPCl_2 + 2CH_3COOH \xrightarrow[-HCl]{70^\circ C} CH_3CSEt + CH_3CCl + 1/n\left[-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-\right]_n.$$

According to the findings of ^{31}P NMR spectroscopy, *S*-ethyl phenylphosphonochloridothioite reacts with acetic acid at 0 °C to form phenyldichlorophosphine and products derived from its stepwise acidolysis—phenylphosphonous acid and its monochloride.[102]

In their reactions with α,β-unsaturated acids dialkyl phosphorochloridodithioites behave similarly to other P(III) acid chlorides, being converted to the corresponding diethyl β-chloroformylalkylphosphonodithioates:[126]

$$(EtS)_2PCl + CH_2{=}CR{-}COOH \rightarrow (EtS)_2P\underset{\underset{O}{\|}}{C}H_2\underset{\underset{R}{|}}{C}HC(O)Cl$$
R=H, Me.

In studies on the reactions of acyl phosphorodithioites with mineral and organic acids[123,127] it was established that, in contrast to their oxygen analogues which react with acids according to the Arbuzov reaction mechanism, in these compounds replacement of the acetoxyl group on the trivalent phosphorus atom occurs with retention of its coordination:

$$(RS)_2POCOMe + HX \rightleftarrows (RS)_2PX + MeCOOH$$
R=Et, Pr; X=Cl, OCOPh, $(RO)_2P(S)S$

In this case the possiblity of transacylation of the acetoxyl group in acyl phosphite was demonstrated experimentally for the first time.[123]

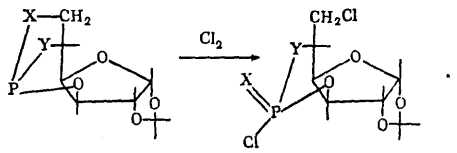
4. Reactions of TTPA with halogens and halogenated electrophilic reagents

The discovery by A E Arbuzov of the rearrangement of trivalent phosphorus acid esters to pentavalent phosphorus acid esters by treatment with alkyl halides formed the start of a systematic study of P(III) derivatives in reactions with halogenated electrophilic reagents. It is obvious that these studies could not also cover TTPA. By studying the chemical behaviour of the latter in reactions with alkyl and acyl halides in the 1960's and 1970's, with the most detailed treatment given in one review,[15] it was possible to establish some of these reaction mechanisms. It was found that in a number of cases the classical Arbuzov reaction route does not occur but the alkylthio group on the trivalent phosphorus atom is replaced and its coordination is retained. Moreover, there was a complete range of halogenated electrophilic reagents used up in this connection and there were virtually no studies on the reactions of TTPA with other compounds containing a halogen atom. At the beginning of the 1980's both in the USSR and abroad studies were published on the chemical behaviour of TTPA in reactions with halogens and halogenated reagents. Of particular interest are the results of those studies in which, as in the case of alkyl and acyl halides, there are deviations from the classical route of the Arbuzov reaction.

It was shown in 1980[76] that chlorine cleaves the S–Ge bond in *S*-germyl phosphorodifluoridothioite.

$$F_2P\overset{\overset{S}{\|}}{S}GeH_3 + Cl_2 \rightarrow F_2P\overset{\overset{S}{\|}}{C}l + ClGeH_3.$$

An interesting mechanism was found[128] in a study of the chlorination of 3,5,6-bicyclophosphorithioites of sugars:



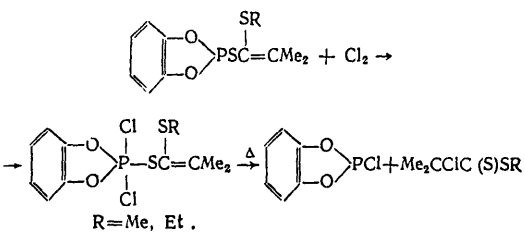
It was shown that the direction of chlorination is determined stereochemically, in all cases nucleophilic substitution being most favourable on the sterically accessible primary C(6) carbon atom.[128]

On mixing equimolar quantities of diphenylphosphinothioite ester and iodine, unstable quasiphosphonium compounds were subsequently obtained.[116]

$$Ph_2PSR + I_2 \xrightarrow[CH_2Cl_2]{-30^\circ C} Ph_2\overset{I}{\overset{|}{\overset{+}{P}}}SRI^- \xrightarrow[-EtI]{(R=Et)} Ph_2P\overset{\overset{S}{\|}}{I}.$$

When R = Et, the quasiphosphonium compound decomposes in accordance with the second stage of the Arbuzov reaction.

Quasiphosphonium compounds[35] as well as chlorophosphoranes[43] are also formed by chlorination of 2-chloro-4,5-benzo-1,3,2-diheterophospholanes that contain an endocyclic P–S bond. As a result of the reaction between chlorine and *S*-vinyl pyrocatechyl phosphorothioite, the first examples of vinylthiochlorophosphoranes were obtained, partially decomposing when distilled under vacuum.[129] In this case products from replacement of the vinylthio group on the trivalent phosphorus atom—pyrocatechyl phosphorochloridite and methyl α-chloroisobutyrodithioate—are isolated:



R=Me, Et.

Chlorination and bromination of phosphorotrithioites take place with the formation of substitution products—dialkyl phosphorohalodithioites:[130]

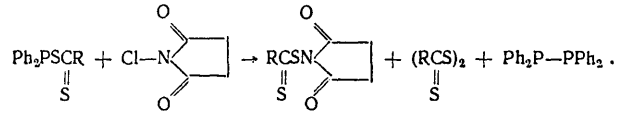
$$2(RS)_3P + Hal_2 \rightarrow (RS)_2PHal + (RS)_3PS + RHal$$
R=Me, Et, Pr; Hal=Cl, Br.

In this reaction phosphorotetrathioate and the respective alkyl halides are formed as by-products.[130]

The chlorination of trialkyl phosphorotrithioites with phosphorus pentachloride takes place in a similar manner:[130]

$$2(RS)_3P + PCl_5 \rightarrow (RS)_2PCl + (RS)_3PS + RCl + PCl_3$$
R=Et, Pr

The reaction of thioacyl phosphinothioites with *N*-chlorosuccinimide probably also leads to replacement of the *S*-thioacyl group by a chlorine atom, but products derived from further reactions are isolated in this case:[55]



The possibility that TTPA take part in exchange reactions with sulphenyl chlorides was first shown in 1980:[19]

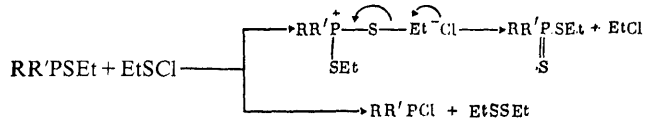
$$(CF_nCl_{3-n}S)_xPCl_{3-x} + xCF_nCl_{3-n}SCl \xrightarrow{-PCl_3} x(CF_nCl_{3-n}S)_2 .$$

The rate of this reaction decreases as the degree of chlorination of the reaction partners increases.

It was later found[131] that in the reaction between methyl phosphorodichloridothioite and trifluoromethylsulphenyl chloride the Arbuzov rearrangement does not occur and *S*-(trifluromethylthiomethyl) phosphorodichloridothioite is unexpectedly formed:

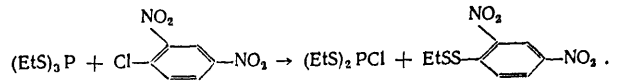
$$CH_3SPCl_2 + CF_3SCl \rightarrow CF_3SCH_2SPCl_2 + HCl .$$

Retention of the same coordination of the phosphorus atom together with an Arbuzov rearrangement also take place for the reactions of phosphorothioites and phosphinothioites with ethylsulphenyl chloride:[132]

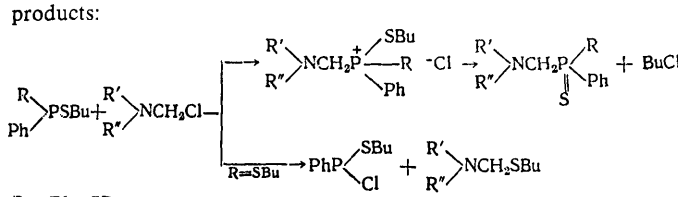


R=R′=SEt; R=Et, R′=Ph .

The course of the reaction is determined by the temperature, use of solvents, presence of acidic catalysts, and the nature of the sulphenyl chloride.[132] In particular, replacement of ethylsulphenyl chloride by 2,4-dinitrophenylsulphenyl chloride in a reaction with triethyl phosphorotrithioite has the result that the Arbuzov reaction pathway does not occur in this case but an alkylthio group on the trivalent phosphorus atom is replaced by a chlorine atom to give phosphorochloridodithioite and 2,4-dinitrophenyl ethyl disulphide:[132]



During the last ten years the study of the chemical behaviour of TTPA in reactions with alkyl and acyl halides has been continued. It transpired that chloromethyl derivatives of amines behave in a similar manner to alkyl halides in reactions with P(III) acid thioesters.[133] While phosphinothioites react with them on the phosphorus atom to form Arbuzov reaction products, phosphonodithioites give products from substitution of the alkylthio group on the trivalent phosphorus atom as well as Arbuzov rearrangement products:

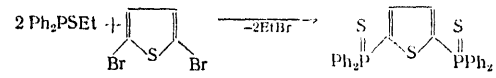


R = Ph, SBu.

The course of the reaction is determined by the polarity of the C—Cl bond; as the latter increases there is a greater tendency towards a substitution reaction.[133]

Phosphoramidothioites also react with alkyl halides by two routes—the Arbuzov reaction pathway and replacement of an alkylthio group.[134] The occurrence of a particular route is determined by the nature of the initial reactants and the presence of a catalyst ($ZnCl_2$).

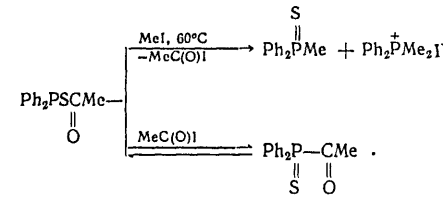
Mixed P(III) acid *O,S*-thioesters react with alkyl halides[36] and 2,5-dibromothiophene[135] in a complex and unclear manner.[135] Only in the case of reaction of the latter with *S*-ethyl diphenylphosphinothioite was it possible to isolate 2,5-bis(diphenylphosphinothioyl)-thiophene:[135]



New data has been obtained on the reactions of phosphorotrithioites with alkyl halides. Until recently it was generally thought[15] that these reactions occur with retention of the same coordination of the phosphorus atom. However, the first example of the formation of only classical Arbuzov reaction products was recently found:[136]

$$(EtS)_3P + MeI \rightarrow (EtS)_2P(=S)Me + EtI .$$

S-Acetyl diphenylphosphinothioite reacts with methyl iodide in an interesting manner.[59] Depending on the process conditions, either methyldiphenylphosphine sulphide and dimethyldiphenylphosphonium iodide or acetyldiphenylphosphine sulphide can be obtained, with the latter formed by a reversible isomerisation of the initial acetyl phosphinothioite under mild conditions by the action of trace quantities of acetyl iodide:[59]



In contrast to this, in the reaction between *S,S*-dialkyl acetyl phosphorodithioites and carboxylic acid halides the coordination of the phosphorus atom remains the same:[123,137]

$$(RS)_2POCOMe + R'C(O)X \rightarrow (RS)_2PX + R'C(O)OC(O)Me$$
R=Et, Pr; R′=Me, CCl_3, Ph; X=Cl, Br .

Dialkyl phosphoramidodithioites also react in a similar manner:[138]

$$(RS)_2PNEt_2 + R'C(O)X \rightarrow (RS)_2PX + R'C(O)NEt_2$$
R=Et, Pr; R′=Me, Ph; X=Cl, Br .

The Arbuzov reaction route, which is typical for the oxygen analogues, namely, acyl phosphites and phosphoramidites, does not occur in a single case, and the functional group is replaced by a halogen atom to give the corresponding phosphorohalodithioites.

In studies on the reactions of TTPA with acyl halides,[123,138,139] the effect of different factors, including the presence of acidic catalysts, on their rate was determined, and it was possible[140] to propose a general acid-catalysed mechanism for the reaction between TTPA and carboxylic acid halides.

$$(RS)_2P—A + HX \rightleftharpoons (RS)_2P—X + HA \xrightarrow{R'C(O)X} (RS)_2PX + R'C(O) + HX$$
A=SR, NR_2, OCOR′

Retention of the same coordination of the phosphorus atom also occurred in reactions of TTPA with polyhalomethanes. Thus, trialkyl phosphorotrithioites undergo a reaction with CCl_4 to form trichloromethylphosphonodithioite, phosphorochloridodithioite, and disulphide:[134,141]

$$2\,(RS)_3P + CCl_4 \rightarrow (RS)_2PCCl_3 + (RS)_2PCl + RSSR$$
$$R=Et,\ Pr,\ Bu\ .$$

At the same time, trichlorobromomethane under similar conditions gives phosphorotetrathioate and alkyl bromide together with trichloromethylphosphonodithioite:[134]

$$2\,(EtS)_3P + CCl_3Br \rightarrow (EtS)_2PCCl_3 + (EtS)_3PS + EtBr\ .$$

This contrast in the final reaction products is due to the different routes of side reactions.[134]

When phosphoramidothioites react with CCl_4 the alkylthio group on the trivalent phosphorus atom is also replaced and the coordination remains the same.[134,142] However, in this case the sole reaction products are the corresponding P(III) acid chlorides and trichloromethyl alkyl sulphide.

$$\begin{matrix} R' \\ Et_2N \end{matrix}\!\!>\!P\!-\!SR + CCl_4 \rightarrow \begin{matrix} R' \\ Et_2N \end{matrix}\!\!>\!P\!-\!Cl + CCl_3SR$$
$$R' = Et_2N,\ SR;\ R = Et,\ Pr\ .$$

In the case of phosphoramidothioites this reaction takes place only in the presence of Lewis acids.[142]

It was recently established that, in contrast to trialkyl phosphites, phosphorothioites[143] and phosphonothioites[144] reacted with dichloroacetylene not by the classical Arbuzov rearrangement route but they formed the previously unknown products derived by 'insertion' of dichloroacetylene into the P–S bond:

$$R'P(SR)_2 + Cl\!-\!C\equiv C\!-\!Cl \rightarrow \begin{matrix} R' \\ RS \end{matrix}\!\!>\!P\!-\!C(Cl)=C(Cl)\!-\!SR$$
$$R' = Et,\ Ph,\ SR;\ R = Et,\ Pr\ .$$

5. Addition of TTPA to multiple bonds and to olefin oxides

Addition reactions of TTPA to C=O, C=C, C=N, N=N, and other multiple bonds have until recently constituted a little-studied area of organophosphorus chemistry; this was related to the low nucleophilicity of the trivalent phosphorus atom in TTPA. The preparation of new types of TTPA and the use of a number of synthetic procedures, in particular, the introduction of a third reagent into the reaction mixture, have made it possible in recent years to extend considerably the range of addition reactions involving TTPA.

(a) Addition to a carbon–oxygen multiple bond

Reactions with aldehydes and ketones. Phosphorotrithioites react with benzaldehyde at 130 °C in a complex manner to give α-alkylthiobenzylphosphonodithioates, trialkyl phosphorotrithioates, and 1-phenyl-1,1-bis(alkylthio)methanes:[145]

$$(EtS)_3P + PhCHO \xrightarrow{180^\circ C} (EtS)_2P(O)\!-\!CHPh(SEt) + (EtS)_3PO + (EtS)_2CHPh$$
$$(EtS)_3P + PhCHO \xrightarrow{200^\circ C} (EtS)_3PS + EtSCH_2Ph$$

It was shown[145] that the course of the reaction depends on the temperature. When this is increased to 200 °C, phosphorotetrathioate and ethyl benzyl sulphide are formed.

An effective synthetic procedure that made it possible to add on P(III) acid thioesters to aldehydes and ketones under mild conditions was the introduction of a third electrophilic reagent which served as an activator into the reaction mixture. Thus, phosphonothioites and phosphorothioites in the presence of an equimolar quantity of dry HCl underwent reaction with benzaldehyde[145] and acetone[146] even at room temperature to form α-alkylthio-substituted phosphonodithioates and phosphinothioates. The latter are formed as complexes with HCl, dissociating on distillation to give the final products;

$$RP(SEt)_2 + R'R''C{=}O + HCl \rightarrow \left[\begin{matrix} R & O\cdots HCl \\ & \| \\ & P\!-\!CR'R'' \\ EtS & SEt \end{matrix}\right] \xrightarrow[-HCl]{\Delta} \begin{matrix} R & O \\ & \| \\ & P\!-\!CR'R'' \\ EtS & SEt \end{matrix}$$
$$R = EtS,\ Et$$

Complex-formation apparently inhibits these reactions in the presence of catalytic quantities of HCl by deactivating the latter, so an equimolar quantity is required.[146]

At the same time, the reaction of *S*-acetyl diphenylphosphinothioite with benzaldehyde in the presence of HCl gives bis[α-(diphenylphosphoryl)benzyl] sulphide, which is isolated from the reaction mixture as a complex with two moles of HCl. In addition to that, α-acetoxybenzyldiphenylphosphine sulphide is formed in small quantity:[147]

$$Ph_2PSCMe(O) + PhCHO + HCl \rightarrow (Ph_2P(O)CHPh)_2S\cdot 2HCl + Ph_2P(S)\!-\!CHPh(OCOMe)$$
$$(Ph_2P(O)CHPh)_2S \xleftarrow{2Et_4N}\ -2Et_4N\cdot HCl$$

This reaction route involves the initial replacement of the thioacetyl group by the action of HCl.[147]

When equimolar quantities of trimethylhalosilanes are used as activating agents in the reactions of phosphinothioites with benzaldehyde, two types of reaction take place depending on the nature of the halosilane. Benzaldehyde reacts with *S*-ethyl diphenylphosphinothioite in the presence of trimethylchlorosilane under mild conditions (–60 to –50 °C), resulting in the isolation of α-siloxybenzylphosphine sulphide as an addition product:[149]

$$Ph_2PSEt + PhCHO + Me_3SiCl \xrightarrow{200^\circ C} Ph_2P(S)\!-\!CHPh(SEt) + Ph_2PCl + (Me_3Si)_2O\ .$$

In contrast to trimethylchlorosilane, trimethyliodosilane can be used to carry out the reaction of phosphinothioites with benzaldehyde under mild conditions (–60 to –50 °C), resulting in the isolation of α-siloxybenzylphosphine sulphide as an addition product:[149]

$$\begin{matrix} Ph \\ R \end{matrix}\!\!>\!P\!-\!SEt + PhCHO + Me_3SiI \rightarrow \left[\begin{matrix} Ph & OSiMe_3 \\ & | \\ R & P\!-\!CHPh\ I^- \\ & | \\ & SEt \end{matrix}\right] \xrightarrow{-EtI} \begin{matrix} Ph & S \\ & \| \\ R & P\!-\!CHPh \\ & | \\ & OSiMe_3 \end{matrix}$$
$$R = Et,\ Ph$$

The formation of an intermediate quasiphosphonium compound has been detected by studying this reaction using ^{31}P NMR spectroscopy at different temperatures.[149] It was suggested[149] that coordination of the silicon atom with the oxygen of the carbonyl group must precede nucleophilic attack by the phosphorus atom.

By using PCl_3 as a third electrophilic reagent in the reaction of phosphorotrithioites with ketones it was possible to obtain a number of α-alkylthioalkylphosphonodichloridates:[150]

$$(RS)_3P + 3R'R''C{=}O + 2PCl_3 \rightarrow 3Cl_2P(O)CR'(SR)R''$$

R = Et, Pr; R′ = R″=Me; R′=Et, R″=Me .

The formation of the latter is evidently due to an initial exchange reaction between phosphorotrithioite and PCl_3 which is already known in the literature[12] followed by addition of the resulting alkyl phosphorodichloridothioite to the carbonyl compound. It has been established[151] that the reaction of *S*-alkyl phosphorodichloridothioites with aldehydes and ketones takes place with retention of the P–Cl bond and cleavage of the P–S bond, in contrast to other P(III) acid chlorides:

$$Cl_2PSEt + RR'C{=}O \rightarrow Cl_2P(O)CRR'(SEt)$$

R=R′=Me; R=H, R′=Ph .

Hydrogen chloride catalyses this reaction.

It should be noted that before the study of Al'fonsov and co-workers[151] there was only information in the literature about the reactions of P(III) thioacid chlorides with carbonyl compounds in the presence of proton-containing reactants. Thus, reaction of P(III) thioacid chlorides with aldehydes and ketones in the presence of an equimolar quantity of water gives *S*-alkyl esters of α-hydroxy-substituted phosphinothioates and phosphonodithioates:[102]

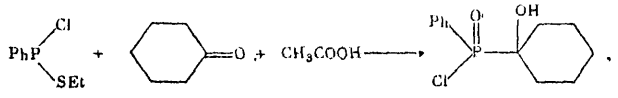
$$(RS)(R')P(O)Cl + H_2O \xrightarrow{-HCl} (RS)(R')P(O)H \xrightarrow{R'''R''C{=}O} (RS)(R')P(O)CR''R'''(OH)$$

R′ = Et, Ph, RS; R = Me, Et, Pr; R″ = H, Me

R‴ = Me, Pr, $(CH_2)_4$, $(CH_2)_5$, CCl_3, Ph, *o*-$O_2NC_6H_4$.

A detailed study of this reaction using ^{31}P NMR spectroscopy formed the basis of the proposal by Kardanov and co-workers[102] that the reaction takes place via hydrolysis of the acid chlorides followed by addition of the resulting P(III) thioacids to the carbonyl compound.

Replacement of water by acetic acid results in the formation of a product that does not contain sulphur:[102]



Recently[152] a simple and convenient method for the preparation of alkythio-substituted phosphinothioates and phosphonodithioates was developed on the basis of the reaction of P(III) thioacid chlorides with carbonyl compounds in the presence of thiols:

$$(R)(EtS)P(O)Cl + R'R''C{=}O + EtSH \rightarrow (R)(EtS)P(O)CR'(SEt)R'' + HCl$$

R = Et, EtS; R′=R″=Me; R′=H, R″—Ph .

However, compounds with an activated carbonyl group, in particular, acetyl phosphonates, do not undergo this reaction.[153] At the same time, the latter react with diethyl phosphorochloridodithioite in the presence of triethylamine to form α-(diethoxyphosphoryl)vinyl phosphorodithioites:[154]

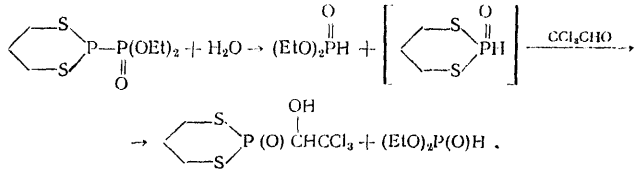
$$(EtS)_2PCl + (EtO)_2P(O)CH_3 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} (EtS)_2POC(OEt)_2{=}CH_2 .$$

Other anhydride derivatives of P(III) thioacids have only been studied in a reaction with chloral. Thus, cyclic[155] and acyclic[110] acyl phosphorodithioites react with it to form new α-acetoxy-β,β,β-trichloroethylphosphonodithioates:

$$R_2POCOCX_3 + CCl_3CHO \rightarrow R_2P(O)CH(OCOCX_3)CCl_3$$

R=EtS, X=H; R_2 = SCH_2CH_2S, X=F .

2-Diethoxyphosphoryl-1,3,2-dithiaphosphorinane does not react with chloral even on boiling, but when water is added to the reaction mixture the P–P bond is cleaved even at room temperature to form 2-oxo-2-(β,β,β-trichloro-α-hydroxyethyl)-1,3,2-dithiaphosphorinane:[156]



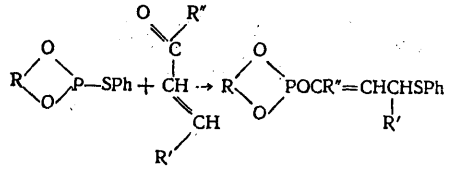
In a study of the addition of P(III) thioacid amides to carbonyl compounds it was established that the nature of the latter has no effect on the course of their reaction with phosphoranilidodithioites, in which α-anilidoaralkylphosphonodithioiates are formed:[157]

$$(EtS)_2PNHPh + n\text{-}XC_6H_4CHO \rightarrow (EtS)_2P(O)CH(NHPh)C_6H_4X\text{-}n$$

X = H, NO_2 .

There was not a single case where products with a P=N bond, namely, phosphonimidodithioates, which are characteristic for reactions of dialkyl phosphoranilidites with carbonyl compounds containing electron-withdrawing substituents, were formed.[157]

Reactions with conjugated carbonyl compounds. The reactions of TTPA with conjugated carbonyl systems, usually giving pentavalent phosphorus compounds, had by the end of the 1970's been studied in quite a detailed manner.[158] At the beginning of the 1980's, Ragulin and co-workers[159] showed that retention of the same coordination of the trivalent phosphorus atom in these reactions was possible by insertion of α,β-unsaturated aldehydes and ketones into the exocyclic P–S bond of phenyl ethylene- and 1,3-propylene-phosphorothioites:[159]

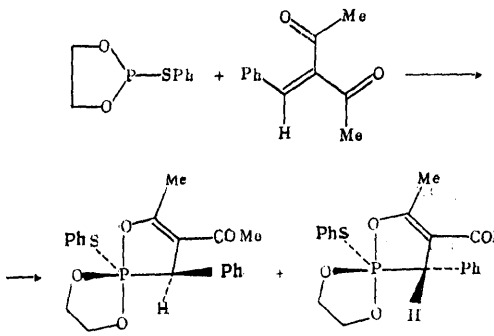


R = CH_3CH_2, $CH_3CH_2CH_2$; R′ = H, Me, Ph; R″ = H, Me .

The rate of condensation decreases when the β-carbon atom of the conjugated system is shielded.

At the same time, insertion of 3-benzylideneacetylacetone in a reaction with phenyl ethylenephosphorothioite results in the formation of a mixture of diastereomeric spirophosphoranes

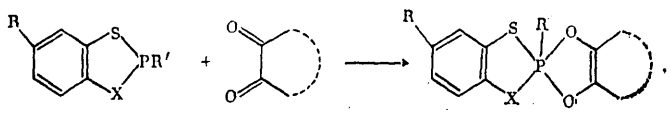
containing a P–S bond:[160]



anti – *syn* –

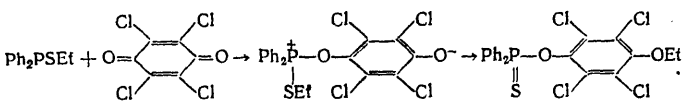
In this case the stereoisomer with the *syn*-configuration is the kinetically favourable product and the *anti*-isomer is the thermodynamically favourable reaction product. The fact that a thermodynamically nonequilibrium mixture of diastereomers is formed was taken by Ragulin and co-workers[160] as positive evidence for an almost synchronous 1,4-cycloaddition mechanism.

Spirophosphoranes containing a P–S bond are also obtained by reaction of α-dicarbonyl compounds with 1,3,2-dithia-[37] and 1,3,2-thiaza-phospholanes:[46]



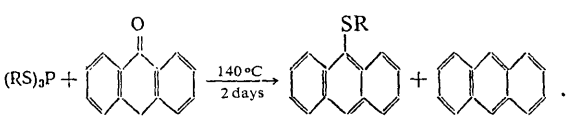
R=H, Me ; R′=Et, Ph ; X=S, NH

Ethyl diphenylphosphinothioite reacts with chloranil in benzene to form *p*-ethoxytetrachlorophenyl diphenylphosphinothioate:[161]



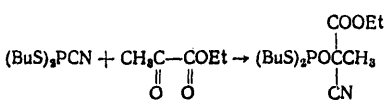
When benzene is replaced by the more polar DMSO and DMF it is possible to stop the process at the stage where a bipolar ion is formed, probably by stabilisation of the quasiphosphonium centre with solvent molecules. A study of this reaction by means of chemically induced polarisation of ^{31}P nuclei showed that there was also a radical route for formation of the final product.[161]

The reaction of trialkyl phosphorotrithioite with anthrone gives 9-alkythioanthracene and anthracene:[162]



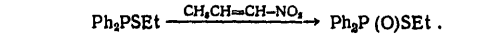
R = Et, Pr, iso-Pr, Bu, iso-Bu

P(III) thioacid cyanides react with ethyl pyruvate, retaining the same coordination of the phosphorus atom and forming α-cyanoalkyl esters of P(III) thioacids.[163]



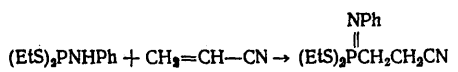
(b) Addition to other multiple bonds

Up to the present time there have been only isolated reports in the literature about the reactions of TTPA with compounds containing C=C, C=N, N=N, and other multiple bonds, which generally take place with retention of the P–S bond. When *S*-ethyl diphenylphosphinothioite reacts with 1-nitro-1-propene, instead of attack by the phosphorus atom on the β-carbon atom of the nitroolefin as occurs in the case of the oxygen analogues, only oxidation of the initial phosphinothioite occurs:[164]

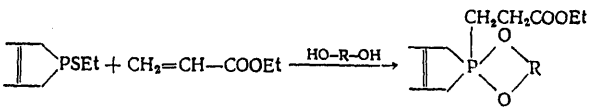


Using ^{31}P NMR spectroscopy, chemically induced polarisation of ^{31}P nuclei was detected on the initial and final products, so it could be assumed[164] that the reaction took place according to a one-electron transfer mechanism.

It was established[165] that cyclic phosphonodithioites do not react with acrylonitrile, while dialkyl phosphoranilidodithioites slowly add on to the latter with the formation of β-cyanoethylphosphonimidodithioates:[113]

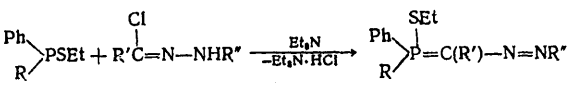


In reactions of phosphinothioites with ethyl acrylate in the presence of aliphatic and aromatic glycols the formation of cyclic phosphoranes was demonstrated:[165]



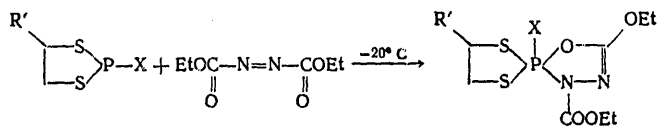
In this case there is probably an initial substitution of the alkythio group on the phosphorus atom.

The first examples of azomethylenephosphoranes containing a P–S bond were obtained in a study of the reaction of P(III) acid thioesters with nitrilimines in the presence of a base:[166,167]



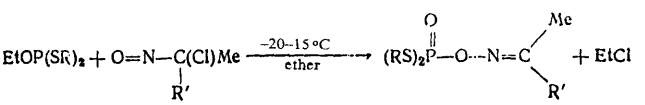
R=Ph, SEt; R′=MeC(O), PhC(O), EtOC(O)
R″ = Ph, *p*-CrC_6H_4, *p*-$O_2NC_6H_4$

A new approach to the synthesis of certain spirophosphoranes containing a dithiophospholane residue is the reaction of cyclic amides and esters of phosphorodithious acid with diethyl azodicarboxylate in chloroform:[168]



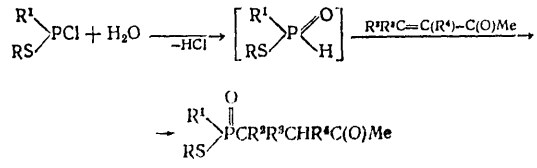
X=NMe_2, OMe; R′=H, Me

The previously unknown *O*-iminophosphonodithioates were readily formed by opening of the N=O bond in α-chloronitrosolkanes on treatment with mixed *O*,*S*-phosphorodithioites:[169]



R=Et, Pr, Bu; R′=Cl, Me

P(III) acid chlorides add on to a C=C bond in the presence of H_2O [170] in a similar manner to the reaction with carbonyl compounds:[102]

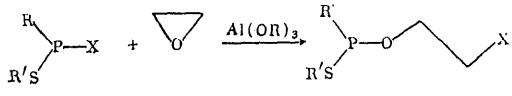


R = Et, Pr, Ph; R^1 = Et, Ph; R^2 = R^3 = R^4 = H, Me.

In the reaction of *S*-phenyl phenylphosphonochloridothioite the formation of a cyclic product—1,2-oxaphosphol-4-ene—occurs together with γ-ketophosphinothioates.[170] The proposed spontaneous cyclisation of γ-ketophosphinothioate was not confirmed experimentally.

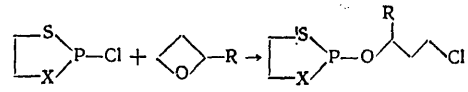
(c) Addition to olefin oxides

In the mid-1970's there were reports[171,172] in the patent literature about the development of a method for hydroxyalkylation of P(III) thioacid chlorides with olefin oxides in the presence of organoaluminium catalysts:



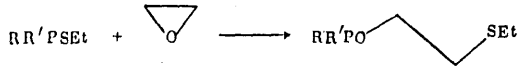
X = Cl, Br; R′ = alkyl, R′S, R′O, R'_2N.

This reaction was subsequently extended to cyclic P(III) thioacid chlorides and oxetanes and it transpired that scission of the 2-methyloxetane ring occurs on the C–O bond through the primary carbon atom in the absence of catalysts:



X = O, S, NBu-t; R = H, Me.

Only in the mid-1980's was the possibility shown for the first time that olefin oxides could be inserted into the P–S bond of phosphinothioites[174] and phosphoramidothioites:[175]



R = Et, R′ = Ph; R = R′ = Ph, NEt_2; R = EtS, R′ = Et_2N.

The reactions are catalysed by organic acids, Lewis acids, and bases.

6. Exchange reactions in a number of TTPA

Exchange reactions in a number of TTPA can be successfully used for the synthesis of various organophosphorus compounds. However, these studies were only elaborated at the end of the 1970's, as a result of which it was established that exchange can be accompanied by processes leading to a change in coordination of the P(III) atom together with retention of the same valency for phosphorus. In this case the effect of different factors (nature of the reactants, temperature, presence of catalysts) on the rate and course of these reactions was shown.

P(III) acid thioesters have been studied in the greatest detail in reactions with phosphorus trihalides,[176,177] which provided the basis for the development of synthetic methods not only for P(III) thioacid chlorides as already reported in the literature but also for the previously unknown phosphoromono-[177] and phosphorodi-bromidothioites.[178]

$$(RS)_3P + 2PX_3 \rightarrow 3RSPX_2;\ 2(RS)_3P + PX_3 \rightarrow 3(RS)_2PX$$

R = Me, Et, Bu; X = Cl, Br.

It was later shown[179] that a similar reaction of tribenzyl phosphorotrithioite with phosphorus tribromide at 180 °C is accompanied by a change in coordination of the phosphorus atom and culminates in the formation of benzylphosphonothioic dibromide, although initial exchange products have been detected by ^{31}P NMR spectroscopy:

$$(PhCH_2S)_3P + 2PBr_3 \rightarrow 3PhCH_2P(S)Br_2.$$

In contrast to the reaction with phosphorus trihalides, the reaction between phosphorotrithioites and ethylphenylchlorophosphine is a reversible process:[177]

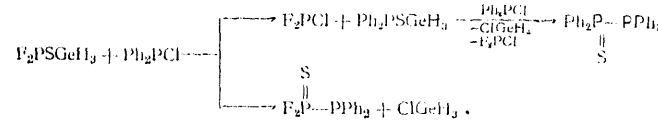
$$(RS)_3P + EtPhPCl \rightleftharpoons (RS)_2PCl + EtPhPSR$$

R = Me, Et, Pr.

At the same time, ethyl diphenylphosphinothioite reacts with diphenylchlorophosphine under severe conditions to form a complex mixture consisting of tetraphenyldiphosphine, ethyldiphenylphosphine sulphide, and diphenylchlorophosphine sulphide:[92]

$$Ph_2PSEt + Ph_2PCl \xrightarrow{250^\circ C} Ph_2P(S)PPh_2 + Ph_2PEt + Ph_2P(S)Cl.$$

The reaction of *S*-germyl phosphorodifluoridothioite with diphenylchlorophosphine is also complex; cleavage of the S–Ge bond occurs together with formation of exchange products:[76]



At the beginning of the 1960's it was shown[176] that the reaction between trimethyl and tributyl phosphorotrithioites in the presence of trace amounts of HCl gives an equilibrium mixture consisting of four phosphorothioites:

$$(RS)_3P + (R'S)_3P \rightleftharpoons (RS)_2PSR' + RSP(SR')_2$$

R = Me; R′ = Et, Bu.

It was established later[106] that the exchange of alkylthio groups in a number of phosphorotrithioites occurs only in the presence of catalytic quantities of acids and bases, the rate of exchange increasing on changing from acidic to basic catalysts.

The reaction of P(III) thioesters with trialkyl phosphites has only been studied in the case of Schrader's anhydride reacting with triethyl phosphite,[121] as a result of which a compound with a $P^{(III)}-P^{(V)}$ bond—*tris*(diethylphosphoryl)phosphine—is formed:

$$[(EtO)_2P(S)]_3P + 3(EtO)_3P \rightarrow [(EtO)_2P(O)]_3P + 3(EtO)_2PSEt.$$

There is no information in the literature about the exchange of groups between P(III) acid thioesters and triaminophosphines, but the reactions of the latter with phosphoromono- and phosphorodichloridothioites[177] and also with 1,3,2-thiazaphospholanes containing an exocyclic P–Cl bond[180] have been studied, so it was possible to

obtain P(III) acid derivatives containing both a P–S bond and a P–N bond in the molecule:

$$(EtS)_2PCl + (Et_2N)_3P \underset{-40\,^\circ C}{\overset{20\,^\circ C}{\rightleftharpoons}} (EtS)_2PNEt_2 + (Et_2N)_2PCl$$
$$(EtS)_2P{-}\overset{+}{P}(NEt_2)_3Cl^-$$

More recently, in a study[181] of the reaction between diethyl phosphorochloridodithioite with hexaethyltriaminophosphine at low temperatures using ^{31}P NMR specroscopy it was possible to identify the formation of a quasiphosphonium compound with a P–P bond, which on increasing the temperature decomposed with the subsequent formation of exchange products. A quasiphosphonium compound with a P–P bond is also formed by reaction of diethyl phosphorochloridodithioite with tripropylphosphine;[181] this compound is converted at 0 °C to tripropylethylphosphonium chloride:

$$(EtS)_2PCl + Pr_3P \underset{0\,^\circ C}{\overset{-60\,^\circ C}{\rightleftharpoons}} (EtS)_2P{-}\overset{+}{P}Pr_3\ Cl^- \longrightarrow Pr_3\overset{+}{P}SEt\ Cl^-$$

Products with a P–P bond were also obtained in the case of the reaction between diethyl phosphorochloridodithioite and silyl phosphites:[124]

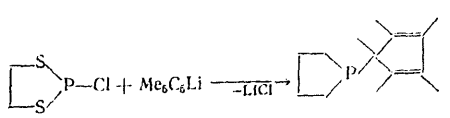
$$(EtS)_2PCl + (RO)_2POSiMe_3 \xrightarrow{-Me_3SiCl} (EtS)_2P{-}\underset{\underset{O}{\|}}{P}(OR)_2$$
R=Et, Me_3Si.

The reaction takes place under mild conditions and is accompanied by the liberation of heat.

7. Reactions of TTPA with organometallic and complex compounds

In recent years studies on the reactions of TTPA with organometallic and complex compounds have been published in the literature. This is related to the fact that a number of metal-complex compounds containing TTPA as ligands have been used as catalysts for liquid-phase hydrogenation[182] and hydroformylation.[183] Moreover, new types and classes of organophosphorus compounds, including those with an unusual structure and coordination of the phosphorus atom, have been obtained from reactions of TTPA with organometallic compounds.

Thus, in the reaction of pentamethylcyclopentadienyllithium with 2-chloro-1,3,2-dithiaphospholane, 2-(pentamethyl-2,4-cyclopentadiene-1-yl)-1,3,2-dithiaphospholane is formed, having a 'fluxional' structure as a result of a 1,5-sigmatropic rearrangement of the dithiaphospholane residue:[184]



Previously unknown compounds with a pentavalent tricoordinated phosphorus atom—*bis*(methylene)phosphoranes—were synthesised from alkyl or aryl phosphorodichloridothioites and lithium *bis*(trimethylsilyl)methanide:[185,186]

$$RS{-}PCl_2 + 3LiCCl(SiMe_3)_2 \xrightarrow[-3LiCl\ -Cl_2C(SiMe_3)_2]{-110\,^\circ C} RS{-}P\!\left(C(SiMe_3)_2\right)_2$$
R=iso-Pr, C_5H_{11}, Ph.

Cleavage of the P–S bond in TTPA on treatment with organolithium compounds was shown only in the case of the reaction between *S*-thiobenzoyl diphenylphosphinothioite and phenyllithium:[55]

$$Ph_2PSCPh + PhLi \rightarrow Ph_3P + PhCS_2^-Li^+$$
(S)

The cleavage of the P–S bond in P(III) acid thioesters by organic hydrides of Group 4b metals was studied in greater detail.[187,188] On the basis of these investigations, for the first time a general method was developed for the synthesis of a new class of organophosphorus compounds—alkyl- and phenyl-alkylthiophosphines[189] and the previously unknown acyclic thioesters of hypophosphorous acid:[190]

$$RP(SR')_2 + Bu_3SnH \rightarrow RP\!\left(\overset{SR'}{H}\right) + Bu_3SnSR'$$
R=Me, Et, iso-Bu, Ph, SR'; R'=Me, Et, Pr.

It is interesting that in the reaction of trialkylstannanes with trichloromethylphosphonodithioite the P–S bond is retained while a C–Cl bond in the trichloromethyl group is cleaved:[188]

$$CCl_3P(SEt)_2 + R_3SnH \rightarrow CHCl_2P(SEt)_2 + R_3SnCl$$
R = Et, Bu.

At the same time, it is not possible to use complex alkali metal hydrides, in particular, lithium aluminium hydride, as reducing agents in reactions with TTPA for carrying out a selective reduction, since all the P–S bonds are cleaved in phosphinothioites, phosphonothioites,[191,192] and phosphorodiamidothioites,[192] resulting in the formation of the corresponding primary or secondary phosphines and hypophosphorous acid diamides:

$$PhP(SEt)_2 \xrightarrow[\text{dibenzo-18-crown-6}]{LiAlH_4} PhPH_2$$
$$(Et_2N)_2PSR \xrightarrow[\text{ether}]{LiAlH_4} (Et_2N)_2PH.$$

It was shown for the first time[191,192] that the use of crown ethers as phase-transfer catalysts in these reactions considerably increases the rate of reduction and the yields of the final products.

During the last ten years there has been a considerable increase in interest concerning metal derivatives of TTPA, particularly in transition metal complexes. A number of mono- and di-substituted phosphinothioite and phosphonodithioite complexes of chromium,[193–196] molybdenum,[194,195,197] and tungsten[194,195] have been obtained from transition metal carbonyl complexes containing readily detachable ligands such as tetrahydrofuran (THF) or norbornadiene (NBD):

$$M(CO)_5THF + R_2PSR' \xrightarrow{-THF} M(CO)_5PR_2SR'$$
$$cis\text{-}M(CO)_4NBD + 2RP\!\left(\overset{S}{S}\!>\!R''\right) \xrightarrow{-NBD} cis\text{-}M(CO)_4\left(RP\!\left(\overset{S}{S}\!>\!R''\right)\right)_2$$
M=Cr, Mo, W; R, R'=CH_3, CF_3; R''=CH_2CH_2, *o*-C_6H_4.

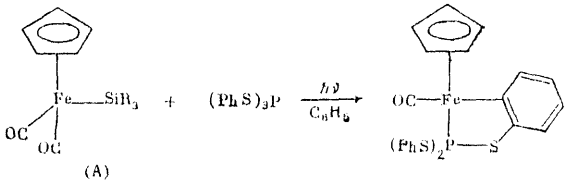
It was established that in all cases phosphorus coordinates with the metal atom, and the rate of ligand exchange depends on the nature of the substituents and the metal atom.[194,195] It should be noted that in the case of disubstituted complexes the compound with a *cis*-configuration that is formed initially can be converted to the *trans*-isomer, with the rate of isomerisation depending on the nature of the substituents, the metal atom, and the temperature.[195,196] The reaction of tetracarbonyl(norbornadiene)molybdenum with *S*-germyl phosphorodifluoridothioite takes place in a similar manner.[76]

More recently the synthesis of phosphinothioites of binuclear manganese carbonyl complexes has been carried out[198] by direct displacement of carbon monoxide from manganese carbonyls:

$$Mn_2(CO)_{10} + (CF_3)_2PSR \xrightarrow{90\text{-}130^\circ C} Mn_2(CO)_8P(CF_3)_2SR$$

R = alkyl, aryl, perfluoroalkyl, perfluoroaryl, $P(CF_3)_2$

Cyclometallated iron complexes with a triphenyl phosphorotrithioite ligand are readily formed by UV irradiation of a complex of the type (A) in the presence of triphenyl phosphorotrithioite:[199]



The replacement of ligands in platinum complexes with the involvement of *S*-germyl phosphorodifluoridothioite has been studied.[76]

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Thus, the introduction of alkythio groups on to the trivalent phosphorus atom produces a substantial change in the reactivity of P(III) acid derivatives. The Arbuzov reaction route, which is typical for oxygen analogues of TTPA, does not occur in the majority of cases and substitution at the trivalent phosphorus atom with retention of the same coordination takes place. This trend is particularly marked in the reactions of TTPA with acids and halogenated electrophilic reagents. The addition of TTPA to carbonyl compounds resulting in the cleavage of a P—S bond, as a rule, only occurs in the presence of a third reagent which assumes the role of activator for the process.

The effect of different factors, including acidic catalysts, on the rate of substitution and exchange reactions involving TTPA has been established, placing them in the same series with other trivalent phosphorus acid derivatives.

The mechanism established for the chemical behaviour of TTPA in substitution and addition reactions now make it possible not only to carry out the directed synthesis of compounds with a predetermined structure and properties but also to predict the course of TTPA reactions that have not yet been studied. Everything that has been reported above and the existence of a considerable number of convenient methods for obtaining TTPA mean that further studies of this class of compounds will have future potential.

References

1. US P. 3 360 573
2. USSR P. 293 039; *Byull. Izobret.*, 1971, (5) 111
3. Japanese Appl. 52-74 660; *Ref. Zh. Khim.*, 1978, 10T53
4. Japanese Appl. 52-109 547; *Ref. Zh. Khim.*, 1978, 23T100
5. French Appl. 2 375 243
6. USSR P. 317 286; *Byull. Izobret.*, 1981, (34) 320
7. B. Appl. 1 377 282; *Izobr. v SSSR za Rubezhom*, 1975, (19) No. 9
8. Japanese Appl. 53-20 798; *Izobr. v SSSR i za Rubezhom*, 1979, (57) No. 1
9. USSR P. 825 538; *Byull. Izobret.*, 1981, (16) 101
10. US P. 254 370; *Chem. Abs.*, 1951, **45** 57
11. C Wu *J. Am. Chem. Soc.*, 1965, **87** 2522
12. E E Nifant'ev *Khimiya Fosfororganicheskikh Soedinenii* (The Chemistry of Organophosphorus Compounds), Izd. MGU, Moscow, 1971
13. D Purdela, R Vilchanu *The Chemistry of Organophosphorus Compounds* (Translated into Russian), Izd. Khimiya, Moscow, 1972
14. B E Ivanov, V F Zheltukhin *Usp. Khim.*, 1970, **39**(5) 779 [English translation in *Russ. Chem. Rev.*, 1970(5)]
15. E A Krasil'nikova *Usp. Khim.*, 1977, **46**(9) 1638 [English translation in *Russ. Chem. Rev.*, 1977(9)]
16. V A Naumov, L V Vilkov *Molekulyarnaya Struktura Fosfororganicheskikh Soedinenii* (The Molecular Structure of Organophosphorus Compounds), Izd. Nauka, Moscow, 1986
17. C Brown, R Hudson, G Wartew *Phosphorus Sulfur*, 1978, **5** 121
18. C Brown, R Hudson, G Wartew *J. Chem. Soc., Perkin Trans. I*, 1979, 1799
19. A Haas, D Winkler *Z. Anorg. Allg. Chem.*, 1980, **468** 68
20. F A Mamedov, F N Mamedov, M A Mirzoeva *Azerb. Khim. Zh.*, 1981, (5) 33
21. W Zeiss, A Pointner, C Engelhardt, H Klehr *Z. Anorg. Allg. Chem.*, 1981, **475** 256
22. Japanese Appl. 55-39 557; *Izobr. v SSSR i za Rubezhom*, 1981, (55) No. 7
23. US P. 4 237 075; *Izobr. v SSSR i za Rubezhom*, 1981, (55) No. 14
24. French Appl. 2 383 190; *Izobr. v SSSR i za Rubezhom*, 1979, (55) No. 6
25. S Pastor, J Spivack, L Eteinhuebe *Phosphorus Sulfur*, 1985, **22** 169
26. USSR P. 757 538; *Byull. Izobret.*, 1980, (31) 93
27. J I Calquhoun, W McFarlane *J. Chem. Soc., Dalton Trans.*, 1977, 1674
28. C C Chang, R C Haltiwinger, A D Norman *Inorg. Chem.*, 1978, **17** 2056
29. BRD Appl. 2 658 368
30. B. Appl. 1 581 079
31. S Kobayashi, M Suzuki, T Saegusa *Bull. Chem. Soc. Jpn.*, 1985, **58** 2153
32. US P. 4 107 168; *Izobr. v SSSR i za Rubezhom*, 1979, (55) No. 8
33. BRD P. 2 809 492; *Chem. Abs.*, 1979, **90** 103 401
34. A R Burilov, M A Pudovik, L N Usmanova, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 2401
35. D Denney, D Denney, L Lin *Khuasyue Syuebao, Acta Chim. Sin.*, 1984, **42** 340; *Ref. Zh. Khim.*, 1984, 23Zh365
36. C H Chen, B A Donatelli, N Zumbulyadis *Synthesis*, 1978, 667
37. A Sua, R Holmes *J. Organomet. Chem.*, 1978, **156** 253
38. J-P Dutasta, J Martin, J-B Robert *J. Org. Chem.*, 1977, **42** 1662
39. D Denney, D Denney, L Lin *Phosphorus Sulfur*, 1982, **13** 1
40. L Horner, M Jordan *Phosphorus Sulfur*, 1980, **8** 235
41. E Niecke, R Rüger *Angew. Chem.*, 1982, **94** 70
42. A M Kuliev, Sh R Aliev, F N Mamedov, et al. *Zh. Obshch. Khim.*, 1977, **47** 2492
43. D Stolberg, J Gloede, K Andrä *Z. Anorg. Allg. Chem.*, 1985, **527** 180
44. P Dalla Groce, S Maiorana *Synthesis*, 1984, 980
45. M A Pudovik, Yu B Mikhailov, L K Kibardina, et al. *Zh. Obshch. Khim.*, 1985, **55** 2185

46. M A Pudovik, Yu B Mikhailov, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1108
47. M A Pudovik, Yu B Mikhailov, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 2468
48. P A Gurevich T V Komina, G Yu Klimentova, et al. *Khim.-Farm. Zh.*, 1984, **18** 833
49. P A Gurevich, A I Razumov, T V Komina, et al. *Zh. Obshch. Khim.*, 1985, **55** 1327
50. K Iurkschat, C Mügge, A Tzschach, et al. *Tetrahedron Lett.*, 1982, **23** 1345
51. E E Nifant'ev, M P Koroteev, S A Ermishkina, et al. *Zh. Obshch. Khim.*, 1978, **48** 1904
52. E E Nifant'ev, M P Koroteev, S A Lysenko, N K Kochetkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1441
53. Yu G Gololobov, M N Danchenko *Zh. Obshch. Khim.*, 1979, **49** 2623
54. M N Danchenko, Yu G Gololobov *Zh. Obshch. Khim.*, 1982, **52** 2205
55. S Kato, M Goto, R Hattori, et al. *Chem. Ber.*, 1985, **118** 1668
56. M N Danchenko, A D Sinitsa *Zh. Obshch. Khim.*, 1986, **56** 1773
57. E A V Ebsworth, M C Huntley, D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1984, 2301
58. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 932
59. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 2203
60. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 559
61. D M Malenko, A D Sinitsa *Zh. Obshch. Khim.*, 1986, **56** 1654
62. E E Nifant'ev, A P Tuseev, A I Val'dman, et al. *Zh. Obshch. Khim.*, 1978, **48** 1473
63. N I Shvetsov-Shilovskii, D P Nesterenko, A A Stepanova *Zh. Obshch. Khim.*, 1979, **49** 1896
64. M A Pudovik, I A Aleksandrova, L K Kibardina, et al. *Zh. Obshch. Khim.*, 1980, **50** 1199
65. M A Pudovik, L K Kibardina, I A Aleksandrova, et al. *Zh. Obshch. Khim.*, 1981, **51** 28
66. M A Pudovik, L K Kibardina, I A Aleksandrova, et al. *Zh. Obshch. Khim.*, 1981, **51** 530
67. H Vetter, H North *Chem. Ber.*, 1963, **96** 1308
68. USSR P. 765 303; *Byull. Izobret.*, 1980, (35) 151
69. S Kh Nurtdinov, S V Khairullina, V K Khairullin, et al. *Zh. Obshch. Khim.*, 1983, **53** 785
70. M A Vasyanina, I K Pokrovskaya, N P Safina, V K Khairullin *Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov* (The Chemistry and Technology of Heteroorganic Compounds) (Edited by P A Kirpichnikov), Izd. Kazan. Khim.-Tekhnol. Instituta, Kazan', 1983, p. 3
71. USSR P. 643 509 (1977); *Byull. Izobret.*, 1979, (3) 88
72. R Light, L Hutchins, R Paine, C Compana *Inorg. Chem.*, 1980, **19** 3597
73. K Gosling, J Miller *Inorg. Nucl. Chem. Lett.*, 1973, **9** 355
74. C Glidewell *J. Organomet. Chem.*, 1977, **142** 171
75. G Fritz, D Hanke *Z. Anorg. Allg. Chem.*, 1986, **537** 17
76. E A W Ebsworth, E K Macdonald, D W H Rankin *Monatsh. Chem.*, 1980, **111** 221
77. D Arnold, E Gromie D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1977, 1999
78. E P Lebedev, M D Mizhiritskii, V A Baburina, E N Ofitserov *Zh. Obshch. Khim.*, 1979, **49** 1730
79. J Heinicke, A Tzschach *Phosphorus Sulfur*, 1984, **20** 347
80. J Grobe, D Le Van, J Nientiedt *Z. Naturforsch., B*, 1986, **41** 149
81. V D Romanenko, A V Ruban, N N Kalibabchuk, et al. *Zh. Obshch. Khim.*, 1981, **51** 1726
82. U Dressler, E Niecke, S Pohl, et al. *Chem. Commun.*, 1986, 1086
83. R Appel, C Casser *Chem. Ber.*, 1985, **118** 3419
84. E Niecke, E Symalla *Chimia*, 1985, **39** 320
85. L Horner, M Jordan *Phosphorus Sulfur*, 1980, **8** 221
86. S Kh Nurtdinov, N M Ismagilova, T A Fakhrutdinova, T V Zykova *Zh. Obshch. Khim.*, 1983, **53** 1045
87. L Horner, M Jordan *Phosphorus Sulfur*, 1980, **8** 215
88. J Omelanczuk, M Mikolaiczyk *Tetrahedron Lett.*, 1984, **25** 2493
89. A Schmidpeter, K Karaghiosoff, C Cleve, D Schomburg *Angew. Chem.*, 1985, **97** 125
90. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2619
91. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 2698
92. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 851
93. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik, *Zh. Obshch. Khim.*, 1983, **53** 1713
94. M N Danchenko, I Yu Budileva, A D Sinitsa *Zh. Obshch. Khim.*, 1985, **55** 939
95. J Grosse, W Pieper, H Neumaier *Angew. Chem.*, 1982, **94** 560
96. F Ando, J Koketsu, Y Ishii *Bull. Chem. Soc. Jpn.*, 1978, **51** 1481
97. M N Dimukhametov, I A Nuretdinov *Zh. Obshch. Khim.*, 1984, **54** 1913
98. O G Sinyashin, Candidate's Thesis in Chemical Sciences, Kazan' University, Kazan', 1981
99. V P Kostin, O G Sinyashin A A Karelov, et al. *Zh. Obshch. Khim.*, 1985, **55** 2175
100. L V Ermanson, N N Godovikov, V S Blagoveshchenskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 423
101. E E Nifant'ev, A S Chechetkin, V E Blagoveshchenskii, A M Sokurenko *Zh. Obshch. Khim.*, 1983, **53** 2695
102. N A Kardanov, N P Provotorova, P V Petrovskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2114
103. E N Ofitserov, O G Sinyashin, N V Ivasyuk, et al. *Zh. Obshch. Khim.*, 1980, **50** 1217
104. D S Yufit, Yu T Struchkov, M A Pudovik, et al. *Dokl. Akad. Nauk SSSR*, 1980, **255** 1190
105. E Gromie, G Hunter, D W H Rankin *Angew. Chem.*, 1980, **92** 323
106. O G Sinyashin, E S Batyeva, A N Pudovik, E N Ofitserov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2133
107. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 218
108. M Movsum-zade, S R Aliev, F N Mamedov *Zh. Obshch. Khim.*, 1980, **50** 2698
109. US P. 4 140 514; *Chem. Abs.*, 1979, **91** 91 340
110. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 703
111. E N Ofitserov, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1981, **51** 738
112. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 2701

113. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 498
114. E S Batyeva, E N Ofitserov, O G Sinyashin, et al. *Zh. Obshch. Khim.*, 1980, **50** 2396
115. E N Ofitserov, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1980, **50** 222
116. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 2199
117. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1671
118. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 540
119. E N Ofitserov, O G Sinyashin, N V Ivasyuk, et al. *Zh. Obshch. Khim.*, 1981, **51** 468
120. O G Sinyashin, T N Sinyashina, E S Batyeva, et al. *Zh. Obshch. Khim.*, 1982, **52** 2438
121. L V Ermanson, V S Blagoveshchenskii, N N Godovikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1689
122. L V Ermanson, V S Blagoveshchenskii, N N Godovikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2788
123. O G Sinyashin, V P Kostin, E S Batyeva, et al. *Zh. Obshch. Khim.*, 1983, **53** 1706
124. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 704
125. E N Ofitserov, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 691
126. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 1253
127. O G Sinyashin, V P Kostin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 472
128. E E Nifant'ev, M P Koroteev, S A Lysenko *Carbohydr. Res.*, 1982, **111** 67
129. M N Danchenko, A D Sinitsa *Zh. Obshch. Khim.*, 1984, **54** 473
130. O G Sinyashin, Sh A Karimullin, D A Pudovik, et al. *Zh. Obshch. Khim.*, 1984, **54** 2458
131. A Haas, W Kortmann *Z. Anorg. Allg. Chem., 1983,* **501** 79
132. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 2463
133. B E Ivanov, S S Krokhina, T V Chichkanova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 178
134. O G Sinyashin, Sh A Karimullin, V P Kostin, et al. *Zh. Obshch. Khim.*, 1986, **56** 1700
135. E A Krasil'nikova, O L Nevzorova, V V Sentemov *Zh. Obshch. Khim.*, 1985, **55** 1283
136. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 713
137. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1673
138. O G Sinyashin, V P Kostin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 502
139. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1386
140. E S Batyeva, O G Sinyashin, V A Al'fonsov, et al. *Trudy VII Konferentsii 'Khimiya i Primenenie Fosfororganicheskikh Soedinenii'* (Proceedings of the VIIth Conference on the Chemistry and Use of Organophosphorus Compounds), Izd. Nauka, Leningrad, 1986
141. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 453
142. V F Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 1183
143. O G Sinyashin, V A Subanov, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1209
144. USSR P. 1 249 019; *Byull. Izobret.*, 1986, (29) 99
145. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 709
146. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 1634
147. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 1905
148. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 689
149. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 535
150. I S Nizamov, V A Al'fonsov, A G Trusenev, et al. *Zh. Obshch. Khim.*, 1986, **56** 216
151. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2413
152. USSR P. 1 177 305; *Byull. Izobret.*, 1985, (33) 85
153. I S Nizamov, Abstract of Candidate's Thesis in Chemical Sciences, Kazan' University, Kazan', 1985
154. V A Al'fonsov, G U Zamaletdinova, I S Nizamov, et al. *Zh. Obshch. Khim.*, 1984, **54** 1485
155. I V Konovalova, V F Mironov, E N Ofitserov, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 690
156. L V Ermanson, N N Godovikov, V S Blagoveshchenskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 427
157. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1643
158. N A Razumova, A A Petrov, Zh L Evtikhov, et al. *Trudy IV Konferentsii 'Khimiya i Primenenie Fosfororganicheskikh Soedinenii'* (Proceedings of the IVth Conference on the Chemistry and Use of Organophosphorus Compounds), Izd. Nauka, Moscow, 1972, p. 100
159. V V Ragulin, N A Razumova, V I Zakharov, A A Petrov *Zh. Obshch. Khim.*, 1980, **50** 462
160. V V Ragulin, V I Zakharov, A A Petrov, N A Razumova *Zh. Obshch. Khim.*, 1981, **51** 34
161. V A Al'fonsov, O M Dianova, E I Gol'dfarb, et al. *Zh. Obshch. Khim.*, 1982, **52** 924
162. M Tomano, T Ikeda, J Koketsu *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1984, 1158
163. A N Pudovik, G V Romanov, V N Volkova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 934
164. V A Al'fonsov, R D Gareev, E I Gol'dfarb, et al. *Zh. Obshch. Khim.*, 1982, **52** 441
165. P Beer, R Edwards, D Hall, et al. *Phosphorus Sulfur*, 1983, **17** 283
166. V I Namestnikov, L A Tamm, V N Chistokletov *Zh. Obshch. Khim.*, 1985, **55** 695
167. V I Namestnikov, L A Tamm, V N Chistokletov *Zh. Obshch. Khim.*, 1985, **55** 710
168. J-P Majoral, R Kraemer, T N'Gando M'Pondo, J Navech *Tetrahedron Lett.*, 1980, **21** 1307
169. I V Martynov, L A Chepakova, V K Brel', V B Sokolov *Zh. Obshch. Khim.*, 1986, **56** 2420
170. F S Mukhametov, R M Eliseenkova, N I Rizpolozhenskii *Zh. Obshch. Khim.*, 1980, **50** 222
171. BRD Appl. 2 407 006
172. B. Appl. 1 458 851
173. L Z Nikonova, O I Nuretdinova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 918

174. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 726
175. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985 **55** 1860
176. K Moedritzer, G Burch, J Van Wazer, H Hofmeister *Inorg. Chem.*, 1963, 1152
177. O G Sinyashin, E N Ofitserov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1981, **51** 2410
178. V A Naumov, O N Kataeva, O G Sinyashin *Zh. Strukt. Khim.*, 1984, **25**(3) 79
179. P S Khokhlov, L S Berseneva, N S Savenkov *Zh. Obshch. Khim.*, 1984, **54** 972
180. M A Pudovik, Yu B Mikhailov, T A Malykh, et al. *Zh. Obshch. Khim.*, 1980, **50** 1677
181. V A Al'fonsov, G U Zamaletdinova, K M Enikeev, et al. *Zh. Obshch. Khim.*, 1986, **56** 1697
182. US P. 3 110 747; *Chem. Abs.*, 1964, **60** 7504
183. US P. 3 351 666; *Chem. Abs.*, 1968, **68** 42 004
184. P Jutzi, H Saleske *Chem. Ber.*, 1984, **117** 222
185. R Appel, K Dunker, E Gaitzsch, T Gaitzsch *Z. Chem.*, 1984, **24** 384
186. R Appel, E Gaitzsch, K Dunker, F Knoch *Chem. Ber.*, 1986, **119** 535
187. P Dehnert, J Grobe, D Le Van *Z. Naturforsch., B*, 1981, **36** 48
188. O G Sinyashin, I Yu Gorshunov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 2198
189. USSR P. 1 122 668; *Byull. Izobret.*, 1984, (41) 88
190. USSR P. 1 114 680; *Byull. Izobret.*, 1984, (35) 60
191. O G Sinyashin, I Yu Gorshunov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 1917
192. O G Sinyashin, I Yu Gorshunov, N V Ivasyuk, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1394
193. J Grobe, D Le Van *Z. Naturforsch., B*, 1979, **34** 1653
194. J Grobe, D Le Van *Z. Anorg. Allg. Chem.*, 1984, **518** 36
195. J Grobe, M Köhne-Wächter, D Le Van *Z. Anorg. Allg. Chem.*, 1984, **519** 67
196. J Grobe, D Le Van, J Szameitat *J. Organomet. Chem.*, 1985, **289** 341
197. J Grobe, D Le Van *Z. Naturforsch., B*, 1980, **35** 694
198. J Grobe, J Vatter, D Rehder *Z. Naturforsch.*, 1985, **40** 975
199. G Cervean, G Chanviere, E Colomer, R Corrin *J. Organomet. Chem.*, 1981, **210** 343