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Structure and Reactivity of Esters of Thio-acids of Three-coordinated Phosphorus

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The structure and the chemical behaviour of thio-esters of three-coordinated phosphorus $R_nP(SR')_{3-n}$ ($n = 0-2$) are examined, and their reactions are discussed with electrophilic reagents differing both in the number and in the nature of the electrophilic centres. The peculiar character of such reactions is due primarily to the presence of two competing nucleophilic centres to the ambidenticity of the phosphorus(III)-sulphur(II) group, and to the high reactivity of two-coordinated sulphur (thionic and thiolic) in esters of three- and four-coordinated phosphorus. A list of 170 references is included.

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I. INTRODUCTION

The chemistry of derivatives of three-coordinated phosphorus is now a well studied field. Structural features and regularities in the chemical behaviour of these compounds have been quite widely discussed in several review papers [1-4] and in monographs published during recent years [5-8].

The structure and the reactivity of compounds of three-coordinated phosphorus containing a phosphorus–sulphur bond have either not been discussed at all in these works [5] or have been only incompletely considered [4,7,8]. However, esters of thio-acids of phosphorus have extremely characteristic properties, distinguishing them strongly from the well studied oxygen analogues. The few papers and their contradictions prevented until recently a comprehensive view of the reactivity of these compounds. Only a series of investigations on the interaction between these esters and several electrophilic reagents, published during recent years, have made it possible to note several general rules controlling these processes.

Esters of thio-acids of three-coordinated phosphorus possess two nucleophilic reaction centres—phosphorus and sulphur—the main feature of the bond between these atoms being that both elements belong to the third period and have electron shells of closely similar structure. Hence considerable competition may be expected between the two atoms in intramolecular donor–acceptor interaction, as well as in reactions with electrophilic and nucleophilic reagents.

The literature shows no abatement of the controversy on the bond structure and intramolecular donor–acceptor interactions in compounds of elements in the third period—silicon, phosphorus, sulphur, and chlorine—especially on the capacity of the lone pairs of electrons on phosphorus(III) and sulphur(II) atoms for p,π and p,d interaction. Some workers [6,9-24] have attempted not only to detect but also in several cases to estimate a $+M$ effect in phosphorus(III), whereas others [3,7,25] give results that they regard as evidence of the absence of such an effect. It has been assumed that the p,π effect of sulphur(II) is slight [16, 26-28], but larger than that of phosphorus [3].

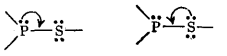
The legitimacy of using ideas on the participation of d orbitals in forming chemical bonds of both σ and π types has also been discussed. Several workers consider [26,29-35] that even with phosphorus(III) and sulphur(II) the possibility of the participation of $3d$ orbitals in hybridisation cannot be completely excluded. The involvement of d orbitals in π bonding explains several peculiarities of compounds of elements in the third period in comparison with the corresponding compounds of elements in the second period [3,36-43]. In the view of other authors [44-46] the role of d orbitals cannot be significant because of their high energy. Attempts have recently been made to explain the peculiarity of compounds of elements in the third period without regard to the main structural feature—the presence of vacant d orbitals in the valency layer—of the electron shells of their atoms [47-51]. The opinion has been expressed [51] that the d-orbital concept cannot be correctly used in describing structural features of compounds of elements in the third period.

Within the scope of the method of molecular orbitals the concept of the participation of d orbitals need not in general be introduced into the description of bond formation in molecules containing phosphorus with coordination numbers 3–6. In the valence bond method, which retains the classical structural formula with its two-centre, two-electron bond, d orbitals are enlisted both for describing bonds and in the theory of electron displacements (p,d and π,d effects). In the discussion of the acceptor properties of phosphorus an attempt has been made to replace the d-orbital concept ($-M$ effect of the phosphorus atom) by that of a negative hyperconjugation effect [51]. At the present time, however, such substitution of one effect by another hardly changes the situation with respect to qualitative ideas on electron displacements in organic molecules.

Data on intramolecular donor–acceptor effects in compounds containing phosphorus–phosphorus and sulphur–sulphur bonds are of especial interest in connection with this problem. The ultraviolet spectra of cyclopolyphosphines have been interpreted [52-57] as supporting a $+M$ effect, which is justified also by quantum-mechanical calculations [54]. Similarly in diphosphines, also on the basis of ultraviolet spectra, the possibility of combined p,d effects has been suggested [58], as a consequence of which both phosphorus atoms are simultaneously donors and acceptors of lone pairs of electrons, which is apparent

in the chemical properties of diphosphines[59]. Similar effects are assumed in natural sulphur, in dihydrogen disulphide, and in dialkyl disulphides[26], and are confirmed also by the abnormally high energy of dissociation of the sulphur–sulphur bond[26,60].

Similarly, the group $>\ddot{P}-\ddot{S}-$ is an ambident system, in which two types of mesomeric displacements



may theoretically occur, the first representing a $+M$ effect and the second a $-M$ effect of the phosphorus atom. In terms of the theory of resonance the ambident system is a resonance hybrid of three structures:

$$>\ddot{P}-\ddot{S}- \leftrightarrow >\overline{P}..=\overset{+}{S} \leftrightarrow >\overset{+}{P}=\overline{S}: .$$

A qualitative estimate has been made of the donor–acceptor interactions in the phosphorus–sulphur bond[61], which are obviously determined primarily by the energies of the highest occupied orbitals and the lowest vacant orbitals of both atoms. Comparison of data[62] on ionisation potentials, electron affinities, and electronegativities of phosphorus and sulphur atoms (Table 1) indicates that sulphur possesses more clearly defined electron-accepting properties ($-I$ and $-M$ effects) than does the phosphorus atom.

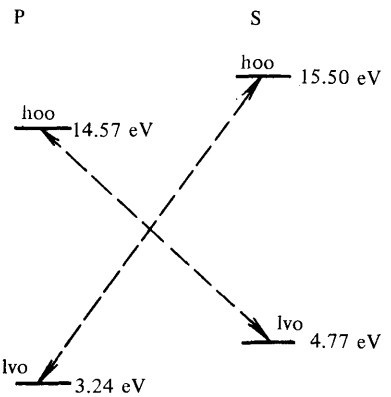


Figure 1. Relative arrangement of highest occupied orbitals (hoo) and lowest vacant orbitals (lvo) of phosphorus and sulphur atoms†.

The energy difference between the highest occupied level of phosphorus and the lowest vacant level of sulphur is actually smaller than the corresponding energy difference between sulphur and phosphorus (9.8 and 12.26 eV—Fig. 1)†. Hence electron displacements towards the sulphur atom are energetically more probable. However, the opposite interaction cannot be completely excluded[63]. This is made still more probable by the negative inductive and mesomeric effects of sulphur conferring a considerable positive charge on the phosphorus, which may be partly balanced by reverse π bonding. Quite a high degree of delocalisation of electron shells may be expected in such a system from the close proximity of the energy states of phosphorus and sulphur atoms.

† Broken lines are drawn in Fig. 1 to indicate probable electron displacements, not the transfer of an electron from one energy level to another.

Table 1. Ionisation potentials I, valency electron affinities A, and orbital electronegativities Oel of atoms (for the sp^3-hybrid state)[62].

Element	I, eV	A, eV	Oel
Phosphorus	14.57	3.24	2.79
Sulphur	15.50	4.77	3.21

II. ELECTRONIC EFFECTS IN ESTERS OF THIO-ACIDS OF THREE-COORDINATED PHOSPHORUS

The question of electron displacements in compounds $R_nP(SR')_{3-n}$ is probably part of the more general problem, already discussed in a review[3] and in several papers[15,64], of the nature of the interaction of a three-coordinated phosphorus atom with substituents containing a π-electron system. Among the latter are e.g. the phenyl, vinyl, and ethynyl radicals, the carbonyl group, and obviously groups containing a two-coordinated sulphur atom. It may be supposed that the phosphorus atom in such systems is able to develop both donor and acceptor properties. No generally accepted opinion has yet been reached on which of these effects is inherent in a three-coordinated phosphorus atom in a static (non-reacting) molecule[15,64,65].

Probably no definite conclusions on the direction of electron displacements can at present be drawn from data on dipole moments. The contradictoriness of published values[66–75] is not surprising, since the dipole moment of a molecule is a function of several factors acting simultaneously, whose combined effect is extremely difficult to assess[76,77]. In molecules containing atoms having lone pairs of electrons the dipole moment depends not only on the dimensions, the electronegativities of the atoms, and the bond angles, but mainly on the type of hybridisation of the orbital of the lone pair. Several authors[69,72] made calculations having equated the dipole moment of the lone pair to that of the phosphorus–carbon bond, which can hardly be accepted as correct[77]. The type of hybridisation has been taken into account in calculating dipole moments for several phosphorus(III) compounds[73–75]. However, a method of calculation[78] that had been criticised[31] was used to determine the character of the hybridisation. Nor do the ultraviolet spectra provide an unambiguous indication of the nature of the conjugation in aromatic phosphines[3,6,7,58,79–84].

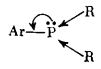
Electronic effects in compounds containing three-coordinated phosphorus have been discussed in terms of proton and phosphorus-31 nuclear magnetic resonance[35,72,85–91]. Attempts were made[87–91] to relate the phosphorus-31 chemical shifts wich such parameters as the electronegativities of substituents, bond angles, degree of π bonding, type of hybridisation, character of the lone pair, etc. However, it has not yet proved possible to develop a general theory relating the chemical shift of the phosphorus atom with the structure of the molecules. The most comprehensive investigation[35] also is evidently not free from defects, and has been criticised by several workers[90,92,93].

Nevertheless, certain considerations pertaining to the character of possible interactions of a three-coordinated

phosphorus atom with the π-electron system of an aromatic ring can be expressed on the basis of published ^{31}P n.m.r. data [72,94,95]. Table 2 lists a series of compounds (Nos. 1–9) in which replacement of an alkyl by a phenyl group leads to a down-field shift in the phosphorus-31 resonance signal, e.g.

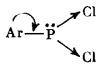
$$\underset{+20.4\text{ ppm}}{(C_2H_5)_3P} > \underset{+16.0\text{ ppm}}{(C_2H_5)_2P{-}C_6H_5} > \underset{+8.0\text{ ppm}}{(C_6H_5)_3P}\ .$$

A low-field displacement of a signal can be attributed to an inductive effect. However, the ethyl and phenyl groups have closely similar electronegativities (2.6 and 2.8), [96,97] differing little from that of the phosphorus atom itself (2.79 for tetrahedral hybridisation [62]). This donor effect may perhaps be regarded as a consequence of p,π conjugation of the lone pair of the phosphorus with the aromatic ring, which is favoured by $+I$ effects of the alkyl groups:



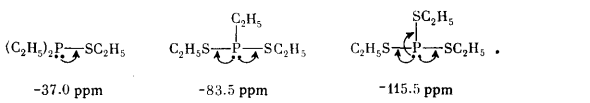
The alkoxycarbonyl group in compounds of the type R_2PCOOR' has a strong electron-accepting action [98], as is indicated by the down-field shift in the resonance signal of the phosphorus nucleus (compounds No. 21–23 compared with No. 1 in Table 2), the infrared absorption by the carbonyl group at 1695–1685 cm^{-1}, and certain chemical properties of such compounds. Acetyl phosphides exhibit [100,101] opposite electron displacements, perhaps promoted by the $+I$ effect of the alkyl groups.

On the other hand, the presence of strongly electron-accepting groups (e.g. halogen atoms) attached to the phosphorus atom produces a high-field shift in the resonance signals when ethyl is replaced by phenyl (compounds No. 10–20 in Table 2), which can probably be explained by a π,d effect:



Comparison of values of $\delta(^{31}P)$ in several series—(I) Nos. 24 and 25, (II) 26 and 27, and (III) 28 and 29 in Table 2—shows that, relative to propenyl, an alkyl group displaces the resonance signal up-field in the presence of such electron-accepting groups as chloro, alkoxyl, and dialkylamino attached to the phosphorus [99]. Unfortunately, the correlation between $\delta(^{31}P)$ and the structure of substituents bound to the phosphorus atom is satisfactory only for a limited number of compounds of similar structure, and available data are insufficient for final conclusions to be reached.

Comparison of the chemical shifts of phosphorus nuclei in a series of tervalent thio-esters (Table 3) permits an analogous discussion of the electron displacements (in terms of inductive and mesomeric effects) in the ground state of molecules [19,61] in conformity with the above structure of the phosphorus–sulphur bond. Experimental values of $\delta(^{31}P)$ suggest that one or other type of electron displacement will develop (predominate) depending on the nature of the groups R and R', as well as on the number of sulphur atoms combined with the phosphorus (Table 3). In all the series investigated [19,61] the successive replacement of alkyl or phenyl by alkylthio (phenylthio) results in a down-field shift in the resonance signal—Table 3, series (I), compounds No. 1, 5, and 15); (II) Nos. 3, 4, and 15; and (III) Nos. 2, 9, and 13—so that the donor effect of the phosphorus increases with the number of alkylthio-groups because of the strong electron-accepting properties of the sulphur atom, e.g.



Similarly, the replacement of alkylthio by phenylthio produces a low-field shift of the resonance signal in all the cases examined, which is obviously due to the more strongly developed electron-accepting properties of the phenylthio-group—series (I), Nos. 1 and 2, (II) Nos. 4 and 7, (III) Nos. 5 and 9, (IV) Nos. 11 and 12, and (V) Nos. 13 and 15—but in several cases—(I) Nos. 1, 3, and 16; (II) Nos. 4 and 5, and (III) Nos. 7 and 9—a high-field shift of the phosphorus-31 resonance signal is observed.

Strengthened shielding of the phosphorus nucleus can evidently be attributed to displacement of electrons as in the π,d effect, e.g. in the sequence

$$\underset{-37\text{ ppm}}{(C_2H_5)_2PSC_2H_5} < \underset{-32.5\text{ ppm}}{(C_2H_5)(C_6H_5)PSC_2H_5} < \underset{-26.5\text{ ppm}}{(C_6H_5)_2PSC_2H_5}$$

Table 2. Phosphorus-31 chemical shifts in compounds PXYZ.

No.	X	Y	Z	δ, ppm	Ref.	No.	X	Y	Z	δ, ppm	Ref.
1	C_2H_5	C_2H_5	C_2H_5	+20.4	94	16	Cl	Cl	ClC_6H_4	−158.5*	–
2	C_2H_5	C_2H_5	C_6H_5	+16.0	94	17	Cl	C_6H_5	C_2H_5	−119.0*	–
3	C_6H_5	C_6H_5	C_6H_5	+8.0	94	18	Cl	C_6H_5	C_6H_5	−81.5*	–
				+5.6	72	19	Br	C_2H_5	C_2H_5	−117.0	94
4	H	CH_3	C_2H_5	+77.5	94	20	Br	C_6H_5	C_6H_5	−70.0	94
5	H	CH_3	C_6H_5	+72.4	94	21	C_2H_5	C_2H_5	$COOCH_3$	+8.0	98
6	C_2H_5	C_2H_5	ClC_6H_4	+15.9	72	22	C_2H_5	C_2H_5	$COOC_2H_5$	+9.6	93
7	C_6H_5	C_6H_5	ClC_6H_4	+6.6	72	23	C_2H_5	C_2H_5	$COOC_3H_7$	+9.6	98
8	C_2H_5	C_2H_5	$CH_3OC_6H_4$	+17.6	72	24	C_3H_5	$N(CH_3)_2$	$N(CH_3)_2$	−98.0	99
9	C_6H_5	C_6H_5	$CH_3OC_6H_4$	+6.1	72	25	C_3H_7	$N(CH_3)_2$	$N(CH_3)_2$	−102.0	99
10	Cl	Cl	C_6H_5	−166*	–	26	C_3H_5	OC_3H_7	OC_3H_7	−151.0	99
11	Cl	Cl	C_2H_5	−196*	–	27	C_3H_7	OC_3H_7	OC_3H_7	−157.0	99
12	Br	Br	C_6H_5	−152	94	28	C_3H_5	Cl	Cl	−159.0	99
13	Br	Br	C_2H_5	−194	94	29	C_3H_7	Cl	Cl	−135.0	99
14	Cl	CH_3	C_6H_5	−83.4	94						
15	Cl	CH_3	C_2H_5	−105.2*	–						

*Values obtained in our laboratory.

Table 3. Phosphorus-31 chemical shifts in compounds PXY(SR).[61]

No.	X	Y	SR	δ, ppm	No.	X	Y	SR	δ, ppm
1	C_2H_5	C_2H_5	SC_2H_5	−37.0	9	C_2H_5	SC_6H_5	SC_6H_5	−100.0
2	C_2H_5	C_6H_5	SC_6H_5	−39.0	10	C_4H_9	SC_2H_5	SC_2H_5	−80.5
3	C_6H_5	C_6H_5	SC_2H_5	−26.5	11	CH_3	SC_2H_5	SC_2H_5	−71.0
4	C_6H_5	SC_2H_5	SC_2H_5	−75.0	12	CH_3	SC_6H_5	SC_2H_5	−86.5
5	C_2H_5	SC_2H_5	SC_2H_5	−83.5	13	SC_6H_5	SC_6H_5	SC_6H_5	−180.0
6	C_6H_5	SC_3H_7	SC_3H_7	−78.0	14	SCH_3	SCH_3	SCH_3	−125.0
7	C_6H_5	SC_6H_5	SC_6H_5	−90.0	15	SC_2H_5	SC_2H_5	SC_2H_5	−115.5
8	C_3H_7	SC_2H_5	SC_2H_5	−81.0	16	C_2H_5	C_6H_5	SC_2H_5	−32.5

Thus in this series of compounds phosphorus exhibits acceptor properties towards the phenyl radical.

Hence the ^{31}P n.m.r. data listed in Tables 2 and 3 indicate that three-coordinated phosphorus may develop either a donor or an acceptor character depending on the nature of the substituents.

Alkyl groups (ethyl, propyl, butyl) make almost the same contribution to the resonance signal, as is indicated by closely similar values of $\delta(^{31}P)$ for compounds Nos. 5, 8, and 10 in Table 3. An exception is the methyl group, which causes a larger up-field shift of the resonance signal than does phenyl—series (I) Nos. 11 and 4, and (II) Nos. 12 and 7. Similarly strong shielding of the phosphorus nucleus by a methyl group has been explained[71] by hyperconjugation:

$$H_3CP(SR')_2 \leftrightarrow H^+CH_2^-P(SR')_2 .$$

Several workers have shown[102-117] that the phosphorus atom is able to exhibit both a definite acceptor and a donor character even in a dynamic state. This is especially apparent in reactions in which the phosphorus, while not acting as a reaction centre, helps to stabilise the transition state. In some cases[112,113,118] phosphorus exerts an acceptor effect, and the carbanions formed in the reaction are stabilised by *d*-orbital resonance. A similar *d*-orbital effect is observed with silicon and sulphur atoms in the reactions of vinylsilanes[119] and vinyl sulphides[26,120]. In other cases[17,109,110], however, the low energy barrier to pyramidal inversion in certain three-coordinated phosphorus derivatives has been attributed to considerable strengthening in the transition state of the donor effect of phosphorus(III) in the static molecule. According to modern ideas in theoretical chemistry, dynamic electronic effects do not necessarily operate in the same direction as electron displacements in the static molecule[121].

III. DUAL REACTIVITY (AMBIDENTICITY) OF PHOSPHORUS(III) THIO-ACIDS TOWARDS ALKYL HALIDES

Compounds containing a $\rangle\ddot{P}-\ddot{S}-$ group occupy a special place among ambident derivatives of three-coordinated phosphorus such as esters, amides, and thioesters. Two types of reactions—electrophilic addition A_E at the lone pair and nucleophilic substitution S_N—characterise derivatives of three-coordinated phosphorus in conformity with the special structure of its electron shell and depending on the structure of its nearest neighbours and the nature of the reagent[4-6,102]. The same types of reactions occur readily also with compounds containing two-coordinated sulphur[26]. Because of the close similarity in the electron configurations of phosphorus and sulphur atoms, the mechanisms of their reactions should have much in common. This must obviously be borne in mind when considering the interaction of the esters $R_nP(SR')_{3-n}$ with electrophilic reagents.

1. Ability of Esters $R_nP(SR')_{3-n}$ to form Onium Derivatives

An element possessing a lone pair of electrons is able to form onium—oxonium, ammonium, phosphonium, sulphonium, etc.—compounds on reaction with electrophilic reagents. Esters of type $R_nP(SR')_{3-n}$ can therefore reasonably be expected to form onium derivatives of two types—quasi-phosphonium and quasi-sulphonium[122-124]:

$$\rangle\ddot{P}-\ddot{S}-R' + R''X \rightarrow \left[\rangle P\begin{matrix}R''\\ \ddot{S}R'\end{matrix}\right]^+X^- ,$$

(I)

$$\rangle\ddot{P}-\ddot{S}-R' + R''X \rightarrow \left[\rangle\ddot{P}-\begin{matrix}R''\\ \ddot{S}\end{matrix}-R'\right]^+X^- .$$

(II)

The quasi-sulphonium structure ascribed[124] to products of the alkylation of trialkyl (triaryl) phosphorotrithioites has since been confirmed[22] by their proton magnetic resonance spectra. Several workers have isolated quasi-phosphonium compounds by treating alkyl dialkylphosphinothioites with alkyl halides[22,123,125] and with other electrophilic reagents[126].

Interesting results have been obtained from the alkylation of dialkyl alkylphosphonodithioites, which form[22,61] mixtures of onium derivatives of both types, the quantitative relations between which vary with the structure of R and R′. To interpret the reactivities of compounds containing P−S, S−P−S, and $S-P\begin{matrix}S\\ \diagdown\\ \diagup\\ S\end{matrix}$ groups use has been made[61,127] of Pearson's concept of hard and soft acids and bases[128,129]. In the ambident system sulphur is a "hard", and phosphorus a "soft", basic centre (sulphur is more electronegative and less polarisable than phosphorus). In esters of type $R_2P.S.R'$, therefore, phosphorus undergoes electrophilic attack by a "soft" electrophilic centre (an sp^3-hybrid carbon atom in an alkyl halide), with formation of quasi-phosphonium derivatives of type (I).

The esters $RP(SR')_2$ contain three nucleophilic centres—one "soft" (the phosphorus atom) and two "hard" (the sulphur atoms)—and the displacement of electron density towards the latter weakens the nucleophilic character of the phosphorus atom and increases the probability of attack by an electrophilic species on the "hard" sulphur atom, even if such species is a "soft" acid. As a consequence, a mixture of quasi-phosphonium (I) and quasi-sulphonium

(II) derivatives is formed. In trialkyl phosphorotrithioites four donor centres are competing. The three sulphur atoms greatly deplete the electronic environment of the phosphorus atom, and hence weaken its nucleophilic character. Furthermore, the probability factor favouring attack on the sulphur increases. All this leads to the formation of quasi-sulphonium derivatives (II). The steric factor may play some part, but no information has been published on the role of steric hindrance in these reactions.

Thus the ability to form quasi-sulphonium compounds[61] falls in the sequence

$$(RS)_3P > (RS)_2PR' > RSPR'_2.$$

2. Thio-esters of Three-coordinated Phosphorus in the Arbuzov Reaction

The mechanism of the action of alkyl halides on oxygen-containing esters of three-coordinated phosphorus has been studied quite well, although few quantitative data on this reaction are yet available[4-6]. The number of investigations on the behaviour of $R_nP(SR')_{3-n}$ esters ($n = 0-2$) in the Arbuzov reaction is at present quite insignificant.

The peculiar behaviour of diphenylphosphinothious esters with alkyl halides was first investigated by Arbuzov, whose results were reported at the Twelfth Congress of Russian Naturalists and Physicians in 1910.[122] He found that "esters of general type $(C_6H_5)_2P.SR$, as derivatives of tervalent phosphorus and like the corresponding oxygen compounds, isomerise under the influence of alkyl iodides into sulphides containing quinquevalent phosphorus, of general type $(C_6H_5)_2PS.R$. However, the isomerisation of sulphur-containing esters is complicated by secondary reactions, viz. the formation of small quantities of tetra-substituted phosphonium iodides and probably esters of formula $(C_6H_5)_2PSSR$".[123]

Dialkyl- and alkylaryl-phosphinothious esters undergo similar reactions[125,131]. Arbuzov suggested the scheme[122]

$$R_2P(SR') + R''X \rightarrow R_2P(S)R'' + R'X\ , \quad (1)$$

$$2R_2P(SR') \rightarrow R_2PR' + R_2P(S)(SR')\ , \quad (2)$$

$$R_2PR' + R''X \rightarrow [R_2PR'R'']^+X^-\ . \quad (3)$$

Equation (1) represents the main reaction, while (2) and (3) are secondary processes.

Kabachnik et al.[124] showed that trialkyl phosphorotrithioites react unusually with preservation of the coordination number of the phosphorus atom:

$$(RS)_3P + R'X \rightarrow \underset{(II)}{\left[(RS)_2P{-}\overset{\displaystyle R'}{\overset{|}{S}}{-}R\right]^+}X^- \rightarrow (RS)_2PX + R'{-}S{-}R\ .$$

They isolated the acid chlorides $(RS)_2PX$ and the dialkyl sulphides, thus showing for the first time that the reaction may take place at the sulphur atom, not at phosphorus. Decomposition of the quasi-sulphonium salt (II) can evidently be regarded as nucleophilic substitution at three-coordinated phosphorus, the electrophilic character of which is enhanced by the positively charged sulphur.

Mixed *O*- and *S*-esters of phosphorous acid[130] react with alkyl halides to form both the normal Arbuzov products and several secondary products. The appearance of the latter was attributed to the involvement of a second nucleophilic centre—a sulphur atom—as well as the phosphorus.

The reactions of dialkyl alkyl(or aryl)phosphonodithioites are most complicated[132,133]. The researchers[61,127,132,134] suggested a scheme involving several parallel and consecutive processes, each of which could be reproduced in separate experiments:

$$\underset{(III)}{RP(SR')_2} + \underset{(IV)}{R''X} \rightarrow \underset{(V)}{R''R'P(S)SR'} + \underset{(VI)}{R'X} + \underset{(VII)}{RP(SR')X} + \underset{(VIII)}{R'{-}S{-}R''}$$

$$\underset{(IX)}{RP(S)(SR')_2} + \underset{(X)}{RR''P(SR')} \qquad \underset{(XI)}{RR''\ddot{P}(S)X} + \underset{(XII)}{R'{-}S{-}R'}$$

$$(X) + (IV) \rightarrow \underset{(XIII)}{RR''_2P(S)} + (VI)$$

$$(IX) + (VI) \rightarrow \underset{(XIV)}{RP(S)(SR')X} + (XII)\ .$$

Compounds (V) and (VI) are products of an Arbuzov reaction, and are obviously formed by the breakdown of a quasi-phosphonium (I) type of intermediate. The products (VII) and (VIII) result from reaction at a sulphur atom, with intermediate formation of quasi-sulphonium derivatives of type (II). Compounds (IX)–(XIV) are formed by secondary processes occurring in the reaction mixture[61,134]. The above scheme shows that the complexity is due not only to the dual reactivity (ambidenticity) of these compounds but also to the ease of occurrence of secondary reactions among starting materials and products[61,127,134].

It is by no means always possible to isolate and identify all the products indicated in the above scheme[61,127]. Their reasons for this are the highly reactive character of compounds containing a phosphorus–sulphur bond and the complexity of their isolation consequent on the formation of difficultly separable azeotropic mixtures. In most cases successful separation can be achieved only by means of column, gas–liquid, and thin-layer chromatography[135,136]. Formation of certain products—(XI) (VII), (XIV)—was detected when the course of the process was monitored by ^{31}P n.m.r. spectroscopy[61,127,142].

The extremely complicated problem of the relative proportions of the first and second types of reaction (at phosphorus and at sulphur respectively) has been only partly solved[61,127,142]. This work has shown that the structure of the alkyl halide has a significant influence firstly on the extent of reaction at phosphorus and sulphur atoms, and secondly on the reaction velocity. Table 4 gives data on the main reaction products containing phosphorus—(V), (IX), and (X)—obtained from the ratio of the integral intensities of the resonance peaks of the phosphorus nucleus, together with quantitative data, obtained by gas–liquid chromatography, on the contents of the dialkyl sulphides (VIII) and (XII).[127,137] The considerable quantities of the normal Arbuzov reaction product (V) and the low contents (0.5–11.0%) of the dialkyl sulphide (VIII) in the reaction mixture obtained from n-alkyl bromides and the esters (III) indicate that the proportion of reaction at the sulphur is insignificant. The dialkyl sulphide (VIII) was not isolated from the reaction with benzyl bromide, so that in this case reaction at the sulphur probably does not take place at all. In the reactions with secondary and tertiary alkyl bromides the yield of the normal Arbuzov reaction product (V) falls (24–30%), while the yield of the dialkyl sulphide (VIII) increases (9.0–31.4%).

On the basis of the results all the alkyl bromides investigated can be arranged in the sequence

$$t\text{-}C_4H_9 > iso\text{-}C_4H_9 > s\text{-}C_4H_9 \simeq iso\text{-}C_3H_7 > n\text{-}C_4H_9 > n\text{-}C_3H_7 > C_2H_5 > CH_3 > C_3H_5 > C_6H_5CH_2$$

according to their tendency to react with the sulphur[61]. This experimental rule can be stated in terms of the concept of soft and hard acids and bases[61]: the hardness of the sp^3 carbon atom in alkyl halides increases in a homologous series and also on passing from primary to secondary and to tertiary compounds[129].

Table 4. Yields (%) of product of the reaction $RP(SR')_2 + R''X$.

R	R′	R″	$\begin{matrix}R\\R''\end{matrix}\!>\!P(=S)\!-\!SR'$ (V)	$R\!-\!P(=S)(SR')_2$ (IX)	RR''_2P (X)	R′—S—R″ (VIII)	R′—S—R′ (XII)
C_6H_5	n-C_4H_9	CH_3	56.5	15.8	14.8	4.3	8.6
C_6H_5	n-C_4H_9	C_2H_5	48.2	17.7	14.3	5.4	12.6
C_6H_5	n-C_4H_9	n-C_3H_7	41.5	21.3	19.0	7.2	9.6
C_6H_5	n-C_4H_9	n-C_4H_9	36.7	17.7	13.5	10.0	—
C_6H_5	n-C_4H_9	s-C_4H_9	30.3	22.5	19.8	15.4	11.8
C_6H_5	n-C_4H_9	t-C_4H_9	24.0	26.1	—	31.4	18.5
C_6H_5	n-C_3H_7	n-C_3H_7	48.3	19.1	18.5	4.3	—
C_6H_5	n-C_3H_7	iso-C_3H_7	28.4	31.9	25.4	9.1	2.0
C_6H_5	n-C_3H_7	n-C_3H_7	41.0	27.7	21.7	5.2	—
C_6H_5	n-C_3H_7	iso-C_3H_7	26.0	23.6	21.2	21.1	8.1
C_6H_5	n-C_3H_7	iso-C_4H_9	29.0	16.0	13.7	24.7	16.0
C_6H_5	n-C_3H_7	n-C_4H_9	42.9	23.5	13.5	11.6	7.7
C_6H_5	n-C_4H_9	C_6H_5	63.0	12.4	12.2	0.3	11.7
C_6H_5	n-C_4H_9	$C_6H_5CH_2$	55.3	18.9	16.3	—	9.4

The rate curves in Fig. 2 have been plotted from the variation in the concentration of the initial ester $C_6H_5P.(SC_3H_7)_2$ during its reaction with several alkyl bromides determined from the ^{31}P n.m.r. spectra [61,127,142]. In order of decreasing rate of reaction with $RP(SR')_2$ the alkyl bromides examined form the sequence

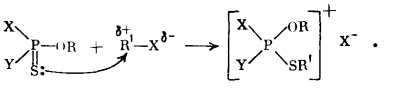
$$CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9 > t\text{-}C_4H_9 \simeq iso\text{-}C_4H_9 > iso\text{-}C_3H_7 > s\text{-}C_4H_9.$$

The principal secondary processes complicating the reaction are [61,127,134] firstly the exchange of sulphur atoms—reductive desulphurisation—and secondly interaction of esters of four-coordinated phosphorus like (V) and (IX) with the alkyl halides [137]. These reactions are due to the ability of both thionic and thiolic sulphur atoms (like phosphorus) to react both with electrophilic and with nucleophilic reagents, because of the presence of lone pairs of electrons and vacant *d* orbitals. Thus a two-coordinated sulphur atom reacts with several nucleophilic reagents, including the three-coordinated phosphorus atom [138–140]. Reactions of several phosphorus(III) compounds with a thiophosphoryl group have been reported [61, 127,134,140,141,143–145]:

$$X_3\ddot{P} + S{=}P\lessdot \rightarrow X_3P{=}S + \ddot{P}\lessdot .$$

The tendency to react with thionic sulphur is not simply related to the nucleophilic character of the reagent, so that the use by certain authors of the terms "thiophilicity" [26,138] or "S-nucleophilicity" [26,139] seems entirely justified.

On the other hand, sulphur(II) is able to react with electrophilic reagents [26]. The high donor power of sulphur in the thiophosphoryl group $\rangle P{=}S$ has been investigated by several workers [146–149]. The substituents X and Y favour reaction if they enhance the nucleophilic character of sulphur [148]:



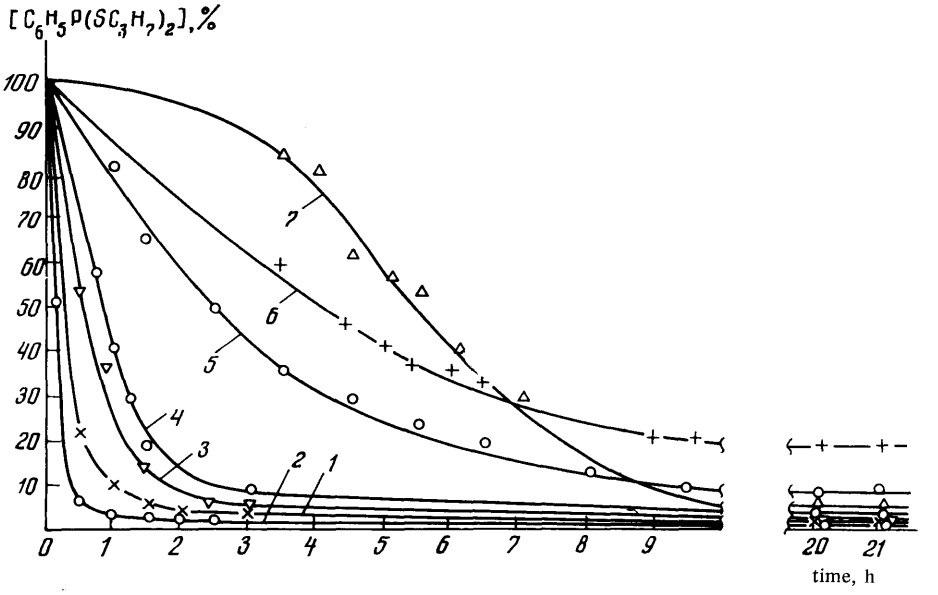


Figure 2. Variation of concentration of $C_6H_5P(SC_3H_7)_2$ with time during reaction with alkyl bromides: 1) CH_3Br; 2) C_2H_5Br; 3) n-C_3H_7Br; 4) n-C_4H_9Br; 5) t-C_4H_9Br; 6) iso-C_3H_7Br; 7) s-C_4H_9Br.

Examination of a series of compounds revealed[148] that the infrared absorption frequencies of the thiophosphoryl group can serve as a criterion of reactivity towards electrophilic reagents. Contradictory information has been published on the behaviour of thiolic sulphur towards such reagents: some authors assume[147,148] that thiolic sulphur in the group PO.SR does not react; other publications[137,150,151] report that reaction does occur. The two sulphur atoms in the group PS.SR may compete, for under mild conditions the thionic sulphur reacts, but on heating the thiolic sulphur may also be involved[137]:

$$RR'P(S)SR'' + R'''Br \begin{cases} \longrightarrow RR'P(S)SR''' + R''Br \\ \xrightarrow[\text{heat}]{} RR'P(S)Br + R''-S-R''' \end{cases}.$$

IV. REACTIONS WITH HALOGENOCARBONYL REAGENTS

Descriptions have appeared of the reactions of sulphur-containing esters $R_nP(SR')_{3-n}$ with several types of halogenocarbonyl compounds—acetyl chloride[124,152-154], chloral[155-157], chloroacetic and chloroformic esters[61,127,142,158-162], and chlorinated and brominated acetyl chlorides[61,127,163].

Reactions with chloral are complicated, and the reaction mechanism has not been elucidated. In several cases the multicomponent mixture contains vinyl ethers[157], whose presence suggests that the reaction proceeds partly in conformity with Perkov's scheme.

Acetyl chloride acts on trialkyl phosphorotrithioites, phosphorothious chlorides[124], alkyl(or aryl)phosphonodithious[152] and dialkylphosphinothious[125] esters, and also mixed *O*,*S*-phosphites[153] at a sulphur atom:

$$\rangle P-S-R + CH_3COCl \rightarrow \rangle P-Cl + CH_3COSR$$

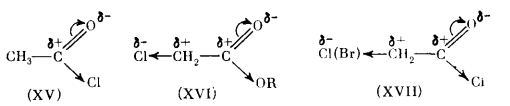
Acyl chlorides act on phospho(i)namidothious esters initially at the nitrogen atom[154]:

$$\begin{matrix} R'S \\ R \end{matrix}\!\!\rangle P-NR''_2 + CH_3COCl \rightarrow \begin{matrix} R'S \\ R \end{matrix}\!\!\rangle P-Cl + CH_3CONR''_2 .$$

The sulphur atom is then attacked:

$$\begin{matrix} R'S \\ R \end{matrix}\!\!\rangle P-Cl + ClCOCH_3 \rightarrow \begin{matrix} Cl \\ Cl \end{matrix}\!\!\rangle P-R + CH_3COSR' .$$

Esters and chlorides of chloro(or bromo)acetic acid differ from acetyl chloride in the nature and number of electrophilic centres:



(XV) (XVI) (XVII)

In chloroacetic esters (XVI) the methylene carbon atom in the sp^3-hybrid state is a soft electrophilic centre, whereas the carbonyl carbon atom in the sp^2-hybrid state is a hard Lewis acid. It would appear that dual reactivity—reaction of the soft electrophilic centre with phosphorus and of the hard electrophilic centre with sulphur—might be expected in chloroacetic esters. In all the reported cases, however, only one type of reaction—of R_2PSR' and $RP(SR')_2$ esters according to the usual Arbuzov scheme—has been observed[158,159], obviously with intermediate formation of a quasi-phosphonium product:

$$\rangle P-S-R' + (XVI) \rightarrow \left[\rangle P\begin{matrix} SR' \\ CH_2COOR \end{matrix}\right]^+ Cl^- \rightarrow \rangle P(S)CH_2COOR + R'Cl .$$

The reaction is complicated by secondary processes[159], such as nucleophilic attack by phosphorus(III) on thionic sulphur

$$R_2P\begin{matrix} S \\ CH_2COOR'' \end{matrix} + :P\begin{matrix} R \\ SR' \end{matrix} \rightarrow R_2\ddot{P}CH_2COOR'' + R_2P(S)SR'$$

with subsequent formation of a phosphonium salt

$$R_2PCH_2COOR'' + ClCH_2COOR'' \rightarrow [R_2P(CH_2COOR'')_2]^+ Cl^- .$$

In the case of esters of the $RP(SR')_2$ type the quasi-phosphonium salt then breaks down:

$$\left[\begin{matrix} SR' \\ | \\ R-P-CH_2COOR'' \\ | \\ CH_2COOR'' \end{matrix}\right]^+ Cl^- \rightarrow RP(S)(CH_2COOR'')_2 + R'Cl .$$

The probable reason for the complete absence of the second type of reaction—involving sulphur—is that the carbonyl carbon is a considerably less active electrophilic centre in these compounds than is the sp^3 carbon atom of the methylene group ($C_{sp^3} > C_{sp^2}$).

Replacement of the alkoxy-group by halogens produces a sharp increase in activity of the sp^2-hybrid carbon atom, and chloroacetyl and bromoacetyl chlorides (XVII) react with ethyl(and phenyl)phosphonodithious esters in two ways—at the phosphorus and sulphur atoms—also accompanied by secondary processes[61,127,169]:

$$RP(SR')_2 + Cl(Br)CH_2COCl \rightarrow RP(Cl)SR' + Cl(Br)CH_2COSR' , \quad (4)$$
$$RP(Cl)SR' + Cl(Br)CH_2COCl \rightarrow RPCl_2 + Cl(Br)CH_2COSR' , \quad (5)$$
$$RP(SR')_2 + Cl(Br)CH_2COCl \rightarrow RP(S)(SR')(CH_2COCl) + R'Cl(Br) , \quad (6)$$
$$RP(S)(SR')(CH_2COCl) + RP(Cl)(SR') \rightarrow RP(SR')(CH_2COCl) + RP(S)Cl(SR') , \quad (7)$$
$$RP(S)(SR')(CH_2COCl) + RP(SR')_2 \rightarrow RP(SR')(CH_2COCl) + RP(S)(SR')_2 . \quad (8)$$

Chloroacetyl chloride reacts initially only with the sulphur (Eqns. 4 and 5) by means of the carbonyl electrophilic centre. Under more severe conditions the Arbuzov reaction (6) also takes place. Bromoacetyl chloride reacts with a thioester $RP(SR')_2$ simultaneously at the two nucleophilic centres (4)–(6), with the phosphorus attacking the methylene carbon, and the sulphur attacking the carbonyl carbon. Such behaviour can conveniently be explained in terms of soft and hard acids and bases: phosphorus and methylenic carbon atoms are soft reaction centres, whereas sulphur and carbonyl atoms are hard centres.

Chloroformic esters ClCOOR'' react with phosphonodithious and phosphinothious esters only at the phosphorus atom[160,162]. Reaction with esters of the latter type can be represented by two consecutive processes[162]:

$$R_2PSR' + ClCOOR'' \rightarrow R_2P(S)COOR'' + R'Cl ,$$
$$R_2P(S)COOR'' + R_2PSR' \rightarrow R_2P(S)SR' + R_2PCOOR'' .$$

This appears somewhat unexpected, since there are data[164] indicating that chloroformic ester is a stronger acylating agent than is acetyl chloride, which acts only on the sulphur atom in all types of esters $R_nP(SR')_{3-n}$, as noted above. The electrophilic centre in chloroformic ester is surrounded by three strongly electronegative groups, and therefore carries a high positive charge:

$$Cl \leftarrow \overset{\overset{O}{\|}}{C} \rightarrow OR'' .$$

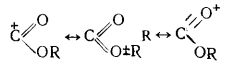
Chloroformic esters should be hard acids. However, the sequence of diminishing hardness [129]

$$CH_3COCl > ClCH_2COCl > ClCOOC_2H_5$$

indicates that chloroformic ester is a less active hard reagent, at least in certain reactions.

Furthermore [164], sodium salts of keto–enols are attacked by chloroformic ester at oxygen (a hard centre), but copper salts at carbon (a soft centre). This can be explained by Nesmeyanov and Kabachnik's concept of dual reactivity [165]. In the case of the copper salt of acetoacetic ester the reaction involves migration of the reaction centre. This is considered [164,165] to occur when the active reagent is strongly electrophilic (i.e. is a hard acid according to Pearson), and the carbon–metal bond is unionised.

With regard to the reactivity of chloroformic ester in the above reaction, the observed features of its chemical behaviour are most consistent with Kornblum's rule [166]. An electrophilic reagent may change its reactivity not only according to the nature of the nucleophile, for even in the same reaction its tendency to react with the softer centre of an ambident system increases on passing from an S_N1 to an S_N2 mechanism [121,166]. Hence chloroformic ester will interact preferentially with a hard centre (sulphur) only if the reaction conditions favour an S_N1 process. If, however, the reaction mechanism is closer to the S_N2 type, reaction must be expected at a soft centre, i.e. at phosphorus. This ester is obviously little able to form a stable intermediate carbocation and hence react by an S_N1 mechanism: the negative inductive effects of the carbonyl oxygen and of the alkoxy-group, which impair the stability of the carbocation, are stronger than stabilising resonance effects of the type



The slowness of S_N1 reaction with α-halogenated ketones is explained similarly [167].

On the other hand, steric hindrance to formation of the transition state in S_N2 processes is absent from the chloroformic ester molecule owing to the planar structure of the sp^2-hybrid carbon atom. Further stabilisation of the transition state may result from overlap of the electron shell of the nucleophilic species with the π-electron system of the carbonyl group. As a consequence of these factors chloroformic ester shows a greater tendency to react by an S_N2 mechanism and therefore to attack the soft centre of the system—the phosphorus atom.

It is clear from the literature also that chloromethyl ether, like chloroformic ester, reacts with the sodium salts of keto–enols at the oxygen atom [168], and with the copper salts at a carbon atom [164]. The tendency of halogenated ethers to react by an S_N2 mechanism can probably be explained also by their ability to interact with the soft centre—the phosphorus atom [170]:

$$R_2PSR' + ClCH_2OR' \rightarrow R_2P(S)CH_2OR' + R'Cl\,, \quad (9)$$

$$R_2P(S)CH_2OR' + R_2PSR' \rightarrow R_2\overset{+}{P}CH_2OR' + R_2P(S)SR'\,, \quad (10)$$

$$R_2\overset{+}{P}CH_2OR' + ClCH_2OR' \rightarrow [R_2P(CH_2OR')_2]^+Cl^-\,. \quad (11)$$

Thus the results for the reactivities of halogenocarbonyl compounds (and of chloromethyl ethers and esters) towards thio-esters of three-coordinated phosphorus $R_nP(SR')_{3-n}$ ($n = 0-2$) enable them to be arranged in the sequence

$$ClCOOR \approx ClCH_2OR \approx ClCH_2COOR > BrCH_2COCl > ClCH_2COCl > RCOCl$$

of diminishing softness towards the phosphorus atom [61,127]. The tendency of the electrophilic reagent to attack a hard centre in the ambident system—a sulphur atom—increases in the same sequence.

REFERENCES

1. A. I. Razumov, Zhur. Obshch. Khim., 29, 1635 (1959).
2. A. N. Pudovik and V. A. Kukhtin, Uspekhi Khim., 28, 96 (1959).
3. E. N. Tsvetkov and M. I. Kabachnik, Uspekhi Khim., 40, 177 (1971) [Russ. Chem. Rev., No. 1 (1971)].
4. B. E. Ivanov and V. F. Zheltukhin, Uspekhi Khim., 39, 773 (1970) [Russ. Chem. Rev., No. 5 (1970)].
5. R. F. Hudson, "Organophosphorus Compounds—Structure and Reaction Mechanisms" (Translated into Russian), Mir, Moscow, 1967.
6. A. J. Kirby and S. G. Warren, "Organic Chemistry of Phosphorus" (Translated into Russian), Mir, Moscow, 1971.
7. D. Purdela and R. Vilceanu, "Chemistry of Organophosphorus Compounds and their Acid Derivatives" (Translated into Russian), Khimiya, Moscow, 1972.
8. E. E. Nifant'ev, "Khimiya Fosfororganicheskikh Soedinenii" (Chemistry of Organophosphorus Compounds), Izd. Moskov. Gos. Univ., 1971.
9. I. P. Romm, E. M. Sadykova, E. I. Gur'yanova, I. D. Kolli, and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, 195, 372 (1970).
10. O. A. Yakutina, G. V. Ratovskii, Yu. I. Frolov, L. M. Sergienko, and V. G. Rozinov, Teor. Eksper. Khim., 7, 514 (1971).
11. L. M. Epshtein, Z. S. Novikova, L. D. Ashkinadze, and N. V. Kostylev, Dokl. Akad. Nauk SSSR, 184, 1346 (1969).
12. I. P. Romm, E. M. Sadykova, E. N. Gur'yanova, and I. D. Kolli, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii, Trudy II Konferentsii" (Chemistry and Application of Organophosphorus Compounds—Proceedings of the Second Conference), Nauka, Moscow, 1974, p. 287.
13. I. P. Romm, E. M. Sadykova, E. N. Gur'yanova, and I. D. Kolli, Zhur. Obshch. Khim., 43, 728 (1973).
14. I. P. Borisova and L. N. Petrov, Zhur. Strukt. Khim., 13, 701 (1972).
15. I. P. Romm and E. N. Gur'yanova, Zhur. Strukt. Khim., 46, 455 (1976).
16. S. N. Borisov, M. G. Voronkov, and E. Ya. Lukevits, "Kremneorganicheskie Proizvodnye Fosfora i Sery" (Organosilicon Derivatives of Phosphorus and Sulphur), Khimiya, Leningrad, 1968, p. 80.
17. R. D. Baechler and K. Mislow, J. Amer. Chem. Soc., 92, 4758 (1970).
18. W. B. Farnham, A. W. Herriott, and K. Mislow, J. Amer. Chem. Soc., 91, 6878 (1969).
19. A. I. Razumov, E. A. Krasil'nikova, T. V. Zykova, N. I. Sinitsyna, R. A. Salakhutdinov, and N. N. Bankovskaya, Zhur. Obshch. Khim., 42, 1250 (1972).
20. E. A. V. Ebsworth, C. Glidewell, and G. M. Sheldrick, J. Chem. Soc. A, 352 (1969).
21. I. P. Romm, V. V. Kopytov, and E. N. Gur'yanova, Zhur. Obshch. Khim., 40, 671 (1970).
22. E. A. Krasil'nikova, T. V. Zykova, A. I. Razumov, and N. I. Sinitsyna, Zhur. Obshch. Khim., 40, 2159 (1970).
23. A. I. Razumov, E. A. Krasil'nikova, N. I. Sinitsyna, T. V. Zykova, R. A. Salakhutdinov, and N. N. Bankovskaya, in "Materialy Vsesoyuznoi Konferentsii po Issledovaniyu Stroeniya Organicheskikh Soedinenii Fizicheskimi Metodami" (Proceedings of an All-Union Conference on the Investigation of the Structure of Organic Compounds by Physical Methods), Kazan, 1971.

24. R.R. Shagidullin, A.V. Chernova, E.A. Ishmaeva, and A.N. Pudovik, Dokl. Akad. Nauk SSSR, 179, 135 (1967).
25. B.I. Stepanov, A.I. Bokanov, and V.I. Svergun, Zhur. Obshch. Khim., 41, 533 (1971).
26. S. Oae, "Chemistry of Organic Sulphur Compounds" (Translated into Russian), Khimiya, Moscow, 1975.
27. R.M. Salinger and R. West, J. Organometallic Chem., 11, 631 (1968).
28. A.N. Egorochkin, N.M. Vyazankin, M.N. Bochkarev, V.T. Bychkov, and V.N. Burov, Zhur. Obshch. Khim., 38, 396 (1968).
29. F.A. Cotton and G. Wilkinson, "Modern Inorganic Chemistry" (Translated into Russian), Mir, Moscow, 1969, Chapters 1 and 2.
30. C. Coulson, "Valence" (Translated into Russian), Mir, Moscow, 1965.
31. E.M. Shustorovich, Zhur. Vses. Khim. Obshch. Mendeleeva, 17, 277 (1972).
32. C.A. Burns and W. Gordy, Phys. Rev., 92, 274 (1953).
33. R.S. Mulliken, J. Amer. Chem. Soc., 77, 887 (1955).
34. L. Pauling and M. Simonetta, J. Chem. Phys., 20, 29 (1952).
35. J.H. Letcher and J.R. Van Wazer, Topics Phosphorus Chem., 5, 75, 169 (1967).
36. L.V. Orlovskaya, "Vliyanie Vysshikh AO na Fizicheskie i Khimicheskie Svoistva Soedinenii Neperekhodnykh Elementov, Tezisy Dokladov Konferentsii" (Effect of Higher Atomic Orbitals on the Physical and Chemical Properties of Compounds of Non-transition Elements—Abstracts of Conference Papers), Riga, 1971, p. 122.
37. M.G. Guntfest, Yu. V. Kolodyazhnyi, V.E. Udre, M.G. Voronkov, and O.A. Osipov, "Vliyanie Vysshikh AO na Fizicheskie i Khimicheskie Svoistva Soedinenii Neperekhodnykh Elementov, Tezisy Dokladov Konferentsii" (Effect of Higher Atomic Orbitals on the Physical and Chemical Properties of Compounds of Non-transition Elements—Abstracts of Conference Papers), Riga, 1971, p. 170.
38. B.A. Trofimov, E.I. Kositsina, N.I. Shergina, S.G. Shevchenko, and E.I. Vyalykh, Izv. Akad. Nauk SSSR, Ser. Khim., 1581 (1971).
39. W.W. Robertson and F.A. Matsen, J. Amer. Chem. Soc., 72, 5248 (1950).
40. J.P. Roberts and M.C. Caserio, "Foundations of Organic Chemistry" (Translated into Russian), Mir, Moscow, 1968.
41. H.H. Jaffé, Uspekhi Khim., 26, 2060 (1957).
42. T. Fueno, O. Kajimoto, K. Izawa, and M. Masago, Bull. Chem. Soc. Japan, 46, 1418 (1973).
43. O. Kajimoto, M. Kobayashi, and T. Fueno, Bull. Chem. Soc. Japan, 46, 1488, 1425, 2316 (1973).
44. J.R. van Wazer, "Phosphorus and Its Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1962.
45. O.P. Charkin, see Ref. 36, p. 7.
46. O.P. Charkin, Zhur. Vses. Khim. Obshch. Mendeleeva, 17, 258 (1972).
47. B.A. Trofimov, N.I. Shergina, E.I. Kositsina, E.P. Vyalykh, S.V. Amosova, N.K. Gusarova, and M.G. Voronkov, Reaktsionn. Sposob. Org. Soed., 10, 766 (1973).
48. B.A. Trofimov, G.A. Kalabin, V.M. Bzhezovskii, N.G. Gusarova, D.F. Kushnarev, and S.V. Amosova, Reaktsionn. Sposob. Org. Soed., 11, 365 (1974).
49. L.M. Epshtein, L.D. Ashkinadze, S.O. Gorelik, N.I. Gambaryan, D.A. Bochvar, and L.A. Kazitsina, Izv. Akad. Nauk SSSR, Ser. Khim., 65 (1974).
50. E.M. Shustorovich, "Khimicheskaya Svyaz' v Koordinatsionnykh Soedineniyakh" (Chemical Bonding in Coordination Compounds), Znanie, Moscow, 1975.
51. D.A. Bochvar, N.P. Gambaryan, and L.M. Epshtein, Uspekhi Khim., 45, 1316 (1976) [Russ. Chem. Rev., No. 7 (1976)].
52. A.H. Cowley, Chem. Rev., 65, 617 (1965).
53. A.H. Cowley and R.P. Pinnell, Topics Phosphorus Chem., 4, 1 (1967).
54. W. Mahjer and A.B. Burg, J. Amer. Chem. Soc., 79, 251 (1957); 80, 6161 (1958).
55. W.A. Henderson, M. Epstein, and F.S. Seichter, J. Amer. Chem. Soc., 85, 2461 (1963).
56. L. Maier, Helv. Chim. Acta, 49, 1119 (1966).
57. W. Mahler, J. Amer. Chem. Soc., 86, 2306 (1964).
58. L.B. Grant and A.B. Burg, J. Amer. Chem. Soc., 84, 1834 (1962).
59. J.B. Lambert, G.F. Jackson, and D.C. Mueller, J. Amer. Chem. Soc., 90, 6401 (1968).
60. L.V. Gurbich, G.V. Kochevtsev, V.N. Kondrat'ev, Yu.A. Lebedev, V.A. Medvedev, V.K. Potapov, and Yu.S. Khodeev, "Energii Razryva Khimicheskikh Svyazei, Potentsialy Ionizatsii i Srodstvo k Elektronu" (Energies of Rupture of Chemical Bonds, Ionisation Potentials, and Electron Affinities), Nauka, Moscow, 1974.
61. E.A. Krasil'nikova, Doctoral Thesis, Kirov Kazan Institute of Chemical Technology, 1973.
62. J. Hinze and H.H. Jaffé, J. Amer. Chem. Soc., 84, 540 (1962).
63. J.N. Murrell, S.F.A. Kettle, and J.M. Tedder, "Theory of Valency" (Translated into Russian), Mir, Moscow, 1968, p. 404.
64. E.N. Tsvetkov, Zhur. Obshch. Khim., 45, 490 (1975).
65. O.A. Raevskii, A.N. Vereshchagin, Yu. P. Donskaya, F.G. Khalitov, I.G. Malakhova, and E.N. Tsvetkov, Izv. Akad. Nauk SSSR, Ser. Khim., 453 (1974).
66. Zh.S. Galuashvili, I.P. Romm, E.N. Gur'yanova, N.N. Korneev, and K.A. Kocheskov, Izv. Akad. Nauk SSSR, Ser. Khim., 2713 (1975).
67. F.A. Gianturco, J. Chem. Soc. A, 1293 (1969).
68. G. Kodama, J.R. Weaver, J. La Rochette, and R.W. Parry, Inorg. Chem., 5, 710 (1966).
69. H. Schindlbauer and G. Hajek, Chem. Ber., 96, 2601 (1963).
70. H. Goetz and S. Domin, Annalen, 704, 1 (1967).
71. S.O. Grim, W. McFarlane, and E.T. Davidoff, J. Org. Chem., 32, 781 (1967).
72. H. Goetz, H. Hadamik, and H. Juds, Annalen, 737, 132 (1970).
73. E.I. Matrosov and G.M. Petrov, "V Vsesoyuznaya Konferentsiya po Khimii Fosfororganicheskikh Soedinenii, Tezisy Dokladov" (Fifth All-Union Conference on the Chemistry of Organophosphorus Compounds—Abstracts of Papers), Moscow, 1972, p. 131.
74. E.I. Matrosov, G.M. Petrov, and M.I. Kabachnik, Zhur. Strukt. Khim., 15, 250 (1974).
75. E.I. Matrosov, G.M. Petrov, and M.I. Kabachnik, Zhur. Strukt. Khim., 15, 255 (1974).
76. M.G. Voronkov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1688 (1961).
77. K. Ryde, "Textbook of Physical Organic Chemistry" (Translated into Russian), Mir, Moscow, 1972, p. 114.

78. E.N. Tsvetkov, D.A. Bochvar, and M.I. Kabachnik, Teor. Eksper. Khim., 3, 3 (1967).
79. H.H. Jaffé and L.D. Freedman, J. Amer. Chem. Soc., 74, 1069 (1952).
80. C.N.R. Rao, J. Ramachandran, and A. Balasubramanian, Canad. J. Chem., 39, 171 (1961).
81. H. Schindlbauer and V. Hilzensauer, Monatsh., 98, 1196 (1967).
82. G.P. Schiemenz, Naturwiss., 53, 476 (1966).
83. G. Shaw, J.K. Becconsall, R.M. Canadine, and R. Murray, Chem. Comm., 425 (1966).
84. B.I. Stepanov, A.M. Bokanov, B.I. Korolev, and V.A. Plakhov, in "Khimiya Organicheskikh Soedinenii Fosfora" (Chemistry of Organic Compounds of Phosphorus), Nauka, Leningrad, 1967, p. 162.
85. W. Drenth, Colloq. Int. CNRS, No. 182, 91 (1970).
86. K.S. Mingaleeva, L.A. Tamm, V.N. Chistoklerov, and A.A. Petrov, Zhur. Obshch. Khim., 44, 103 (1974).
87. C.J. Jameson and H.S. Gutowsky, J. Chem. Phys., 44, 1214 (1964).
88. J.R. Van Wazer, C.F. Callis, J.N. Shoolery, and R.C. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).
89. H.S. Gutowsky and J. Larman, J. Amer. Chem. Soc., 87, 3815 (1965).
90. B.I. Ionin, Zhur. Obshch. Khim., 38, 1659 (1968).
91. A.I. Razumov, S.V. Yalymova, Yu. Yu. Samitov, V.V. Moskva, T.V. Zykova, G.F. Nazvanova, and R.A. Salakhutdinov, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii, Trudy V Konferentsii" (Chemistry and Application of Organophosphorus Compounds—Proceedings of the Fifth Conference), Nauka, Moscow, 1974, p. 318.
92. J.M. Murray, R. Schmizier, E. Grundemann, and H. Teichmann, J. Chem. Soc. B, 1714 (1971).
93. E.S. Kozlov and E.N. Gaidamaka, Teor. Eksper. Khim., 8, 420 (1972).
94. E. Fluck, "Die kernmagnetische Resonanz und ihre Anwendung in der anorganische Chemie", Berlin, 1963.
95. B.I. Ionin, Doctoral Thesis, Lensovet Leningrad Institute of Technology, 1970.
96. C.W.N. Cumper, A.A. Foxton, J. Read, and A.J. Vogel, J. Chem. Soc., 430 (1964).
97. S.S. Batsanov, Uspekhi Khim., 37, 778 (1968) [Russ. Chem. Rev., No. 5 (1968)].
98. E.A. Krasil'nikova, N.A. Moskova, and A.I. Razumov, Zhur. Obshch. Khim., 39, 216 (1969).
99. A.I. Razumov, B.G. Liorber, and T.V. Zykova, Zhur. Obshch. Khim., 40, 1704 (1970).
100. R.G. Kostyanowsky, V.V. Jakshin, and S.L. Zimont, Tetrahedron, 24, 2995 (1968).
101. R.G. Kostyanovskii and V.V. Yakshin, Izv. Akad. Nauk SSSR, Ser. Khim., 478 (1969).
102. N.A. Razumova, Doctoral Thesis, Lensovet Leningrad Institute of Technology, 1971.
103. E.N. Tsvetkov, M.I. Kabachnik, and D.I. Lobanov, Teor. Eksper. Khim., 1, 729 (1965).
104. E.N. Tsvetkov, M.I. Kabachnik, and D.I. Lobanov, Teor. Eksper. Khim., 2, 458 (1966).
105. E.N. Tsvetkov, D.I. Lobanov, L.A. Izosenkova, and M.I. Kabachnik, Zhur. Obshch. Khim., 40, 500, 2383 (1970).
106. E.A. Jakovleva, E.N. Tsvetkov, D.I. Lobanov, A.J. Snatenstein, and M.I. Kabachnik, Tetrahedron, 25, 1165 (1969).
107. J.B. Lambert, G.F. Jackson, and D.C. Mueller, J. Amer. Chem. Soc., 90, 6401 (1968).
108. E.A.V. Ebsworth, C. Glidewell, and G.M. Sheldrick, J. Chem. Soc. A, 352 (1969).
109. R.D. Baechler and K. Mislow, J. Amer. Chem. Soc., 92, 3090 (1970).
110. J.B. Lambert, G.F. Jackson, and D.C. Mueller, J. Amer. Chem. Soc., 92, 3093 (1970).
111. Chang-Jung-Yü, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii, Trudy II Konferentsii" (Chemistry and Application of Organophosphorus Compounds—Proceedings of the Second Conference), Moscow, 1962, p. 310.
112. D.J. Peterson and H.R. Hays, J. Org. Chem., 30, 1939 (1965).
113. D.J. Peterson, J. Org. Chem., 31, 950 (1966).
114. A.N. Pudovik, Uspekhi Khim., 23, 575 (1954).
115. M.I. Kabachnik, T.Ya. Medved', Yu.M. Polikarpov, and K.S. Yudina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1584 (1962).
116. D.I. Lobanov, E.N. Tsvetkov, E.V. Saltanova, E.A. Yakovleva, A.N. Shatenshtein, and M.I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 2050 (1968).
117. E.A. Yakovleva, G.G. Isaeva, M.M. Makhamatkhanov, A.N. Zhidkova, E.N. Tsvetkov, M.I. Kabachnik, and A.N. Shatenshtein, Zhur. Obshch. Khim., 40, 1626 (1970).
118. M.I. Kabachnik, E.N. Tsvetkov, and Chang-Jung-Yü, Zhur. Obshch. Khim., 32, 3340 (1962).
119. D. Seyferth, Progr. Inorg. Chem., 31, 950 (1966).
120. W.E. Parham and R.F. Motter, J. Amer. Chem. Soc., 81, 2146 (1959).
121. H. Becker, "Einführung in die Elektronentheorie organisch-chemischer Reaktionen" (Translated into Russian), Mir, Moscow, 1965, p. 89.
122. A.E. Arbuzov, Zhur. Russ. Fiz.-khim. Obshch., 42, 549 (1910).
123. A.E. Arbuzov, "Izbrannye Trudy" (Selected Works), Akad. Nauk SSSR, Moscow, 1952, p. 226.
124. A.D. Divinskii, M.I. Kabachnik, and V.V. Sidorenko, Dokl. Akad. Nauk SSSR, 60, 999 (1948).
125. N.I. Rizpolozhenskii and V.D. Akamsin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 370 (1969).
126. A.I. Razumov, E.A. Krasil'nikova, N.A. Moskva, T.V. Zykova, and R.A. Salakhutdinov, Zhur. Obshch. Khim., 41, 1498 (1971).
127. G.V. Orlova, Candidate's Thesis, Kirov Kazan Institute of Chemical Technology, 1973.
128. R.G. Pearson and J. Songstag, J. Amer. Chem. Soc., 89, 1827 (1967).
129. S.A. Shevelev, Uspekhi Khim., 39, 1773 (1970) [Russ. Chem. Rev., No. 10 (1970)].
130. A.E. Arbuzov and K.V. Nikonorov, Dokl. Akad. Nauk SSSR, 62, 75 (1948).
131. V.D. Akamsin and N.I. Rizpolozhenskii, Dokl. Akad. Nauk SSSR, 168, 867 (1966).
132. E.A. Krasil'nikova, A.M. Potapov, and A.I. Razumov, Zhur. Obshch. Khim., 36, 609, 1098, 1101 (1968).
133. B.A. Arbuzov, N.I. Rizpolozhenskii, and M.A. Zvereva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 179 (1957).
134. A.M. Potapov, Candidate's Thesis, Kirov Kazan Institute of Chemical Technology, 1967.
135. A.M. Potapov, E.A. Krasil'nikova, A.I. Razumov, and S.Yu. Baigil'dina, Zhur. Obshch. Khim., 40, 546 (1970).
136. E.A. Krasil'nikova, A.M. Potapov, and A.I. Razumov, Zhur. Obshch. Khim., 38, 1556 (1968).

137. E.A.Krasil'nikova, A.I.Razumov, I.M.Starshov, G.V.Orlov, M.I.Starshov, and L.I.Sergeicheva, Zhur.Obshch.Khim., 45, 1898 (1975).
138. T.Hakabayashi, J.Tsurugi, S.Kawamura, T.Kitao, M.Ui, and M.Nose, J.Org.Chem., 31, 4174 (1966).
139. A.G.Parker and M.Kharasch, Chem.Rev., 59, 383 (1953).
140. H.E.Ulmer, L.C.D.Groenweghe, and L.Maier, J.Inorg.Nuclear Chem., 20, 82 (1961).
141. E.A.Krasil'nikova, A.M.Potapov, and A.I.Razumov, Zhur.Obshch.Khim., 37, 1409, 2365 (1967).
142. E.A.Krasil'nikova, T.V.Zykova, A.I.Razumov, I.M.Starshov, G.V.Orlova, M.I.Starshov, and R.A.Salakhutdinov, Zhur.Obshch.Khim., 43, 1701 (1973).
143. V.V.Moskva, G.R.Nazvanova, T.V.Zykova, A.N.Razumov, and R.A.Salakhutdinov, Zhur. Obshch.Khim., 42, 314 (1972).
144. V.K.Khairullin, M.A.Vasyanina, G.V.Dmitrieva, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 2767 (1971).
145. A.O.Vizel', V.K.Krupnov, and B.S.Arbuzov, Izv. Akad.Nauk SSSR, Ser.Khim., 181 (1972).
146. A.J.Burn and J.G.Cadogan, J.Chem.Soc., 5532 (1961).
147. H.Teichmann and C.Hilgetag, Chem.Ber., 96, 1454, 1465 (1963).
148. L.V.Nesterov, A.Ya.Kessel', Yu.Yu.Samitov, and A.A.Musina, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii, Trudy IV Konferentsii" (Chemistry and Application of Organophosphorus Compounds—Proceedings of the Fourth Conference), Nauka, Moscow, 1972, p.261.
149. H.Teichmann and G.Hilgetag, Angew.Chem., 79, 1077 (1967).
150. A.J.Burn, J.G.Cadogan, and H.N.Moulden, J.Chem.Soc., 5542 (1961).
151. I.V.Murav'ev and B.I.Kotovich, see Ref.73, p.140.
152. V.D.Akamsin and N.I.Rizpolozhenskii, Izv.Akad. Nauk SSSR, Ser.Khim., 493 (1966).
153. D.Minich, N.I.Rizpolozhenskii, V.D.Akamsin, and O.A.Raevskii, Izv.Akad.Nauk SSSR, Ser.Khim., 876 (1969).
154. N.I.Rizpolozhenskii and V.D.Akamsin, Izv.Akad. Nauk SSSR, Ser.Khim., 1398 (1968).
155. J.F.Allen and O.H.Johnson, J.Amer.Chem.Soc., 77, 2871 (1955).
156. G.Schrader, BRD P.954 244 (1956); Chem.Abs., 53, 11 305 (1959).
157. G.Schrader, BRD P.1 058 046 (1959); Chem.Abs., 55, 13 319 (1961).
158. E.A.Krasil'nikova, N.A.Moskva, and A.I.Razumov, Zhur.Obshch.Khim., 40, 2765 (1970).
159. A.I.Razumov, E.A.Krasil'nikova, N.A.Moskva, T.V.Zykova, and L.A.Chemodanova, Zhur.Obshch. Khim., 41, 2402 (1971).
160. A.I.Razumov, E.A.Krasil'nikova, N.A.Moskva, T.V.Zykova, and R.M.Salakhutdinov, Zhur. Obshch.Khim., 41, 1498 (1971).
161. E.A.Krasil'nikova, N.A.Moskva, A.I.Razumov, and G.V.Shtatnova, Zhur.Obshch.Khim., 41, 1502 (1971).
162. N.A.Moskva, Candidate's Thesis, Kirov Kazan Institute of Chemical Technology, 1970.
163. E.A.Krasil'nikova, A.N.Razumov, G.V.Orlova, and N.A.Moskva, Zhur.Obshch.Khim., 42, 2578 (1972).
164. O.A.Reutov, "Teoreticheskie Osnovy Organicheskoi Khimii" (Theoretical Foundations of Organic Chemistry), Izd.Moskov.Gos.Univ., 1964.
165. A.N.Nesmeyanov and M.N.Kabachnik, Zhur. Obshch.Khim., 25, 41 (1955).
166. N.Kornblum and R.Brawn, J.Amer.Chem.Soc., 85, 1359 (1963); 86, 2681 (1964).
167. E.L.Eliel, in "Steric Effects in Organic Chemistry" edited by M.S.Newman (Translated into Russian), Inostr.Lit., Moscow, 1960, p.153.
168. M.Kornblum and R.Seitrer, J.Amer.Chem.Soc., 83, 3668 (1961).
169. E.A.Krasil'nikova, A.I.Razumov, T.V.Zykova, and G.V.Orlova, Zhur.Obshch.Khim., 46, 2748 (1976).
170. E.A.Krasil'nikova, A.I.Razumov, E.V.Bayandina, and V.G.Zarinova, Zhur.Obshch.Khim., 41, 1173 (1971).

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