Translated from *Uspekhi Khimii*, 54, 2044-2075 (1985) U.D.C. 547.26'118

Isothiocyanates of Phosphorus Acids, *N*-Phosphorylated Thionocarbamates and Thioureas

R.M.Kamalov, M.G.Zimin, and A.N.Pudovik

Current data on the synthesis, structures, the activities, and practical applications of the isothiocyanates of tri-coordinate, tetracoordinate, pentacoordinate, and hexacoordinate phosphorus acids and *N*-phosphorylated and *N*-thiophosphorylated thiocarbamates, dithiocarbamates, and thioureas are examined and surveyed.
The bibliography includes 223 references.

CONTENTS

I. Introduction 1210
II. Isothiocyanates of phosphorus acids 1210
III. *N*-Phosphorylated thiocarbamates and dithiocarbamates 1218
IV. *N*-Phosphorylated thioureas 1219

I. INTRODUCTION

Compounds in which the isothiocyanato-group is linked directly to the phosphorus atom have been attracting increasing attention by investigators, because, owing to their high reactivity, they serve as valuable starting materials and intermediates for the synthesis of a wide variety of organophosphorus compounds which are of both theoretical and practical importance.

Approximately 15 years have elapsed since the publication of the first reviews[1,2] devoted to the methods of synthesis, physicochemical properties, and applications of the isothiocyanates of phosphorus acids. During this period, the chemistry of phosphorylated isothiocyanates has developed further. It has now become necessary to survey and as far as possible arrange systematically the extensive and interesting data which have been published in recent years on this topic in the world chemical literature. Extremely unstable phosphorylated thiocyanates with the structure P–S–C≡N were synthesised and investigated for the first time during the last decade.[3-6] These compounds are intermediates in many methods of synthesis of isothiocyanates of phosphorus acids and for this reason we thought it desirable to consider them also in the present review.

According to patent data, the isothiocyanates of phosphorus acids have found applications as pesticidal[7,8] and bactericidal[9-12] preparations, as antitear and antiwear additives to lubricating oils,[13] as additives to natural and synthetic materials imparting fire resistance,[7,9,14,15] as stabilisers of polyoxymethylene,[16] as components of a cadmium-plating electrolyte which increase the corrosion resistance of the coating,[17] and as starting materials for the preparation of cation-exchange membranes.[18] In addition polymeric materials with fire-resistant properties whose molecules contain the P–N=C=S group have been synthesised.[19,20]

Among the products obtained from phosphorus-containing isothiocyanates, *N*-phosphorylated and *N*-thiophosphorylated thiocarbamates, dithiocarbamates, and thioureas occupy a special place in view of the wide variety of their practical applications. The methods of synthesis of *N*-(thio)phosphorylated thio- and dithio-carbamates, based on the reactions involving the addition of alcohols, alkoxides, mercapto-compounds, and certain acids to phosphorylated isothiocyanates, are therefore described in a special section of this review. The synthesis and properties of phosphorylated thioureas are examined in the concluding section of our review, which includes only data published after the review articles on phosphorus-containing thioureas.[1,21] In Sections III and IV we thought it essential to discuss not only the addition of various proton-donating reagents to the isothiocyanato-group but also other reactions leading to *N*-phosphorylated thio- and dithiocarbamates and thioureas. Heterocyclic derivatives in which the thiocarbamoyl group is incorporated in a ring are an exception; the chemistry of these compounds has been fairly completely described in another review[22] and is not considered in the present article.

II. ISOTHIOCYANATES OF PHOSPHORUS ACIDS

1. Methods of Synthesis

Various derivatives of tricoordinate, tetracoordinate, pentacoordinate, and hexacoordinate phosphorus containing the isothiocyanato-group linked directly to the phosphorus atom have now been obtained. Previous reviews[1,2] described the methods of their synthesis by the reactions of phosphorus acid halides with salts of thiocyanic acid or trimethylsilyl isothiocyanate, of partial esters of phosphorus(III) acids with thiocyanogen, of salts of dialkylphosphorodithioic acids with bromocyanogen, and of pyrophosphates and metaphosphonodithioates with potassium thiocyanate.

The first of the methods listed above continues to be the most convenient and most widely used because of the ready availability of the starting compounds.[3,4,7,23-40]

The interaction of phosphonochloridothioites with lead thiocyanate in ether leads to the formation of *S*-alkyl alkyl(aryl)phosphonoisothiocyanatidothioites (I):[23]

$$2R^1(R^2S)PCl + Pb(SCN)_2 \rightarrow 2R^1(R^2S)PNCS + PbCl_2. \quad (I)$$

The reactions of pentavalent phosphorus acids halides with potassium thiocyanate (or silver thiocyanate) yielded the corresponding isothiocyanates and dithiocyanates (II):[7,24-27]

$$R_nP(X)Hal_{(3-n)} + (3-n)\,KSCN \rightarrow R_nP(X)(NCS)_{3-n} + (3-n)\,KHal;$$
$$X = O, S;\ Hal = Cl, Br;\ n = 1, 2 \quad (II).$$

The reactions are usually carried out in acetone or acetonitrile between 5° and 100 °C.

Investigators have devoted much attention to the synthesis of isothiocyanates containing the phosphazene and other inorganic rings. Isothiocyanato-derivatives of phosphazenes (III) can be obtained by treating chlorophosphazenes with alkali metal or ammonium thiocyanates in organic solvents:[28]

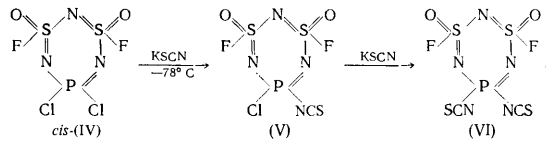
$$(NPCl_2)_n + 2n\text{KSCN} \rightarrow [NP(NCS)_2]_n + 2n\text{KCl};$$
$$n = 3, 4. \qquad \text{(III)}$$

The synthesis of fluoroisothiocyanatophosphazenes by the reaction of the corresponding monochloro- or monobromoperfluorophosphazenes with potassium or silver thiocyanate has been described.[29,30] Tetrachlorodiisothiocyanatocyclotriphosphazene has been synthesised by the reaction of $(NPCl_2)_3$ with potassium or ammonium thiocyanates.[31,32] Hexachlorodiisothiocyanato- and tetrachlorotetraisothiocyanatocyclotetraphosphazenes have been obtained analogously.[33]

It has been shown[34] that, on refluxing with KSCN in acetonitrile, 1,3,5-trichloro-1,3,5-triphenoxycyclotriphosphazene gives rise to a 96% yield of the corresponding triisothiocyanato-derivative. However, the reaction under the same conditions involving 1,3,5-tributoxy-1,3,5-trichlorocyclotriphosphazene yielded butyl thiocyanate and an oligometric product whose molecules were made up of phosphazene rings joined by P–O–P linkages and containing exocyclic butoxy- and thiocyanato-groups.

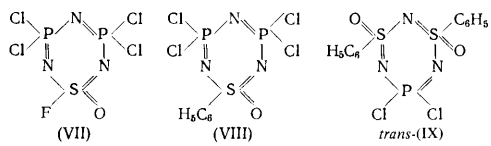
After treating compound (IV), having the *cis*-configuration, with potassium thiocyanate, the monoisothiocyanato-compounds (V) and the diisothiocyanato-compounds (VI) were isolated:[35]

Scheme 1



cis-(IV) (V) (VI)

Monoisothiocyanato-derivatives in the form of two (*cis*- and *trans*-) isomers have been obtained in proportions of 1:1 from compounds (VII) and (VIII) and compound (IX) having the *trans*-configuration:[36]



(VII) (VIII) *trans*-(IX)

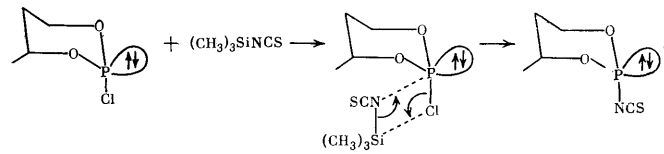
Two and four isothiocyanato-groups can be introduced into compounds (VII)–(IX) under appropriate conditions.[36]

The interaction of trimethylsilyl isothiocyanate with the chlorides of tricoordinate and tetracoordinate phosphorus acids may entail the complete exchange of halogen atoms for isothiocyanato-groups:[41,42]

$$R_{3-n}P(X)Cl_n + n\,(CH_3)_3SiNCS \rightarrow R_{3-n}P(X)(NCS)_n + n\,(CH_3)_3SiCl;$$
$$n = 1, 2, 3;\ X = \text{unshared electron pair of O and S.}$$

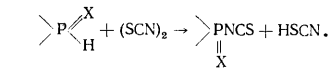
It has been demonstrated by ^1H NMR for the chloride of 1,3-butylenephosphorous acid that the reactions proceed stereospecifically with retention of the configuration at the phosphorus atom.[41] It can be shown that the reaction involves a cyclic electron transfer (Scheme 2), although one cannot rule out the possibility that the substitution takes place with the inversion and subsequent epimerisation of the reaction product at a high temperature:

Scheme 2



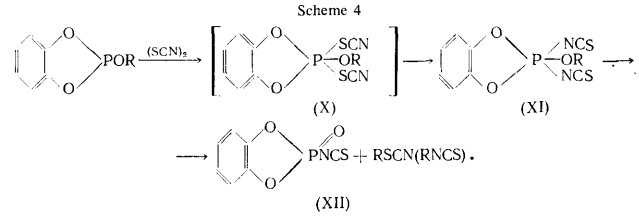
Various, including optically active, isothiocyanates of tetracoordinate phosphorus acids have been obtained in accordance with Scheme 3:[4,6,37]

Scheme 3



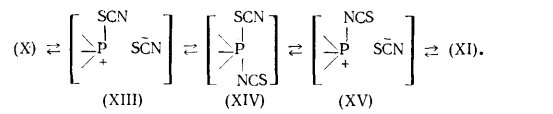
o-Phenylene phosphoroisothiocyanatidate (XII) is formed when alkyl *o*-phenylene phosphites are acted upon by thiocyanogen.[43] The diisothiocyanatophosphoranes (XI), which are stable at −40 °C and, for R = C_6H_5, also at room temperature, arise in the first stage of this reaction (Scheme 4). An increase of temperature leads to the decomposition of compounds (XI) into the phosphoroisothiocyanatidate (XII) and an alkyl thiocyanate or an alkyl isothiocyanate depending on the structure of the substituent R. When R was a primary alkyl group, an alkyl thiocyanate was formed but, when R was a secondary alkyl group, a mixture of thio- and isothio-cyanates was isolated:[44]

Scheme 4



(XII)

It has been suggested[43] that the reaction begins with the concerted addition of $(SCN)_2$ to the phosphorus atom with formation of the intermediate (X), whose conversion into the isomer (XI) is believed[43] to proceed via the equilibrium between the phosphonium structures (XIII) and (XV) and the phosphorane structure (XIV):



(XIII) (XIV) (XV)

The interaction of triphenylphosphine with thiocyanogen at −40 °C in CH_2Cl_2 leads to the phosphonium salt (XVI):[44,45]

$$(C_6H_5)_3P + (SCN)_2 \rightarrow (C_6H_5)_3\overset{+}{P}NCS\ \overline{SCN}.$$
$$\text{(XVI)}$$

When organophosphorus acids are added to the salt (XVI), phosphorylated isothiocyanates are formed in a high yield.[44] Phosphoranes and phosphonium salts of type (XI) and (XVI), containing isothiocyanato-groups, can also be obtained in a quantitative yield by the stepwise substitution of the chlorine atoms in the corresponding dichlorophosphoranes on treatment with trimethylsilyl isothiocyanates[46] or metal thiocyanates in the presence of a crown-ether.[44,46]

Phosphorus acid isothiocyanates are formed in the reactions of phosphorodithioic acids with cyanamides[47,48] and of phosphorothioic and phosphorodithioic acids with organic cyanates and thiocyanates[49–51] and also in the three-component reaction of diphenylphosphinous acid, ammonium

thiocyanate, and HCl.[52] None of these reactions are of preparative value for the synthesis of phosphorylated isothiocyanates because of the low yields and the difficulty of isolating pure products from the reaction mixture. However, a convenient method has been proposed for the synthesis of phosphoroisothiocyanatidothioates (XVII) [51,53] by the reaction of phosphorodithioic acids with an excess of alkyl thiocyanates at 80–100 °C:

$$R^1SCN + (R^2O)_2PSSH \xrightarrow{80-100^\circ C} \underset{(XVII)}{(R^2O)_2P(S)NCS} + R^1SH.$$

The reactions of bisphosphinyl disulphides (XVIII) with cyanide anion proceed via a stage involving the formation of the phosphinothioate anion (XIX) and the phosphinic thiocyanate (XX) which rearranges to the phosphinic isothiocyanate (XXI) (Scheme 5).[54] The final reaction products are the pyrophosphinomonothiomic anhydrides (XXII). When bulky substituents (for example, t-C_4H_9 or C_6H_5) are introduced at the phosphorus atom, the reactions stop at the stage involving the formation of the isothiocyanates (XXI):

Scheme 5

$$\underset{(XVIII)}{\left[R^1R^2P(O)S\right]_2} + CN^- \longrightarrow R^1R^2P(O)\!-\!S\!-\!S\!-\!P(O)R^1R^2 \longrightarrow$$
$$\longrightarrow \underset{(XIX)}{R^1R^2P(S)O^-} + \underset{(XX)}{\left[R^1R^2P(O)SCN\right]} \longrightarrow$$
$$\longrightarrow \underset{(XXI)}{R^1R^2P(O)NCS} + (XIX) \longrightarrow \underset{(XXII)}{R^1R^2P(O)OP(S)R^1R^2} + \bar{S}CN.$$

It has been shown by ^1H NMR that the fluoride of methylphosphonoisothiocyanatidic acid disproportionates with formation of the difluoride and the diisothiocyanate of methylphosphonic acid on heating (at 80 °C) for 10 weeks.[27]

In many cases phosphorylated isothiocyanates are synthesised by reactions of compounds already containing the P–NCS groups, which are accompanied by an increase of the coordination number of the phosphorus atom. Thus dialkyl phosphoroisothiocyanatidites enter into the Arbuzov reaction with alkylsulphenyl chlorides and are converted into *SO*-dialkyl phosphoroisothiocyanatidothioates (XXIV):[55]

$$\underset{(XXIII)}{(R^1O)_2PNCS} + R^2SCl \rightarrow \underset{(XXIV)}{(R^1O)(R^2S)P(O)NCS} + R^1Cl.$$

Vinyl phosphoroisothiocyanatidates and phosphorodiisothiocyanatidates can be obtained by means of the Perkow reactions from phosphoromono- and phosphorodiisothiocyanitidites, trichloroacetylphosphonate [40] and halogenopyruvate[56,57] esters, and hexachloroacetone.[57] Isothiocyanatospirophosphoranes have been synthesised by the reaction of the isothiocyanates of cyclic phosphorous acids with tetrachlorobenzoquinone [39] and dienes.[58]

A tetraisothiocyanato-derivative of hexacoordinate phosphorus (XXVI) has been synthesised from diaryloxytriisothiocyanatophosphorane (XXV) and tetraalkylammonium thiocyanate:[59]

$$\underset{(XXV)}{(C_6H_5O)_2P(NCS)_3} + Alk_4\overset{+}{N}\,N\bar{C}S \rightarrow \underset{(XXVI)}{(C_6H_5O)_2\bar{P}(NCS)_4Alk_4\overset{+}{N}}.$$

2. Phosphorothiocyanatidates and Their Rearrangement to Phosphoroisothiocyanatidates

In many of the reactions considered above one might have expected the initial formation of phosphorothiocyanatidates, which can rearrange to phosphoroisothiocyanatidates.

The first examples of phosphoroisothiocyanatidates were obtained as early as the beginning of this century, but were erroneously assumed to be the thiocyanato-derivatives.[1] The error was not corrected until the middle 1950's and in subsequent years it was established that phosphorothiocyanatidates are extremely unstable and exhibit a pronounced tendency towards isomerising to the isothiocyanatidates. The first reliable report of the synthesis of a phosphorothiocyanatidate, namely dineopentyl phosphorothiocyanatidate (XXVII), was published in 1972.[3] Compound (XXVII) was obtained by treating dineopentyl phosphorylsulphenyl chloride (XXVIII) with silver cyanide[3] or (better) with trimethylsilyl cyanide[60] in methylene chloride in the absence of atmospheric moisture and oxygen at −5 °C. At room temperature the rapid and irreversible rearrangement of the thiocyanato-derivative (XXVII) to the corresponding isothiocyanato-derivative (XXIX) is observed, the latter having being also synthesised by an independent procedure:

$$\underset{(XXVIII)}{[(CH_3)_3CCH_2O]_2P(O)SCl} + AgCN \rightarrow \underset{(XXVII)}{[(CH_3)_3CCH_2O]_2P(O)SCN}$$
$$\underset{(XXVIII)}{[(CH_3)_3CCH_2O]_2P(O)Cl} + KSCN \rightarrow \underset{(XXIX)}{[(CH_3)_3CCH_2O]_2P(O)NCS}.$$

Phosphorothiocyanatidothioates, which proved to be more stable than their oxygen analogues, have been synthesised by the same method.[4] Later new examples of the synthesis of similar compounds were published.[4–6,37,54,60–63] Stereochemical study of the rearrangement of phosphorothiocyanatidates to phosphoroisothiocyanatidates using diastereoisomeric cyclic[4,37] and optically active acyclic[5] model systems showed that it proceeds with total inversion of the configuration at the phosphorus atom. It has been noted that the isomerisation is accelerated in the presence of nucleophiles,[4,5] which was confirmed by the fact that carefully purified phosphorothiocyanatidates are stable in the absence of access by atmospheric oxygen. Their stability also increases in the presence of BF_3, which functions as a "nucleophile trapping agent".[4]

The authors suggest that the mechanism involving nucleophilic substitution at the phosphoryl centre is the most likely for the rearrangement.[4,5] Under the influence of atmospheric moisture or some other nucleophiles present in the reaction mixture at low concentrations, the thiocyanate anion is generated from the phosphorothiocyanatidates (XXX) via Scheme 6 at the beginning of the reaction. As a result of the nucleophilic attack by the nitrogen atom (a hard base) on the phosphorus atom of the thiocyanate anion (a hard acid centre) of the phosphorothiocyanatidate (XXX), the phosphoroisothiocyanatidate (XXXI) is then formed:

Scheme 6

$$Nu^- + \underset{(XXX)}{>P(X)SCN} \longrightarrow >P(X)Nu + S\bar{C}N;$$

$$S\bar{C}N + \underset{(XXX)}{X\!>\!P\!-\!SCN} \longrightarrow \underset{(XXXII)}{\left[SCN\!-\!\overset{X^-}{P}\!-\!SCN\right]^{\neq}} \longrightarrow$$

$$\longrightarrow \underset{(XXXI)}{SCN\!-\!P\!<^{X}} + S\bar{C}N.$$

An addition–elimination mechanism with formation of a short-lived phosphorane intermediate having a trigonal-bipyramidal structure with the SCN groups in the apical positions cannot be ruled out, according to the authors,[5] for the substitution reaction considered. However, they give preference to the concerted mechanism with the transition state (XXXII) [reaction of the $S_N2(P)$ type] having the same geometry (Scheme 6).

Special investigations have shown[4,6] that many reactions leading to phosphoroisothiocyanatidates involve the formation of the corresponding thiocyanatidates as intermediates. The reactions of phosphorus acid halides with potassium thiocyanate have attracted particular attention in this connection. The available facts indicate that phosphorothiocyanatidates are not formed as intermediates in these reactions.

3. The Properties of Phosphoroisothiocyanatidates

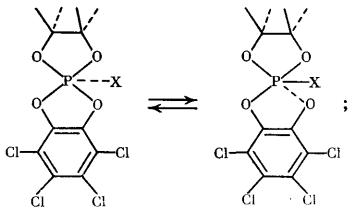
(a) Studies on Phosphoroisothiocyanatidates by Physicochemical Methods

Some data on the IR, NMR, and UV spectra of phosphorylatedisothiocyanates have been published in earlier reviews.[1,2]

In the IR spectra the ν_{as} absorption bands of the isothiocyanato-group linked to the phosphorus atom are in the range 1990–2000 cm^{-1};[29,64] in the range 730–910 cm^{-1}, intense ν(P–N) bands are present.[64] The ν(P=O) bands are located in the range 1220–1280 cm^{-1} [64] and the ν(P=S) frequencies are also close to the usual values.

It has been noted[35,36] that the introduction of the NCS group into the cyclic compounds (IV), (VII), (VIII), and (IX) induces an appreciable (up to 30 p.p.m. per NCS group) downfield shift of the signals due to the phosphorus nuclei in the ^{31}P NMR spectra.

By recording the NMR spectra over a range of temperatures, Trippett et al.[39] determined the free energy of activation ΔG^* for the pseudorotation (XXXIIIa) ⇌ (XXXb) of the isothiocyanato-group, which proved to be 17.8 kcal mol^{-1}.



(XXXIIIa) X = NCS, NCO, Cl (XXXIIIb).

The quantity ΔG^* for the isocyanato-group is 17.5 kcal mol^{-1}. In terms of their apicophilic properties, both these groups (NCO and NCS) are close to the chlorine atom, for which ΔG^* is 17.8 kcal mol^{-1}.

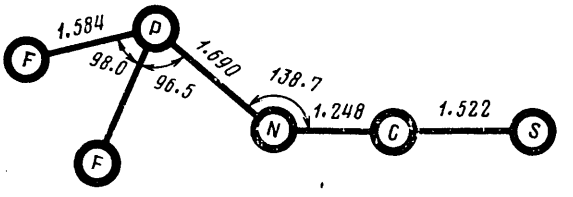
The mass spectra of diethyl phosphoroisothiocyanatidate,[65] hexaisothiocyanatocyclotriphosphazene, and octaisothiocyanatocyclotetraphosphazene [66] have been investigated. The characteristic processes involving the decomposition of diethyl phosphoroisocyanatidate [65] involve the initial rupture of the P–N bond or the decomposition of ethoxy-groups, accompanied by the loss of the CH_3, C_2H_3, and C_2H_4 fragments. The mass spectra of cyclic isothiocyanates [66] indicate a greater stability of the phosphazene ring. The fragmentation of the NCS group takes place either with the elimination of the sulphur atom or with the loss of a S_2 molecule, or with the elimination of a CS_2 molecule. Data for the mass spectra of phosphoroisothiocyanatidates can also be found in other communications.[32,35,36,67]

The crystal and molecular structures of the isothiocyanates of trimeric [68] and tetrameric [69] cyclophosphazenes have been investigated by X-ray diffraction. The results have lead to the conclusion that the P–N linkage in the fragment



has a certain amount of double bond character.

A wider range of physicochemical methods have been used by investigators in the study of the molecular structure of difluoroisothiocyanatophosphine F_2PNCS (XXXIV).[70–73] The IR and Raman spectra in the gas phase, in the intermediate and far regions, have been obtained and discussed.[70,71] It has been demonstrated by photoelectron spectroscopy[72] that the lowest ionisation potentials in the molecule of compound (XXXIV) are those of the electrons of one of the π-bonds of the NCS group (10.2 eV) and the unshared electron pair of the phosphorus atom (11.9 eV). The parameters of the bond lengths and angles have been determined by electron diffraction[70] and have been refined[73] by employing a combination of electron diffaction and ^1H NMR methods in a liquid crystal solvent (see Figure). It has been shown[70] that the isothiocyanato-group is in the *trans*-position with respect to the FPF bisector.



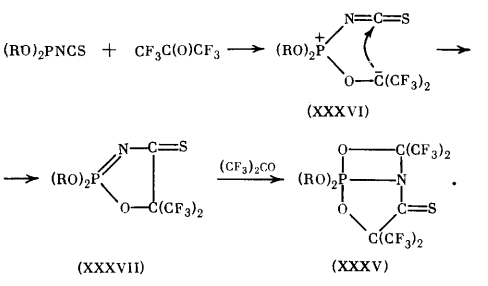
The bond lengths (Å) and valence angles (degrees) in the molecule of difluoroisothiocyanatophosphine (XXXIV).[173]

(b) Reactions of the Isothiocyanates of Phosphorus(III) Acids

Reactions involving an increase of the coordination number of the phosphorus atom and cycloaddition reactions with participation of the PN=C=S fragment, which plays the role of a 1,3-dipolar reagent, are most characteristic of phosphorus-(III) acid isothiocyanates.

The first example of the cycloaddition reaction has been described by Trippett and co-workers,[74] who investigated the interaction of hexafluoroacetone with dialkyl phosphoroisothiocyanatidites. A crystalline 1 : 2 adduct, the bicyclic phosphorane (XXXV), was obtained as a result:

Scheme 7



(XXXVI) (XXXVII) (XXXV)

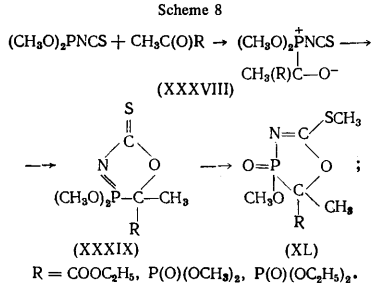
The betaine (XXXVI) (Scheme 7) is formed in the first stage and then cyclises to the imide (XXXVII), which is subjected to electrophilic attack by a second hexafluoroacetone molecule with the consequent formation of the bicyclic phosphorane

(XXXV). The strain in the trigonal bipyramid of the phosphorane becomes minimal, according to the authors,[74] when both rings occupy axial-equatorial positions and the nitrogen atom is then located in the equatorial position.

In subsequent studies a wide variety of carbonyl, imino-, and other unsaturated compounds were made to undergo the cycloaddition reaction with phosphorus(III) isothiocyanates.[40,75-78]

The interaction of dimethyl phosphoroisothiocyanatidite with acetyl phosphonates[75] and pyruvate esters[40] begins with nucleophilic attack by the phosphorus atom on the carbon atom of the carbonyl group. The dipolar ion (XXXVIII) cyclises to the intermediate (XXXIX) with a phosphimide linkage (Scheme 8). The subsequent imide–imide rearrangement with *S*-alkylation leads to substituted 3-methoxy-2-methyl-5-methylthio-3-oxo-1,4,3-oxaza-4-phospholens (XL):

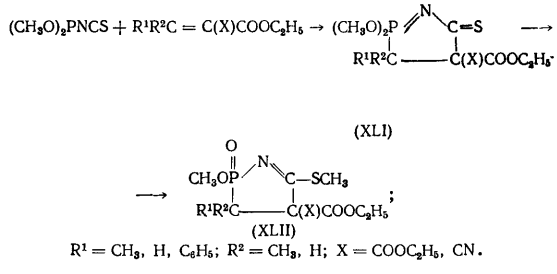
Scheme 8



(XXXVIII) (XXXIX) (XL)

R = $COOC_2H_5$, $P(O)(OCH_3)_2$, $P(O)(OC_2H_5)_2$.

In the reactions of dimethyl phosphoroisothiocyanatidite with esters of methylene- and ethylidene-malonic acids[76] and alkylidene derivatives of cyanoacetic ester,[77] the intermediates (XLI) with a P=N bond are also stabilised by the imide–imide rearrangement, being converted into *S*-alkylated products (XLII), which are formed as a mixture of the geometrical isomers:

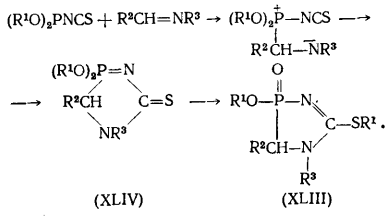


(XLI) (XLII)

R^1 = CH_3, H, C_6H_5; R^2 = CH_3, H; X = $COOC_2H_5$, CN.

It has been noted that the alkylidene derivatives of cyanoacetic ester are more reactive than the alkylidene derivatives of malonic ester as a consequence of the higher degree of polarisation of the double bond by the cyano-group.

The interaction of dialkyl phosphoroisothiocyanatidites with *N*-methylbenzylideneamine and *N*-phenyl and *N*-methyltrichloroethylideneamines results in the formation of 1,2-substituted 3-alkoxy-5-alkylthio-3-oxo-1,4,3-diaza-4-phospholens (XLIII):[78]

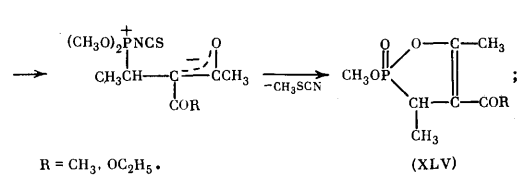


(XLIV) (XLIII)

When dimethyl phosphoroisothiocyanatidite was made to react with *N*-methyltrichloroethylideneamine, the authors isolated the products of the hydrolysis of the intermediate (XLIV) with a P=N bond—3-methoxy-1-methyl-3-oxo-2-trichloromethyl-1,4,3-diazaphospholan-5-thione.

In certain reactions of phosphoroisothiocyanatidites with unsaturated compounds the cycloaddition products involving the isothiocyanato-group are not formed and the pseudohalogen properties characteristic of this group are manifested. Thus the reactions of dimethyl phosphoroisothiocyanatidite with ethylideneacetylacetone and ethylideneacetoacetic ester lead to the formation of 4-substituted 2-methoxy-3,5-dimethyl-2-oxo-1,2-oxa-4-phospholens (XLV) and methyl thiocyanate (Scheme 9):[76]

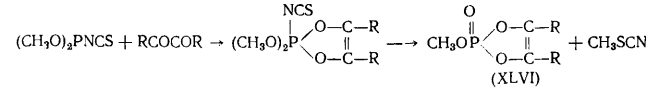
Scheme 9



R = CH_3, OC_2H_5. (XLV)

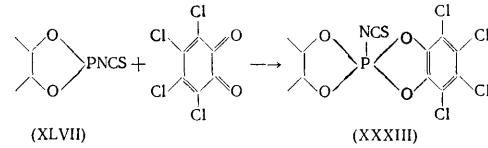
The reaction proceeds via a 1,4-cycloaddition mechanism with subsequent dealkylation in conformity with the second stage of the Arbuzov rearrangement.

The interactions of dimethyl phosphoroisothiocyanatidite with diacetyl and benzil lead similarly to the formation of 4,5-dimethyl- and 4,5-diphenyl-derivatives of 2-methoxy-2-oxo-1,3,2-dioxa-4-phospholens (XLVI):[79]



(XLVI)

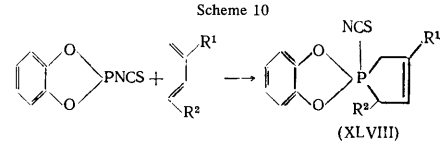
The reactions of α-dicarbonyl compounds with the isothiocyanates of cyclic phosphorous acids stop at the stage involving the formation of isothiocyanatospirophosphoranes, which is illustrated by the formation of compound (XXXIII) by the reaction of isothiocyanates of the 1,3,2-dioxaphospholan series (XLVII) with tetrachloro-*o*-benzoquinone:[39]



(XLVII) (XXXIII)

An analogous reaction in accordance with Scheme 10, which results in the formation of isothiocyanatophosphoranes (XLVII), takes place when *o*-phenylene phosphoroisothiocyanatidite reacts with 1,3-dienes, such as divinyl, isoprene, piperylene, and chloroprene:[58]

Scheme 10

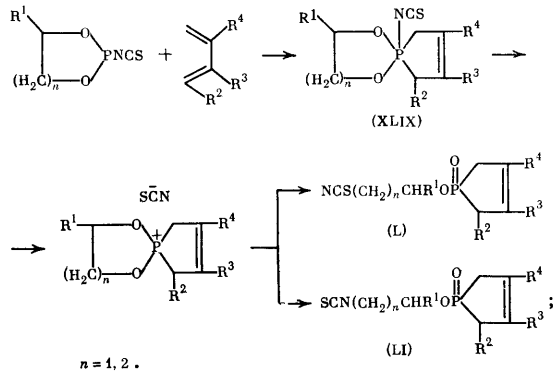


(XLVIII)

The reactivity of the dienes in condensation with phosphoroisothiocyanatidites decreases in the sequence isoprene > divinyl > piperylene > chloroprene. These data permit the conclusion that the phosphorus-containing component behaves as an electrophile. The condensation of ethylene and 1,3-butylene phosphoroisothiocyanatidites[80,81] with the same dienes does not stop at the isothiocyanatophosphorane (XLIX) stage. The phosphorane undergoes the second stage of the

Arbuzov rearrangement, giving rise to compounds of tetracoordinate phosphorus (L) and (LI):

Scheme 11



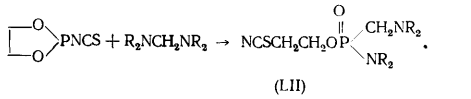
(XLIX)

$n = 1, 2$.

The reactions with piperlyene and 2,3-dimethylbuta-1,3-diene afford only the thiocyanates (L), while in the case of divinyl, isoprene, and chloroprene two products were isolated in each case: the thiocyanate (L) and the isothiocyanate (LI).

After the thiocyanate anion has been removed from the intermediate adduct (XLIX) (Scheme 11), it can attack the most hydrogenated carbon atom of the ester group via the sulphur or nitrogen atom. Attack via the sulphur atom is preferred, because the highest negative charge is concentrated on it at the instant of the removal of the thiocyanate anion. Indeed in all cases the yield of thiocyanates predominates.

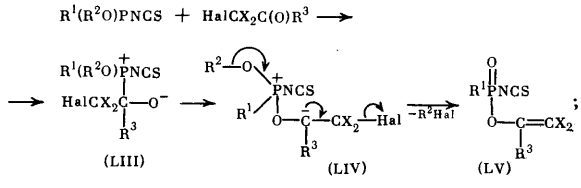
Treatment of ethylene phosphoroisothiocyanatidite with various methylenediamines including dipiperidinylmethane and di-4-morpholinylmethane yielded thiocyanatoethyl aminomethylphosphonamidates (LII).[82] These reactions apparently proceed via a mechanism similar to that described above:



(LII)

Phosphoromono- and phosphorodi-isothiocyanatidites react with α-halogenocarbonyl compounds to form the products of the Perkow reaction via Scheme 12. This has been demonstrated in relation to halogenopyruvate esters,[56,57] hexachloroacetone,[57] and trichloroacetylphosphonate esters.[40] In these reactions phosphoroisothiocyanatidites behave like trialkyl phosphites. According to Scheme 12, the reactions begin with the nucleophilic attack by the phosphorus atom on the carbon atom involved in the C=O bond with formation of the dipolar ion (LIII), which undergoes the phosphonate–phosphate rearrangement to the dipolar ion (LIV). The subsequent elimination of the alkyl halide leads to the vinyl phosphates (LV).

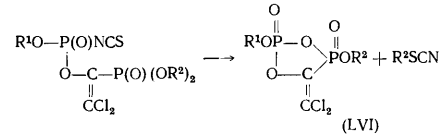
Scheme 12



(LIII) (LIV) (LV)

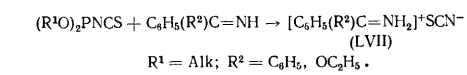
R^1 = AlkO, NCS; R^2 = Alk; R^3 = CCl_3, $COOC_2H_5$, $P(O)(OR)_2$; X = H, Cl.

The vinyl phosphates, formed in the reaction with trichloroacetyl phosphonates, are capable of cyclising to a dioxadiphospholans (LVI):[40]



(LVI)

The main product of the reaction of dialkyl phosphoroisothiocyanatidites with imines having a mobile hydrogen atom, for example, with diphenylketimine and benzimidoethyl ether, are immonium thiocyanates (LVII). The structure of the phosphorus-containing products was not established:[78]



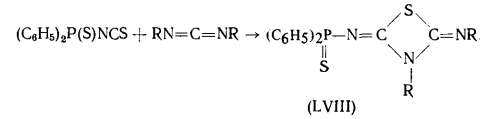
(LVII)

R^1 = Alk; R^2 = C_6H_5, OC_2H_5.

(c) Reactions of the Isothiocyanates of Tetracoordinate Phosphorus Acids

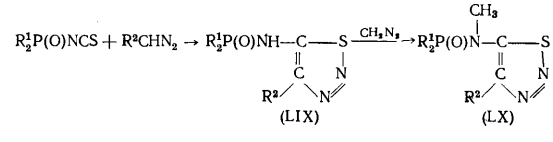
Reactions involving the addition of various nucleophiles to the NCS group are most characteristic of the isothiocyanates of tetracoordinate phosphorus acids. These reactions will be considered in the corresponding Sections devoted to the methods of synthesis of N-phosphorylated thio- and dithiocarbonates and thioureas. In the present Section we shall deal with other reactions of the isothiocyanates of tetracoordinate phosphorus acids, mainly their cycloaddition reactions.

The reactions of diphenylphosphinothioic isothiocyanate with dicyclohexyl- and diisopropyl-carbodiimides, leading to 1,3-thiazetidine derivatives (LVIII), and not 1,3-diazetidine derivatives as had been stated previously in the literature, have been described:[83]



(LVIII)

The interaction of phosphorylated isothiocyanates with diazomethane or phenyldiazomethane leads to the formation of the corresponding 5-(*N*-phosphinyl)amino-1,2,3-thiadiazoles (LIX):[84]

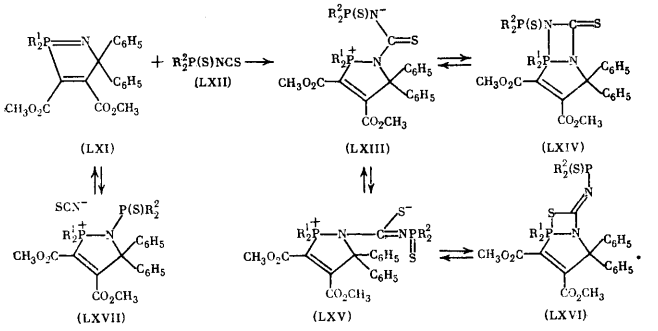


(LIX) (LX)

When the reactions are carried out with a large excess of diazomethane, 5-(*N*-methyl-N-phosphinyl)amino-1,2,3-thiadiazoles (LX, $R^2 = CH_3$) are formed. The involvement of phenylphosphonic diisothiocyanate and phosphoric triisothiocyanate in these reactions does not lead to the expected thiadiazoles, but the structure of the products formed has not been established. Dimethyl- and diphenyl-phosphinothioic isothiocyanates react with azaphospholans (LXI) to form cyclic [2 + 2]-adducts.[85] The phosphorylated isothiocyanates (LXII) (as well as isothiocyanates without phosphorus) add via the C=S bond to the phosphazine group in azaphospholes (LXI) with formation of compounds (LXVI)

containing the 1,3,2-λ^5-thiazaphosphetidine ring:

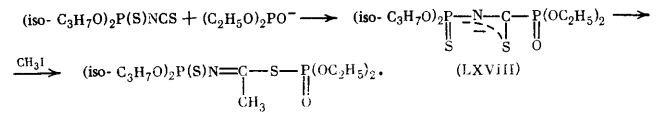
Scheme 13



When compounds (LXVI) are dissolved, the equilibrium (LXVI) ⇌ (LXV) ⇌ (LXIII) ⇌ (LXIV) is established. In the case of the dimethylphosphinyl group, it is displaced towards the form (LXIV) to a greater extent than in the case of the diphenylphosphinothioyl group. With increase of temperature to 70–90 °C, the reversible migration proceeds so rapidly that the ^{1}H NMR spectra exhibit a coalescence of the δ_{PCH_3} signals for (LXIV) and (LXV). The rearrangement proceeds intramolecularly and not via the reverse dissociation (LXVI) ⇌ (LXI) + (LXII) ⇌ (LXIV), which is demonstrated by the fact that the azaphosphole (LXI) added in excess is not involved in the coalescence. Yet another isomer-adduct (LXVII) is formed when the reaction is carried out in benzene, from which it crystallises.

It has been established by ^{31}P NMR that compound (LXVII) is converted into an equilibrium mixture of compounds (LXIV) and (LXVI) via compounds (LXIII) and (LXV) in $CHCl_3$ and more slowly in a benzene suspension.

The mesomeric anion (LXVIII) formed in the reaction of diisopropyl phosphoroisothiocyanatidothioate with sodium diethyl phosphite exhibits the 1,2-C → S mitration of the phosphoryl group in methylation:[86]



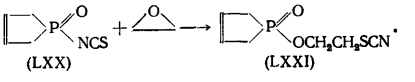
The SCN group manifests pseudohalogen properties in certain reactions of the isothiocyanates of tetracoordinate phosphorus acids. For example, phosphorylated aminoheterocycles of type (LXIX) are formed (Scheme 14) in the reactions with aminobenzazoles, benzazolone imines,[87] 2-aminothiazoles, and 2-aminothiazolines:[88]

Scheme 14

$$R^1R^2P(X)NCS + H_2NHet \rightarrow \underset{(LXIX)}{R^1R^2P(X)NHHet} + HNCS;$$

Het = heterocyclic group

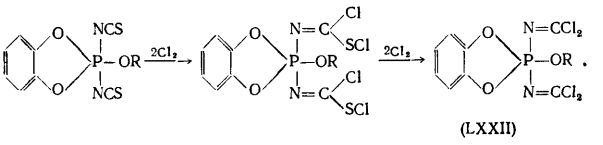
Epoxyethane is capable of being inserted in the P–N bond of the phosphorylated isothiocyanates. Isothiacyanatophosphine oxide (LXX) has been converted in this way into the 2-thiocyanatoethyl phosphinate (LXXI):[80]



The reaction with molecular chlorine, leading to phosphorylated isocyanide dichloride (see, for example, Roessky and Janssen[30] and Derkach and Liptuga[89]), are extremely characteristic of the isothiocyanates of phosphorus acids. Many other examples of similar reactions have been quoted in a review.[1]

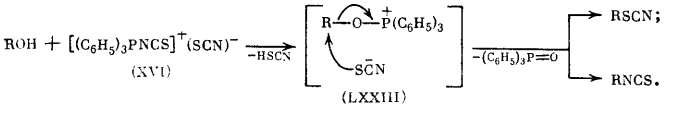
(d) Chemical Reactions of Isothiocyanates with the Phosphorane or Phosphonium Structure

Alkoxydiisothiocyanato-*o*-phenylenedioxyphosphoranes are smoothly chlorinated at −80 °C by 4 moles of chlorine to give compound (LXXII):[43]



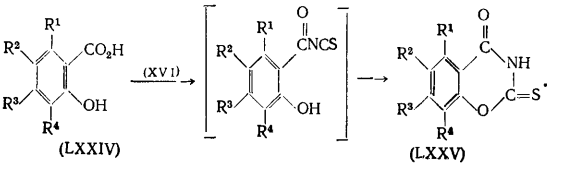
The adduct of triphenylphosphine and thiocyanogen—the phosphonium salt (XVI), described in 1977,[45] permits the synthesis of thio- and isothio-cyanates, disubstituted thioureas, amides, phosphimides, and other compounds in high yields and under mild conditions.[44,45,90–98] The adduct converts via Scheme 15 primary alcohols into thiocyanates, tertiary alcohols into isothiocyanates, and secondary alcohols into a mixture of both products[44,45] in almost quantitative yields:

Scheme 15



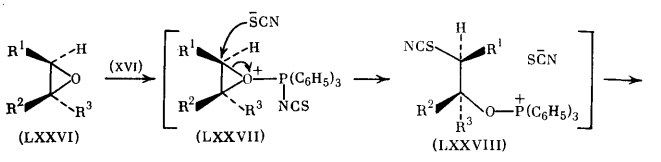
The reactions proceed via the intermediate (LXXIII), the formation of thio- or isothio-cyanates depending on the ambident character of the thiocyanate anion. Carboxylic acids give rise to acyl isothiocyanates in this reaction.[44]

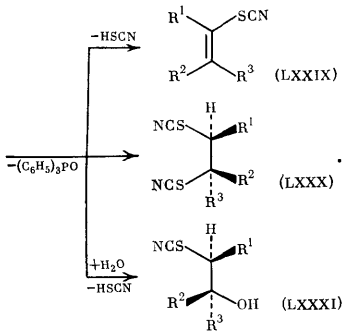
2-Thiono-3,4-dihydro-2*H*-1,3-benzoxazin-4-ones (LXXV) have been obtained in 70% yields by treating substituted salicylic acids (LXXIV) with the salt (XVI):[90]



The epoxides (LXXVI) react with the phosphonium salt (XVI) via Scheme 16 under mild conditions with the opening of the oxiran ring and the formation of mono- and di-isothiocyanato-derivatives.[94,98] The interaction of α,β-epoxyketones leads to α-thiocyanatovinyl ketones (LXXIX, R^1 = R^4CO). Regiospecific thiocyanation of monosubstituted or 1,2-disubstituted epoxides leads to the corresponding vicinal dithiocyanates (LXXX), *threo*-dithiocyanates and *erythro*-dithiocyanates being formed respectively from *trans*- and *cis*-epoxides. The reactions of 1,1-disubstituted epoxides give rise to vicinal *threo*-thiocyanatohydrins (LXXXI):

Scheme 16

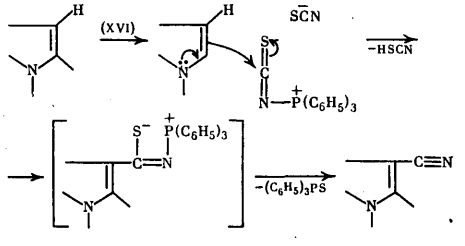




It has been suggested[98] that the electrophilic phosphorus atom of the phosphonium salt (XVI) attacks the oxygen atom of the oxiran ring with formation of the intermediate (LXXVII), which is then subjected to nucleophilic attack by the thiocyanate anion. This results in the opening of the oxiran ring and the formation of the β-thiocyanatoalkoxyphosphonium salt (LXXVIII), resembling the intermediate formed in the reactions with alcohols. In the case of α,β-epoxyketones the intermediate (LXXVIII) undergoes ready α-deprotonation by the thiocyanate anion, accompanied by the spontaneous elimination of triphenylphosphine oxide and the formation of α-thiocyanatovinyl ketones (LXXIX). The regiospecificity of the reactions can be accounted for by the stabilising effect of the neighbouring carbonyl group.

The intermediate (LXXVII), formed from monosubstituted and 1,2-disubstituted epoxides, is attacked by the thiocyanate anion at the least substituted carbon atom. A second SCN group then displaces triphenylphosphine oxide from compound (LXXVIII) via nucleophilic substitution with formation of vicinal dithiocyanates (LXXX). When the substitution by the thiocyanate anion is hindered by steric factors, as happens, for example, in the intermediate (LXXVIII) obtained from 1,1-disubstituted epoxides, hydrolysis takes place readily and leads to the formation of vicinal thiocyanatohydrins (LXXXI) and triphenylphosphine oxides.

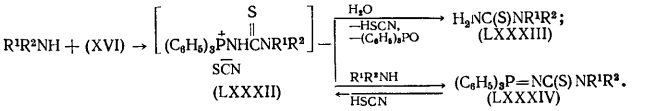
The use of the phosphonium salt (XVI) makes it possible to achieve the cyanation of pyrroles, indoles, and enamines under mild conditions and in satisfactory yields.[45,97]



The cyanation of pyrroles takes place selectively in the 2-position when the latter is unsubstituted. Otherwise, the cyano-group is introduced into the less reactive 3-position. The reactions of the salt (XVI) with indoles also proceed selectively with formation of products in which the cyano-group is in the 3-position. If an alcoholic group is present in the indole or pyrrole molecule, then its thiocyanation takes place in competition with the cyanation of the heterocycle. However, the introduction of an acyl protecting group makes it possible to avoid the first reaction.

Yet another application of the phosphonium salt (XVI) involves its use in the synthesis of substituted thioureas and amides.[91-93,95] In the first stage of the reactions with the amines, the phosphonium salts (LXXXII) are formed (Scheme 17), being converted into the corresponding 1,1-disubstituted thioureas (LXXXIII) in a high yield on treatment with aqueous acetonitrile:[91,95]

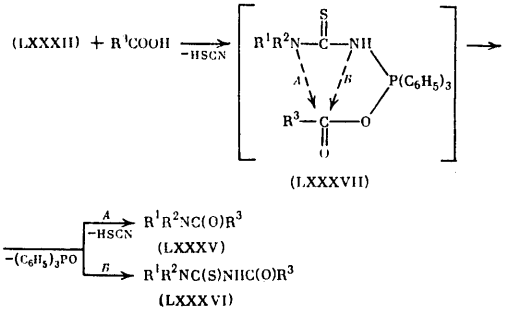
Scheme 17



The intermediate formation of compound (LXXXII) has been confirmed by chemical reactions. When the phosphonium salt (XVI) is treated with an excess of the amine, the phosphine imine (LXXXIV) is formed and is smoothly converted into the corresponding thiourea and triphenylphosphine oxide when it is treated with an aqueous solution of thiocyanic acid.

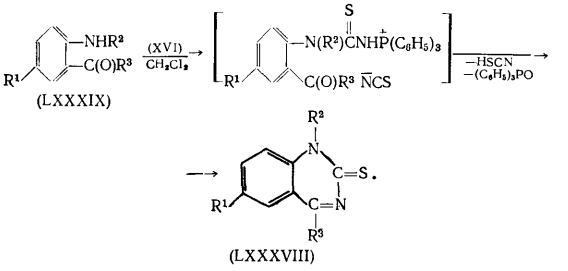
If carboxylic acids are introduced into the reaction instead of the aqueous acetonitrile, the corresponding amides (LXXXV) and/or acylthioureas (LXXXVI) are formed, depending on the structure of the initial amine and carboxylic acid:

Scheme 18



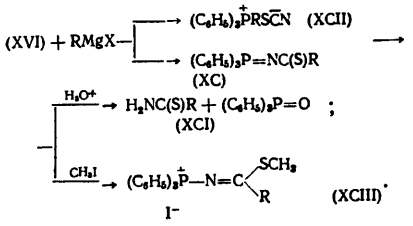
The reactions apparently begin with the attack by the carboxylate anion on the phosphorus atom in the salt (LXXXII) and lead to the intermediate (LXXXVII). The latter split off triphenylphosphine oxide and are converted either into the amide (LXXXV) via a six-membered cyclic transition state (pathway *A*) or into the acylthiourea (LXXXVI) via a four-centre transition state (pathway *B*). With the increase of the size of the substituents in the amine and the carboxylic acid, the yield of the amides (LXXXVI) diminishes, while that of the thioureas (LXXXVI) increases, which can be accounted for by the smaller dependence of the reaction via pathway *B* on the steric factor, because in this case the substituents can be located in the *trans*-position.

The adduct of triphenylphosphine with thiocyanogen (XVI) has been used also in the synthesis of 2-thiono-1,2-dihydroquinazolines (LXXXVIII) from readily available *o*-acylanilines (LXXXIX):[92,95]



The reaction of organomagnesium compounds with the adduct (XVI) proceeds with formation of phosphine imine intermediates (XC) which are converted into the thioamides

(XCI) on acid hydrolysis:[93]



In the absence of acid, it is possible to isolate compound (XC) and a small amount of the phosphonium salt (XCII). The phosphine imine (SC) is methylated by methyl iodide to the phosphonium salt (XCIII).

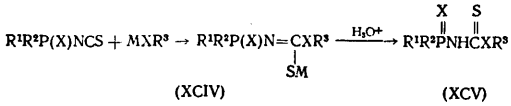
Thus the reaction of alcohols, epoxides, carboxylic acids, and organophosphorus acids and the adduct of triphenylphosphine and thiocyanogen begins with the nucleophilic attack on the phosphorus atom, which leads to the formation of phosphonium salts of the type (LXXIII) and (LXXVII). The reactions with amines, enamines, organomagnesium compounds, pyrroles, and indoles begin with the nucleophilic addition to the NCS group. Depending on the structure, the intermediates formed in these reactions on treatment with different reagents give rise to a whole range of practically important substances.[93]

III. *N*-PHOSPHORYLATED THIO- AND DITHIO-CARBAMATES

It is known that the esters of tetracoordinate phosphorus acids and derivatives of thio- and dithio-carbamic acids constitute the two most numerous classes of chemical substances among the pesticidal preparations employed nowadays. The study of the biological activity of phosphorylated thio- and dithio-carbamates, in the molecule of which phosphorus-containing and thiocarbamate fragments are combined, is therefore of great interest. Substances with bactericidal,[11] antihelminthic,[99-101] insectoacaricidal,[102-105] and other pesticidal activities[106-108] have been found among *N*-phosphorylated thio- and dithiocarbamates. In addition, *N*-phosphorylated thiocarbamates can be used as antioxidants for synthetic resins and as additives to motor fuels,[104] while *N*-thiophosphoryldithiocarbamates can be employed as complex-forming agents and extractants.[109]

1. Methods of Synthesis of *N*-Phosphorylated Thio- and Dithio-Carbamates

The synthesis of organophosphorus thio- and dithiocarbamates from phosphorus-containing isothiocyanates or mixtures of tetracoordinate phosphorus acid chlorides and potassium thiocyanate on treatment with alcohols, mercaptans, or, better, with their metal derivatives has been described.[1] The *S*-metallated derivatives of *N*-(thio)phosphorylated isothio(dithio)carbamates (XCIV) formed in the latter case are converted into thio(dithio)carbamates (XCV) after acidification:

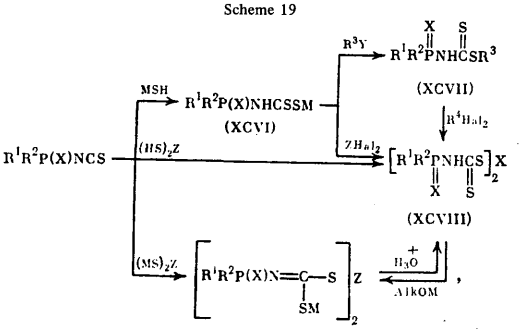


where X = O or S and M is an alkali metal. These metals have remained of key importance also in subsequent studies. Thus *S*-butyl-*N*-diphenylphosphinyl dithiocarbamate has been obtained by the reaction of diphenylphosphinyl isothiocyanate with sodium butanethiolate in the presence of triethylamine on subsequent treatment with NH_4Cl.[110]

The addition of alcohols to the NCS groups of 1,1,3,3-tetrachloro-5,5-diisothiocyanatocyclotriphosphazene,[31,32] 3,9-diisothiocyanato-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecane 3,6-dioxide, and the analogous bissulphide [104] led to the formation of the corresponding phosphorus-containing bisthionocarbamates.

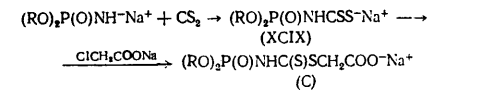
The salts of *N*-(thio)phosphorylated dithiocarbamic acids (XCVI), formed when the thioisocyanates of tetracoordinate phosphorus acids are treated with alkali metal hydrogen sulphides,[105,106,111-116] are converted into the dithiocarbamates (XCVII) on alkylation.[103,106,113] Reaction of the salts (XCVI) with alkylene or oxydimethylene dihalides leads to bisphosphoryldithiocarbamates (XCVIII):[105,117]

Scheme 19

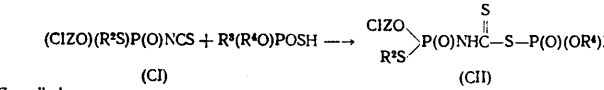


where X = O or S, M = Li, Na, K, or NH_4, Y = halogen or Ts [tosyl? (Ed.of Translation)], and Z = $(CH_2)_2O$ or a substituted or unsubstituted alkylene. In addition, compounds (XCVIII) can be obtained by treating phosphoroisothio(thio)cyanatidates with dithiols[99,117-119] or alkali metal dithiolates with subsequent acidification[101-103,105,117] and also by the reaction of dithiocarbamates (XCVII) with alkylene dihalides in the presence of bases.[117]

The possibility of obtaining *S*-sodium dialkylphosphoryldithiocarbamates (XCIX) from sodium phosphoramides and carbon disulphide has been demonstrated.[120] When compounds (XCIX) are treated with sodium chloroacetate, the paste-like sodium *S*-[*N*-(dialkylphosphoryl)thiocarbamoyl] acetates (C) are formed:

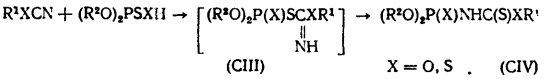


Certain acids can also be made to add to the isothiocyanato-group. In particular, the partial esters of phosphonomonothioic acids interact with phosphoroisothiocyanatidothioates (CI) to form *NS*-diphosphorylated dithiocarbamates (CII):[108]



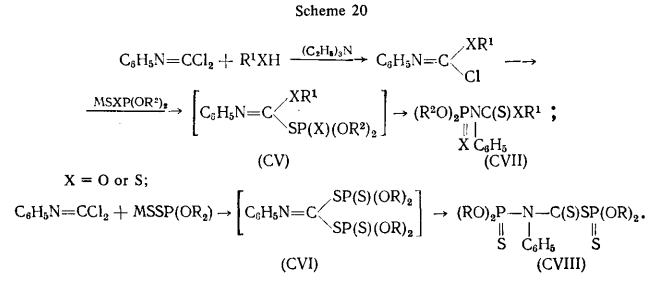
Z = alkylene.

Phosphoromonothioic and phosphorodithioic acids are capable of adding tothe C≡N bond in cyanates and thiocyanates, the adducts (CIII) rearranging readily to *N*-(thio)phosphorylated thio- or dithio-carbamates (CIV):[50,51]

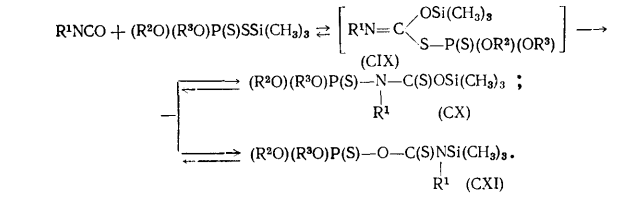


When the chlorine atoms in phenyl isocyanide dichloride are substituted via a series of stages by an alkoxy- or alkylthio-group and then by a dialkyl phosphorothioate or phosphorodithioate group (Scheme 20), *S*-(thio)phosphorylated isothio- or isodithio-carbamates (CV) are formed.[107,121] The interaction of phenyl isocyanide dichloride with salts of dialkylphosphorodithioic acids lead to analogous compounds (CVI).[107,122] However, in contrast to patent data,[123–125] it has been shown[107,121,122] that compounds (CV) and (CVI) are unstable and in the course of the process undergo an irreversible rearrangement to the phosphorylated dithiocarbamates (CVII) and (CVIII). When salts of dialkylphosphoromonothioic acids are involved in the reaction, derivatives with a P=O group are produced:[107,121]

Scheme 20

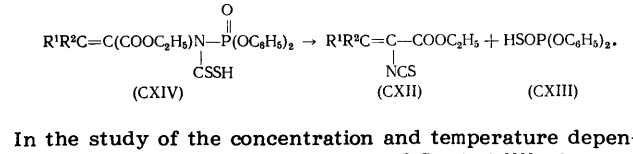


The interaction of *S*-trimethylsilyl phosphorodithioates with isocyanate leads to the adducts (CIX) which are capable of reversible isomerisation to both *N*-thiophosphorylated [compounds (CX)] and *O*-thiophosphorylated [compounds (CXI)] trimethylsilyl thionocarbamates:[126]

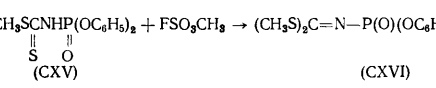


2. The Properties of *N*-Phosphorylthiocarbamates

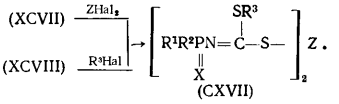
The reactions involving the addition of alcohols and mercaptans to the isothiocyanates of tetracoordinate phosphorus acids are reversible.[1] Even at room temperature *N*-(thio)phosphorylated thio- and dithio-carbamates (CIV) decompose to phosphoroisothio(thio)cyanatidates and alcohols or thiols.[50,51] An interesting decomposition into the isothiocyanate (CXII) and diphenylphosphoromonothioic acid has been observed on heating dithiocarbamates having the structure (CXIV):[127]



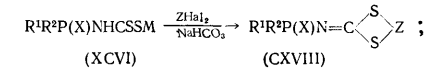
In the study of the concentration and temperature dependence of the IR spectra of solutions of *S*-alkyl *NN*-dialkylthiophosphoryldithiocarbamates, no thione–thiol tautomerism has been observed.[109] Nevertheless the alkylation of *N*-(thio)phosphorylated thio- and dithio-carbamates by different alkylating agents always leads to *S*-alkylated and not *N*-alkylated products. Thus, on treatment with methyl fluorosulphate, the dithiocarbamate (CXV) is converted into the *N*-phosphorylated imidodithiocarbonate (CXVI):[128]



Diphosphorylated bisimidodithiocarbonates (CXVII) are formed on reaction of *N*-phosphorylated dithiocarbamates (XCVII) with alkylene dihalides[103] and of diphosphorylated dithiocarbamates (CXVIII) [99,102,117,119] or their metal derivatives[103,118] with alkyl halides:

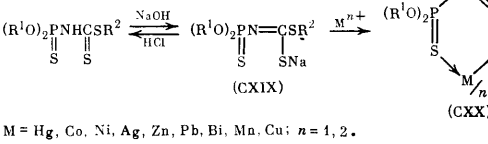


On treatment with alkylene dihalides in the presence of bases, the salts of *N*-(thio)phosphoryldithiocarbamic acids (XCVI) cyclise to *N*-(thio)phosphorylated imino-1,3-dithietans[106,111,112,115,116,129–136] or imino-1,3-dithiolans (CXVIII),[114] which have found practical application as broad spectrum pesticides:



Z = alkylene.

N-Thiophosphorylated dithiocarbamates are weak acids with $pK_a \cong 7.5$ (in aqueous alcoholic mixtures) [51,109] and are converted on treatment with alkalies into water-soluble *S*-metal derivatives (CXIX):[51]



M = Hg, Co, Ni, Ag, Zn, Pb, Bi, Mn, Cu; $n = 1, 2$.

Treatment of derivatives of compound (CXIX) by salts of thiophilic metals leads to the formation of stable complexes (CXX), which can be extracted from organic media by organic solvents, which makes it possible to employ *S*-alkyl-*NN*-dialkylthiophosphoryldithiocarbamates as extractants.[109]

IV. *N*-PHOSPHORYLATED THIOUREAS

Numerous publications devoted to the methods of synthesis and reactions of *N*-phosphorylated thioureas and also to their practical use in industry, agriculture, medicine, and veterinary science have appeared in recent years.

Numerous investigations have been devoted to the biological activity of *N*-phosphorylated thioureas. According to literature data, substances exhibiting carcinostatic and immunostimulating,[137] bactericidal,[10–12,138–142] anthelminthic,[55,143–154] arthropocidal,[55,155] nematocidal,[55,143,155,156] insectoacaricidal,[104,143,156,157] herbicidal,[140,157,158] fungicidal,[38,157,159–163] and other pesticidal[107,164,165] activities as well as preparations used to destroy ectoparasites,[166] for the prophylaxis and treatment of coccidiosis,[167] and in the therapy of radiation sickness[168] have been found among them.

In addition, the use of *N*-phosphorylated thioureas as additives to lubricating oils[169,170] and motor fuels,[104,171,172] as antioxidants for synthetic resins,[104] as additives to reduce the combustibility of organic substances,[14,15,171–174] as fire-resistant polymeric materials,[19,20] as plasticisers,[165] and as extractants[175,176] is of extremely great value.

1. Methods of Synthesis of *N*-Phosphorylated Thioureas

The method of synthesis of *N*-phosphorylated thioureas most frequently employed involves the addition of ammonia,[37,104] aliphatic amines,[5,6,30–32,51,54,60,67,104,110,143,148,155,156,164,168,169,177–179] aromatic amines,[38,47,49–51,104,110,141,146–149,151,152,154,159–162,164,169,177,178,180–186] and heterocyclic amines[38,104,137–139,141,142,159,163,164,169,186] to the NCS group in the isothiocyanates of tetracoordinate phosphorus acids. Reactions with alkylene-diamines[144,157,169] and arylenediamines[145,147,149,150,166,187,188] result in the formation of bisphosphorylated thioureas. The corresponding *N*-phosphorylated thiosemicarbazides have been isolated in the reactions with hydrazines.[38,138,139,189–191] The reactions usually proceed very readily at room temperature and lead to the formation of the required compounds in high yields.

The kinetics of the reactions of phosphoroisothiocyanatidates with aniline have been studied by IR spectroscopy:[180]

$$R_2P(O)NCS + C_6H_5NH_2 \rightarrow R_2P(O)NHC(S)NHC_6H_5\ ;$$
$$R = C_2H_5,\ C_6H_5O,\ C_2H_5,\ C_2H_5O.$$

It was found that the reactions are of second kinetic order. Phosphorylated isothiocyanates and phenyl isothiocyanates can be arranged in the following sequence in terms of their reactivities:

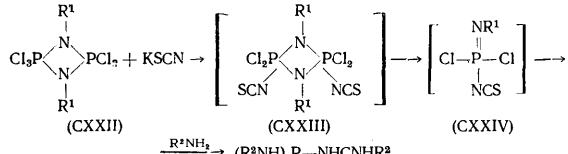
$$(C_6H_5O)_2P(O)NCS \gg (C_6H_5)_2P(O)NCS \approx (C_2H_5O)_2P(O)NCS > (C_2H_5)_2P(O)NCS > C_6H_5NCS.$$

The reactions are completed faster in acetone and dioxan than in CCl_4, which has been explained[180] by the influence of the unshared electron pairs of the oxygen atoms in the molecules of the first two solvents.

Optically active *N*-phosphorylated thioureas have been obtained by the reaction of amines with optically active phosphorylated isothiocyanates.[5,6,37,60] The reaction of the ^{32}P-labelled diphenylphosphinothioic isothiocyanate with the ε-amino-groups of the lysine side chains in proteins has been used to introduce a radioactive label into γ-globulin.[67] *N'*-hydantoinyl-*N''*-phosphorylthioureas have been obtained from the corresponding disubstituted 5-aminohydantoins and dialkyl phosphoroisothiocyanatidates and phosphoroisothiocyanatidothioates.[163]

The synthesis of thioureidophosphazoarenes (CXXI) via Scheme 21 by treatment of *NN'*-diarylhexachlorocyclophosphazans (CXXII) initially with KSCN and then with aromatic or heterocyclic amines in acetone at 0 °C has been described. It is suggested that the process proceeds via the intermediate (CXXIII) and (CXXIV):

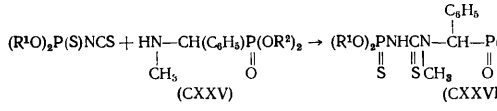
Scheme 21



(CXXII) (CXXIII) (CXXIV)

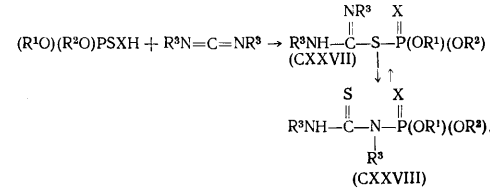
$\xrightarrow{R^2NH_2}$ $(R^2NH)_2P(NR^1)NHCNHR^2$ (S) (CXXI).

Bisphosphorylated thioureas (CXXVI) are formed in the reactions of α-aminophosphonates (CXXV) with phosphoroisothiocyanatidothioates:[51]



(CXXV) (CXXVI)

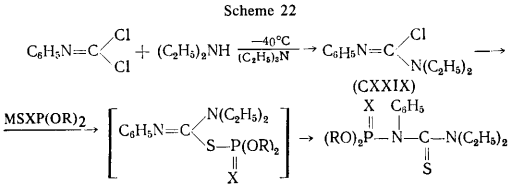
Together with the reactions of phosphorylated isothiocyanates with amines, other methods have also been used to synthesise *N*-phosphorylated thioureas, because the reactions of the amines are not free from certain limitations. In particular, thioureas in which the nitrogen atom linked to the phosphorus atom is fully substituted cannot be synthesised by these reactions. This can be achieved, for example, with the aid of the reactions of phosphorothioic and phosphorodithioic acids with carbodiimides.[140,192–199] The products of the addition of the thioacids of tetracoordinate phosphorus to the C–N bond in compounds (CXXVII), which have the isothiourea structure, can rearrange to *N*-(thio)phosphorylated thioureas (CXXVIII) in addition to undergoing other reactions. In certain cases (when R^3 = isopropyl or cyclohexyl) the rearrangement is reversible, but under the usual conditions the equilibrium is almost fully displaced towards the isomer (CXXVIII). The study of the stereochemistry of the conversion of *S*-phosphorylisothioureas into *N*-phosphorylthioureas[197,198] demonstrated the complete retention of the configuration at the phosphorus atom:



(CXXVII) (CXXVIII)

An analogous rearrangement of *S*-(thio)phosphorylated isothioureas to *N*-(thio)phosphoryl thioureas has been observed in the reaction of diethyl phosphorodithioic acid with cyanamide[48] and in exchange reactions of salts of dialkyl phosphorothioic and dialkyl phosphorodithioic acids with *NN*-diethyl-*N'*-phenylchloroformamidine (CXXIX) (Scheme 22):[107]

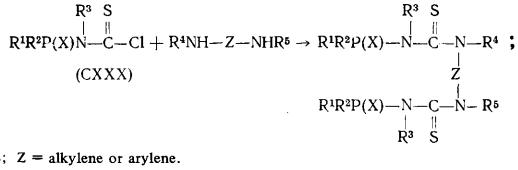
Scheme 22



(CXXIX)

M = Na, K, NH_4; X = O or S.

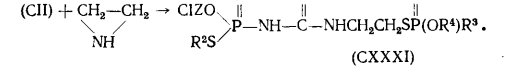
Phosphoryl- and thiophosphoryl-thiocarbamoyl chlorides (CXXX) can condense with amines[155,156] and alkylene- and arylene-diamines[157] to form the corresponding mono- or bis-(thio)phosphorylthioureas:



(CXXX)

X = O or S; Z = alkylene or arylene.

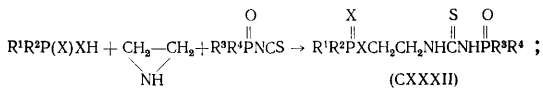
Diphosphorylated thioureas (CXXXI) have been synthesised from *NS*-diphosphorylated dithiocarbamates (CI) and ethyleneimine:[200]



(CXXXI)

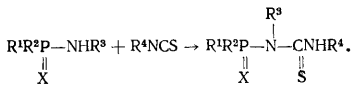
Analogous products (CXXXII) have been isolated in three-component reactions of the acid esters of phosphonic, phosphonodithioic, phosphonotrithioic, or phosphorodiamidodithioic acids with phorphoryl isothiocyanates and

ethyleneimine.[165,201,202] The corresponding *NS*-diphosphorylated thio- or dithio-carbamates of type (CII) are apparently formed in these reactions as intermediates:



$R^1 = AlkX, ArX, AlkNH;\ R^2 = Alk, Ar, AlkNH;\ X = O \text{ or } S.$

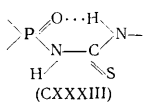
According to patent data,[155,156] phosphorylated thioureas can be obtained by adding the amides of tetracoordinate phosphorus acids to organic isothiocyanates:



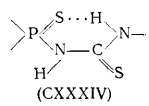
The addition of *cis*- and *trans*-2-amido-4-methyl-2-oxo-1,3,2-dioxaphosphorinanes to cyclohexyl isothiocyanate takes place in the presence of sodium hydride.[37] Diaminotetrakis(dimethylamino)cyclotriphosphazene reacts with phenyl isothiocyanate in boiling benzene to form a monosubstituted derivative of thiourea.[28]

2. The Properties of *N*-(Thio)Phosphorylated Thioureas

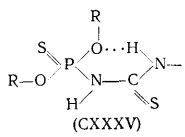
It has been established by IR spectroscopy[203] that *N*-phosphorylated and *N*-thiophosphorylated thioureas do not exhibit a tendency towards the thione–thiol tautomerism both in polar and in non-polar solvents. In a study of the concentration dependence of the IR spectra, it was found that these compounds are associated both in the crystalline state and in concentrated solutions as a result of the formation of intermolecular hydrogen bonds involving the P–NH, C=S, and P=S groups. In dilute solutions in CCl_4 an equilibrium is established between the self-associated species and their monomers. The intermolecular hydrogen bonds (CXXXIII), (CXXXIV), and (CXXXV) make a significant contribution to the stabilisation of the monomeric forms:



(CXXXIII)

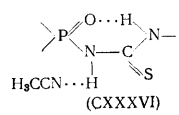


(CXXXIV)

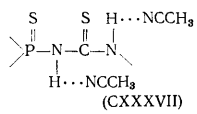


(CXXXV)

Heteroassociated 1:1 and 1:2 species arise in acetonitrile for the phosphoryl [compound (CXXXVI)] and thiophosphoryl [compound (CXXXVII)] derivatives respectively:

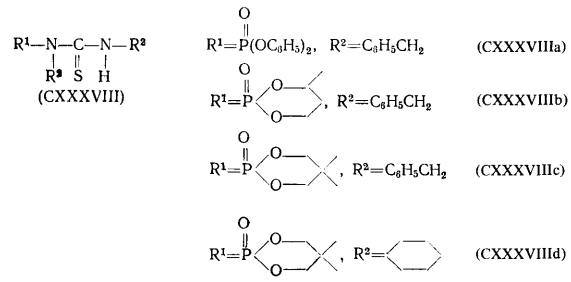


(CXXXVI)



(CXXXVII)

The X-ray diffraction study of *NN'*-dibenzyl-*N*-diphenylphosphorylthiourea (CXXXVIIIa),[204] *NN'*-dibenzyl-*N*-(4-methyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (CXXXVIIIb),[198] *NN'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (CXXXVIIIc), and *NN'*-dicyclohexyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (CXXXVIIId)[205] revealed significant structural and conformational differences between the dibenzyl derivatives (CXXXVIII, a–c) and the dicyclohexyl derivative (CXXXVIIId):



(CXXXVIII)

$R^1=P(OC_6H_5)_2$, $R^2=C_6H_5CH_2$ (CXXXVIIIa)

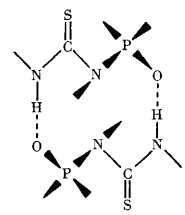
$R^1=$, $R^2=C_6H_5CH_2$ (CXXXVIIIb)

$R^1=$, $R^2=C_6H_5CH_2$ (CXXXVIIIc)

$R^1=$, $R^2=$ (CXXXVIIId)

In compounds (CXXXVIII, a–c) the sulphur and phosphorus atoms occupy virtually antiperiplanar positions about the SC–NP bond (torsional angle of about 160°). The thiourea fragment in the dibenzyl derivatives (CXXXVIII, a–c) is planar. A chelate six-membered ring is formed in these molecules via the intramolecular NH...O=P hydrogen bond.

The presence of the two bulky cyclohexyl substituents in the molecule of compound (CXXXVIIId) disturbs the planarity of the thiourea skeleton. The deviation of the phosphorus atom from the plane of the nitrogen and sulphur atoms in compound (CXXXVIIId) amounts to 1.435 Å while in compound (CXXXVIIIc) it is only 0.490 Å. The P–N–C–S torsional angle is 91°, so that the non-bonding S...P distance, amounting to 3.73 Å in compound (CXXXVIIId), is much shorter than in compound (CXXXVIIIc) (4.242 Å). The rotation about the PN  bond in compound (CXXXVIIId) is restricted owing to the interaction of the α-protons of the cyclohexane ring with the phosphoryl oxygen; the rotation about the PN–CS bond is also hindered. The thiourea (CXXXVIIId) gives rise to the dimers (CXXXIX) in the crystalline state, which are stabilised by intermolecular hydrogen bonds:

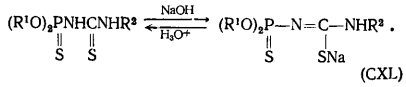


(CXXXIX)

The structural and conformational differences between the thioureas of types (CXXXVIII, a–c) and (CXXXVIIId) are also shown in the NMR spectra. The spin–spin coupling constants ^3J(P–N–C–H) for *NN'*-dicyclohexyl- and *NN'*-diisopropyl-phosphorylthioureas are unusually high (20.5 to 25.4 Hz) compared with other *N*-phosphorylated thioureas (9.5–10.0 Hz). For the thiophosphoryl derivatives, the difference between the ^3J(PH) is not quite so significant, but it does exist. On the basis of the invariance of the constants ^3J(PH) when the solvents are varied, the authors[199] concluded that the most stable conformations of the *NN'*-disubstituted phosphorylthioureas (CXXXVIII) are identical in the crystalline state and in solution.

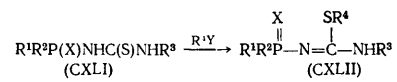
Like *N*-thiophosphoryldithiocarbamates, *N'*-substituted *N*-dialkylthiophosphorylthioureas are weak acids with $pK_a \cong 8.8$ (in an aqueous alcoholic medium) [51,176,203] and form water-soluble salts (CXL) with alkalies or alkali metal

alkoxides:[51]



(CXL)

Like *N*-(thio)phosphoryl(di)thiocarbamates, the thioureas (CXLI) are alkylated by various alkylating agents with formation of *S*-alkyl-*N*-(thio)phosphorylisothioureas (CXLII):[179,206–210]

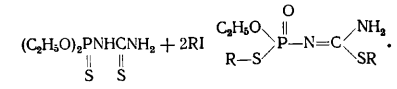


(CXLI) (CXLII)

R^4Y = AlkHal, AlkOTs, $AlkCHN_2$, Alk_2SO_4.

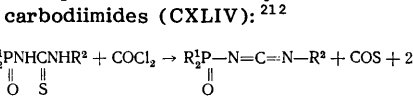
The alkylation is sometimes accompanied by the Pishchimuka rearrangement:[208]

Scheme 23



The interaction of *N*-(thio)phosphorylthiourea with Methylene Blue in 85% ethanol leads to the reduction of the dye to a substituted phenothiazine, thiourea dimerising under these conditions.[211]

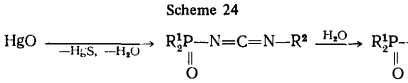
The reactions of the phosphorylthioureas (CXLIII) with phosgene in the presence of tertiary bases lead to phosphorylated carbodiimides (CXLIV):[212]



(CXLIII) (CXLIV)

The carbodiimides (CXLIV) can be obtained from compound (CXLIII) by desulphurisation with mercury(II) oxide in boiling benzene in accordance with Scheme 24. It is then essential to bind the water evolved, since otherwise the phosphorylated ureas (CXLV) are formed:[212]

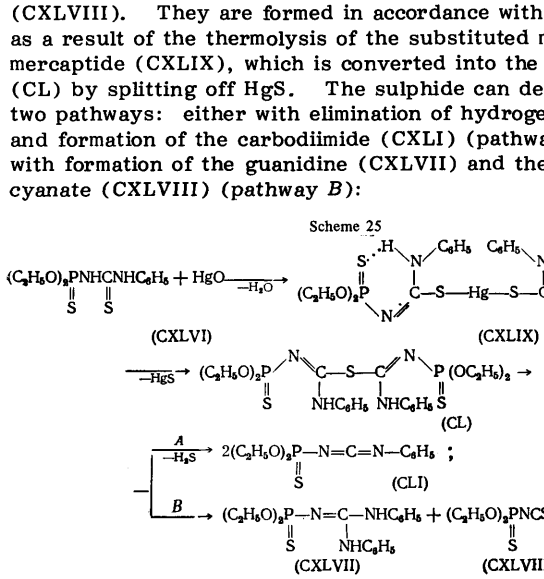
Scheme 24



(CXLIII) (CXLIV) (CXLV)

According to Grapov et al.[213], the yield of the thiophosphorylated carbodiimides is low when this method is used. The main products of the reaction of the thiourea (CXLVI) with mercury(II) oxide are compounds (CXLVII) and (CXLVIII). They are formed in accordance with Scheme 25 as a result of the thermolysis of the substituted mercury mercaptide (CXLIX), which is converted into the sulphide (CL) by splitting off HgS. The sulphide can decompose via two pathways: either with elimination of hydrogen sulphide and formation of the carbodiimide (CXLI) (pathway *A*) or with formation of the guanidine (CXLVII) and the isothiocyanate (CXLVIII) (pathway *B*):

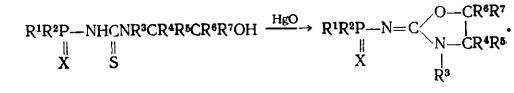
Scheme 25



(CXLVI) (CXLIX) (CL) (CLI) (CXLVII) (CXLVIII)

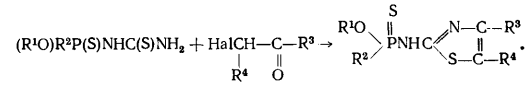
When *N*-phosphoryl- and *N*-thiophosphoryl-thiourea are heated with HgO in the presence of alcohols, mercaptans, and amines, the corresponding phosphorylated and thiophosphorylated isoureas, isothioureas, and guanidines are formed.[213,214]

The products of the addition of aminoalcohols to phosphorylated isothiocyanates (CLII) cyclise to *N*-phosphorylimino-oxazolidines (CLIII) under the influence of mercury(II) oxide with elimination of hydrogen sulphide:[215–219]



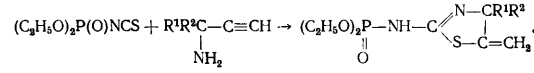
(CLII) (CLIII)

The reactions of thiophosphorylated thioureas with α-halogenoketones lead to the formation of phosphorus-containing aminothiazoles (CLIV):[220]



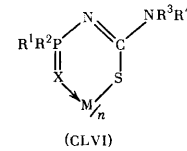
(CLIV)

Diethyl *N*-(2-thiazolinyl)phosphoramidates (CLV) are the products of the reaction of diethyl phosphoroisothiocyanatidate with substituted propargylamines:[221,222]



(CLV)

The molecules of phosphorylated thioureas contain several centres capable of forming a coordinate bond with metal ions. It has been reported in two reviews[1,21] that the formation of stable mono- or bi-ligand chelates of type (CLVI) is characteristic of these compounds. The complex formation reaction is accompanied by the displacement of one or two protons:

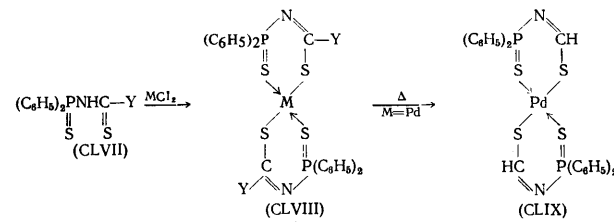


(CLVI)

X = O, S; M = Co(II), Ni(II), Cu(I); n = 1, 2

New data concerning the formation of complexes by *N*-(thio)-phosphorylthioureas with metal ions have been published.[51,150,152,156,175–178,186,223]

Ojima and co-workers[177,178] investigated the complex formation reactions between diphenylphosphinothioylthioureas (CLVII) and nickel(II), palladium(II), and cobalt(II) ions, which leads to the formation of 1 : 2 chelates having the structure (CLVIII):



(CLVII) (CLVIII) (CLIX)

Y = $N(CH_3)_2$, $N(C_2H_5)_2$, NHC_6H_5; M = Co(II), Ni(II), Pd(II).

In the reaction with palladium(II) ions (for R = NHC_6H_5), another chelate is isolated together with the complex (CLVIII) to which the structure (CLIX) was attributed on the basis of

IR spectroscopic, X-ray diffraction, and elemental analyses. The authors[178] believe that, when the complex (CLVIII) is heated, the ligand is partly destroyed, but the six-membered ring is retained.

The complexes with the nickel(II) and palladium(II) ions are diamagnetic at room temperature, which indicates their planar configuration. The IR and UV spectra confirm this. The cobalt(II) complexes are paramagnetic and have a tetrahedral configuration. On formation of complexes with copper(II) ions, the copper is reduced to the univalent state, but the reaction products could not be isolated in this instance.

A study of complex formation reactions of the thioureas (CLVII, R = phenylamino, *m*-tolylamino, α- and β-naphthylamino, or piperidinyl) with nickel(II) ions showed that the complexes have the 1:2 composition and in most cases have a planar structure.[186]

The formation of complexes by *N*-thiophosphorylthioureas with nickel, cobalt, mercury, and silver ions and the structures of the resulting chelates have been investigated[176,223] by spectrophotometric, potentiometric, IR spectroscopic, and ^{31}P NMR methods.

In view of the ability of *N*-thiophosphorylthioureas to form chelates which can be extracted from aqueous media by organic solvents, they can be used as extractants in analytical chemistry. Thus it has been shown[175,176] that many metal ions [Cu, Co, Ag, Cd, Au, Al, Mo, Ni, Gg, Ga, In, Bi, Pd, Pb, Zn, Mn(II), Tl, Ti] can be extracted from aqueous solutions of different acidity in the form of complexes with the aid of *NN*-diisopropyl-*N'*-phenylthiophosphorylthiourea. A procedure for the group concentration of microadmixtures of heavy metal ions in their chemical-spectroscopic analysis has been developed on the basis of the extraction properties of this compound.[175]

---o0o---

The data presented show that phosphorylated isothiocyanates as well as *N*-phosphorylated monothio- and dithiocarbamates and thioureas, which are genetically related to the isothiocyanates, possess a broad spectrum of properties useful in practice. Presumably further studies in this interesting field of organophosphorus chemistry will be directed towards a deepening of our knowledge of the structure and properties of these important and useful compounds, towards the search for new possibilities in their practical application, and also towards the development of the most technological processes for their synthesis.

REFERENCES

1. G.I.Derkatsch and Sh.M.Ivanova, Z.Chem., 1969, **9**, 369.
2. M.O.Lozinskii, G.I.Derkach, P.S.Pel'kis, and Zh.M.Ivanova, Symposium, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods for the Investigation of Organic Compounds), Izd.Khimiya, Moscow, 1971, Book 22, p.166.
3. A.Lopusinski and J.Michalski, Angew.Chem., 1972, **84**, 896.
4. A.Lopusinski, J.Michalski, and W.J.Stec, Annalen, 1977, 924.
5. A.Lopusinski, L.Luczak, J.Michalski, M.M.Kabachnik, and M.Moriyama, Tetrahedron, 1981, **37**, 2011.
6. A.Lopusinski, L.Luczak, and J.Michalski, Tetrahedron, 1982, **38**, 679.
7. BRD Appl.1921461 (1969); Chem.Abs., 1970, **72**, 42770.
8. Japanese P.50-21538 (1975); Ref.Zhur.Khim., 1976, 200352.
9. USSR P.244326 (1968); Byul.Izobret., 1969(18), 26.
10. Acc.British Appl.1318312 (1973); Izobr.za Rub., 1973, **15**(10), 36.
11. Acc.British Appl.1318313 (1973); Isobr.za Rub., 1973, **15**(10), 37.
12. BRD Appl.2039365 (1971); Chem.Abs., 1972, **76**, 141018.
13. Japanese P.47-48483 (1972); Chem.Abs., 1973, **79**, 147946.
14. Japanese P.49-31956 (1974); Ref.Zhur.Khim., 1975, 8T652.
15. Japanese P.49-31957 (1974); Ref.Zhur.Khim., 1975, 8T653.
16. Japanese P.41028 (1970); Ref.Zhur.Khim., 1972, 4S332.
17. USSR P.910862 (1980); Byul.Izobret., 1982(9), 121.
18. Japanese Appl.53-149188 (1978); Ref.Zhur.Khim., 1980, 11T615.
19. Japanese P.49-7276 (1974); Ref.Zhur.Khim., 1974, 23S601.
20. Japanese P.49-11838 (1974); Ref.Zhur.Khim., 1974, 22S419.
21. H.A.Friedman, Org.Prep.and Proced.Int., 1977, **9**, 209.
22. L.V.Razvodovskaya, A.F.Grapov, and N.N.Mel'nikov, Uspekhi Khim., 1982, **51**, 239 [Russ. Chem.Rev., 1982(2)].
23. USSR P.242167 (1968); Byul.Izobret., 1969(15), 24.
24. US P.3621083 (1971).
25. USSR P.286638 (1969); Byul.Izobret., 1970(34), 214.
26. G.I.Derkach and N.I.Liptuga, Symposium, "Metody Polucheniya Khimicheskikh Reaktivov i Preparatov" (Methods for the Synthesis of Chemical Reagents and Preparations), Izd.IREA, Moscow, 1969, Vol.19, p.55.
27. J.G.Riess and R.Bender, Bull.Soc.chim.France, 1972, 3700.
28. H.R.Allcock, "Phosphorus–Nitrogen Compounds" (Translated into Russian), Izd.Mir, Moscow, 1976.
29. T.Chivers, R.T.Oakley, and N.L.Paddock, J.Chem.Soc.(A), 1970, 2324.
30. H.W.Roessky and E.Janssen, Z.Naturforsch., 1974, **29b**, 174.
31. T.Moeller and R.L.Dieck, Synth.Inorg.and Metal-org.Chem., 1972, **2**(1), 19.
32. R.L.Dieck and T.Moeller, J.Inorg.and Nucl.Chem., 1973, **35**(1), 75.
33. R.L.Dieck and T.Moeller, Inorg.and Nucl.Chem. Letters, 1972, **8**, 763.
34. K.Brantd, V.V.Kireev, V.V.Korshak, and B.R.Tsokolaev, Zhur.Obshch.Khim., 1978, **48**, 358.
35. E.Klei and J.C.Grampel, Z.Naturforsch., 1976, **31b**, 1035.
36. E.Klei and J.C.Grampel, Rec.Trav.chim., 1978, **97**, 307.
37. A.Lopusinski, J.Michalski, and W.J.Stec, Bull. Acad.Pol.Sci.Ser.Sci.chim., 1975, **23**, 229.
38. N.N.Mel'nikov, T.P.Krylova, and I.L.Vladimirova, Zhur.Obshch.Khim., 1977, **47**, 1711.
39. J.Brierley, J.I.Dicktein, and S.Trippett, Phosph. and Sulfur, 1979, **7**, 167.
40. I.V.Konovalova, R.D.Gareev, L.A.Burnaeva, N.K.Novikova, T.A.Faskhutdinova, and A.N.Pudovik, Zhur.Obshch.Khim., 1980, **50**, 1451.

41. E.N.Ofitserov, T.A.Zyablikova, E.S.Batyeva, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1380.
42. A.N.Pudovik, G.V.Romanov, and T.Ya.Stepanova, Zhur.Obshch.Khim., 1979, **49**, 1425.
43. E.Krawczyk, J.Michalski, M.Pakulski, and A.Skowronska, Tetrahedron Lett., 1977, 2019.
44. J.Burski, J.Kieszkowski, J.Michalski, M.Pakulski, and A.Skowronska, Chem.Comm., 1978, 940.
45. Y.Tamura, T.Kawasaki, M.Adachi, M.Tanio, and Y.Kita, Tetrahedron Lett., 1977, 4417.
46. A.Skowronska, M.Pakulski, and J.Michalski, in "International Conference on Phosphorus Chemistry, Halle (GDR)", 1979, p.141.
47. I.M.Kosinskaya, N.P.Pisanenko, and V.I.Kal'chenko, Zhur.Obshch.Khim., 1976, **46**(10), 2227.
48. H.Fedgenhäuer and R.Moll, Z.Chem., 1980, **20**, 141.
49. A.N.Pudovik, R.A.Cherkasov, M.G.Zimin, and R.M.Kamalov, Zhur.Obshch.Khim., 1978, **48**, 2645.
50. M.G.Zimin, R.M.Kamalov, R.A.Cherkasov, and A.N.Pudovik, Zhur.Obshch.Khim., 1982, **52**, 482.
51. M.G.Zimin, R.M.Kamalov, R.A.Cherkasov, and A.N.Pudovik, Phosph.and Sulfur, 1982, **13**, 371.
52. I.Ojima, K.Akiba, and N.Inamoto, Bull.Chem.Soc. Japan, 1969, **42**, 2975.
53. USSR P.726102 (1978); Byul.Izobret., 1980(13), 130.
54. A.Lopusinski and J.Michalski, Bull.Acad.Pol.Sci. Ser.Sci.Chim., 1975, **23**, 411.
55. British Appl.205319 (1981); Chem.Abs., 1981, **95**, 97048.
56. USSR P.819110 (1979); Byul.Izobret., 1981(13), 98.
57. I.V.Konovalova, L.A.Burnaeva, I.K.Novikova, O.S.Kedrova, and A.N.Pudovik, Zhur.Obshch. Khim., 1981, **51**, 995.
58. N.A.Razumova and F.V.Bagrov, Zhur.Obshch. Khim., 1970, **40**, 1241.
59. A.Skowronska and M.Pakulski, in "International Conference on Phosphorus Chemistry, Halle (GDR)", 1979, p.422.
60. A.Lopusinski, J.Michalski, and W.J.Stec, Angew. Chem., 1975, **87**, 134.
61. A.Lopusinski, J.Michalski, and W.J.Stec, Bull. Acad.Pol.Sci.Ser.Sci.Chim., 1975, **23**, 235.
62. J.Michalski, A.Lopusinski, W.J.Stec, and W.Fluck, Z.Naturforsch., 1976, **31b**, 1431.
63. J.Michalski, A.Lopusinski, and L.Luczak, "IX Mezhdunarodnyi Simpozium po Khimii Organicheskikh Soedinenii Sery" (The IXth International Symposium on the Chemistry of Organosulphur Compounds), Riga, 1980, p.164.
64. G.I.Derkach, Zh.M.Ivanova, and N.I.Liptuga, Symposium, "Khimiya Organicheskikh Soedinenii Fosfora (Zhurnal Obshchei Khimii)" [The Chemistry of Organophosphorus Compounds (Journal of General Chemistry)], Izd.Nauka, Leningrad, 1967, p.72.
65. S.Treppendahl, P.Jakobsen, and J.Wieczorkowski, Acta Chem.Scand., 1974, **28**, 657.
66. A.J.Wagner and T.Moeller, J.Chem.Soc.A, 1971, 596.
67. R.A.Spencer, J.M.Swan, and S.H.Wright, Austral. J.Chem., 1969, **22**, 2359.
68. J.B.Faught, T.Moeller, and I.C.Paul, Inorg.Chem., 1970, **9**, 1656.
69. J.B.Faught, Canad.J.Chem., 1972, **50**, 1315.
70. D.W.H.Rankin and S.J.Cyvin, J.Chem.Soc., Dalton Trans., 1972, 1277.
71. S.Cradock, E.A.V.Ebsworth, M.L.McConnell, D.W.H.Rankin, and M.R.Todd, J.Chem.Soc., Dalton Trans., 1977, 1925.
72. S.Cradock and D.W.H.Rankin, J.Chem.Soc., Faraday Trans.II, 1972, 940.
73. P.D.Blair, J.Mol.Structure, 1983, **97**, 147.
74. E.Duff, S.Trippett, and P.J.Whittle, J.Chem. Soc., Perkin Trans.I, 1973, 972.
75. USSR P.700519 (1978); Byul.Izobret., 1979(44), 100.
76. I.V.Konovalova, N.V.Mikhailova, R.D.Gareev, L.A.Burnaeva, T.V.Anufrieva, and A.N.Pudovik, Zhur.Obshch.Khim., 1981, **51**, 989.
77. I.V.Konovalova, N.V.Mikhailova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., 1982, **52**, 1290.
78. I.V.Konovalova, M.V.Cherkina, E.G.Yarkova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch. Khim., 1981, **51**, 993.
79. I.V.Konovalova, L.A.Burnaeva, N.M.Kashtanova, and A.N.Pudovik, Zhur.Obshch.Khim., 1982, **52**, 1965.
80. N.A.Razumova, A.A.Petrov, and Zh.L.Evtikhov, Zhur.Obshch.Khim., 1968, **38**, 2542.
81. N.A.Razumova, Zh.L.Evtikhov, and A.A.Petrov, Zhur.Obshch.Khim., 1969, **39**, 1419.
82. USSR P.722918 (1978); Byul.Izobret., 1980(11), 83.
83. I.Ojima and N.Inamoto, Chem.Comm., 1970, 1629.
84. G.Tomaschewski and D.Zanke, Z.Chem., 1970, **10**, 145.
85. A.Schmidpeter and T.Griegern, Angew.Chem., 1978, **90**, 469.
86. A.N.Pudovik and M.G.Zimin, Uspekhi Khim., 1983, **52**, 1803 [Russ.Chem.Rev., 1983(11)].
87. A.Aripov, A.F.Grapov, and N.N.Mel'nikov, Symposium, "Sintez i Primenenie Novych Khimicheskikh Preparatov Protiv Vilta Khlopchatnika" (The Synthesis and Applications of New Chemical Preparations against Cotton Wilt), Tashkent, Uzbekistan, 1975, p.12.
88. L.V.Razvodovskaya, A.F.Grapov, S.I.Orlov, E.Sh.Khasan'yanova, and N.N.Mel'nikov, Zhur. Obshch.Khim., 1980, **50**, 329.
89. G.I.Derkach and N.I.Liptuga, Symosium, "Metody Polucheniya Khimicheskikh Reaktivov i Preparatov" (Methods for the Synthesis of Chemical Reagents and Preparations), Izd.IREA, Moscow, 1969, Vol.19, p.53.
90. Y.Tamura, T.Kawasaki, M.Tanio, and Y.Kita, Chem.Ind., 1978, 806.
91. Y.Tamura, M.Adachi, T.Kawasaki, and Y.Kita, Tetrahedron Lett., 1978, 1753.
92. Y.Tamura, T.Kawasaki, M.Tanio, and Y.Kita, Synthesis, 1979, 120.
93. Y.Tamura, T.Kawasaki, M.Adachi, and Y.Kita, Synthesis, 1979, 887.
94. Y.Tamura, T.Kawasaki, N.Gohda, and Y.Kita, Tetrahedron Lett., 1979, 1129.
95. Y.Tamura, T.Kawasaki, M.Adachi, and Y.Kita, Chem.Pharm.Bull., 1979, **27**, 1636.
96. Y.Tamura, Y.Kita, and T.Kawasaki, J.Synth.Org. Chem.Jap., 1980, **38**, 891.
97. Y.Tamura, M.Adachi, T.Kawasaki, H.Yasuda, and Y.Kita, J.Chem.Soc., Perkin Trans.I, 1980, 1132.
98. Y.Tamura, T.Kawasaki, H.Yasuda, N.Gohda, and Y.Kita, J.Chem.Soc., Perkin Trans.I, 1981, 1577.
99. US P.3691283 (1972); Chem.Abs., 1972, **77**, 156345.
100. US P.3671631 (1972).
101. Acc.British Appl.1321368 (1973); Izobr.za Rub., 1973, **15**(1), 12.
102. South African P.6801720 (1968); Chem.Abs., 1969, **70**, 86572.

103. US P.3719757 (1973).
104. US P.3528975 (1970).
105. US P.3719700 (1973).
106. South African P.6801064 (1968); Chem.Abs., 1969, **70**, 77933.
107. M.G.Zimin, R.M.Kamalov, M.M.Afanas'ev, and A.N.Pudovik, Zhur.Obshch.Khim., 1985, **55**, 506.
108. USSR P.449060 (1972); Byul.Izobret., 1974(41), 49.
109. V.F.Toropova, G.A.Lazareva, M.G.Zimin, and R.M.Kamalov, Zhur.Anal.Khim., 1983, **38**, 1574.
110. G.Tomaschewski and D.Zanke, Z.Chem., 1970, **10**, 117.
111. US P.4065466 (1977).
112. US P.4067882 (1978).
113. US P.3519709 (1970).
114. US P.3476837 (1969).
115. BRD Appl.2726128 (1977); Chem.Abs., 1978, **88**, 105302.
116. BRD Appl.2726129 (1977); Chem.Abs., 1978, **88**, 105303.
117. US P.3705211 (1972).
118. US P.3852397 (1974).
119. BRD Appl.2408697 (1974); Chem.Abs., 1974, **81**, 169167.
120. A.I.Ginak, K.A.V'yunov, E.G.Sochilin, G.M.Sheshina, T.V.Ratnikova, and V.N.Lepilin, Trudy Leningrad.Tekhnol.Inst.im.Lensoveta, 1975, **5**(1), 6.
121. USSR P.977459 (1981); Byul.Izobret., 1982(44), 94.
122. USSR P.959405 (1981); Byul.Izobret., 1982(45), 283.
123. BRD P.1138389 (1963).
124. BRD P.1141277 (1963).
125. Japanese P.24399 (1963); Ref.Zhur.Khim., 1966, 8N472.
126. G.A.Kutyrev, A.V.Lygin, R.A.Cherkasov, and A.N.Pudovik, Zhur.Obshch.Khim., 1982, **52**, 501.
127. D.Hoppe, Angew.Chem., 1973, **85**, 909.
128. G.E.Struve, C.Gazzola, and G.L.Kenyon, J.Org. Chem., 1977, **42**, 4035.
129. US P.3470207 (1969).
130. US P.3553319 (1971).
131. US P.4070372 (1978).
132. French Appl.2413395 (1979); Ref.Zhur.Khim., 1980, 18O264.
133. Belgian P.862479 (1978); Chem.Abs., 1979, **90**, 38903.
134. Dutch P.7712731 (1979); Chem.Abs., 1979, **91**, 135625.
135. B.P.1569224 (1980).
136. Swiss P.632275 (1982).
137. BRD Appl.2727550 (1970); Chem.Abs., 1979, **90**, 121395.
138. US P.3660413 (1972).
139. US P.3992373 (1976).
140. Polish P.108330 (1981).
141. F.I.Abdel-Hay, M.A.Omara, A.A.El-Barbary, and M.El-Badawi, Z.Naturforsch., 1979, **34b**, 297.
142. BRD P.2405894 (1974); Chem.Abs., 1975, **82**, 43439.
143. BRD Appl.2708863 (1977); Chem.Abs., 1978, **88**, 22431.
144. BRD Appl.2728321 (1978); Chem.Abs., 1978, **88**, 120771.
145. BRD Appl.2739215 (1978); Chem.Abs., 1978, **89**, 24005.
146. US P.4076809 (1978).
147. US P.4086336 (1978); Chem.Abs., 1978, **89**, 108754.
148. US P.4139614 (1979).
149. US P.4170648 (1979).
150. US P.4234575 (1980).
151. US P.4239708 (1980).
152. US P.4269829 (1981).
153. US P.4276290 (1981).
154. Polish P.101294 (1979).
155. US P.4087521 (1978).
156. US P.4259330 (1981).
157. US P.4120957 (1978).
158. US P.3904654 (1975).
159. Japanese P.4440 (1969); Ref.Zhur.Khim., 1970, 1N718.
160. Japanese P.48-40744 (1973); Ref.Zhur.Khim., 1974 18N631.
161. Japanese P.50-20127 (1975); Ref.Zhur.Khim., 1975, 20O353.
162. Japanese P.54-14170 (1979); Ref.Zhur.Khim., 1980, 10O342.
163. L.M.Myl'nikova, Ya.A.Mandel'baum, and R.S.Soifer, Zhur.Obshch.Khim., 1980, **50**, 1319.
164. Ru-Yu Chen and Hu Shi-xian, in "Conf.internat.de chimie du phosphore, Nice (France)", 1983, Abstracts, Poster 20.
165. USSR P.368274 (1971); Byul.Izobret., 1973(9), 95.
166. US P.4137310 (1979); Chem.Abs., 1979, **90**, 186634.
167. Japanese Appl.53-34724 (1978); Ref.Zhur.Khim., 1979, 5O316.
168. BRD Appl.2847064 (1980); Ref.Zhur.Khim., 1981, 9O50.
169. Europ.Pat.Appl.1949 (1979); Chem.Abs., 1980, **92**, 25353.
170. USSR P.876701 (1980); Byul.Izobret., 1981(40), 98.
171. US P.3965127 (1976).
172. US P.3980618 (1976).
173. USSR P.632702 (1977); Byul.Izobret., 1978(42), 86.
174. USSR P.896119 (1980); Byul.Izobret., 1982(1), 136.
175. USSR P.828010 (1978); Byul,Izobret., 1981(17), 179.
176. G.A.Lazareva, M.G.Zimin, R.G.Islamov, R.M.Kamalov, and V.F.Toropova, Symposium, "Fosfororganicheskie Soedineniya i Polimery" (Organophosphorus Compounds and Polymers), Izd.Chuvash.Gos.Univ., Cheboksary, 1983, p.547.
177. I.Ojima, T.Iwamoto, T.Onishi, N.Inamoto, and K.Tamaru, Chem.Comm., 1969, 1501.
178. I.Ojima, T.Onishi, N.Inamoto, and K.Tamaru, Bull. Chem.Soc.Japan, 1971, **44**, 2150.
179. L.Ya.Bogel'fer, A.F.Grapov, V.V.Negrebetskii, V.N.Zontova, and N.N.Mel'nikov, Zhur.Obshch. Khim., 1981, **51**, 1203.
180. G.Tomaschewski and D.Zanke, Z.Chem., 1971, **11**, 384.
181. BRD Appl.2346241 (1974); Chem.Abs., 1974, **81**, 37407.
182. Swiss P.596228 (1978); Chem.Abs., 1978, **89**, 24007.
183. USSR P.407891 (1971); Byul.Izobret., 1973(47), 81.
184. US P.3845176 (1974).
185. USSR P.535755 (1973); Byul.Izobret., 1976(43), 167.
186. A.Ziegler, V.P.Botha, and I.Haiduc, Inorg.Chim. Acta, 1975, **15**(2), 123.
187. USSR P.410009 (1972); Byul.Izobret., 1974(1), 80.
188. US P.4229383 (1980).
189. H.-J.Jahns, Z.Chem., 1970, **10**, 435.
190. N.N.Mel'nikov, L.V.Razvodovskaya, N.N.Vorob'eva, V.D.Li, T.A.Karaseva, G.V.Golovkin, L.Ya.Bogel'fer, V.V.Negrebetskii, and A.F.Grapov, Zhur.Obshch.Khim., 1983, **53**, 1693.
191. USSR P.411082 (1971); Byul.Izobret., 1974(2), 76.

192. M.Mikolajczyk, P.Kielbasinski, and Z.Goszczynska, J.Org.Chem., 1977, **42**, 3629.
193. M.Mikolajczyk and P.Kielbasinski, Tetrahedron, 1981, **37**, 233.
194. C.Blonski, M.B.Gasc, A.Klaebe, J.J.Perie, R.Roques, J.P.Declarcq, and G.Germain, J.Chem. Soc., Perkin Trans.II, 1982, 7.
195. C.Blonski, M.B.Gasc, A.Klaebe, and J.J.Perie, Tetrahedron Lett., 1982, **23**, 2773.
196. G.Etemad-Moghadam, C.Blonski, M.B.Gasc, J.J.Perie, and A.Klaebe, Phosph.and Sulfur, 1983, **14**, 367.
197. P.Kielbasinski, A.Sut, and M.Mikolajczyk, "IX Mezhdunarodnyi Simpozium po Khimii Organicheskikh Soedinenii Sery" (The IXth International Symposium on the Chemistry of Organosulphur Compounds), Riga, 1980, p.182.
198. J.Karolak-Wojciechowska, M.W.Wieczorek, M.Mikolajczyk, A.Sut, P.Kielbasinski, Y.T.Struchov, and M.Y.Antipin, Acta Cryst., 1983, C**39**, 587.
199. M.Mikolajczyk, P.Kielbasinski, and W.Basinski, J.Org.Chem., 1984, **49**, 899.
200. USSR P.435248 (1972); Byul.Izobret., 1974(25), 82.
201. USSR P.368275 (1971); Byul.Izobret., 1973(9), 95.
202. USSR P.411091 (1972); Byul.Izobret., 1974(2), 78.
203. R.G.Islamov, M.G.Zimin, R.M.Kamalov, I.S.Pominov, and A.N.Pudovik, Zhur.Obshch.Khim., 1983, **53**, 2659.
204. J.Karolak-Wojciechowska, M.Wieczorek, M.Mijolajczyk, P.Kielbasinski, Y.T.Struchkov, and M.Y.Antipin, Acta Cryst., 1979, **35**, 877.
205. J.Karolak-Wojciechowska, M.W.Wieczorek, Y.T.Struchkov, M.Y.Antipin, M.Mikolajczyk, P.Kielbasinski, and A.Sut, Phosph.and Sulfur, 1983, **17**, 141.
206. Czech P.181950 (1980); Ref.Zhur.Khim., 1981, 7N119.
207. L.Kuruc, Š.Truchlin, and Š.Kovač, Chem.Zvesti, 1978, **32**, 524.
208. L.Kuruc, Š.Kovač, Š.Truchlin, V.Konečny, and J.Sustek, Chem.Zvesti, 1979, **33**, 803.
209. L.Kuruc, V.Konečny, Š.Kovač, Š.Truchlin, and M.Kurucova, Chem.Zvesti, 1980, **34**, 668.
210. L.Kuruc, V.Konečny, Š.Kovač, and Š.Truchlin, Chem.Zvesti, 1981, **35**, 373.
211. V.A.Aleksenko, M.M.Kremlev, and V.I.Dulova, Vop.Khim.i Khim.Tekhnol., 1979(53), 6.
212. G.Tomaschewski, B.Breitfeld, and D.Zanke, Tetrahedron Lett., 1969, 3191.
213. A.F.Grapov, V.N.Zontova, and N.N.Mel'nikov, Dokl.Akad.Nauk SSSR, 1980, **251**, 882.
214. V.N.Zontova, A.F.Grapov, and N.N.Mel'nikov, Zhur.Obshch.Khim., 1982, **52**, 64.
215. DDR P.71659 (1970).
216. US P.3714176 (1973).
217. US P.3803312 (1974).
218. US P.3876781 (1975).
219. US P.3880998 (1975).
220. BRD Appl.2316185 (1974); Ref.Zhur.Khim., 1975, 12O429.
221. I.N.Azerbaev, L.T.Kalkabaeva, and L.A.Tsoi, Symposium, "Khimiya Atsetilena i Tekhnologiya Karbida Kal'tsiya" (The Chemistry of Acetylene and the Technology of Calcium Carbide), Alma-Ata, Kazakhstan, 1972, p.155.
222. I.N.Azerbaev, L.T.Kalkabaeva, and L.A.Tsoi, Symposium, "Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena" (Reports at the IVth All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol.1, 159.
223. V.I.Dulova, M.M.Kremlev, and V.A.Aleksenko, Zhur.Neorg.Khim., 1974, **19**, 441 [Russ.J.Inorg. Chem., 1974(2)].

Ul'yanov-Lenin Kazan State University