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Phosphorus-containing Polysulphides (Methods of Synthesis and Chemical Properties)

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The methods of synthesis and chemical properties of compounds containing the $>\!\overset{X}{\overset{\|}{P}}-(S)_n-$ (X = O or S, n = 2-4) fragment are examined. The unusual chemical behaviour of phosphorus-containing polysulphides in the reactions with nucleophiles and electrophiles is discussed.
The bibliography includes 170 references.

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I. INTRODUCTION

Despite the fact that phosphorus-containing polysulphides have been know for a long time, their chemical properties have begun to be studied in detail only in recent years. Nevertheless the presence of phosphorus-containing fragments introduces a definite specificity into the chemical behaviour of these compounds, which differ appreciably in their reactivity from aliphatic and aromatic polysulphides.[1] It must also be emphasised that phosphorus-containing polysulphides are the starting materials for the synthesis of a wide variety of organophosphorus compounds, including those which are difficult to obtain by other means.

This review is devoted to phosphorus-containing polysulphides—the "symmetrical" polysulphides (I), in the molecules of which the polysulphide bridge links two phosphorus-containing groups, and the "asymmetric" polysulphides (II), where there is only one such group. This review is a first attempt at a survey of the methods of synthesis and chemical properties of these compounds.

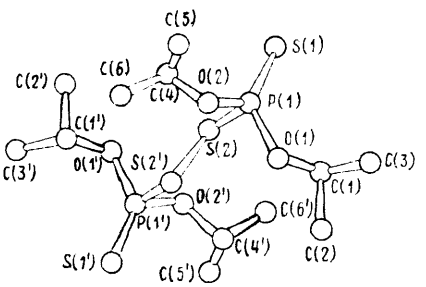
$$\underset{(I)}{R_2\overset{X}{\overset{\|}{P}}-S_n-\overset{X}{\overset{\|}{P}}R_2} \qquad \underset{(II)}{R_2\overset{X}{\overset{\|}{P}}-S_n-R'}$$

Here X = O or S, n = 2–4, and R and R′ are various organic and inorganic substituents linked to the phosphorus and sulphur atoms either directly or via the atoms of other elements.

Considerable advances have been made recently in the study of the reactivity of phosphorus-containing polysulphides and also in their employment for the synthesis of new structures among organophosphorus compounds.

II. THE STRUCTURE OF PHOSPHORUS-CONTAINING POLYSULPHIDES

The structure of symmetrical phosphorus-containing polysulphides is examined below in relation to bis(di-isopropoxythiophosphoryl) disulphide investigated by X-ray diffraction (see Figure).[2] The bond lengths and valence angles are indicated in Table 1. The data obtained do not preclude the possibility of the presence of a centre of symmetry located between the two sulphur atoms S(2) and S(2′). The S(2)–S(2′) distance (2.09 Å) is greater than in tetraethylthiuramide sulphide (1.999 Å).[3] The atoms surrounding the phosphorus atom have a distorted tetrahedral configuration; a plane can be drawn through the C(4)–O(2)–P(1)–O(1)–C(1) atoms to within 0.04 Å.



The structure of bis(di-isopropoxythiophosphoryl) disulphide according to Tkachev et al.[2]

Table 1. The bond lengths and valence angles in bis(di-isopropoxythiophosphoryl) disulphide.[2]

Bond length, Å		Valence angles, deg	
S(1)—P(1)	1.89	S(2′)—S(2)—P(1)	99.1
S(2)—P(1)	2.07	S(1)—P(1)—S(2)	102.8
S(2)—S(2′)	2.09	S(1)—P(1)—O(1)	122.0
P(1)—O(1)	1.57	S(1)—P(1)—O(2)	117.0
P(1)—O(2)	1.53	S(2)—P(1)—O(1)	108.0
O(1)—C(1)	1.44	S(2)—P(1)—O(2)	111.0
O(2)—C(4)	1.47	O(1)—P(1)—O(2)	95.0
C(1)—C(2)	1.52	P(1)—O(1)—C(1)	121.0
C(1)—C(3)	1.49	P(1)—O(2)—C(4)	119.0
C(4)—C(5)	1.55	O(1)—C(1)—C(2)	108.0
		O(1)—C(1)—C(3)	104.0
		O(2)—C(4)—C(5)	106.0
		O(2)—C(4)—C(6)	104.0
		C(3)—C(1)—C(2)	112.0
		C(5)—C(4)—C(6)	112.0

In the case of phosphorus-containing tri- and tetrasulphides, the structure of the polysulphide chain is of interest. Combined infrared and Raman spectroscopic data show

that the R–S–$(S)_n$–S–R polysulphide chain in phosphorus-containing polysulphides is unbranched.[4] Table 2 presents the absorption maxima in the infrared and Raman spectra of bis(diethoxythiophosphoryl) polysulphides in the range 400–700 cm^{-1} when the stretching vibration bands of the S–S, P–S, and P=S bonds are located. Evidently the bands which are intense in the Raman spectra have a low intensity in the infrared spectra and conversely. The unbranched nature of the structure of phosphorus-containing polysulphides is indicated by the fact that this feature holds best for centro-symmetric structures.[5] It must be emphasised that the bands cannot be assigned to different conformers, since the relative intensities remain constant as the temperature is altered.

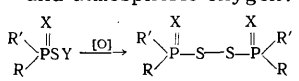
Table 2. The band maxima (ν, cm^{-1}) in the infrared and Raman spectra of bis(diethoxythiophosphoryl) polysulphides (bands of low intensity are indicated in brackets).[4]

P–S–S–P		P–S–S–S–P		P–S–S–S–S–P		Assignment
i.r.	R	i.r.	R	i.r.	R	
—	—	—	—	(452)	452	S–S sym.
—	—	464	465	469	—	S–S asym.
—	485	—	480	—	474	S–S sym.
498	—	501	—	501	—	P–S asym.
—	507	—	(506)	—	(505)	P–S sym.
639	(640)	643	(642)	644	—	P = S asym.
(656)	657	—	655	—	653	P = S sym.

III. METHODS OF SYNTHESIS

1. Symmetrical Phosphorus-containing Disulphides

The commonest method of synthesis of phosphorus-containing disulphides involves the oxidation of phosphorothioic and phosphorodithioic acids or their salts. The oxidants employed are the halogens (chlorine, bromine, and iodine),[6–19,21] hydrogen peroxide,[6,20,22] sodium nitrite (in the presence of sulphuric acid),[22–24] nitrous acid,[25] dimethylsulphoxide,[26] sulphuryl or thionyl chloride,[27–30] potassium hexacyanoferrate(III),[31] and atmospheric oxygen:[32]



where X = O or S, Y = H or a metal, and R and R′ are substituted or unsubstituted alkyl, aryl, alkoxy-, aryloxy-, or amino-group or a fluorine atom.

Best results are achieved when one employs acid salts, since the reactions of certain dialkylphosphorodithioic acids with iodine in an acid medium are reversible.[33] In an alkaline medium the oxidation by iodine proceeds as far as the phosphates and sulphates and it is therefore not possible to obtain disulphides under these conditions.[34,35]

It must be emphasised that, together with the disulphides, trisulphides are formed in yields up to 12% in the oxidation of phosphorodithioic acids by certain oxidants (Br_2, KI + I_2, H_2O_2) in an acid medium.[9,21] Concentrated sulphuric acid converts phosphorodithioic acids into a mixture containing up to 49% of the disulphide, 27% of the trisulphide, and 11% of phosphorothioic acid.[22] The ease of the oxidation of *O,O*-dialkyl phosphorodithioates depends on the nature of the alkyl residue (Table 3).

Phosphorus-containing disulphides with a C–P bond can be obtained from secondary phosphines via stages involving the formation of phosphinothious and phosphinodithioic acids with subsequent oxidation:[38]

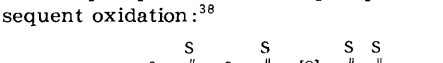
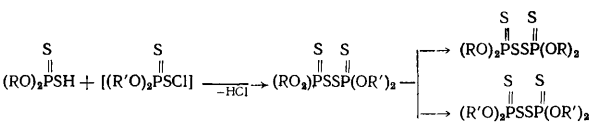


Table 3. The oxidation-reduction potentials *E* for the reaction $(RO)_2P(S)S^- - e \rightarrow (RO)_2P(S)SS(S)P(OR)_2$.[36,37]

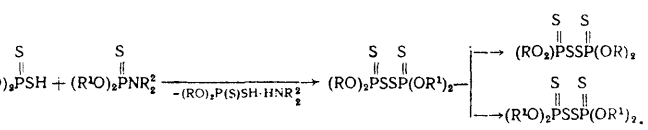
R	*E*, V	R	*E*, V
CH_3	0.315	C_6H_{13}	0.015
C_2H_5	0.255	iso-C_3H_7	0.196
C_3H_7	0.187	iso-C_4H_9	0.158
C_4H_9	0.122	iso-C_5H_{11}	0.086
C_5H_{11}	0.050		

Disulphides are formed from phosphorodithioic acids when the latter interact with dialkoxythiophosphorylsulphenyl chlorides:[39–42]



Symmetrical phosphorus-containing disulphides (R = R′) have been obtained successfully by this method. In the case of various alkyl groups (R and R′), the isolation of the disulphide in a pure form present considerable difficulties owing to the ease of their disproportionation to the corresponding symmetrical disulphides.[40]

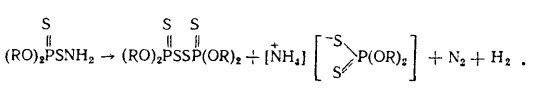
The reactions of phosphorodithioic acids with dialkoxythiophosphorylsulphenamides proceed analogously:[40]



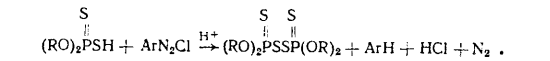
The interaction of *N*-substituted thiophosphorylsulphenamides with phosphorus acid halides in an alkaline medium results in the formation of phosphorus-containing disulphides:[43]



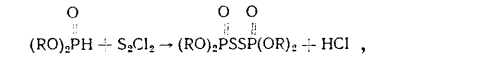
The decomposition of thiophosphorylsulphenamides, which apparently proceeds via a free-radical mechanism, also leads to the formation of disulphides:[44]



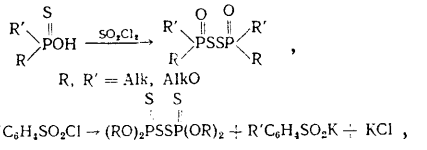
According to Mel'nikov and co-workers,[45,46] the formation of phosphorus-containing disulphides in the reactions of phosphorodithioic acids with diazonium salts in an acid medium also involves a free-radical mechanism:



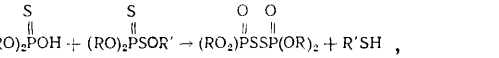
Several specific methods whereby one can obtain bis(dialkoxyphosphoryl) disulphides have been discussed in the literature. These include the reactions of dialkyl phosphites with sulphur monochloride,[47] i.e.



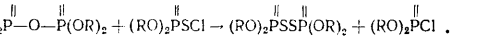
the condensation of acid phosphinothioates, phosphonothioates, phosphorothioates, and phosphorodithioates in the presence of sulphuryl chloride[29,30] or sulphonyl chlorides,[91] i.e.



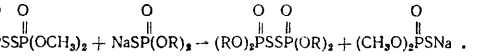
the reactions of *O,O*-dialkylphosphorodithioic acids with *O,O*-dialkyl *S*-methyl phosphorodithioates,[48] i.e.



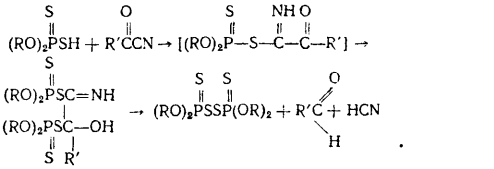
and the interaction of pyrophosphorothioates with dialkoxyphosphorylsulphen chlorides,[49]



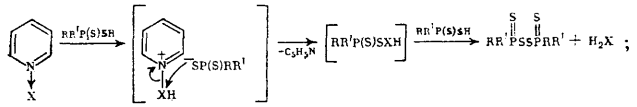
Bis(dialkoxyphosphoryl) disulphides with higher alkyl substituents (propyl and butyl) can be obtained from bis(dimethoxyphosphoryl) disulphide by its interaction with aqueous solutions of the salts of the corresponding phosphorus acids:[20]



Phosphorus-containing disulphides are obtained as side products in certain reactions. For example, the interaction of phosphorodithioic acids with nitriles of pyruvic and benzoylformic acids results in the formation of a bisphosphorylated iminocarbinol, one of the decomposition pathways of which leads to a phosphorus-containing disulphide:[50]



Disulphides are also formed in the reaction of phosphorodithioates with sulphimines, *N*-iminopyridinium betaines, and pyridine *N*-oxide:[51-53]

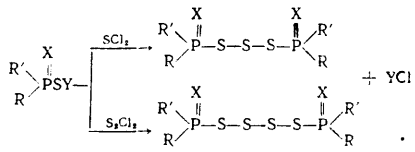


R, R' = C_6H_5, AlkO; X = O, $NC_6H_4NO_2$-4, $NCOC_6H_5$.

2. Symmetrical Phosphorus-containing Tri- and Tetrasulphides

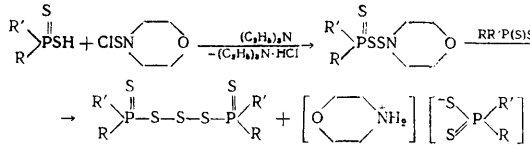
A phosphorus-containing trisulphide was isolated for the first time in the recrystallisation of diethyl phosphinodithioate from carbon disulphide and was described as bis(diethylphosphinyl) trisulphide.[54] A mixture of symmetrical tri- and tetra-sulphides is formed in the interaction of alcohols with phosphorus pentasulphides. Depending on the conditions (temperature, duration of heating), the content of trisulphides in the mixture can then range from 37 to 63% and that of the tetrasulphides from 19 to 28%.[37,55]

The commonest method of synthesis of phosphorus-containing tri- and tetra-sulphides involves the interaction of phosphorodithioic acids or their salts with sulphur di- or mono-chloride:[6,7,56-60]

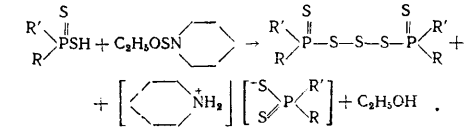


where Y = H or metal, X = O or S, and R,R' is an alkyl-, alkoxy-, or substituted alkoxy-group[6,7,56,58] or R = alkyl and R' = S.[59,60]

Symmetrical phosphorus-containing trisulphides have been obtained from *O,O*-dialkylphosphorodithioic or alkoxyalkylphosphonodithioic acids and morpholinylsulphenyl chloride.[41-61] The reaction apparently proceeds via the intermediate formation of thiophosphoryl morpholino disulphide:

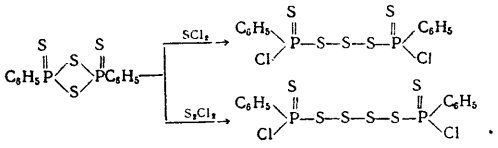


The reaction with ethoxypiperidino sulphide proceeds analogously:[42]

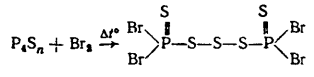


When dialkoxythiophosphoryl *N*-mono(di)alkylamino disulphides were allowed to interact with phosphorothioic acids, bis(dialkoxythiophosphoryl) tetrasulphides were isolated.[62]

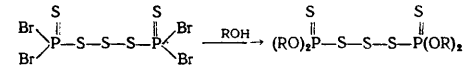
Halogen-substituted phosphorus-containing polysulphides are extremely interesting. Fluorine-substituted polysulphides are obtained by oxidising the corresponding fluorine-containing phosphorodithioic acids.[59,60] Bis(phenylchlorothiophosphonyl) polysulphides are obtained by treating phenylthionophosphine sulphide with sulphur di- or monochloride:[63]



Bis(dibromothiophosphoryl) trisulphides are formed readily when phosphorus polysulphides P_4S_n, where n = 3, 5, or 7, are treated with bromine:[64,65]



The interaction of bis(dibromothiophosphoryl) trisulphides with alcohols gives rise to bis(dialkoxythiophosphoryl) trisulphides:[65]



Individual reactions leading to the formation of phosphorus-containing tri- and tetra-sulphides as side products are known in the literature. Thus bis(diethylthiophosphinyl) trisulphide can be isolated in a low yield in the reaction of bis(dimethylamino)diethylphosphinylborane with sulphur:[66]

$$[(CH_3)_2N]_2BP(C_2H_5)_2 + S \rightarrow (C_2H_5)_2\overset{S}{\overset{\|}{P}}-S-S-S-\overset{S}{\overset{\|}{P}}(C_2H_5)_2 + B_2[N(CH_3)_2]_4 \ .$$

Phosphorus-containing polysulphides are formed together with phosphinodithioic acids and disulphides in the interaction of secondary phosphines with sulphur.[54]

In the oxidation of potassium and nickel salts of *O,O*-diethylphosphorodithioic acids with selenous acid, bis(diethoxythiophosphoryl) tetrasulphide is one of the reaction products.[67]

3. Asymmetric Phosphorus-Containing Polysulphides

Phosphorothioic and phosphorodithioic acids or their salts can be used to synthesise asymmetric phosphorus-containing disulphides. On interaction with various organosulphenyl chlorides, they give rise to a wide variety of disulphides:[42,68-81]

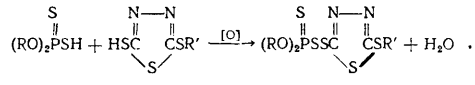
$$(RO)_2\overset{X}{\overset{\|}{P}}SY + ClSR' \rightarrow (RO)_2\overset{X}{\overset{\|}{P}}SSR' + YCl \ ,$$

where X = O or S, Y = H or metal, and R′ = alkyl, substituted alkyl, aryl, substituted aryl, carbamoyl, alkoxycarbonyl, and various ester and heterocyclic groups.

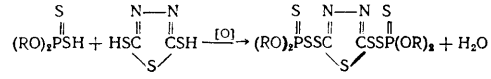
Phosphorodithioic acids react with aminosulphenyl chlorides to form dialkoxythiophosphoryl amino disulphides:[41,61,68-70]

$$(RO)_2\overset{S}{\overset{\|}{P}}SY + ClSNR_2' \rightarrow (RO_2)\overset{S}{\overset{\|}{P}}SSNR_2' + YCl \ .$$

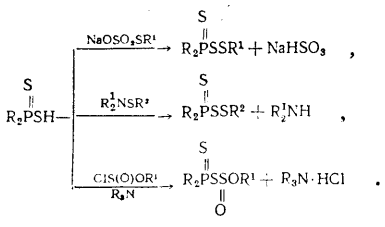
Asymmetric phosphorus-containing disulphides with thiadiazole residues are obtained by the joint oxidation of *O,O*-dialkylphosphorodithioic acids and 2-mercapto-1,3,4-thiadiazoles:[82]



In the presence of a twofold excess of phosphorodithioic acid, compounds with two symmetrical disulphide groups are formed analogously from dimercapto-derivatives:



Asymmetric phosphorus-containing disulphides and sulphonylthio-derivatives can also be obtained by the reaction of phosphorodithioic acids with sodium alkyl thiosulphates,[83] sulphenamides,[61,85] and alkylsulphurous acid chlorides:[84]

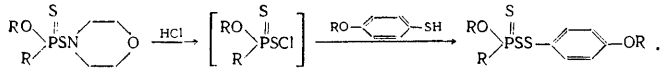


Many asymmetric phosphorus-containing disulphides are obtained by the reaction of dialkoxyphosphoryl- and dialkoxythiophosphoryl-sulphenyl chlorides with compounds containing the mercapto-group:[76,86-88,93]

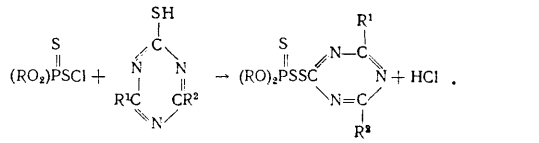
$$(RO)_2\overset{X}{\overset{\|}{P}}SCl + R'SH \rightarrow (RO)_2\overset{X}{\overset{\|}{P}}SSR' + HCl \ .$$

It is noteworthy that, in contrast to phosphorylsulphenyl chlorides, the majority of thiophosphorylsulphenyl chlorides are unstable. However, in many studies these substances were isolated in a pure form using various organophosphorus compounds as intermediates in the synthesis.[39,61,89]

The preparation of asymmetric disulphides from thiophosphorylsulphenamides in the presence of HCl should be assigned to reactions of the same type, since the corresponding thiophosphorylsulphenyl chloride is an intermediate under these conditions:[61]



The interaction of dialkoxythiophosphorylsulphene chlorides with mercaptotriazines in the presence of an acceptor which absorbs the hydrogen chloride evolved leads to dialkoxythiophosphoryl triazinyl disulphides:[90]

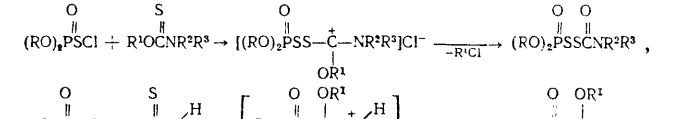


Dialkoxythiophosphorylsulphene chlorides react with derivatives of carbonic and carbamic acids to give the corresponding phosphorus-containing disulphides:[92]

$$(RO)_2\overset{O}{\overset{\|}{P}}SCl + R^1S\overset{X}{\overset{\|}{C}}R^2 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}S\overset{X}{\overset{\|}{C}}R^2 + R^1Cl \ ,$$

where X = O or S, R = alkyl, R^1 = H, a metal, or alkyl, and R^2 = alkoxy-, aryloxy-, or amino-group.

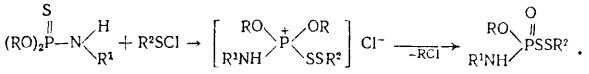
Certain alkoxythiocarbamates also react with dialkoxyphosphorylsulphenyl chlorides. It is remarkable that, depending on the structure of the substituent at the nitrogen atom, final reaction products of different structure are formed:[92]



It has been noted in some reports that, on heating or prolonged storage, compounds containing the thiocarbamoyl residue are converted from the thiolo- into the thiono-form:[92]

$$(RO)_2\overset{O}{\overset{\|}{P}}S\overset{S}{\overset{\|}{C}}NR^1R^2 \rightarrow (RO)_2\overset{S}{\overset{\|}{P}}O\overset{S}{\overset{\|}{C}}NR^1R^2 \ .$$

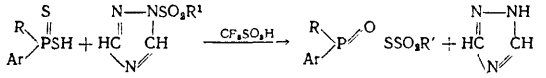
Asymmetric phosphorus-containing disulphides are also the products of the reactions of phosphorothioic acid amides with organosulphenyl chlorides. The formation of a disulphide in this instance is apparently a consequence of the decomposition of the intermediate quasi-phosphonium compound:[94]



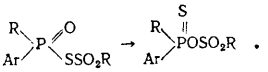
A novel method of synthesis of diethoxyphosphoryl acetyl disulphide from *O,O*-diethyl *S*-methyl phosphorodithioate and thioloacetic acid has been proposed by Michalski and coworkers:[48]

$$(RO)_2\overset{O}{\overset{\|}{P}}OCH_3 + CH_3\overset{O}{\overset{\|}{C}}SH \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}S\overset{O}{\overset{\|}{C}}CH_3 + CH_3OH \ .$$

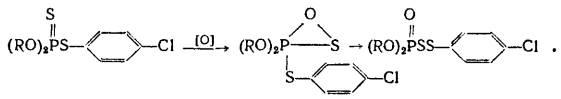
The method of synthesis of sulphonylthio-derivatives by sulphonating sulphotriazoles with alkylarylphosphinodithioic acids in the presence of trifluoromethanesulphonic acid[84] is also of interest:



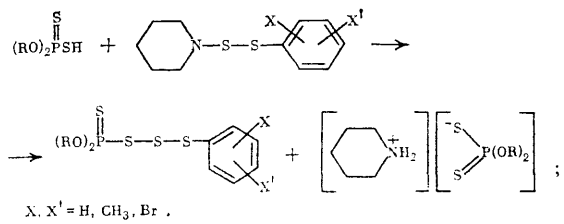
Analogously to compounds containing the thiocarbamoyl residue,[92] *S*-sulphonylphosphinothioates slowly isomerise to the corresponding P–S derivatives at 20 °C:[84]



Asymmetric phosphorus-containing disulphides are obtained by oxidising the esters of phosphorodithioic acid with 3-chloroperbenzoic acid. Three-membered heterocycles are apparently formed as intermediates in this reaction:[95]

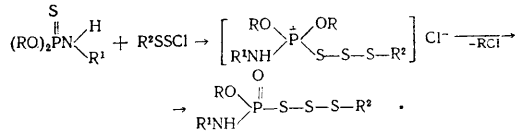


Asymmetric phosphorus-containing trisulphides have been investigated to a much smaller extent. Several examples of the preparation of such compounds have been described in the literature. One of these involves the interaction of *O*,*O*-dialkylphosphorodithioic acids with amino disulphides:[96]



X, X' = H, CH_3, Br .

Trisulphides are also formed in the reactions of phosphorothioic acid amides with organothiosulphene chlorides:[97]



IV. CHEMICAL PROPERTIES

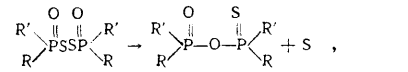
Despite the fact that phosphorus-containing polysulphides are quite readily available, systematic studies of their reactions have been begun comparatively recently and have led to the development of methods of synthesis of a number of classes of organophosphorus compounds whose preparation by other methods presents significant difficulties.[1,97]

The presence of several reaction centres in the molecules of phosphorus-containing polysulphides imparts unusual features to their chemical behaviour. These compounds react with both electrophiles and nucleophiles, the reactions involving and not involving the rupture of the polysulphide chain.

Among the phosphorus-containing polysulphides, the disulphides are the most thoroughly investigated group; tri- and tetra-sulphides have been studied to a much lesser extent.

1. Thermal Stability

The thermal stability of phosphorus-containing polysulphides depends to a large extent on their structure. Thus, whereas bis(diethoxythiophosphoryl) disulphide begins to decompose only at 180 °C,[98] the corresponding dialkyl-, dialkoxy-, and alkylalkoxy-phosphoryl compounds are gradually converted into pyrophosphorothioates, even at room temperature, while on heating the process is rapid:[29]

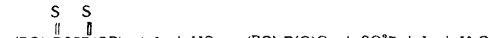


where R and R' = alkyl or alkoxy-group.

Analogous behaviour has also been observed in the series of tri- and tetra-sulphides. Bis(dialkoxythiophosphoryl) trisulphides and bis(dialkoxythiophosphoryl) tetrasulphides are comparatively stable at room temperature, but on heating or prolonged storage they decompose with liberation of sulphur.[4] Bis(dialkoxyphosphoryl) trisulphides and bis(dialkoxyphosphoryl) tetrasulphides are much less stable; they begin to evolve sulphur at room temperature after only several days.[4]

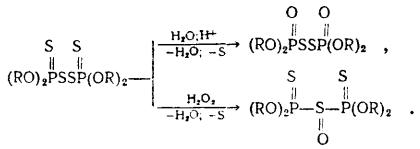
2. Oxidation and Chlorination

Bis(dialkoxythiophosphoryl) disulphides are quantitatively oxidised by iodine in an aqueous alkaline medium:[34,35]

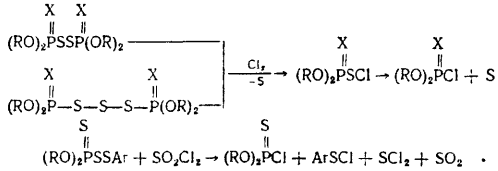


An analogous reaction takes place also when other oxidants are employed.[7]

Depending on the reaction conditions, the oxidation of bis(dialkoxythiophosphoryl) disulphides with hydrogen peroxide can give rise to both bis(dialkoxyphosphoryl) disulphides[99] and bis(dialkoxythiophosphoryl) sulphoxides:[100]



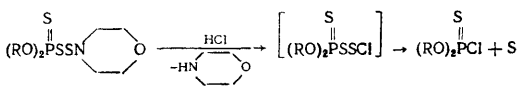
The chlorination of various symmetrical and asymmetric phosphorus-containing disulphides and trisulphides with chlorine or sulphuryl chloride entails the rupture of the polysulphide chain with formation of phosphoryl- or thiophosphoryl- sulphenyl chlorides,[6,9,101–104] but, under the reaction conditions, the latter evolve sulphur, giving rise to phosphorothioic acid chlorides as the final products:



The chlorination or bromination of bis(hexafluorodimethylthiophosphinyl) disulphide leads to the chloride or bromide of hexafluorodimethylphosphinous acid;[105] this disulphide reacts with hydrogen chloride or bromide to form mixtures of hexafluorodimethylphosphinodithioic acid and its halide.[105]

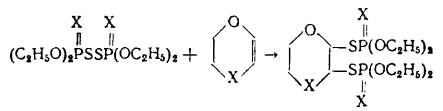
The reaction of dialkoxythiophosphoryl morpholino disulphide with hydrogen chloride proceeds with rupture of the S–N bond. According to Almasi and Plaskucz,[41] the unstable

dialkoxyphosphoryl chloride sulphide is an intermediate in this reaction:



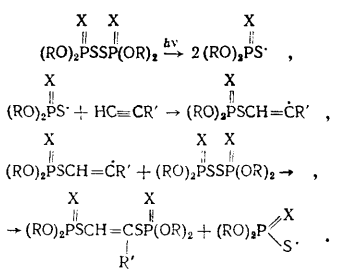
3. Addition to Multiple Bonds

An interesting type of reaction of phosphorus-containing disulphides is addition to multiple bonds.[106,107] Bis(dieth-oxyphosphoryl) bis(diethoxythiophosphoryl) disulphides react with dioxene and thioxene in the presence of iodine to form the corresponding phosphorothioic acid esters:



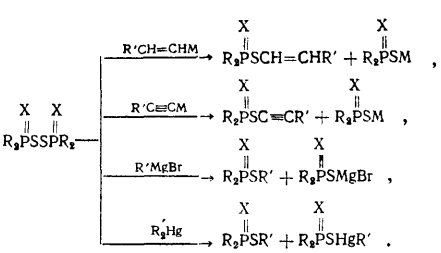
where X = O or S.

The reaction of phosphorus-containing disulphides with acetylenic hydrocarbons takes place under irradiation with ultraviolet light and apparently has a radical mechanism:[108]



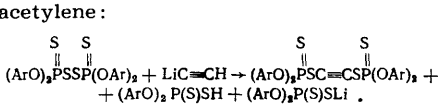
4. Interaction with Organometallic Compounds

Phosphorus-containing disulphides react with organometallic compounds with dissociation of the disulphide bond and the formation of the corresponding phosphorothioic and phosphorodithioic acid esters.[109-113] The literature contains examples of such interaction with alkyl-lithium, alkylpotassium, alkylsodium, metal derivatives of alkenes and alkynes, Grignard reagents,[110-113] and organomercury compounds:[114]

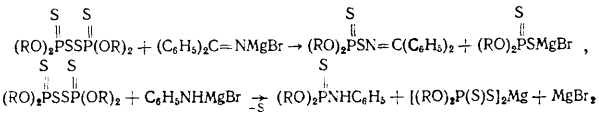


where R = aryl or alkoxy-group, X = O or S, and M is a metal.

Bis-derivatives are also sometimes formed, for example, from lithioacetylene:



The reactions with *N*-magnesio-derivatives either give a low yield of the corresponding sulphenamides or phosphorothioic acid amides are formed as a result of desulphurisation:[113,115]

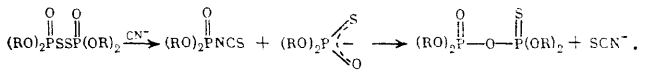


5. Reactions with Hydrocyanic Acid Salts

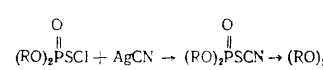
The reactions of hydrocyanic acid salts with bis(thiophosphoryl) disulphides involve the initial formation of the corresponding thiocyanates,[116,117] which subsequently isomerises to the isothiocyanates:



In the case of bis(phosphoryl) disulphides the final products of this reaction are either pyrophosphoromonothioates or, depending on the structure of the groups attached to the phosphorus atom, isothiocyanates:[49,118]



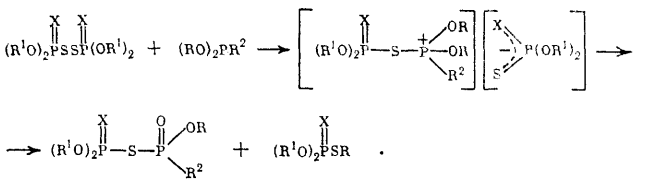
The thiocyanates of *O,O*-dialkylphosphoric acids, obtained by the reaction of phosphorylsulphenyl chlorides with silver cyanide, are stable only in solution at −5 °C. They isomerise at room temperature to the isothiocyanates:[49]



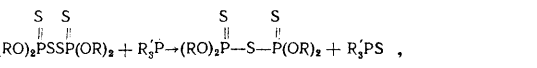
6. Reactions with Tervalent Phosphorus Derivatives

The interactions of bis(phosphoryl) and bis(thiophosphoryl) disulphides with various tervalent phosphoryl derivatives have been studied in detail.[49,119-128] Some of these reactions constitute convenient methods for the synthesis of many organophosphorus derivatives. It is most likely that such reactions proceed via the mechanism of the Arbuzov reaction with formation of an intermediate quasi-phosphonium salt.

The character of the final reaction product depends on the mode of decomposition of this intermediate. Thus bis(dialkoxyphosphoryl) and bis(dialkoxythiophosphoryl) disulphides react with phosphite and phosphonite esters to form pyrophosphates and the esters of phosphorothioic and phosphorodithioic acids,[49,119-123]

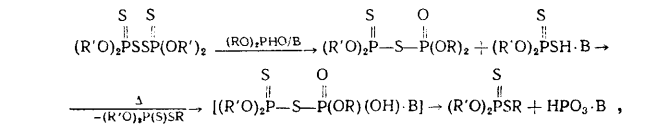


The reactions of phosphorus-containing disulphides with triaryl phosphites, phosphorous acids tris(*N,N*-diethylamide), and triphenylphosphine[123-125] proceed with the desulphurisation of the disulphides and the formation of pyrophosphorotrithioates:



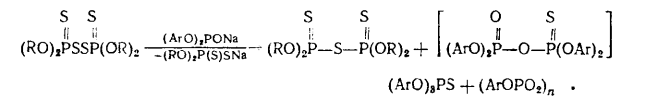
where R = alkyl or phenyl and R′ = phenyl, alkoxy-group, or diethylamino-group.

Bis(dialkoxythiophosphoryl) and bis(diaryloxythiophosphoryl) disulphides react with salts of phosphorous acid in accordance with the mechanism of the Michaelis–Becker reaction:[127,128]



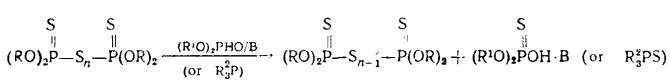
where B is a base.

The formation of pyrophosphorotrithioates and triaryl phosphorothioates has been observed in the reactions of bis(dialkoxythiophosphoryl) disulphides with alkali metal salts of diarylphosphorothioic acids:[124,128]



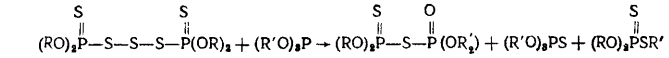
The formation of the triaryl phosphorothioate has been explained by the disproportionation of the tetra-aryl pyrophosphorothioate.

The interaction of phosphorus-containing tri- and tetrasulphides with an equimolar amount of dialkyl or trialkyl phosphite and also triphenylphosphine entails the desulphurisation of these compounds with formation of di- and tri- sulphides respectively:[142]

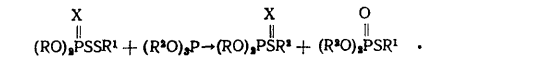


where R and R^1 is an alkyl, R^2 is an alkoxy-group or phenyl, n = 3 or 4, and B is a base.

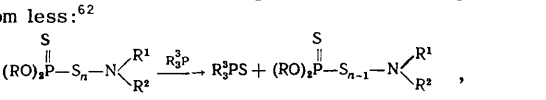
The reactions of phosphorus-containing tri- and tetrasulphides with tervalent phosphorus derivatives apparently proceed analogously to the reactions of the disulphides, via a stage involving the formation of an unstable quasi-phosphonium compound. However, in contrast to the disulphides, the intermediate formed is more polar and its desulphurisation is observed as a consequence of the rupture of the disulphide bond. In the presence of an excess of the di- or tri-aryl sulphite, the reaction does not stop at the stage described above: the disulphides formed react further with the phosphites to form asymmetric pyrophosphorodithioates as well as esters of phosphorothioic and phosphorodithioic acids:[129]



Asymmetric phosphorus-containing disulphides react with triethyl phosphites with rupture of the S–S bond to form the triesters of phosphorothioic and phosphorodithioic acids:[121,126]



In the reaction with trialkyl phosphites or triphenylphosphines, phosphorus-containing amino polysulphides undergo desulphurisation with formation of products containing one sulphur atom less:[62]

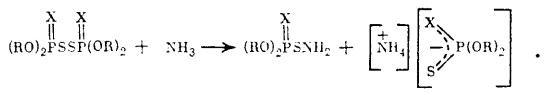


where n = 3 or 4 and R^3 is an alkoxy-group or phenyl.

7. Reactions with Ammonia, Amines, and Hydrazines

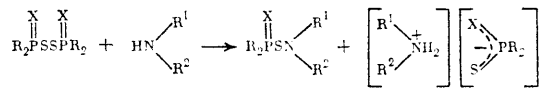
In the reactions of symmetrical phosphorus-containing disulphides with nitrogen-containing bases having a mobile hydrogen atom, the sulphide bond is broken and the corresponding phosphorylsulphenamides and the ammonium salts of phosphorothioic or phosphorodithioic acids are formed. The reaction is general for different amines.[44,130–135] With its aid, thiophosphorylsulphenamides unsubstituted at the nitrogen atom and *N*-monoalkyl-substituted derivatives have become available, whereas it had been impossible to obtain them by the methods known previously.[136]

On reaction with ammonia at approximately 5 °C, bis(dialkoxyphosphoryl) and bis(dialkoxythiophosphoryl) disulphides form high yields of dialkoxyphosphoryl- and dialkoxythiophosphoryl-sulphenamides:[44,137]



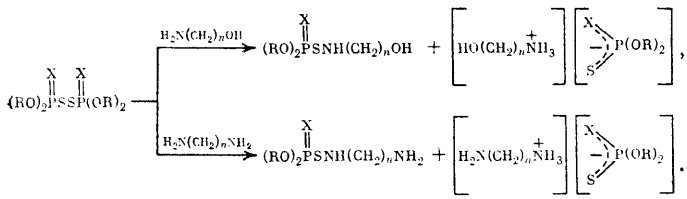
The reaction is rapid and the phosphorylsulphenamides obtained are vacuum-distilled. They are insufficiently stable on storage but are stable at low temperatures and can be used as intermediates in the synthesis of various derivatives.[138]

The substitution of a hydrogen atom in the amide group increases the stability of phosphorylsulphenamides. Thus primary and secondary aliphatic amines react with bis(phosphoryl) and bis(thiophosphoryl) disulphides to form more stable sulphenamides:[130,132,139,140]

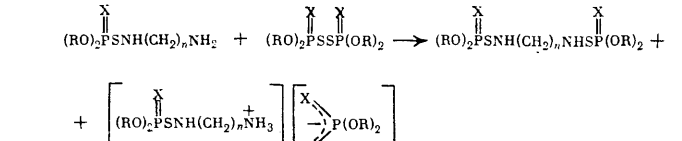


where R is an alkoxy- or aryloxy-group or aryl and X = O or S.

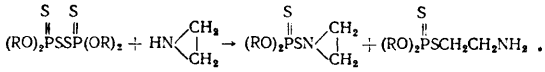
Hydroxyalkylamines and diamines react analogously:[134,141]



Aliphatic diamines can give rise to bisphosphorylated derivatives:[141]

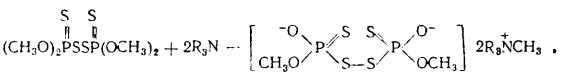


Alicyclic secondary amines react with disulphides in accordance with an analogous mechanism,[140,142] but the reaction with ethyleneimine involves the simultaneous opening of the three-membered ring together with the formation of thiophosphorylethyleneimide:[134]

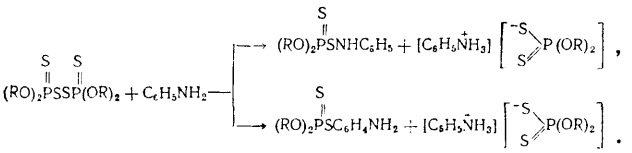


On reaction with tertiary amines, bis(dialkoxythiophosphoryl) disulphides behave as alkylating agents,[143,144] forming the salts of quaternary ammonium bases. This

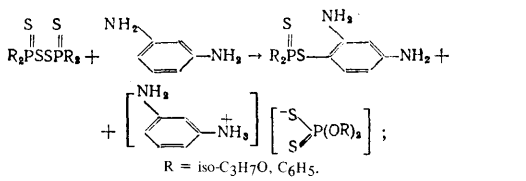
reaction takes place particularly readily with bis(dimethoxythiophosphoryl) disulphide:[143]



Bis(dialkoxythiophosphoryl) disulphides react with aromatic amines in an unusual manner.[145] The reaction with aniline at 90–95 °C takes place with rupture of the sulphide bond via two pathways with formation of *N*-phenylthiophosphorylsulphenamide and the product of the substitution of hydrogen in the aromatic ring by the thiophosphorylmercapto-group:

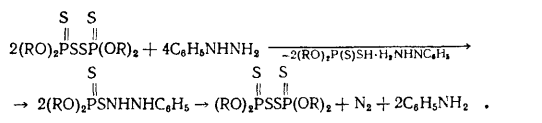


The reaction of phosphorus-containing disulphides with *m*-phenylenediamine proceeds under milder conditions (on heating a mixture of the initial components in benzene) and the main products are *S*-(diaminophenyl)-substituted derivatives of phosphorodithioic acids and substitution takes place in the 4-position of *m*-phenylenediamine:[145]



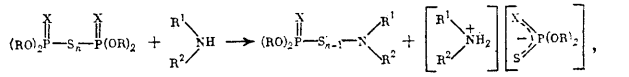
R = iso-C_3H_7O, C_6H_5.

The interaction of phosphorus-containing disulphides with aromatic and aliphatic hydrazines is also interesting. It is not possible to isolate the corresponding thiophosphorylsulphenichydrazide, which apparently decomposes with formation of the initial disulphide, aniline, and nitrogen. In the presence of an excess of phenylhydrazine, the disulphides react almost completely:[131]



In contrast to the reaction with phenylhydrazine, the analogous reaction of disulphides with *N*,*N*-dimethylhydrazine leads to the formation of the dimethylammonium salt of *O*,*O*-dialkylphosphorodithioic acid and not its dimethylhydrazinium salt.[131] This can be explained by the more basic properties of the dimethylamine formed compared with those of the initial dimethylhydrazine.

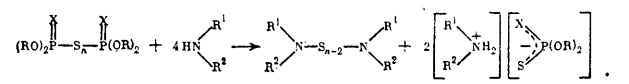
The reactions of phosphorus-containing tri- and tetrasulphides with amines had been virtually uninvestigated previously. Several studies devoted to the interaction of amines with the tri- and tetra-sulphides showed that the main product is the salt of the amine and the corresponding phosphorothioic acid; other phosphorus-containing reaction products could not be isolated.[57,65] It has been established in recent years that, in the interaction of phosphorus-containing tri- and tetra-sulphides with primary and secondary aliphatic or alicyclic amines, the disulphide bond nearest the phosphorus atom is ruptured with formation of the corresponding asymmetric polysulphides containing one sulphur atom less and of the salts of *O*,*O*-dialkylphosphorothioic or *O*,*O*-dialkylphosphorodithioic acids:[147,148]



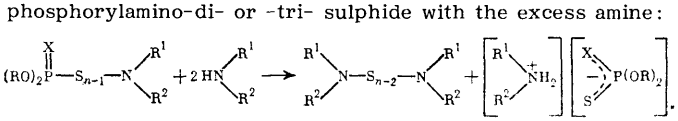
where X = O or S, *n* = 3 or 4, R = alkyl, R^1 = H or alkyl, and R^2 = alkyl (R^1 and R^2 can together form a heterocyclic group).

Dialkoxyphosphoryl *N*-mono(or *N*,*N*-di)alkylamino disulphides are readily vacuum-distilled, while the corresponding dialkoxyphosphoryl and dialkoxythiophosphoryl trisulphides decompose on distillation. The infrared, ^{1}H NMR, and ultraviolet spectra are most informative as regards these compounds. The infrared spectra contain the characteristic absorption band of the N–H group (3320 cm^{-1}), δ_{N-H} = 3.85–4.71 p.p.m. in the ^{1}H NMR spectra, while the ultraviolet spectra exhibit absorption at 226 and 281 nm for the di- and tri-sulphides respectively.[4] The stability of such structures is apparently due to the stabilisation of the molecule by the resonance interaction involving the 3*d* orbitals of the sulphur and phosphorus atoms, which is confirmed by the bathochromic shift of the absorption maximum in the ultraviolet spectra on passing from the disulphide to the trisulphide.[146,149]

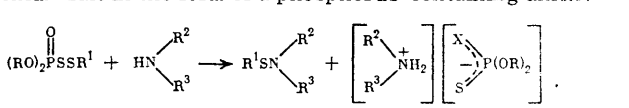
The reactions of tri- and tetra-sulphides with an excess of aliphatic amines result in a quantitative formation of bis(dialkylamino) sulphides or bis(dialkylamino) disulphides together with salts of phosphorothioic or phosphorodithioic acids:



This is explained by the reaction of the intermediate thiophosphorylamino-di- or -tri- sulphide with the excess amine:

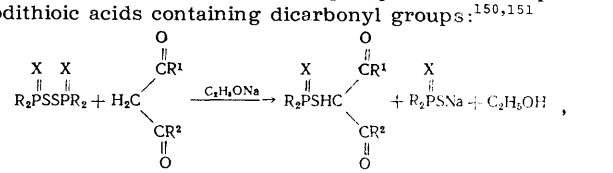


It must be emphasised that, in contrast to the reaction of symmetrical disulphides, the interaction of asymmetric phosphorus-containing disulphides with primary and secondary amines results in the formation of sulphenamides without a phosphorus atom, while the organophosphorus part of the molecule enters into the composition of the corresponding ammonium salt in the form of a phosphorus-containing anion:[94]



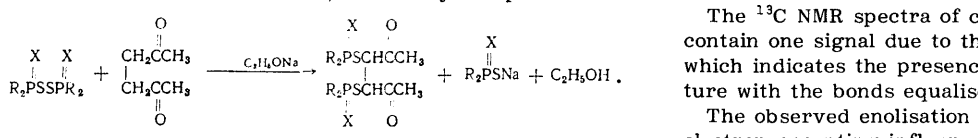
8. Reactions of Phosphorus-containing Polysulphides with a CH Acid

One of the characteristic pathways in the reactions of phosphorus-containing polysulphides involves their interaction with dicarbonyl compounds. Thus the reactions of phosphorus-containing disulphides with β- and γ-dicarbonyl compounds, namely with the sodio-derivatives of acetoacetic ester, acetylacetone, acetoacetanilide, malonic acid ester, and acetonylacetone involve the dissociation of the disulphide bond and the formation of esters of phosphorothioic or phosphorodithioic acids containing dicarbonyl groups:[150,151]



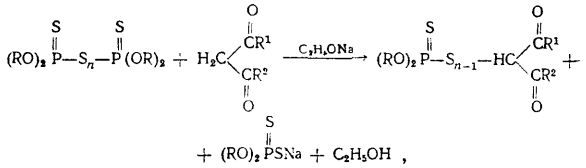
where R = aryl or alkoxy-group, $R^1 = CH_3$ or C_2H_5O, $R^2 = CH_3$, C_2H_5O, or C_2H_5NH, and X = O or S. It must be emphasised that the reaction leads to the formation of the corresponding *C*-derivative.[151]

Depending on the conditions (the ratio of the reactants and process temperature), the sodio-derivatives of γ-dicarbonyl compounds interact with either one disulphide molecule, as in the case of β-dicarbonyl derivatives, or with two such molecules to form disubstituted γ-dicarbonyl compounds:



The more mobile the hydrogen in the molecule of the carbonyl compound, the greater the ease of the reaction with phosphoryl disulphides.

In the interaction of phosphorus-containing tri- and tetrasulphides with the sodio-derivatives of malonic ester, acetoacetic ester, or acetylacetone, the disulphide bond nearest to the phosphorus atom is ruptured and the corresponding asymmetric di- or tri-sulphides are formed together with salts of phosphorodithioic acids:[152]

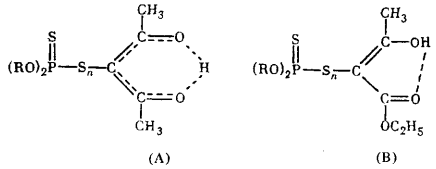


where R = alkyl, R^1 and R^2 = alkoxy-group or CH_3, and $n = 3$ or 4.

Table 4. Spectroscopic characteristics of diacetylmethyl and alkoxycarbonylacetylmethyl dialkoxythiophosphoryl polysulphides.[152]

n	^{1}H NMR spectrum (δ, p.p.m.)		I.r. spectrum (ν, cm^{-1})		^{13}C NMR spectrum (δ, p.p.m.)		U.v. spectrum	
	OH	CH_3	H . . . O	—C=C—	=C—CH_3	=C—OC_2H_5	λ_{max}, nm	lg ε
				Compounds of type (A)				
2	17.1	2.43	1570	—	195.77	—	231	3.1
3	17.6	2.45	1575	—	195.66	—	240	3.9
				Compounds of type (B)				
2	13.7	2.43	1580	1635	184.81	171.59	232	4.1
3	13.7	2.43	1585	1640	184.81	171.68	240	4.6

Analysis of the infrared, ultraviolet, and ^{1}H and ^{13}C NMR spectra showed that the di- and tri-sulphides formed, (A) and (B), are almost wholly enolised in both non-polar solvents and in a pure form. The chemical shift of the signal due to the hydroxyl proton in the ^{1}H NMR spectra (Table 4) indicates the formation of an intramolecular hydrogen bond between the enolic hydroxyl and the oxygen of the carbonyl group:



(A) (B)

Table 4 shows that the chemical shift of the signal of the enolic proton hardly changes with increase of temperature to 70 °C and following a change in the nature of the solvent, which indicates the stability of the chelate structure formed. The number of sulphur atoms in the chain also does not affect the chemical shift. The content of the enolic form in compounds of this type is 98%; on passing from CCl_4 as the solvent to CH_3CN, the content of the keto-form increases to 4%.[152]

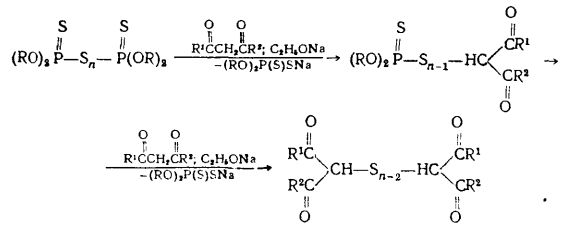
The ^{13}C NMR spectra of compounds of type (A) (Table 4) contain one signal due to the carbon of the carbonyl group, which indicates the presence of a quasi-symmetrical structure with the bonds equalised in pairs.[153]

The observed enolisation is a consequence of the strong electron-accepting influence of the thiophosphoryl disulphide and trisulphide groups, which entails a decrease of the electron density on the methyl carbon atom and hence an increase of the acidity of the CH group.

An increase of the wavelength and of the extinction coefficients in the ultraviolet spectra of compounds of types (A) and (B) (Table 4) on passing from the disulphide to the trisulphide indicates the presence in this compound of an unbranched structure of the polysulphide chain.[154]

The products of the reaction of phosphorus-containing polysulphides with sodiomalonic ester exist in the keto-form, as shown by the absorption band at 1740 cm^{-1} in the infrared spectra, the presence of the signal due to the proton in the CH group (δ = 4.4 p.p.m.), and the absence of the signal of the enolic proton in the ^{1}H NMR spectra.

In the interaction of symmetrical tri- or tetra-sulphides with an excess of a β-dicarbonyl compound, the disulphide bonds closest to the phosphorus atom are ruptured in succession and the corresponding mono- or di-sulphides without phosphorus are formed:[152]

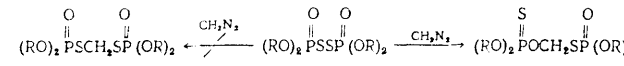


9. The Interaction of Phosphorus-containing Polysulphides with Diazo-compounds

The interaction of phosphorus-containing polysulphides with diazo-compounds has been studied only in recent years.[155-163] It is stated in the literature that aromatic disulphides, in particular diphenyl disulphide, react with the Simmons–Smith reagent (iodomethylzinc iodide ICH_2ZnI) and also with the esters of diazocarboxylic acids in the presence of a catalyst to form the products of the insertion of the corresponding carbene in the disulphide bond. On the other hand, dialkyl sulphides do not react with the Simmons–Smith reagent and the reaction with diazocarboxylic acid esters takes place with only an insignificant yield.[164,165]

These data show that the activity of the disulphides in relation to diazo-compounds is significantly influenced by their structure. The presence of electron-donating substituents reduces and that of electron-accepting substituents increases the reactivity of the disulphides. The latter factor is manifested in the reaction of phosphorus-containing polysulphides with diazo-compounds in reactions of the carbene and non-carbene types.

It is of interest that, in contrast to aromatic disulphides, bis(dialkoxyphosphoryl) disulphides never form products of the insertion of the methylene group in the S–S bond on reaction with an excess of diazomethane in an ethereal solution under various conditions (under irradiation by light from a mercury lamp, in daylight, or in the absence of illumination); this reaction leads to the formation of a low yield of asymmetric products—dialkoxythiophosphoryloxy—dialkoxyphosphorylthiomethanes:[155]

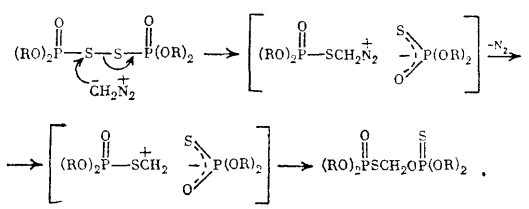


where R = alkyl.

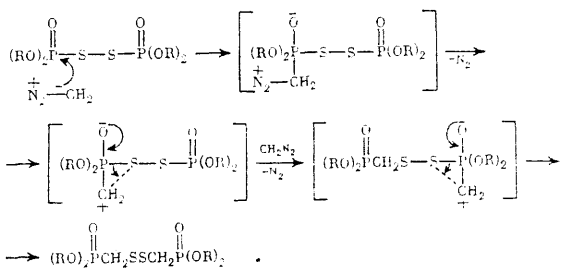
The ^{31}P NMR spectra of these compounds consist of two singlet signals with δ_P = 21–23.7 p.p.m. and 65.2–68.2 p.p.m., which are characteristic of quinquevalent phosphorus in the phosphoryl and thiophosphoryl groups respectively. The ^1H NMR spectra show a doublet of doublets due to the CH_2 group with δ_H = 5.28–5.40 p.p.m. ($^3J_{P(O)H}$ = 19.5 Hz, $^3J_{P(S)H}$ = 13.5 Hz), which also confirms the presence in the molecule of the phosphoryl and thiophosphoryl groups and the asymmetry of the structure formed. The infrared spectra contain an absorption band in the range 1260–1275 cm^{-1} (due to the vibrations of the P=O bond). The absorption band corresponding to the P=S group is shown in the Raman spectra in the range 615–630 cm^{-1}.[155]

Since the given reaction results in the formation of products containing the thiophosphoryl group instead of one of the initial phosphoryl groups, the reaction has been called the phosphoryl–thiophosphoryl rearrangement.[155]

It is believed that, at least in the absence of illumination, bis(dialkoxyphosphoryl) disulphides interact with an undissociated diazomethane molecule. This reaction can be represented by different schemes. One of these involves attack by diazomethane on one of the sulphur atoms with rupture of the disulphide bond and the formation of an intermediate structure with an ambident thiophosphoryl anion and a phosphorus-containing diazonium cation; the last species, which is an unstable intermediate, gives off nitrogen and is converted into the more stable phosphorus-containing carbonium ion, which attacks the rigid end of the triad, namely oxygen, in the $(O\therefore P\therefore S)^-$ ambident system:

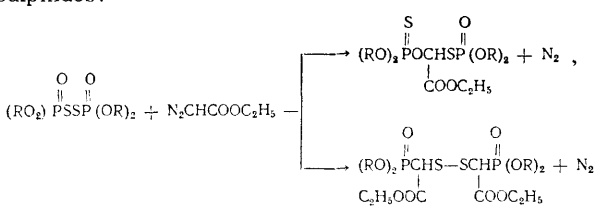


The interaction of bis(dialkoxyphosphoryl) disulphides with diazomethane in the absence of illumination is not restricted to the phosphoryl–thiophosphoryl rearrangement and is accompanied by the formation of the products of insertion of two methylene groups in both P–S bonds of the disulphide with retention of the S–S bond and the symmetry of the structure.[156] The formation of products of the P–S insertion has been represented by a scheme involving successive attack by diazomethane on the phosphorus atom of the disulphide with the intermediate formation of a dipolar diazonium ion, its decomposition to N_2 and a dipolar carbonium ion, and the 1,2-migration of the P(O)SS fragment to the carbonium centre; an analogous sequence of stages after the attack by a second diazomethane molecule leads to the final product:



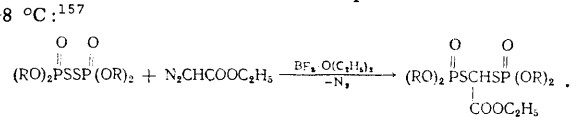
The ^1H NMR spectrum of the products of insertion in the P–S bond of the disulphide (R = iso-C_3H_7) contains a doublet associated with the methylene protons of the CH_2 group having δ_H = 2.21 p.p.m. ($^2J_{PH}$ = 15 Hz). The $^{31}P-\{^1H\}$ NMR spectrum consists of a singlet with δ_P = 24.9 p.p.m.; the infrared spectrum contains an absorption band due to the P=O group in the region of 1260 cm^{-1}.[156]

The interaction of bis(dialkoxyphosphoryl) disulphides with diazoacetic ester involves (as in the reaction with diazomethane) under conditions not promoting the formation of a carbene, involves both the phosphoryl–thiophosphoryl rearrangement with formation of dialkoxythiophosphoryloxy-dialkoxyphosphorylthioacetic esters and the insertion of the ethoxycarbonylmethylene group in both P–S bonds with formations of bis(ethoxycarbonyldialkoxyphosphonomethyl) disulphides:[156]



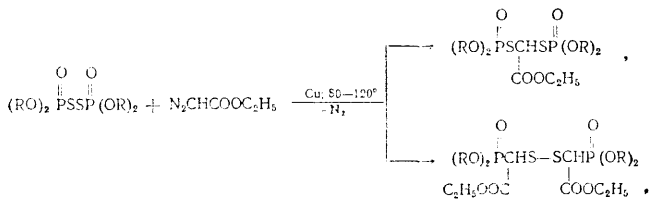
The two competing reactions take place at different rates and, depending on the process conditions, it is therefore possible to obtain each reaction product separately or their mixture in different proportions.

The reaction under the conditions of the catalytic generation of ethoxycarbonylcarbene leads to different results. When bis(dialkoxyphosphoryl) disulphides react with diazoacetic ester in the presence of catalytic amounts of boron trifluoride etherate, bis(dialkoxyphosphorylthio)acetic esters, the products of the insertion of ethoxycarbonylcarbene in the S–S bond, are formed even at temperatures between –20° and +8 °C:[157]

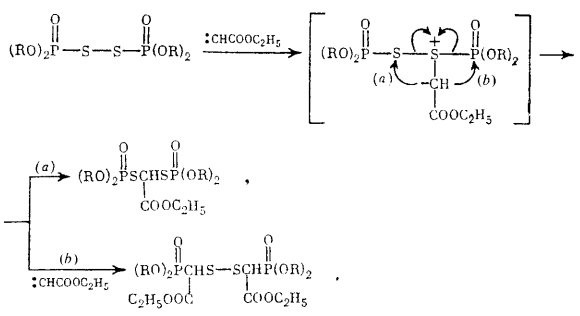


The ^1H NMR spectra of these compounds contain a triplet due to the methylidyne proton of the $CHCOOC_2H_5$ group with δ_H = 4.90–5.04 p.p.m. ($^3J_{PH}$ = 13.5 Hz). A singlet with δ_P = 21.1–21.6 p.p.m. can be observed in the $^{31}P-\{^1H\}$ NMR spectra. The infrared spectra contain absorption bands corresponding to the stretching vibration frequencies of the P=O (1265–1275 cm^{-1}) and C=O (1745 cm^{-1}) bonds.[157]

Under the conditions of the catalytic generation of the carbene in the presence of copper powder at 80 °C in benzene or at 80–120 °C in the absence of the solvent, the formation of the product of the insertion of ethoxycarbonylcarbene in the S–S bond of the disulphide is accompanied by the competing reaction involving insertion in both P–S bonds:[157]

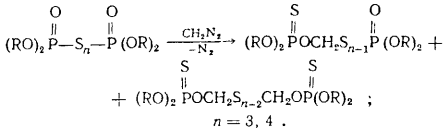


The insertion of ethoxycarbonylcarbene in the S–S bond apparently proceeds via a stage involving the formation of an unstable sulphonium ylide with subsequent 1,2-migration of the phosphorylsulphenyl group from the sulphonium sulphur atom to the ylide carbon atom (pathway *a*). The insertion of ethoxycarbonylcarbene in the P–S bond is also regarded as a process involving the intermediate formation of a sulphonium ylide with subsequent migration of the phosphoryl group from the sulphonium sulphur atom to the ylide carbon atom (pathway *b*):[157]

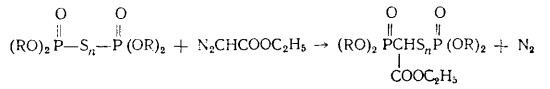


Since insertion in the P–S bond is observed also under conditions which do not promote the formation of carbenes, it is necessary to take into account the possibility of the reaction with an undissociated molecule of the diazo-compound. However, in this case the reaction centre is apparently the phosphorus atom and not the sulphur atom in the disulphide molecule.

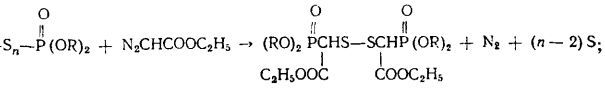
Phosphorus-containing tri- and tetra-sulphides form the products of the phosphoryl–thiophosphoryl rearrangement on interaction with diazomethane:[158]



In the reaction with diazoacetic ester there is no rearrangement and the products of the insertion of the ethoxycarbonylmethylene group in one of the P–S bonds of the polysulphide are formed in a high yield:[159]

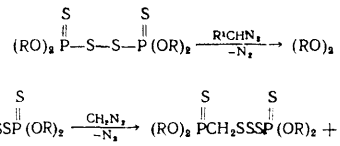


In the presence of an excess of diazoacetic ester, two ethoxycarbonylmethylene groups are inserted in the P–S bonds of the polysulphides and desulphurisation takes place:[159]



$n = 3, 4$.

Reactions analogous to those described above have also been considered in relation to thiophosphoryl di-, tri-, and tetra-sulphides:[160–162]

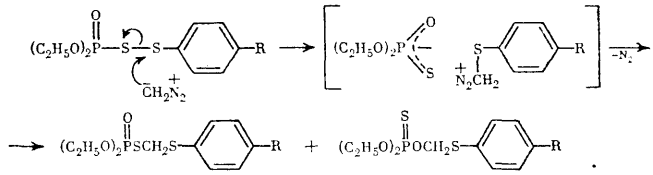


where R = alkyl and R′ = H or $COOC_2H_5$.

In the case of bis(dialkoxythiophosphoryl tetrasulphides the sequence of the insertions of the methylene group initially in one and then in the other S–S bond of the polysulphide has been observed with the aid of ^1H NMR spectroscopy. This is indicated by one doublet due to the protons of the CH_2 group with $\delta_H = 4.02$ p.p.m. ($^3J_{PH} = 18$ Hz), appearing initially in the spectrum, and then by the second doublet with $\delta_H = 3.75$ p.p.m. ($^3J_{PH} = 18$ Hz).[162]

It has been suggested that the phosphoryl–thiophosphoryl rearrangement takes place in the reaction with an undissociated molecule of the diazo-compound, while the S–S insertion is a reaction of the carbene type. The P–S insertion reaction can apparently be both of the carbene and non-carbene types.

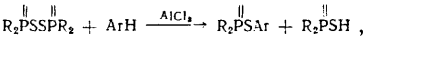
As regards phosphorus-containing disulphides with an asymmetric structure, it has been reported that the methylene group is inserted in the S–S bond of aryl diethoxyphosphoryl disulphide in its interaction with diazomethane.[95] The products of the rearrangement were obtained in an insignificant yield.[166] It is believed that the formation of arylthiodiethoxyphosphorylthiomethane and arylthiodiethoxythiophosphoryloxymethane proceeds via the "diazonium" mechanism; the diazonium cation interacts with the thiophosphoryl anion to a greater extent via the sulphur atom and to a lesser extent via the oxygen atom of the ambident $(O\cdots P\cdots S)^-$ triad:[166]



The reactions of phosphorus-containing polysulphides with diazo-compounds make it possible to obtain organophosphorus compounds which had been difficult to synthesise otherwise or had been altogether unknown and lead to interesting possibilities for the study of the carbene reactions in the chemistry of organophosphorus compounds.

10. The Reactions of Phosphorus-containing Disulphides in the Presence of Lewis Acids

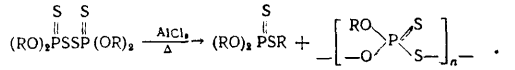
When phosphorus-containing disulphides react with aromatic hydrocarbons and alkyl aryl ethers in the presence of Lewis acids, the corresponding S-aryl esters of phosphorothioic acids are formed:[167,168]



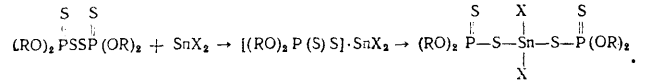
where R = alkoxy-group or phenyl. One must note that, in the case where the unsubstituted alkyl aryl ethers are employed, a mixture of isomers is formed whose separation presents certain difficulties.

When bis(dialkoxythiophosphoryl) disulphides are used, alkylation of the aromatic ring is also observed and in some cases this reaction predominates.[167,168]

In the presence of Lewis acids, bis(dialkoxythiophosphoryl) disulphides are capable of self-alkylation:[167]



The interaction of phosphorus-containing disulphides with tin dihalides is of interest:[169,170]



A complex of tin dihalide is apparently formed initially. The subsequent redistribution of electron density leads to the rupture of the S–S bond and the formation of S–Sn valence bonds.

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Thus the unusual chemical behaviour of phosphorus-containing polysulphides renders this group of compounds extremely promising for use in organic synthesis in order to obtain new types of organophosphorus compounds or compounds of this kind which have been hitherto difficult to obtain.

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