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The Reactivity of 1,3,2-Diheterophospholans Containing a Tricoordinate Phosphorus Atom

M.A.Pudovik, V.V.Ovchinnikov, R.A.Cherkasov, and A.N.Pudovik

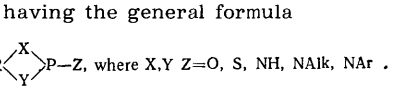
The results of studies on the reactivity of 1,3,2-di-heterophosphacycloalkanes containing a tricoordinate phosphorus atom carried out in recent years are examined and surveyed. Muchattention has been devoted to reactions leading to an increase of the coordination number of the ring phosphorus atom and also to exocyclic and endocyclic substitution reactions. The mechanisms and certain stereochemical characteristics of the reactions of cyclic phosphorus compounds are discussed. In a few instances the reactivities have been estimated quantitatively.
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I. INTRODUCTION

The characteristic features of the reactivity of cyclic compounds of tricoordinate phosphorus were noted previously in a review[1,2]. During the time which has elapsed since then, new interesting data have accumulated, supplementing and deepening the available information about the mechanisms of reactions of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes having the general formula



The description of these reactions is based on ideas about the structures of the intermediates or transition states involving an increase of the coordination number of the phosphorus atom. In many cases the reactivity of these compounds is explained from the standpoint of ring strain. Such inferences are based on the data accumulated hitherto on the cyclic phosphorus compounds: the steric structure of the ring itself and of the exocyclic substituent linked to it, the distribution of electron density in the molecule, the electronic situation at the phosphorus nucleus itself—the character of the hybridisation of its lone electron pair (LEP), and the strength of the phosphorus–heteroatom bond.

The steric structures of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with a tervalent phosphorus atom have been studied in detail by various methods[3-5]. An important feature of the structure of five-membered phosphorus rings compared with the phosphorinane and acyclic analogues is a significantly reduced (93–100°) endocyclic X–P–Y angle. As a consequence of this, the electron density at the centre of the triad is reduced, which is clearly manifested by the deshielding of the phosphorus nucleus, according to ^{31}P NMR data, with decrease of ring size[6]. At the same time the LEP of phosphorus in such compounds has a reduced *p* character compared with the six-membered and acyclic derivatives with similar structures[7] and is therefore less reactive with respect to electrophiles. This factor is responsible for certain specific features of the reactivity of diheterophospholans. Many aspects of a purely synthetic type are not considered in this review. We thought it useful to deduce and as far as possible survey the characteristics of the reactivity of 1,3,2-diheterophosphacycloalkanes with a tervalent phosphorus atom, particular attention being devoted to compounds with a five-membered ring.

II. BASICITY AND COMPLEX FORMATION

Data concerning the ability of phosphorus-containing heterocycles to participate in nucleophilic reactions can be obtained from the analysis of the results of studies of the protonation of these compounds and of their tendency to form metal complexes.

It is known[8] that the introduction of electron-accepting substituents at a tricoordinate phosphorus atom reduces significantly the electron density at this atom, which entails a decrease of nucleophilic reactivity. An analogous effect is observed when phosphorus is incorporated in a ring. Thus the observed high ionisation potential of 1,3-butylene phosphorochloridite (9.90 eV) compared with diethyl phosphorochloridite (9.51 eV) may indicate a weakening of the interaction of the LEP of the phosphorus and oxygen atoms ($n_P - n_O$) on cyclisation[9]. In this respect, the absence of interaction between HCl and five-membered cyclic phosphorochloridites, obtained by the reaction

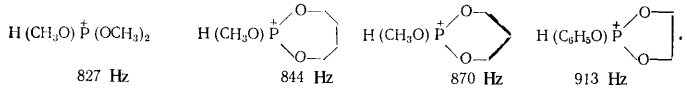


is also striking[10].

Acyclic and cyclic six-membered phosphorochloridites as well as 1,3,2-oxaza- or 1,3,2-diaza-phospholans are obtained only in the presence of hydrogen chloride acceptors[10]. While gaseous HCl does not interact with 2-chloro-1,3,2-dioxaphospholans, on replacement of the chlorine atom by an alkoxy-, alkyl, or dialkyl-amide group the tervalent phosphorus atom can be protonated[11].

An important characteristic of the protonated phosphite is the constant $^1J_{PH}$, which is extremely sensitive to a change in the electronic and steric environment of phosphorus. The

increase of $^1J_{PH}$ on passing from acyclic to six- and five-membered cyclic as well as bicyclic protonated phosphites is consistent with the increase of the s character of the LEP of the phosphorus atom in the initial compounds[11,12]:

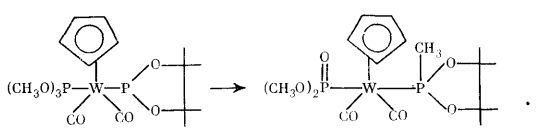


The results of the determination of the proton affinities and ionisation potentials of cyclic phosphites in the gas phase[13] also confirm the earlier conclusion that the basicity of the phosphorus atom decreases in the following sequence of phosphites: acyclic > six-membered > five-membered > bicyclic[14,15], which is associated with the increase of the ring strain in this sequence.

It has been suggested that the repulsion between the LEP of the oxygen and phosphorus atoms increases the energy of the highest occupied molecular orbital of the unshared electron pair of the phosphorus atom in an acyclic phosphite and its proton affinity. The inclusion of a phosphorus(III) atom in a five-membered ring alters the geometry of the pyramidal structure of the phosphorus atom and leads to strain in the cyclic system. As a consequence of this, the degree of hybridisation of the LEP in the ring phosphorus and oxygen atoms changes, their mutual repulsion diminishes, and the protophilic properties of the cyclic phosphite are diminished[13].

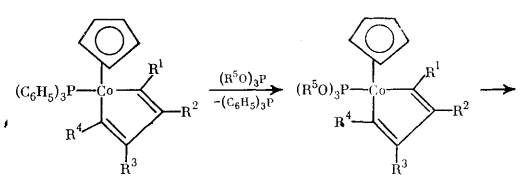
By virtue of the low basicity of phosphorus in dioxaphospholans, 1,2-phenylenephosphophosphorous acid exists in the condensed phase in a form with a tricoordinate phosphorus atom[16]. The presence of a small amount of a similar structure has been noted for the oxathiaphospholan analogue[17]; six-membered cyclic and acyclic diorganylphosphorous acids exist mainly as hydrophosphoryl derivatives $(RO)_2P(O)H$.

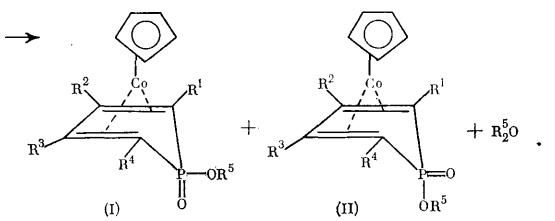
The reduced electron-donating capacity of the LEP of phosphorus in cyclic phosphites is also indicated by data demonstrating a lower stability of their complexes with phenols[18], BH_3, BF_3, and metals[19-21]. It is significant that the basicity of the phosphorus atom in phosphorinane structures and hence the stability of the adducts with BH_3 depend on the steric orientation of the LEP. Thus the equatorial electron pair in six-membered cyclic phosphites is less "basic" than the axial pair[9]. However, the formation of complexes of these compounds with Lewis acids leads to adducts in which the complex-forming agent is in the equatorial and apparently less sterically hindered position[20]. The cyclic phosphites in complexes can undergo intramolecular alkylation[22]:



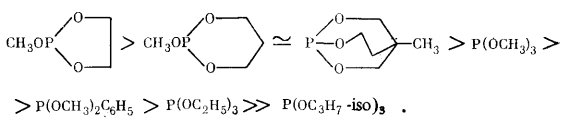
The isomerisation of coordinated phosphites has been noted in substitution reactions proceeding via Scheme 1:[23]

Scheme 1





The use of cyclic phosphites in this reaction showed that at the triphenylphosphine substitution stage the rate of the process is independent of the nature of the phosphite. However, at the stage involving isomerisation of the phosphacyclopentadienyl derivatives (I) and (II) within the complex, the following phosphite activity series was found:

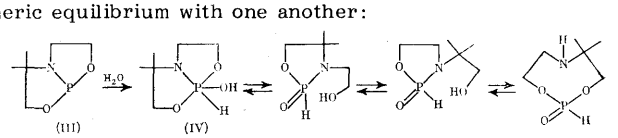


The above sequence can be explained by taking into account the fact that the isomerisation process proceeds via a transition stage with phosphorus(V),[23] in which there is a significant decrease of ring strain in cyclic phosphites. The small steric effect of cyclic dihydroxyalkylene groups compared with alkoxy-groups (particularly with an iso-structure)[23,24] also facilitates the reaction.

III. REACTIONS WITH COMPOUNDS CONTAINING A MOBILE HYDROGEN ATOM

1. Water, Alcohols, and Phenols

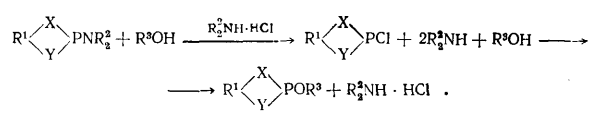
The interaction of cyclic phosphites with water and aqueous organic solvents is used widely as a convenient method of synthesis of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes containing the hydrophosphoryl group[25]. Dioxaphospholans[26,27] and oxazaphospholans[28] unsubstituted in the ring hydrolyse as a rule with ring opening, the hydrolysis being significantly accelerated by acid catalysts[29]. The presence of alkyl substituents at endocyclic carbon atoms greatly stabilises the cyclic fragment and hydrolysis takes place with retention of the ring[29-31]. In the low-temperature hydrolysis of condensed phosphoramidites (III),[32,33] the formation of the hydroxyphosphoranes (IV) was detected by ^{31}P NMR. These compounds are transformed further into derivatives of tetracoordinate phosphorus involved in a tautomeric equilibrium with one another:



The reactions of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with alcohols, phenols, and glycols lead either to exocyclic substitution[34-41] or to the dissociation of one or both endocyclic phosphorus–heteroatom bonds[42-51]. There is also a possibility of the formation of monocyclic phosphoranes or spirophosphoranes with a P–H bond[52-55]; in many instances the reaction products are compounds of hexacoordinate phosphorus[56-59].

The study of the reactions of the amides of cyclic phosphorus acids with proton-donating reagents established the important role of acid catalysis[38,60-62]. Thus alcoholysis of phosphoramidites is accelerated by amine hydrochlorides,

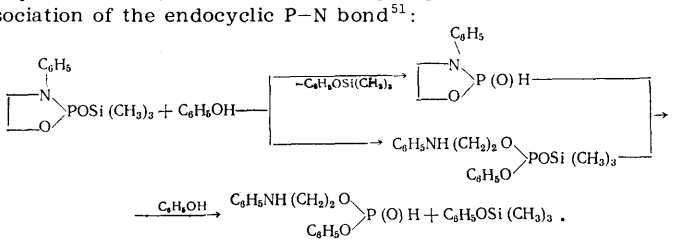
usually present as admixtures in the initial compound. This is accompanied by the intermediate formation of tervalent phosphorus chlorides which are readily esterified with regeneration of the catalyst[62]:



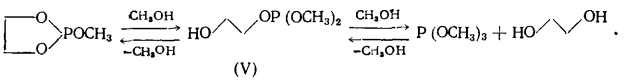
The acceleration of reactions of this type under the conditions of base catalysis has been noted[63].

The rates of the reactions of 2-dimethylamino-1,3,2-dioxaphospholan with phenol, butanol, and t-butyl alcohol in benzene increase with increase of the acidity of the hydroxylated reagent[38]. The reactivity of five-membered cyclic phosphoramidites in a non-catalysed reaction with butanol is significantly higher than that of the corresponding acyclic derivatives[38]; an increase of the number of alkyl substituents in the ring increases the reactivity of cyclic phosphoramidites in these reactions. The interpretation of the results is fairly difficult, particularly since it has been shown by kinetic studies[41] that the first stage of the alcoholysis involves complex formation between the alcohol and the phosphoramidite. According to the authors[41], this hinders comparison of the kinetic parameters of the reaction with the structures of the initial reactants.

The alcoholysis of 1,3,2-oxazaphospholans containing the exocyclic POSi group takes place simultaneously via two pathways—the desilylation of the initial phosphoramidite and dissociation of the endocyclic P–N bond[51]:

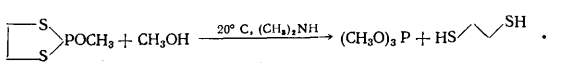


The P–N, P–O, and P–S bond strengths in 1,3,2-diheterophospholans unsubstituted in the carbon component of the ring and also the relative contributions of the *exo*- and *endo*-pathways of the methanolysis depend on different factors and in the first place on the temperature and acidity of the reaction medium and on the basic additives[47,48]. The methanolysis of 2-methoxy-1,3,2-dioxaphospholan does not take place in an alkaline medium; in the absence of bases, equilibrium involving the formation of the intermediate (V) with an open-chain structure has been noted[48]:

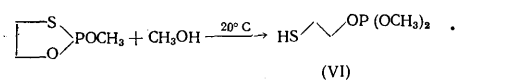


(V)

At 20 °C methanol does not interact with 2-methoxy-1,3,2-dithiaphospholan; the P–O bond is cleaved only at 80 °C in the presence of an excess of methanol. However, after the addition of catalytic amounts of dimethylamine, both P–S bonds of the heterocycle are readily ruptured even at room temperature[47]:

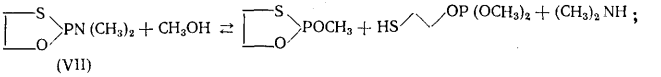


The use of oxathiaphospholan leads to the formation of β-mercaptoethyl dimethyl phosphite(VI):

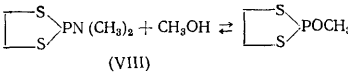


(VI)

The methanolysis of 2-dimethylamino-1,3,2-oxathia- and 2-dimethylamino-1,3,2-dithia-phospholans (VII) and (VIII) in the absence of basic additives is reversible[47]:

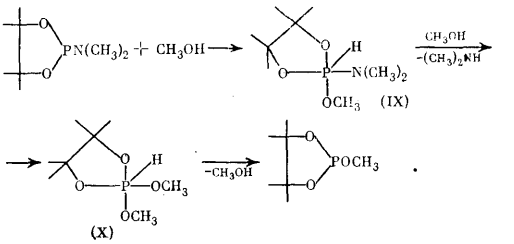


(VII)



(VIII)

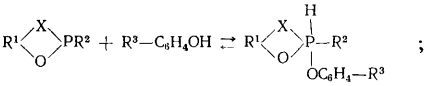
An increasing amount of data confirming that the alcoholysis of 1,3,2-diheterophospholans by alcohols and phenols involves the intermediate formation of structures of the phosphorane type with a P–H bond has been published recently[35,39,52–55]. The formation of the pentacoordinate intermediates (IX) and (X) in the reaction of 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan with methanol has been detected by ^{31}P NMR:[36]



(IX)

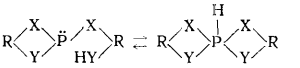
(X)

1,3,2-Dioxa- and 1,3,2-oxaza-phospholans react with substituted phenols also to form addition products which contain a pentacovalent phosphorus atom and are in equilibrium with the initial reactants[53,64]:



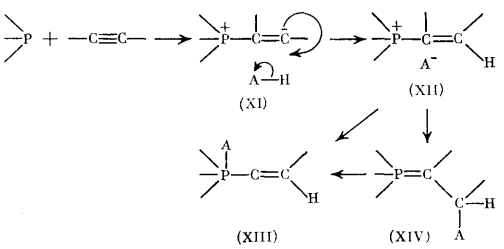
R^1=*o*-C_6H_4—, —$C(CH_3)_2C(CH_3)_2$—; R^2=Alk, Ar; R^3=*p*-NO_2, *p*-Cl, H, *p*-NH_2, *o*-NH_2; X=O, NH.

The formation of a phosphorane is favoured by a decrease of the temperature of the reaction mixture and an increase of the acidity of the phenol. It is believed[53] that the rate-determining stage in these reactions is the protonation of the phosphorus atom. An intramolecular version of such addition has been discovered in the case of 1,3,2-diheterophospholans containing functional groups with a mobile hydrogen atom in the β-position in the exocyclic substituent:



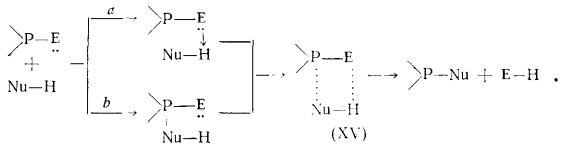
The position of this tautomeric equilibrium depends on the temperature, the nature of the solvent, the heteroatoms in the ring, and the nature of the substituents in the latter. Data on this question have been exhaustively described in a number of communications[65–71], although one should note that the thermodynamic characteristics of such processes, like those of many reactions of 1,3,2-diheterophosphacycloalkanes with proton donors, have not been described in the literature.

The course of the reactions of cyclic phosphites with alcohols in the presence of a third reactant—a compound with a C=C bond, was unexpected[54]:



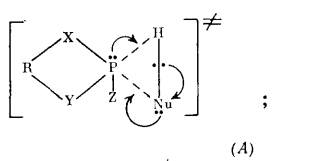
The dipolar ion (XI) formed in the first stage interacts with the proton-donating reactant A–H, leading to the phosphonium intermediate (XII) which is stabilised by being converted into the final phosphorane (XIII) either directly or via the unstable ylide (XIV).

The available experimental data do not allow a single mechanism to be postulated for the interaction of 1,3,2-diheterophosphacycloalkanes with water, alcohols, and phenols. A number of workers have expressed the view that the substitution of an exocyclic group is an S_N2 process [with respect to phosphorus(III)] in which the reactivity of cyclic organophosphorus compounds depends on the ratio of the electronic and steric characteristics of the exchanging groups and also on the nature of the ring heteroatoms[61]. If the exocyclic substituent at the tervalent phosphorus atom is a group which is difficult to eliminate but is fairly basic, there is a possibility of electrophilic cooperation as a result of preliminary protonation (pathway *a*) or protonation after orientation of the nucleophile (pathway *b*):

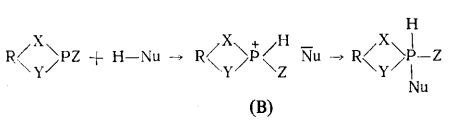


According to Mathis[37], these reactions can proceed via a four-centre cyclic transition (XV) or via the formation of the intermediate (XV) having a similar structure. Such association can take place also with participation of an endocyclic heteroatom[47], whereupon substitution occurs with ring opening.

On the other hand, the data presented in this Section show that, in the course of the reactions of 1,3,2-diheterophospholans with proton-donating reagents, intermediates with a pentacoordinate phosphorus atom probably play an important role. They can be formed via the 1,1-addition of a nucleophile to the tervalent phosphorus atom, or in a single stage via a three-centre transition stage (A), or in two stages via an ionic intermediate (B)†:



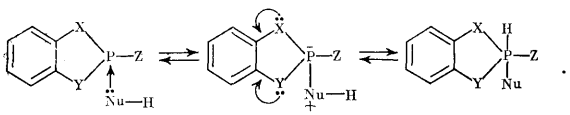
(A)



(B)

†Such reactions are classified in the literature as oxidative addition reactions[72,73].

In those cases where the electrophilicity of phosphorus is fairly high and the negative charge is effectively delocalised in the transition state (or in an anionic intermediate; for example, in benzodiheterophospholans), nucleophilic attack on the tervalent phosphorus atom can precede the proton transfer:

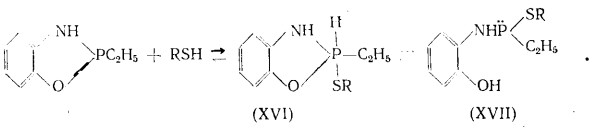


The possibility of the existence of cyclic anions with a tetracoordinate phosphorus atom has been demonstrated in a number of studies[74,75]. There is a possibility of base catalysis in reactions via this pathway[63]. The ability of the phosphorus atom in cyclic compounds to increase fairly readily its coordination number leads in many instances to products with a hexacoordinate phosphorus atom[56–59].

2. Mercaptans and Amines

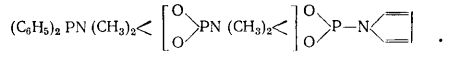
In contrast to alcohols and phenols, mercaptans as a rule convert 1,3,2-diheterophospholans into thiophosphoryl compounds[76,77]. Only in rare instances are exocyclic groups at the tervalent phosphorus atom substituted by an alkylthio-group with retention of the coordination number[63]. The formation of cyclic phosphorothioic acids is observed on interaction of cyclic phosphites with hydrogen sulphide[78–80].

Depending on their structure, 1,3,2-oxazaphospholans react differently with mercaptans. Saturated heterocycles with an alkylene bridge in the molecule undergo "thionation" with retention of the cyclic fragment[63]. On the other hand, 4,5-benzo-1,3,2-oxazophospholans react with mercaptans to form addition products—monocyclic phosphoranes (XVI) with a P–H bond and a small amount of the isomeric phosphonamidothioites (XVII) with a tervalent phosphorus atom[55,81]. Compounds (XVI) and (XVII) are probably involved in a tautomeric equilibrium, which is displaced towards compound (XVI):



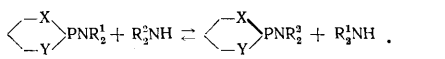
(XVI) (XVII)

The aminolysis of cyclic phosphorus(III) derivatives has been studied in greatest detail in relation to 1,3,2-dioxaphospholans having an exocyclic P–N bond[37]. The reactivity of cyclic phosphoramidites in transamidation is as a rule higher than that of their acyclic analogues and depends on the nature of the attacking and leaving amines. The rate of aminolysis increases with increasing basicity of the amine and the electrophilicity of the phosphorus atom in the sequence[82]



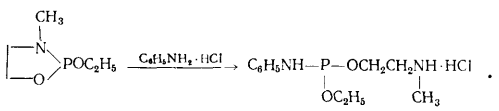
At the same time instances of the substitution of a more basic amine by a less basic amine in the presence of acid admixtures are known. The reactions take place in such cases in the three-component phosphoramidite–acid–amine system via the initial protonation of the phosphoramidite and subsequent formation of an anhydride, which interacts with the less basic amine to form transamidation products[62,83].

On the other hand, in a study of the transamidation of 2-dialkylamino-1,3,2-dioxa- and 1,3-dimethyl-1,3,2-diazaphosphorinanes, it was suggested that the following equilibrium obtains as a rule in the phosphoramidite–amine system[61]:

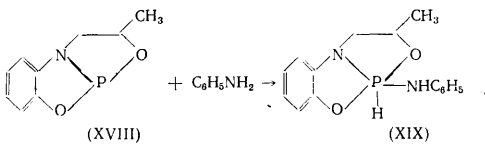


The role of added acid consists in shifting the equilibrium as a result of the binding of the more basic amine. However, this view is apparently valid only when equimolar amounts of the acid are used and does not explain the catalytic influence of the acid reactant on the course of these reactions.

The aminolysis of the endocyclic P–N bond in 1,3,2-oxazaphospholans takes place when aniline hydrochloride is used; in the absence of added additives, these reactions do not occur[84]:

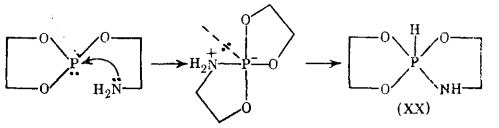


The aminolysis of 1,3,2-diheterophospholans can also proceed via the intermediate formation of phosphoranes with a P–H bond[53]. The present authors have detected addition products of this type by ^{31}P NMR in a study of the interaction of bicyclic phosphoramidites with primary and secondary amines. After mixing the bicyclic compound (XVIII) with aniline at room temperature, a doublet signal was recorded in the ^{31}P NMR spectrum of the reaction mixture ($\delta_{^{31}P}$ = −54 p.p.m., $^1J_{PH}$ = 820 Hz); it refers to the phosphorane (XIX):



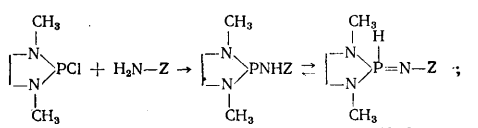
(XVIII) (XIX)

The reaction with diethylamine is accompanied by an exothermic effect and also leads to an addition product with a pentacoordinate phosphorus atom ($\delta_{^{31}P}$ = −42 p.p.m., $^1J_{PH}$ = 820 Hz). The increase of the rate of reaction in the sequence diphenylamine < ethylaniline < diethylamine suggests that in such cases there is nucleophilic attack on the tervalent phosphorus atom, which functions as the electrophilic reactant. An analogous mechanism must be assumed also in cyclisation reactions with formation of spirophosphoranes, for example, compound (XX):[2]



(XX)

Products with an exocyclic secondary amino-group, which in many instances exist in the tautomeric imide form, have been obtained by the amination of 2-halogeno-1,3,2-diazaphospholans[85]:

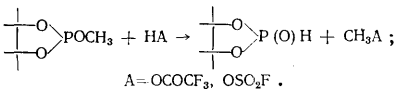


Z=SO_2CF_3, $SO_2C_6H_4$—CH_3, P (S) $(OC_6H_5)_2$, P (S) $(C_6H_5)_2$.

3. Acids

The reactions of 1,3,2-diheterophospholans and 1,3,2-diheterophosphorinanes with strong hydrogen donors, namely carboxylic[48,86–93], sulphonic[53,94,95], and phosphorus-containing acids[96–98], take place in several ways: with ring opening[87,89], with formation of phosphorane and spirophosphorane derivatives[90,91], with formation of disproportionation[48] and polymerisation[92,93] products, and with substitution of an exocyclic group[44,88,89].

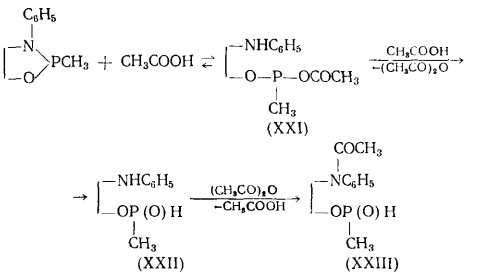
The interaction of the hydrate of toluene-*p*-sulphonic acid with substituted 1,3,2-oxazaphospholans and 1,3,2-oxazaphosphorinanes leads to products of the hydrolytic ring opening[94,95]. When equimolar proportions of the cyclic phosphite and trifluoroacetic or fluorosulphonic acids are used, the ring is not opened; in this case exocyclic dealkylation via the mechanism of the Arbuzov reaction is observed[11]:



A=$OCOCF_3$, OSO_2F .

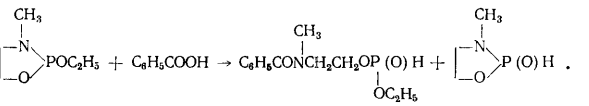
The reactions of strong phosphinic[96] and phosphinodithioic[97] acids with 1,3,2-diheterophosphorinanes resulted in the isolation of mixed anhydrides. The tricoordinate phosphorus atom in the ring of the latter was found to have a reduced nucleophilic reactivity.

The study of the interaction of carboxylic acids with 1,3,2-oxazaphospholans showed that, depending on the structure of the latter, the reactions can involve the nitrogen or phosphorus atom of the P–N ambident system. Protonation of the endocyclic nitrogen atom in saturated 1,3,2-oxazaphospholans leads to ring opening with formation of the phosphonite (XXI). As a result of acidolysis, the latter is converted into the hydrophosphoryl compound (XXII) and the acetic anhydride produced acetylates the amino-group with formation of the compound (XXIII):[89]

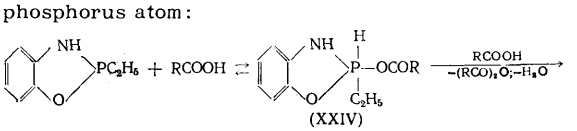


(XXI) (XXII) (XXIII)

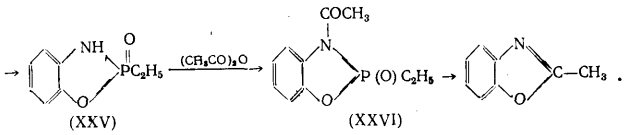
The analogous reaction involving 2-alkoxy-3-alkyl-1,3,2-oxazaphospholans takes place simultaneously via two pathways with formation of linear and cyclic acid phosphites:



2-Ethyl-4,5-benzo-1,3,2-oxazaphospholan reacts with carboxylic acids under mild conditions to form products of the phosphorane type with a P–H bond [compounds (XXIV) [90,91]], which are further converted into compounds (XXV) with a tetracoordinate phosphorus atom. The rate of reaction increases with increase of the strength of the carboxylic acid. The first step in the interaction is probably protonation of the phosphorus atom:



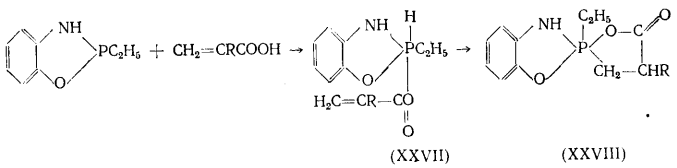
(XXIV)



(XXV) (XXVI)

Acylation of the phosphonate (XXV) by acetic anhydride on heating leads to 2-methylbenzoxazole, formed from the acetylated oxazaphospholan (XXVI).

When α,β-unsaturated carboxylic acids are used, the phosphoranes (XXVII) formed initially are stabilised in a different manner—via intramolecular cyclisation with formation of the spirophosphoranes (XXVIII) with a P–C bond[91]:



(XXVII) (XXVIII)

Analogous reactions of 1,3,2-dioxaphospholans investigated previously lead to the formation of spirophosphoranes and polymeric products[92,93]. The formation of zwitter-ionic intermediates as the result of attack by a phosphonite molecule on the β-carbon atom of the unsaturated acid was postulated for this process[93] (see Section VIII below). However, one cannot rule out the possibility that initial protonation of the phosphorus atom is possible in these reactions too.

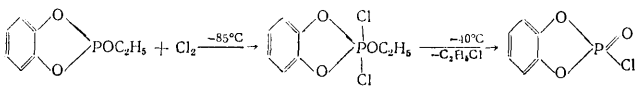
IV. BIPHILIC REACTIONS

Derivatives of tervalent phosphorus can exhibit in many instances a "biphilic" reactivity[99]. "Biphilicity" is understood as the ability of the phosphorus compound not only to supply electrons to the substrate with formation of a σ-bond but also to receive them at the same centre with formation of a σ- or π-bond. Reactions of this type were partly considered in the previous Section devoted to proton-donating reagents. It follows from the foregoing that "biphilic" reactions can be most usefully investigated in relation to cyclic systems in view of the relative stability of the intermediates formed; this makes it possible to investigate the intermediate stages in certain processes.

1. Reactions with Halogens

Depending on their structure, the halogenation of 1,3,2-diheterophospholans can proceed with ring opening and the formation of linear products[100] or it can lead to cyclic phosphates via the mechanism of the Arbuzov reaction[101–103]. In many instances it was possible to note the formation of adducts with a pentacoordinate phosphorus atom[101–106]. The initial formation of phosphonium salts of type (XXIX) has been assumed in these reactions[107]. They can be converted into the final products (XXX) and (XXXI) via two pathways: as a result of the attack by the halide ion on the phosphonium centre (pathway *a*) or as a result of the attack on another electrophilic centre of the molecule—the tervalent phosphorus atom (pathway *b*, Scheme 2):

The chlorination of 2-alkoxy-4,5-benzo-1,3,2-dioxaphospholans in methylene chloride at −85 °C made it possible to detect the formation of the dichlorophosphorane (XXXII) which is converted into the cyclic phosphorochloridate (XXXIII) on raising the temperature to −40 °C:[108–110]



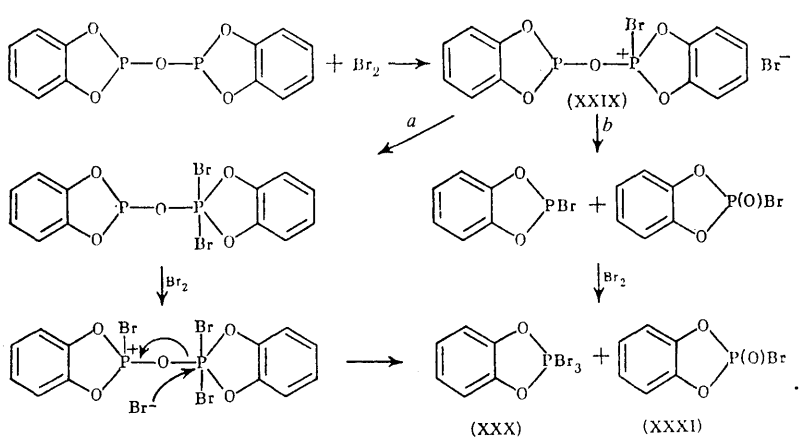
(XXXII) (XXXIII)

The analogous reaction of 4,5-benzo-1,3,2-dioxaphospholan, obtained from the optically active secondary *R*(+)-octyl alcohol, leads to a halogenoalkane with the *S*(−)-configuration[109]. This enabled the authors[109] to suggest that the process illustrated in Scheme 3 proceeds via a stage involving the formation of the dihalogenophosphorane (XXXIV), which is involved in a rapid equilibrium with the phosphonium salt (XXXV).

The dealkylation of the latter via the S_N2 mechanism leads to substitution at the chiral carbon atom with inversion of its configuration. The alternative mechanism with a four-centre transition stage (XXXVI) would lead to the retention of the configuration of the carbon atom in the exocyclic alkoxy-group.

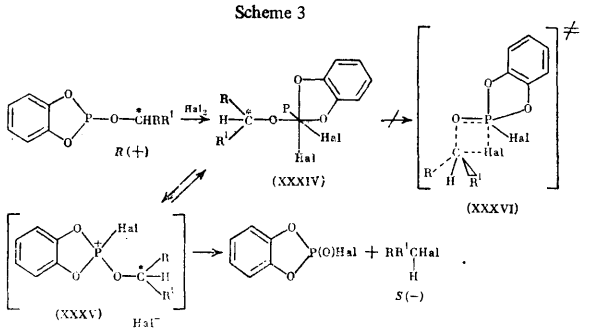
Halogenation of oxazophospholans leads to the opening of the ring at the phosphorus–oxygen bond and the formation of phosphoramidochloridates[111]. The stereochemical result of the halogenation of *cis*- and *trans*-2-methoxy-1,3,2-dioxaphosphorinanes[112] depends on the nature of the halogen: chlorination takes place stereospecifically and bromination yields a mixture of diastereoisomeric products in which one or other diastereoisomer predominates.

Scheme 2



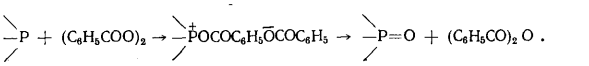
(XXIX) (XXX) (XXXI)

Scheme 3



2. Reactions with Peroxides, Disulphides, and Dithiocyanogen

Cyclic and linear derivatives of tervalent phosphorus are characterised by a high reactivity in reactions with peroxides[113-115]. It has been suggested that the interaction with benzoyl peroxide takes place via the initial attack by the phosphorus atom on the peroxide oxygen with formation of the ion pair (XXXVII):

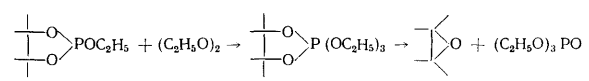


(XXXVII)

The sequence of changes in the reactivity of the cyclic phosphoramidites is analogous to that observed in the reactions with alkyl halides (see Section 5).

The results of a study of the reactions of cyclic phosphites with diethyl peroxide lead to a different conclusion[114]. The rate of this reaction increases in the sequence acyclic phosphites < dioxaphosphorinanes < dioxaphospholans.

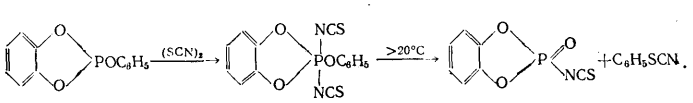
Among the phospholan derivatives, the 4,5-benzo-derivative, in which the phenylenedioxy-substituent exhibits powerful electron accepting properties, shows the highest reactivity. In addition, one should note the instability of the cyclic phosphoranes (XXXVIII) formed in the reaction:



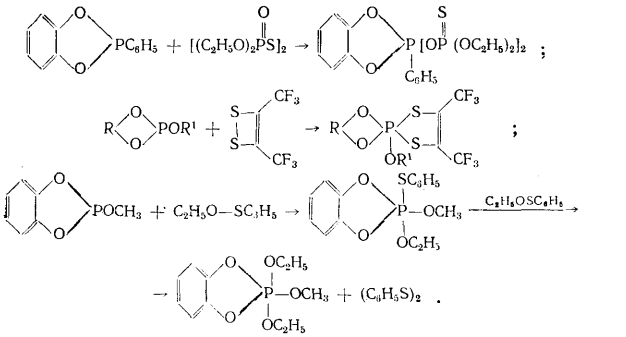
(XXXVIII)

These results are consistent with the concept of the "biphilic" insertion of the phosphorus atom of the cyclic phosphite in the oxygen–oxygen bond of the peroxide. The 1,3,2-diazaphospholan analogues also react with diethyl peroxide to form the corresponding pentacoordinate compounds, but their stability is much lower than that of the intermediates with oxygen-containing rings[116].

A series of reactions accompanied by the "biphilic" insertion of tervalent phosphorus derivatives in the O–S and S–S bonds have been described in the literature. The reaction of 2-phenoxy-4,5-benzo-1,3,2-dioxaphospholan with dithiocyanogen[117] results in the formation of quinquevalent phosphorus compounds containing P–N bonds:



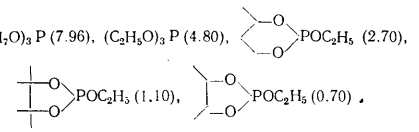
The formation of phosphorane derivatives is observed in the reactions of cyclic phosphites with disulphides[117-119] and compounds containing the O–S bonds[120]:



V. THE ARBUZOV REACTION. REARRANGEMENTS

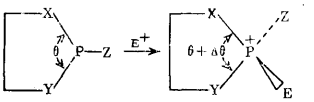
The study of the behaviour of cyclic esters of phosphorus acid in reactions with alkyl halides was initiated by Arbuzov in the 1950's.[121] The structure of the final products of this reaction depends on the ring size and the number and nature of its substituents. According to the results of differential thermal analysis[122], acyclic phosphites enter most readily into the Arbuzov reaction, while their 1,3,2-dioxaphosphorinane and 1,3,2-dioxaphospholan analogues react with greater difficulty. The increase of reactivity corresponds to the increase of electron density at the ring phosphorus atom[2,123].

A study of the comparative reactivities of tervalent phosphorus acid esters with respect to CH_3I established that, on passing from linear trialkyl phosphites to their six- and five-membered cyclic analogues, the rate constant diminishes[124]:



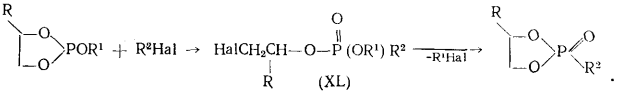
The values of $10^4\ k$ (litre $mol^{-1}\ s^{-1}$) are given in brackets.

The lower reactivity of phospholan derivatives in reactions with electrophiles E^+ is explained from the standpoint of the increasing ring strain ($\theta + \Delta\theta$) in the transition state, because the endocyclic angle increases from 93–98° to 109° in the intermediate (XXXIX) formed with a quaternised phosphorus atom[2,125]:

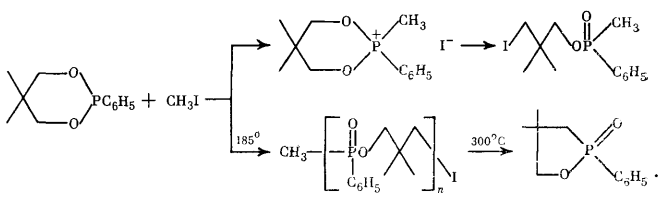


(XXXIX)

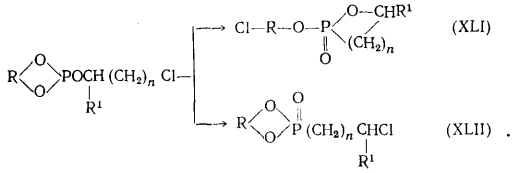
The Arbuzov reaction involving the esters of pinacol- and methoxymethylethylene-phosphorous acids as well as esters with six-membered rings proceeds without ring opening[126]. The reaction involving phosphites with cyclic arylene substituents takes place analogously[127,128]. Unsubstituted or monosubstituted phospholan systems tend to undergo ring opening[129-131], but there is also a possibility of the subsequent cyclisation of the intermediate linear phosphonate (XL):[132,133]



In the reaction of methyl iodide with neopentylene phenylphosphonite[134], there is a possibility of "transcyclisation" at a high temperature with formation of an oxaphospholan derivative together with the usual Arbuzov reaction:



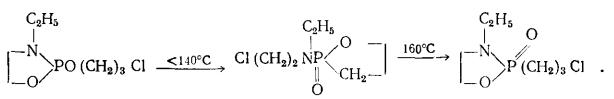
2-(ω-Halogenoalkoxy)-1,3,2-diheterophosphacycloalkanes, formed in the reaction of cyclic phosphorochlorodites with epoxyalkanes, undergo an unusual intramolecular version of the Arbuzov rearrangement[135-144]. The cyclic fragment of the initial phosphite can then be quoted or can be retained depending on the size of the ring, the nature and number of its substituents, and also the structure of the exocyclic halogenoalkyl component[137-145]:



(XLI)

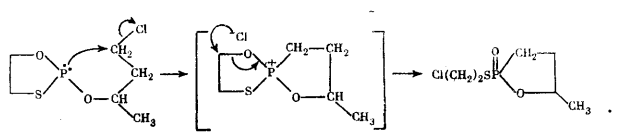
(XLII)

In the majority of instances, intramolecular thermal isomerisation leads to a mixture of the isomeric compounds (XLI) and (XLII). The rearrangement of ethylene and 1,2-propylene phosphite results in the formation of both products; on the other hand, 2,3-butylene phosphites isomerise preferentially to compounds (XLII) with retention of the phospholan ring. The ratio of the isomers formed depends also on temperature. Thus 1,3,2-oxazophospholan (XLIII) isomerises at 140 °C to 1,2-oxaphospholan (XLIV) and an increase of the reaction temperature leads to "transcyclisation" with formation of a compound having the oxazaphospholan structure (XLV):[141]



(XLIII) (XLIV) (XLV)

The ease of isomerisation depends on the nature of the branching of the exocyclic fragment. The introduction of the methyl group in the γ-position in the 3-chloroalkoxymoiety can fully suppress the intramolecular isomerisation of oxazaphospholans; the presence of the methyl group in the α-position facilitates the reaction[141]. These data are satisfactorily consistent with the S_N2 mechanism of the substitution of the halogen by a phosphorus atom at the terminal carbon atom. The rearrangement of the oxathiaphospholans (XLVI) is accompanied by ring opening at the C–O bond[140], probably via the attack by the chloride ion on the carbon of the unsubstituted oxathiaphospholan quasi-phosphonium intermediate (XLVII):



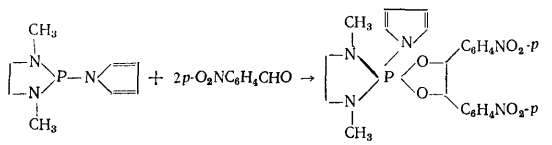
(XLVI) (XLVII)

VI. REACTIONS WITH CARBONYL COMPOUNDS

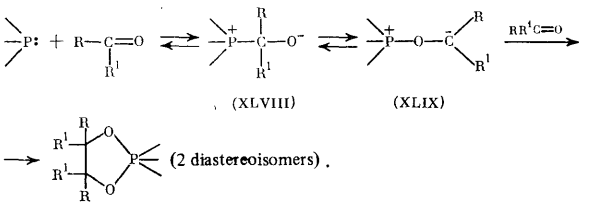
1. Aldehydes and Ketones

Data on the chemical reactions of alkylene phosphites with α-halogenoaldehydes and ketones have been published in a review[10] and will not be considered here. One should only note that α-chloroaldehydes interact with cyclic phosphites to form cyclic and acyclic products of the Perkow reaction, while α-chloroketones react both via the mechanism of the Arbuzov reaction and that of the Perkow reaction.

Various 1,3,2-diheterophospholans interact with aromatic aldehydes and ketones to form 1:2 adducts with the spirophosphorane structure[146-150]:



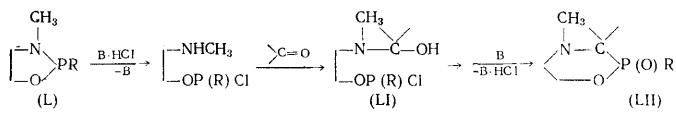
Apparently spiro-cyclisation takes place via the formation of intermediate dipolar structures (XLVIII) and (XLIX), which are converted into compounds with a pentacovalent phosphorus atom on reaction with a second molecule of the carbonyl reagent[1,151]:



(XLVIII) (XLIX)

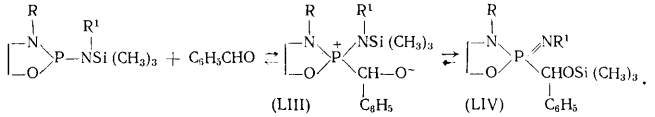
(2 diastereoisomers).

The interaction of oxazaphospholans with aldehydes and ketones is frequently accompanied by the insertion of the latter in the P–N bond, ring expansion, and the formation of 1,4,2-oxazaphosphorinanes[152-156]. In these reactions there is acid catalysis due to an admixture of the hydrochlorides, frequently present in the initial cyclic phosphoramidites[157,158]. Under their influence, the initial dissociation of the P–N bond of the oxazaphospholan (L) takes place[159] and the resulting aminoalkyl phosphorochloridite or phosphonochloridite interacts with the carbonyl compound; the dehydrochlorination of the intermediate (LI) leads to the corresponding 1,4,2-oxazaphosphorinane (LII):



(L) (LI) (LII)

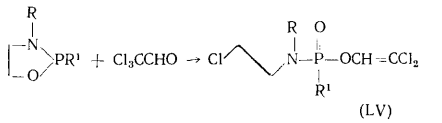
The reactions of carbonyl compounds with 1,3,2-oxazaphospholans containing the silylamino-group in the exocyclic fragment take place readily[160,161]:



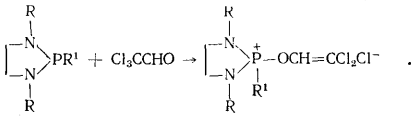
(LIII) (LIV)

The nucleophilic addition of the phosphorus(III) atom of the initial phosphoramidite to the carbonyl group leads to the formation of the dipolar ion (LIII), in which the trimethylsilyl group migrates to the oxy-anionic centre. The cyclic phosphonate (LIV) formed decomposes on heating into the initial component via a stage involving the formation of compound (LIII).[160]

2-Alkoxy-1,3,2-oxaza- and 2-alkoxy-1,3,2-diaza-phospholans react differently with chloral. The formation of products with ring opening, namely β,β-dichlorovinyl phosphates (LV), is characteristic of the former[162], while the latter give rise to cyclic phosphonium chlorides (LVI):[163]



(LV)

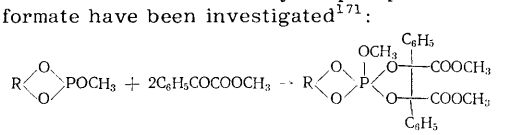


(LVI)

The study of the reactions of substituted 1,3,2-diheterophosphacycloalkanes with chloral and trichloroacetophenone[164] established that the overall sequence of the changes in the reactivity of cyclic phosphites in this process resembles that established in reactions of cyclic phosphites with alkyl halides[165] (see Section V): the reactivity decreases on passing from acyclic derivatives of tervalent phosphorus to their six- and five-membered cyclic analogues. This agrees with the idea that the rate-determining stage in such reactions involves the attack by the phosphorus atom on the carbon atom of the carbonyl group.

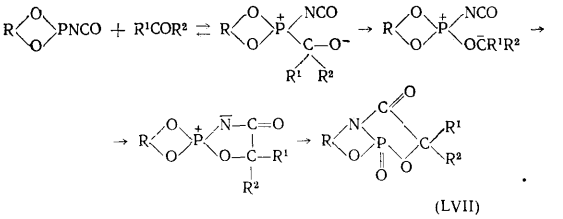
2. Activated Carbonyl and Dicarbonyl Compounds

The reactions of trialkyl phosphites with carbonyl compounds activated by electron-accepting substituents can take place via two pathways[151]: at a low temperature with formation of predominantly pentacoordinate derivatives of phosphorus and at an elevated temperature with formation of the corresponding 2-substituted alkyl phosphonates. In contrast to linear phosphites, the cyclic analogues give rise as a rule to the thermodynamically stable spirophosphoranes. This is observed in the reactions of ethers and amides of alkylene phosphorous acids with esters of α-ketoacids[166] and of 1,3,2-diheterophospholans with phenylbenzoyldiimide[167,168] and the esters and the nitrile of benzoylformic acid[169,170]. The kinetics of the reactions of cyclic phosphites with methyl benzoylformate have been investigated[171]:



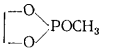
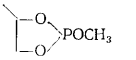
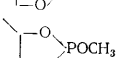
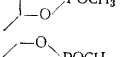
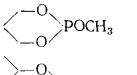
Despite the fact that two ester molecules participate in the reaction, the rate of the process is described by a second order kinetic equation (or first order with respect to each reactant) and the slowest stage is the formation of a dipolar ion of the type $\geq\overset{+}{P}-\underset{|}{C}-O^-$ (XLVIII).[171] The thermodynamic characteristics obtained (Table 1) make it possible to assign the five- and six-membered cyclic analogues to various reaction series: the reactivity of the phospholan derivatives is controlled by the entropy factor, while the reactions of phosphorinane derivatives are subject to control by the enthalpy factor.

The products of the interaction of cyclic phosphoroisocyanatidites with the esters of pyruvic, benzoylformic, and α,β-di-oxobutyric acids and phenylglyoxal[172-174] are the corresponding hetero-derivatives of the bicyclo-octane and bicyclononane series (LVII):



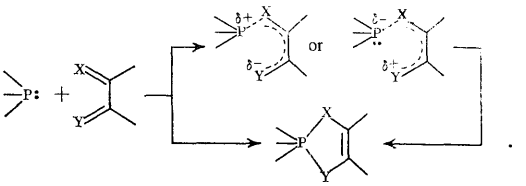
(LVII)

Table 1. Kinetic parameters of the reactions of cyclic phosphites with benzoylformic acid ester at 50 °C.[171]

Phosphite	$10^4 k$, litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
	5.60	16.4	249.5
	9.10	19.3	236.9
	14.02	26.5	210.8
	1.69	5.9	292.7
	2.65	3.8	295.7

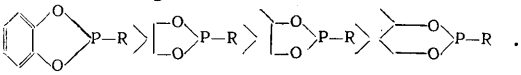
The interaction of cyclic derivatives of tervalent phosphorus with dicarbonyl and saturated carbonyl compounds has been examined in reviews[1,151,175]. 1,3,2-Diheterophospholans react with α,β-unsaturated compounds containing the N=N–C=O and N=C–C=O conjugated systems, which results in the formation of spirophosphorane structures[176-180].

Such processes resemble the cycloaddition reactions, which can proceed either via two stages or synchronously. The characteristics of such reactions are consistent with the mechanism of diene condensation with participation of cyclic phosphites[181-188]:



The rate of reaction depends mainly on the redistribution of electron density in the intermediate reaction complex, which results in the manifestation of the dominant influence of electronic or steric factors (Table 2).

The replacement of acyclic groups by cyclic groups increases significantly the rate and lowers the activation barrier to the reaction owing to the weak electron-donating influence of the 1,3,2-dioxaphospholan fragment compared with the two alkoxy-groups in the transition state. The activity series of cyclic phosphites in diene condensation[181,182] has been established as a function of the ring structure:



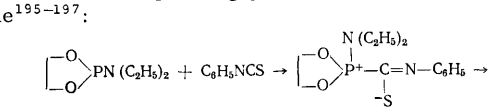
The data obtained most probably indicate nucleophilic attack by the unsaturated reactant; phosphorus then exhibits electrophilic properties[189]. The successive replacement of the oxygen atoms in the diheterophospholan fragment by sulphur apparently increases still further the electron-accepting character of this fragment and increases the rate of condensation[183].

Table 2. Kinetic parameters of the condensation reactions between phosphorochloridites and isoprene[184].

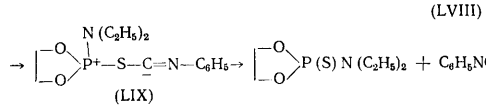
Phosphorochloridite	$10^4 \cdot k$, litre mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
$(C_2H_5O)_2PCl$	0.012	92.8	100.8
	0.97	70.1	150.8
$C_2H_5OPCl_2$	1.26	82.3	116.8

3. Reactions with Isocyanates, Carbon Dioxide, Their Thio-analogues, and Related Compounds

The "insertion reactions" involving isocyanates, isothiocyanates, carbon disulphide, carbon dioxide, and other heterocumulated reagents occupy a special place in the chemistry of tervalent phosphorus acid amides[190,191]. It has been suggested[192] that the reaction takes place via the insertion of the carbonyl reactant in the P–N bond in the ring with formation of an intermediate with a larger cyclic system than in the initial phosphite. However, it was shown subsequently[193,194] that two independent pathways can be followed in these reactions: insertion in the ring of the diheterophosphacycloalkane and its oxidation with formation of a compound having a tetrahedral phosphorus atom. In the interaction of cyclic phosphoramidites with isothiocyanates, dipolar ions with a P–C bond (LVIII) arise in the first stage and readily undergo the mercaptophosphonate–phosphorothioate rearrangement in the course of the reaction to the thiophosphonium intermediate (LIX); the final reaction products are the corresponding phosphoramidothioate and an isonitrile[195–197]:



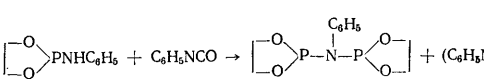
(LVIII)



(LIX)

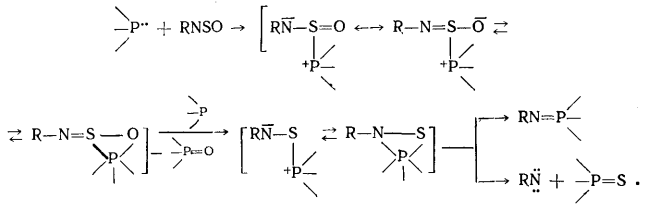
Cyclic phosphoramidites are oxidised analogously by isocyanates.

The presence of a mobile hydrogen atom in the exocyclic amino-group of the 1,3,2-dioxaphospholan permits its disproportionation in the reaction with isocyanate[197,198]:

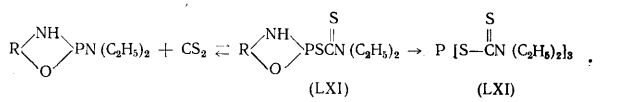


As a consequence of their low nucleophilic reactivity, 1,3,2-diheterophospholans are less reactive in reactions with substituted sulphenylamines than their open-chain analogues[199].

It has been suggested that the process begins with nucleophilic attack by the phosphorus atom on the electrophilic sulphur atom; in the subsequent stages the S–O and P–S bonds in the intermediates formed dissociate simultaneously or in succession. The final products of the reaction are the corresponding phosphoryl, thiophosphoryl, and imidophosphoryl derivatives:



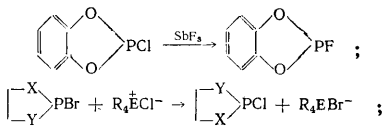
The stability of the products of the insertion of CS_2 and CO_2 in the exocyclic P–N bonds of 1,3,2-dioxaphosphorinanes[200], 1,3,2-oxathiaphospholans, 1,3,2-dithiaphospholans[201], and 1,3,2-oxazaphospholans[202] depends on the structure of the cyclic fragment. As a result of the interaction of carbon disulphide with amides containing a diheteroalkylene cyclic fragment (R = alkylene), stable thiocarbamoyl phosphorothioites (LX) are formed; the reaction of 4,5-benzo-1,3,2-oxazaphospholan (R = *o*-C_6H_4) takes place with subsequent disproportionation of the 1:1 adducts to tris(*N*,*N*-diethylthiocarbamoylthio)phosphine (LXI):



(LXI) (LXI)

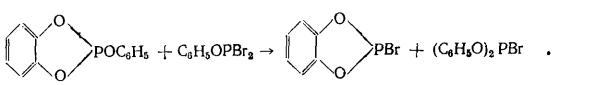
VII. SUBSTITUTION AT THE PHOSPHORUS ATOM ON TREATMENT WITH REAGENTS WITHOUT A MOBILE HYDROGEN ATOM

As already mentioned above, reactions accompanied by the substitution of the exocyclic group at the phosphorus atom are extremely characteristic of cyclic phosphorus derivatives. This is also characteristic of a series of reactions involving reagents without a proton. It has been established[203] that there is rapid intermolecular halogen exchange involving 2-chloro(bromo)-1,3,2-dioxa(oxaza)phospholans. The activation barrier to this process is 20.2 ± 4 kJ mol^{-1}, which agrees with the idea that the mechanism of the exchange involves a four-centre transition state of type (XV) without the preliminary ionisation of the phosphorus–halogen bonds. The exocyclic chlorine is readily substituted by fluorine on treatment with antimony trifluoride and bromine is substituted by chlorine on treatment with ammonium, phosphonium, and arsonium chlorides[204–206]:

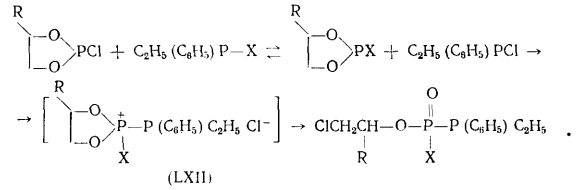


X, Y=O, NR; R=Alk, Ar; E=N, P, As .

The exchange of substituents has been noted in reactions of the full cyclic esters of phosphorous acid[207,208]:

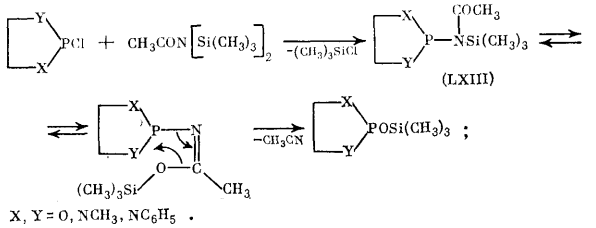


Similar exchange processes have been demonstrated also for cyclic phosphorochloridites when these react with trialkyl phosphites or phosphoramidites[209]. In a few instances these processes are accompanied by ring opening via a mechanism of the type of the Arbuzov rearrangement via an intermediate—the cyclic quasi-phosphonium salt (LXII):[210]



(LXII)

2-Halogeno-1,3,2-diheterophospholans are readily silylated by *N*,*N*-bis(trimethylsilyl)acetamide[211–214]:



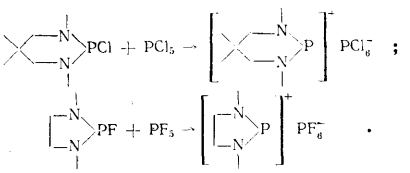
(LXIII)

X, Y = O, NCH_3, NC_6H_5 .

During the reaction, the 2-(*N*-acetyl-*N*-trimethylsilylamino)-1,3,2-diheterophospholans (LXIII) formed initially decompose to the corresponding cyclic silyl phosphites. According to the results of differential thermal analysis, the reactivity of cyclic phosphorohalidites increases on passing from 1,3,2-diazaphospholan to the oxaza- and dioxa-derivatives, i.e. with increasing electrophilicity of the phosphorus atom[211].

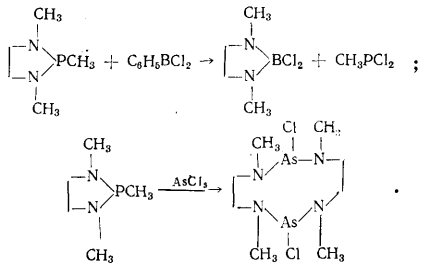
Compounds with a P–P bond can be obtained by treating 2-halogeno-1,3,2-diheterophosphacycloalkanes with metallic sodium[215,216].

Treatment of phosphorohalidites with Lewis acids leads to cyclic cations with a dicoordinate phosphorus atom[19,217]:

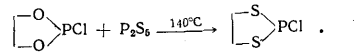


The formation of such compounds has been noted also in the formation of complexes by iron and manganese carbonyls or of fluoroboranes with 1,3,2-diazaphospholans[218–220].

The exchange of phosphorus for other heteroatoms is sometimes observed[205,221]:

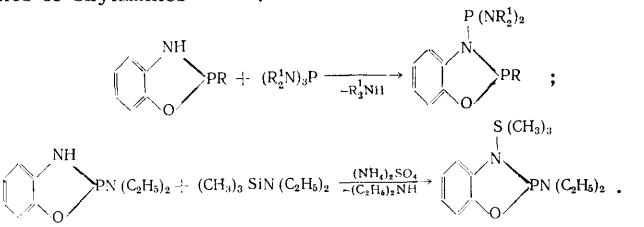


The replacement of the endocyclic oxygen atoms by sulphur in 2-chloro-1,3,2-dioxaphospholan using phosphorus pentasulphide is possible[222]:

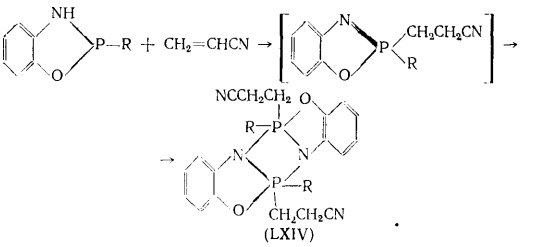


The mechanisms of such reactions have not been determined in detail.

Substitution can take place not only at the phosphorus atom but also at the endocyclic nitrogen atom. 4,5-Benzo-1,3,2-oxazaphospholans readily exchange the mobile hydrogen atoms of the endocyclic amino-group in reactions with triaminophosphines or silylamines[223–229]:



2-Substituted 4,5-benzo-1,3,2-oxaza- and 4,5-benzo-1,3,2-diaza-phospholans readily add to unsaturated compounds with an activated double bond. The addition products formed initially are stabilised via dimerisation to diazadiphosphetidines (LXIV):[229–231]

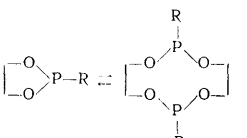


(LXIV)

VIII. RING EXPANSION. POLYMERISATION

In a number of instances cyclic derivatives of tricoordinate phosphorus are capable of spontaneous transformation into dimeric products or oligomers[232]. Thus on standing for a long time, 2-chloro-4,5-benzo-1,3,2-dioxaphospholan is irreversibly converted into oligomeric products, which regenerate the monomeric compound on distillation[233]. A similar reversible transformation of the monomeric 3-methyl-2-phenyl-1,3,2-oxazaphospholan has been noted[193].

The formation of dimers, trimers, and oligomers is particularly characteristic of unsubstituted cyclic derivatives of tervalent phosphorus in which the phosphorus atom is involved in an exocyclic P–C bond. Dioxaphospholans dimerise reversibly to ten-membered cyclic diphosphonites (LXV) in the presence of atmospheric moisture; furthermore, the formation of polymeric compounds is also observed under these conditions[233–237]:



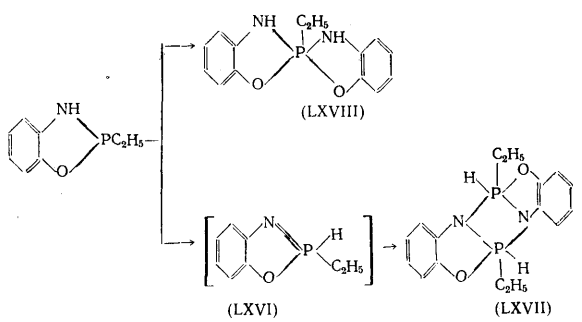
(LXV)

Dimeric derivatives with a similar structure are also formed from 1,3,2-oxazaphospholans[232]. Dimers of type (LXV) retain the properties of tricoordinate phosphorus derivatives —they are oxidised and combine with sulphur[238]. When both endocyclic oxygen atoms are replaced by nitrogen, phospholans lose their tendency to dimerise; ring expansion has not been observed also in the series of 1,3,2-dithiophospholans[236].

After prolonged storage, dioxaphosphorinanes give rise to cyclic dimers and trimers together with polymeric products[239]; in contrast to their five-membered cyclic analogues,

dithiaphosphorinane derivatives with tervalent phosphorus are irreversibly converted into 12-membered cyclic compounds[236].

The dimerisation of 2-ethyl-4,5-benzo-1,3,2-oxazaphospholan takes place in an unusual manner[240]. The phosphonoimidite (LXVI), formed as a result of prototropic isomerisation, dimerises to the diazadiphosphetidine (LXVII); the process is also accompanied by the symmetrisation of the initial phosphonite to give the spirophosphorane (LXVIII):

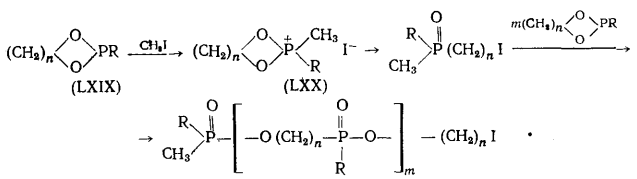


(LXVIII)

(LXVI) (LXVII)

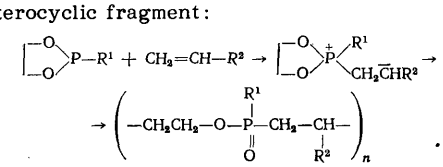
When a ring oxygen atom is replaced by sulphur, the tautomeric prototropic transition does not take place and the formation of the phosphetidine ring is not observed; there is only a reversible transition to a compound having the spirophosphorane structure of type (LXVIII).[241]

The polymerisation and copolymerisation reactions of cyclic derivatives of phosphorus can be initiated by boron trifluoride, sulphuric acid, dimethyl sulphate, and bromocyanoacetamide[242]. The Arbuzov reaction of cyclic phosphites and phosphonites (LXIX) [244] with alkyl halides is used to synthesise oligomers with the phosphorus atom in the main chain; the reaction proceeds via the formation of the quasi-phosphonium salt (LXX), the opening of its ring, and interaction with the next molecule of the phosphacycloalkane:



(LXIX) (LXX)

The polycondensation of the dialkyl esters of phenyl- and ethyl-phosphinous acids with glycols takes place mainly via the intermediate formation of cyclic esters of phosphinous acid[245]. The copolymerisation of cyclic phosphorus(III) derivatives with a wide variety of electrophilic monomers, the so-called alternant polymerisation[93], begins with the formation of the dipolar ion (LXXI): the growth of the polymer chain involves the opening of the ring in the five-membered heterocyclic fragment:



α,β-Unsaturated carboxylic acids, their amides, and sulphonamides as well as ketones have been used as the unsaturated monomers[93].

The data presented in this review demonstrate the unusual reactivity of 1,3,2-diheterophospholans. The characteristics of the geometry of these molecules associated with the incorporation of a tervalent phosphorus atom in a strained five-membered ring alter the character of the hybridisation of the unshared electron pair of the phosphorus atom and weaken the nucleophilic properties of the phosphorus atom compared with acyclic phosphorus(III) derivatives. The distinct tendency of 1,3,2-diheterophospholans to participate in "biphilic" processes with increase of the coordinate number of the phosphorus atom is due to the same causes.

The wide variety of the chemical reactions characteristic of organic phosphorus(III) compounds is supplemented in the case of the cyclic esters, ester-amides, and amides by reactions with ring expansion, "transcyclisation", and spirocyclisation. The comparative instability of the unsubstituted five-membered phosphacycloalkanes containing a phosphorus(III) atom ensures the occurrence of oligomerisation processes, which make these cyclic organophosphorus substances similar to bifunctional monomers.

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