Translated from *Uspekhi Khimii*, 54, 1899-1939 (1985) U.D.C. 547.341

The Reactivity of 1,3,2-Diheterophosphacyclanes Containing a Pentacoordinate Phosphorus Atom

N.A.Polezhaeva and R.A.Cherkasov

Studies on the reactivity of λ^5-1,3,2-diheterophosphacyclanes obtained during the last ten years are examined and described systematically. Data concerning new prototropic and elementotropic processes involving derivatives of pentacoordinate phosphorus are presented. Attention has been concentrated on the elucidation of the influence of the incorporation of a phosphorus(V) atom in the ring on the reactivity of phosphoranes in reactions of various types. The role of phosphorus(V) compounds as intermediates in reactions of phosphorus compounds involving different types of coordination of the phosphorus atom is demonstrated.
The bibliography includes 176 references.

CONTENTS

I.	Introduction	1126
II.	Hydrophosphoranes	1126
III.	Hydroxyphosphoranes. The phosphate-phosphorane tautomerism	1130
IV.	Aminophosphoranes. The phosphimide-phosphorane tautomerism	1137
V.	Other tautomeric transformations of phosphoranes. Phosphorotropic processes	1139
VI.	Thermolysis of phosphoranes	1140
VII.	Nucleophilic substitution at a pentacoordinate phosphorus atom	1142

I. INTRODUCTION

The study of the relation between the structure and reactivity of 1,3,2-diheterophosphacyclanes containing tricoordinate[1] and tetracoordinate[2] phosphorus atoms revealed the specific features of the chemical behaviour of these organophosphorus compounds (OPC) associated with the inclusion of a phosphorus atom in the cyclic molecular skeleton. The reactivity of five-membered cyclic OPC of the above type has been found to be particularly unusual, which was manifested in the kinetic, synthetic, and stereochemical results of the reactions involving them.

In the present review an attempt is made to give a systematic account of the survey of the literature data on the reactivity of heterocyclic compounds of pentacoordinate phosphorus containing in the cyclic fragment, together with the phosphorus(V) atom, two other identical or different heteroatoms (O, N, S), namely λ^5-1,3,2-diheterophosphacyclanes. In a number of instances data on the reactivities of acyclic phosphorus(V) compounds and 1,2-heterophosphacyclanes with a similar ligand environment around the phosphorus atom are adduced for comparison.

In the review literature available hitherto attention has been concentrated on the structural[3-5] and to a lesser extent the synthetic[6-8] chemistry of compounds of pentacoordinate phosphorus. Although modern ideas about the structure, the ligand reorganisation processes, and the role of intermediates of the phosphorane type in the chemical reactions of OPC have been developed precisely in relation to λ^5-1,3,2-diheterophosphacyclanes,[9] the relation between the structure and reactivity of these OPC has been studied systematically only for a few examples.[10] During 1970–1980, new experimental data were obtained which deepened our knowledge about the chemical behaviour of compounds of pentacoordinate phosphorus. New types of phosphoranes were synthesised; some of them are stable models of the intermediates formed in reactions of compounds with different types of coordination of the phosphorus atom. New types of prototropic and elementotropic tautomeric systems, including phosphorotropic systems, containing the phosphorus(V) atom have been discovered. Data concerning the mechanisms of nucleophilic substitution reactions at a pentacoordinate phosphorus atom have been obtained for the first time. New possibilities for the employment of phosphorus(V) compounds in organic synthesis have been demonstrated.[11] The "hydroxyphosphorane concept", which is a compilation of empirical rules governing the structure and character of the ligand and valence isomerisation of the phosphorane molecules, has been developed further.[12]

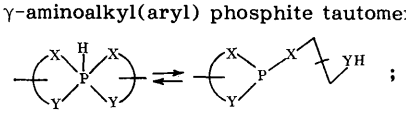
These and other results of the studies during the last ten years are included in the present review. The synthetic and stereochemical aspects of the chemistry of λ^5-1,3,2-diheterophosphacyclanes are used only to the extent that they are necessary for the elucidation of the characteristics of the reactivity of OPC of this type.

II. HYDROPHOSPHORANES

Information about the methods of synthesis and the chemical properties of hydrophosphoranes obtained in the early stages of the development of the chemistry of these compounds of pentacoordinate phosphorus, containing a P–H bond, are presented in the relevant reviews[13-15] and are not included in the present review. The principal characteristic features of the tautomeric processes involving such compounds and the results of the study of their reactivity obtained during recent years are considered here.

1. The Phosphate–Phosphorane Tautomerism

The isolation of the first spirophosphoranes and somewhat later of monocyclic phosphoranes with a P–H fragment (see Pudovik et al.[1] and Arbuzov and Polezhaeva[10] and the literature quoted therein) made it possible to establish the existence of the hydrophosphorane–γ-hydroxyalkyl(aryl) phosphite or γ-aminoalkyl(aryl) phosphite tautomeric equilibrium:



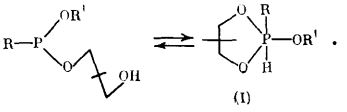
X, Y = NR, O .

The position of this equilibrium depends on the structure of the compound, the medium, and temperature. The phosphorane form is more characteristic of spirocyclanes substituted at the carbon atoms, those containing a secondary amino-group, and unsaturated and aromatic systems. A decrease of temperature promotes an increase of the content of the phosphorus(V) isomer. The introduction of substituents at the endocyclic nitrogen atom in λ^5-oxazaphospholans shifts the equilibrium towards the phosphite.[10,16]

The ease of the phosphorus(V) → phosphorus(III) transition is determined to a large extent by the nature of the endocyclic heteroatoms. For X = Y = O, the equilibrium is displaced towards the spirophosphorane even at room temperature, particularly in the case of substituted rings.[17] For asymmetrically substituted rings, two and sometimes three phosphorus(III) forms can exist in equilibrium with the hydrophosphorane.

Although a correlation between the polarity of the solvent and the content of the phosphite form at equilibrium has not been observed, it has been established that basic solvents shift the equilibrium towards phosphorus(III), while acid solvents shift it towards phosphorus(V).

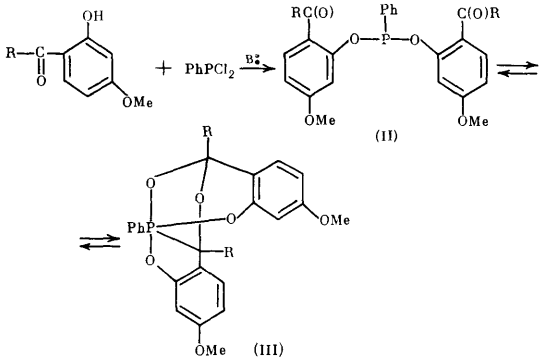
An analogous equilibrium for monocyclic phosphoranes has been detected by ^{31}P NMR; in this case too a decrease of temperature favours the formation of the phosphorus(V) form:



(I)

Hydrophosphoranes of type (I) are interesting because they are intermediates in many reactions of derivatives of tervalent phosphorus with proton-donating reagents (see Pudovik et al.[1] and the literature quoted therein) and also serve as the starting compounds for the synthesis of alkylspirophosphoranes with a P–R bond.[18]

The type of tautomerism described is characteristic mainly of hydrophosphoranes, but the observation of the phosphite–phosphorane tautomerism in the phenylphosphonite (II)–polycyclic phenylphosphorane (III) system has been reported:[19]



(II)

(III)

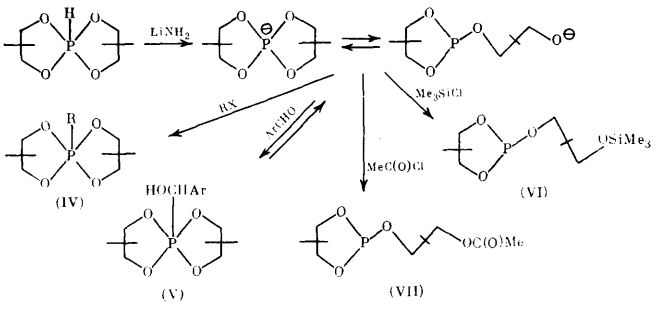
When the polycyclic phosphorane (III) is dissolved in $CHCl_3$, the equilibrium is established in 1 h at 25 °C.

The reactivity of hydrophosphoranes is determined mainly by the phosphite–phosphorane equilibrium and the presence of a fairly mobile P–H proton in the phosphorane isomer. The electrophilic properties of the pentacoordinate phosphorus atom, which predetermine the behaviour of spirophosphoranes and in general of phosphorus(V) derivatives as Lewis acids, play a significant role. In the phosphorus(III) form the reactions can involve one of two nucleophilic centres—the tricoordinate phosphorus atom and the YH(XH) group.

Estimation of the acid properties of hydrophosphoranes[20] demonstrated a decrease of the H-donating capacity following the replacement of endocyclic oxygen atoms by the NH group [apparently as a consequence of the greater $(p-d)_\pi$ donor capacity of the nitrogen atom compared with oxygen[20]] and on transition from spirocyclic to monocyclic hydrophosphoranes. The reactivity of hydrophosphoranes in the reaction with diphenyldiazomethane increases in parallel with the enhancement of the acid properties.[20]

The ease of the abstraction of the P–H proton on treatment of hydrophosphoranes with various metallating agents (metal hydrides and amides and organometallic compounds) is also determined by the structure of the phosphorane.[21,22] Whereas a proton can be abstracted from hydrophosphoranes which are derivatives of pinacol by metal amides (but not hydrides), hydrophosphoranes containing an endocyclic or exocyclic carbonyl group are deprotonated even by diethylamine

According to ^{31}P NMR data, the metallic derivatives of hydrophosphoranes are O anions and not P anions (the $^1J_{PH}$ doublet disappears and the signal of tricoordinate phosphorus appears).[21] However, a dual reactivity is characteristic of these compounds. Their alkylation by alkyl halides, alkenyl halides, and alkyl sulphates gives rise to a product with a spiran structure (IV). In the reactions with aromatic aldehydes the products are α-hydroxyalkylspirophosphoranes (V) which are thermally unstable and on heating regenerate the initial spirophosphorane and the aldehyde. The phosphoranes (V) can be formed also without the participation of metals (see below). Silylation and acylation involve the terminal oxygen atom of the phosphite group and lead to the phosphites (VI) and (VII) respectively.[21] We may note that the reactions of the hydrophosphoranes themselves with acyl chlorides in the presence of tertiary amines also lead to γ-acetoxyalkyl phosphites (VII),[23] while acylation of λ^5-oxazaspirophospholans by acetic anhydride ruptures both P–N bonds:[24]



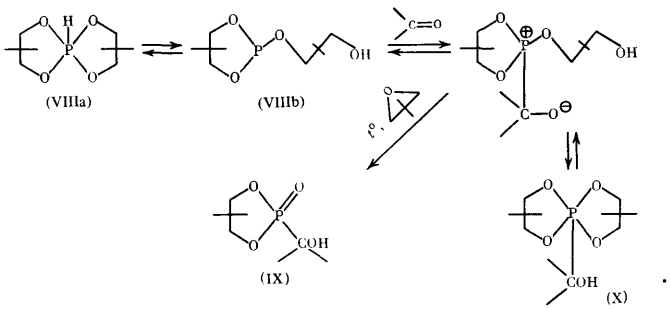
(IV) (V) (VI) (VII)

An analogy with dialkyl phosphites is manifested in these reactions: metallation takes place at the oxygen atom and the subsequent reactions with electrophiles can proceed via both the oxygen and phosphorus atoms.

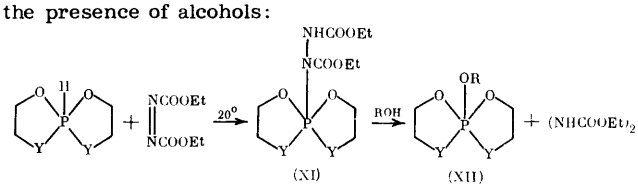
Like dialkylphosphorous acids, hydrophosphoranes interact with aliphatic aldehydes,[21,25] activated ketones, and animals [23,26] and add to electrophilic unsaturated systems.[27,28]

As already stated, although the α-hydroxyalkylspirophosphoranes formed on addition of hydrospirophosphoranes to aldehydes can be isolated, they are unstable and readily decompose. It has been suggested[26] that these reactions involve the nucleophilic addition of the phosphorus(III) atom of the form (VIIIb) to the carbon atoms of the carbonyl group; the dipolar ion, whose formation is promoted by an excess of the carbonyl reagent, is stabilised in two ways:

the elimination of the epoxide leads to cyclic α-hydroxyphosphonates (IX), while cyclisation gives rise to spirophosphoranes (X):



Imines are less reactive in the addition reactions of hydrospirophosphoranes than the aldehydes with a similar structure;[28] in the presence of alcohols cyclic enamines oxidise hydrospirophosphoranes to the corresponding pentaoxaspirophosphoranes.[29] The oxidation products (XII) are obtained ultimately also on interaction with azodicarboxylic ester in the presence of alcohols:

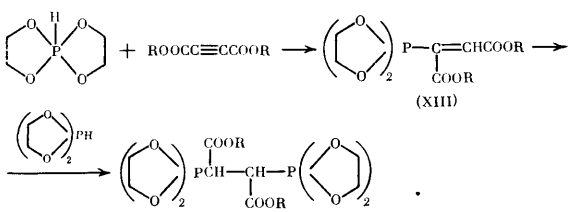


It has been suggested[30] that the adduct (XI) is formed initially, but it is unstable and has not been isolated.

The reactions of hydrospirophosphoranes with aldehydes, ketones, and imines are reversible and their thermodynamically controlled products are phosphoranes with an exocyclic P–C bond. Like the interaction with phenyl azide[31] and with certain other unsaturated systems,[23,25,28,29] these reactions are characteristic only of the hydrophosphoranes which are in equilibrium with the phosphite form; in the absence of the latter, there is no reaction.

In the general case the reactivity of λ^5-1,3,2-diheterophospholans with P–H bonds in reactions with electrophiles depends to a large extent on the nature of the heteroatoms attached to the phosphorus atom. Spirophosphoranes containing even one 1,3,2-oxazaphospholan ring are more reactive than tetrahydroxyspirophosphoranes.[28]

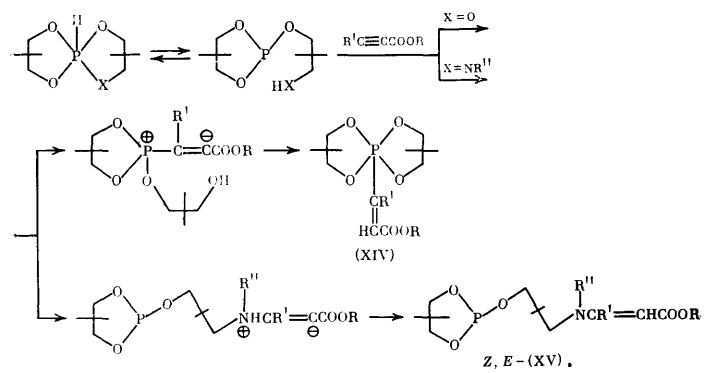
The nature of the endocyclic heteroatom of hydrospirophosphoranes influences also the synthetic result of the reactions involving addition to acetylenic reagents. Tetrahydroxyhydrophosphoranes readily add to acetylenedicarboxylate esters and proprionates with formation of vinylphosphoranes (XIII).[32] The adduct (XIII), which exists in the form of two stereoisomers, which can be separated by crystallisation, combines with a second molecule of hydrophosphorane at an elevated temperature:



It is striking that the P–C bond in the vinylphosphorane is fairly labile and is readily broken on treatment with an alcoholic solution of sodium alkoxide.[33] This can be accounted for by the high electrophilicity of the phosphorus-(V) centre.

If the spirophosphorane contains even one endocyclic P–N bond, then the reaction products are the stereoisomeric phosphites (XV). However, ring-substituted λ^5-oxazaphospholans and λ^5-dioxaphospholans form compounds of pentacoordinate phosphorus of type (XIV). It has been suggested[34] that the phosphite formed is involved in the addition process (Scheme 1); hydrophosphoranes which are not in equilibrium with the phosphorus(III) isomer are inert in such reactions.

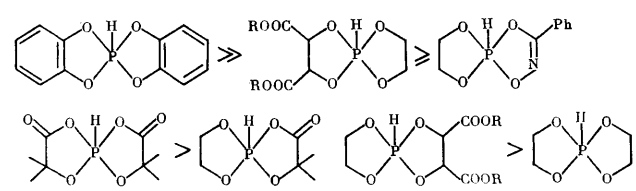
Scheme 1



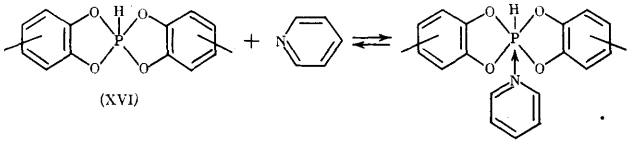
The mechanism presented in Scheme 1 is supported by the fact that alcohols do not react with these acetylenic compounds, whereas secondary amines readily add to them. The interaction of the γ-aminoalkyl cyclic phosphite isomer therefore involves the terminal amino-group like the addition of amines, while the oxa-analogues add as a result of the nucleophilic attack by the tervalent phosphorus atom on the β-carbon atom of the acetylenic group.[32–34]

Vinylphosphoranes of types (XIII) and (XIV) combine with a second hydrospirophosphorane molecule slowly, while the addition of dialkyl phosphites (in the presence of bases) is rapid. This difference has been attributed[33] to the different nucleophilic properties and steric hindrance of the phosphorus centres of the addends. In the addition of vinylphosphoranes, the nucleophile is subjected to a β-directing effect [in relation to phosphorus(V)], as in the analogous reactions of the vinyl derivatives of tricoordinate and tetracoordinate phosphorus. Only the vinylphosphorane obtained from propiolic acid esters (XIV, R' = H) combines with amines at the α-carbon atom.[33] Presumably the β-directing effect under conditions involving competition between the electron-accepting substituents in compound (XIV) is more pronounced for the alkoxycarbonyl group than for the spirophosphoranyl group.

Numerous data demonstrating the manifestation of the Lewis acidity of the phosphorus atom in hydrophosphoranes have been obtained. The following series, based on the weakening of this acidity, which agrees with the decrease of the overall electron-accepting capacity of the substituents in λ^5-diheterophospholan rings, have been found:[22]



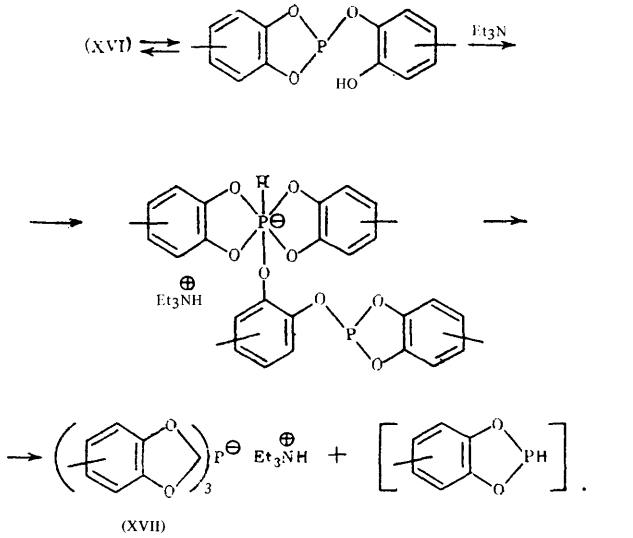
The Lewis acidity of hydrophosphoranes predetermines their capacity for coordination to bases, which increases the coordination number of the phosphorus atom to six:[35]



(XVI)

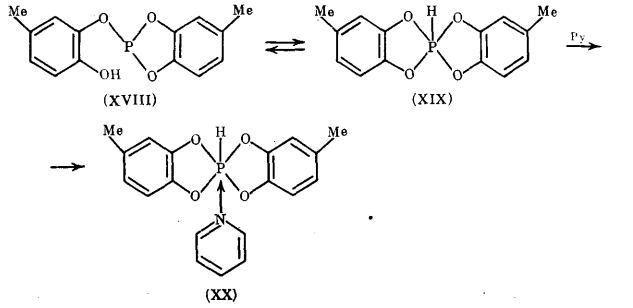
According to ^{31}P NMR data, the reversible reaction of compound (XVI) with pyridine leads to compounds of hexacoordinate phosphorus, whose content in the equilibrium mixture increases with increase of temperature. An analogous phenomenon obtains also when other spirophosphoranes without the P–H fragments are used, but in these cases it is less marked.[36]

The interaction of substituted dibenzohydrospirophosphoranes (XVI) with bases stronger than pyridine (triethylamine, triethylenediamine, and diisopropylamine) leads to the phosphoranes (XVII) as a result of the interaction of the two tautomeric forms of the hydrophosphorane:[37]



(XVII)

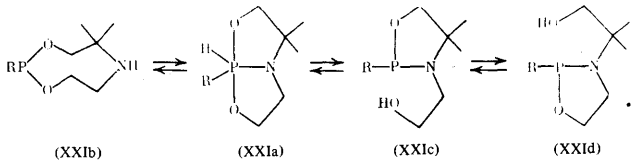
The above data indicate the ability of hydrophosphoranes to be involved in a tautomeric equilibrium with γ-hydroxyalkyl(aryl) phosphites, on the one hand, and (in basic media) with derivatives of hexacoordinate phosphorus, on the other. The presence of both types of equilibria has been established in the (XVIII) ⇌ (XIX) ⇌ (XX) system:[36]



(XVIII) (XIX) (XX)

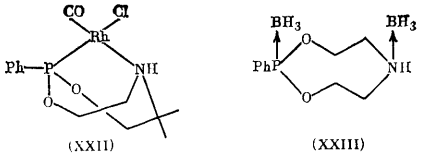
With increase of the amount of pyridine, the equilibrium shifts towards the "phosphorate" (XX).

Tautomerism involving the formation of the forms (XXI, b–d) is potentially possible for the bicyclic hydrophosphoranes (XXIa):



(XXIb) (XXIa) (XXIc) (XXId)

Only the phosphorane (XXIa), which has been found to be involved in the P–H P–D deuterium exchange, has been detected in solution;[38–40] the form containing a phosphorus-(III) atom has been identified in the gas phase by photoelectron spectroscopy.[41] Bicyclohydrophosphoranes combine with phenyl azide.[42] They react with transition metals to form complexes in which the coordinated ligand can exist in a monodentate or bidentate monocyclic phosphite form of type (XXII).[43–46]

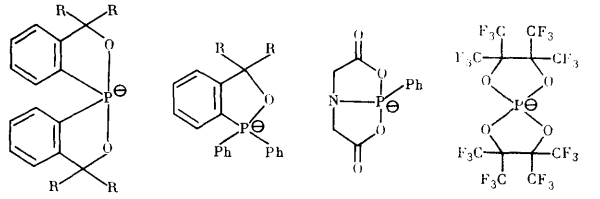


(XXII) (XXIII)

The adduct (XXIII), containing two molecules of the complex-forming agent, has been obtained by the interaction of (XXIa, R = Ph) with $Me_2S.BH_3$.[42]

2. Phosphoranide Anions

As pointed out above, the deprotonation of hydroxyspirophosphoranes results in the formation of phosphoranide anions, which may be involved in a tautomeric equilibrium with phosphite-alkoxides.[47,48] This method of generating stable cyclic phosphoranide anions has been used[48–52] for the synthesis of stable cyclic anionic systems (XXIV)–(XXVII) from the corresponding hydrophosphoranes; the bases employed were butyl-lithium[50,51] or triethylamine:[48,52]

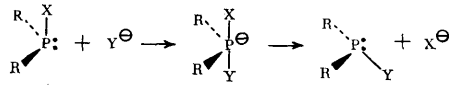


(XXIV) (XXV) (XXVI) (XXVII)

R = Me, CF_3

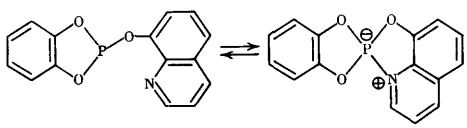
X-Ray diffraction (XRD) data for the anion (XXVII) have shown that it has the structure of a distorted trigonal bipyramid (TBP) with the unshared electron pair (LEP) in the equatorial (*e*) position and with a large difference between the lengths of the axial (*a*) P–O bonds (1.77 and 2.02 Å).[48]

Species of the type of phosphoranide anions have been postulated as unstable intermediates in bimolecular nucleophilic substitution reactions at a tricoordinate phosphorus atom:[1,53]



The isolation and identification of stable phosphoranide anions is of fundamental importance for the understanding of the mechanisms of nucleophilic substitution at the atoms of not only tricoordinate[1] but also tetracoordinate[2] and pentacoordinate (see Section VII) phosphorus atoms, which, at least in cyclic OPC, can proceed via a stage involving the formation of intermediates with an increased, compared with the initial phosphorus compound, coordination number of the central atom.

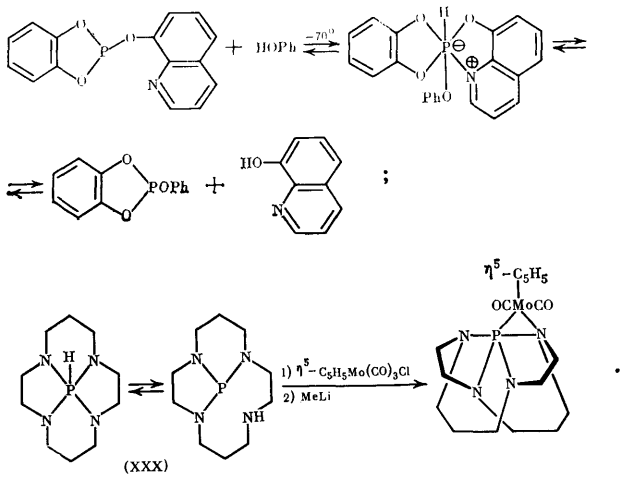
A phosphoranide centre can be formed also intramolecularly:[54]



(XXVIII) (XXIX)

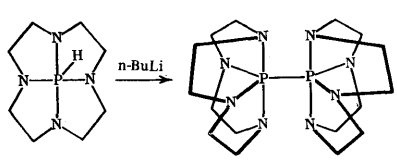
The equilibrium (XXVIII) ⇌ (XXIX), detected by ^{31}P NMR, is strongly displaced towards the form (XXVIII). Intermolecular nucleophilic substitution in this system takes place via an intermediate with a hexacoordinate phosphorus atom.[55]

Unusual polycyclic phosphoranides have been synthesised by the reaction of the hydrophosphorane (XXX) with transition metal compounds.[56] According to XRD data, the phosphorus ligand in these compounds is bidentate and is coordinated to the metal atom via both the phosphoranide and amine centres.

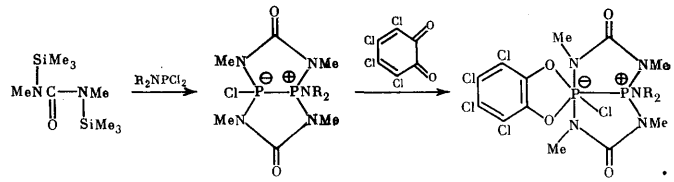


(XXX)

We may note, incidentially, that the first diphosphorane compound with a P(V)–P(V) bond has been obtained from a polycyclic hydrophosphorane:[57]



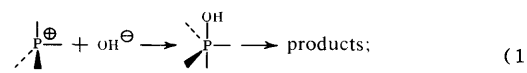
Compound (XXXI) contains a direct bond between the phosphonium and phosphoranide phosphorus atoms. The interaction with chloranil results in the formation of a "phosphoniaphosphorate"—the first compound with a P(IV)–P(VI) bond:[58]



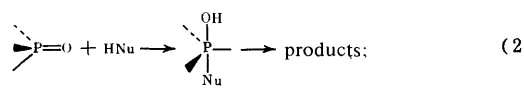
(XXXI)

III. HYDROXYPHOSPHORANES. THE PHOSPHATE–PHOSPHORANE TAUTOMERISM

The development of the chemistry of hydroxyphosphoranes is closely related to modern ideas concerning the mechanism of nucleophilic substitution reactions at a tetrahedral phosphorus atom [$S_N2P(IV)$], which are based on the rules associated with the hydroxyphosphorane concept—intermediates having a TBP structure with a pentacoordinate phosphorus atom are formed in these processes (see Cherkasov et al.[2] and the literature quoted therein). The character of such intermediates determines to a large extent the reactivity of phosphorus(IV) compounds and the synthetic and stereochemical results of nucleophilic substitution reactions. On hydrolysis of phosphonium salts [Eqn.(1)] or solvolysis of phosphoryl compounds by proton-containing nucleophiles [Eqn.(2)], the above TBP intermediates should have the hydroxyphosphorane structure:



(1)



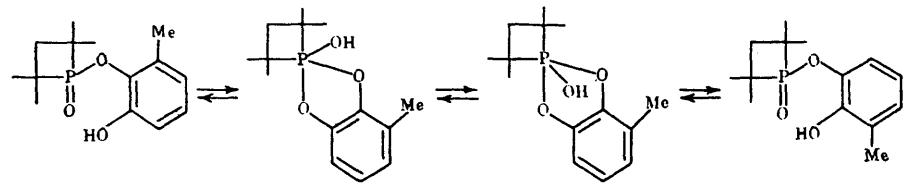
(2)

Nu = nucleophile.

The identification of the hydroxyphosphoranes and the study of their properties are therefore of decisive importance for the demonstration of a two-stage mechanism of the nucleophilic substitution reactions at phosphorus(IV), including biochemical phosphate transfer processes.[2,59,60]

Nevertheless, until the end of the 1970's, the demonstration of the formation of hydroxyphosphoranes in the nucleophilic reactions of phosphorus(IV) remained an unsolved problem. The first unambiguous evidence for the formation of hydroxyphosphoranes was obtained in the study of the interaction of cyclic phosphoryl compounds with proton-containing nucleophiles[2] and the hydroxyphosphoranes were trapped directly and successfully characterised in a study of the isomerisation of γ-hydroxyalkyl(aryl) esters of cyclic quinquevalent phosphorus acids (see Cherkasov et al. and the literature quoted therein[2]). Methods for the synthesis of stable hydroxyphosphoranes were subsequent developed.

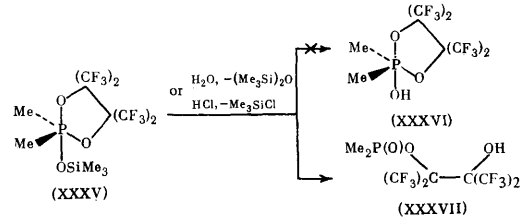
The 5-hydroxy-2-methylphenyl ester of the cyclic four-membered phosphinic acid (XXXII) shows signs in solution of a dynamic equilibrium due to the isomerisation (XXXII) ⇌ (XXXIV) involving the intermediate formation of the hydroxyphosphoranes (XXXIII, a and b):[61]



(XXXII) (XXXIIIa) (XXXIIIb) (XXXIV)

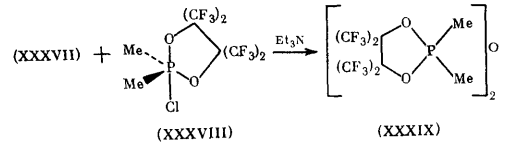
The activation energy for the isomerisation process is 17 kcal mol^{-1}. The concentration of compounds (XXXIII) is insufficient for their direct detection by NMR, but the possibility of their formation has been demonstrated by the reaction of a mixture of compounds (XXXII) and (XXXIV) with diazomethane: the methyl ester of the acid (XXXIII) was obtained in 5% yield. It is striking that the activation barrier to the isomerisation of the acyclic analogues (XXXII) is 24 kcal mol^{-1} for diphenylphosphinate and 28.3 kcal mol^{-1} for diphenylphosphinothioate, which reflects the well known sequence in the decrease of the energy of the TBP on passing from acyclic to monocyclic and spirocyclic structures[2] and the lower stability of mercaptophosphoranes compared with hydroxyphosphoranes.[62]

In this connection we may also note that, when the monocyclic siloxyphosphorane (XXXV) is acidified or cautiously hydrolysed, the product is not the hydroxyphosphorane (XXXVI) but the isomeric γ-hydroxyalkyl phosphinate (XXXVII):[63]



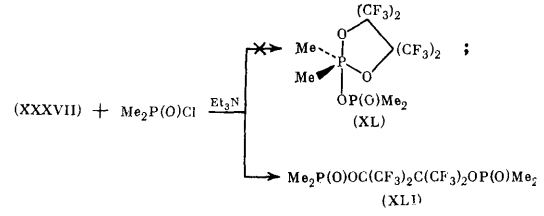
(XXXV) (XXXVI) (XXXVII)

However, it is of interest that the reaction of the phosphinate (XXXVII) with the chlorophosphorane (XXXVIII) proceeds with transfer of the reaction centre and leads to the anhydride of the hypothetical P(V)–OH acid (XXXIX):



(XXXVII) (XXXVIII) (XXXIX)

However, the acyclic chloride of dimethylphosphinic acid converts compound (XXXVII) into the symmetrical bisphosphinate (XLI) and not into the mixed anhydride (XL):[63]

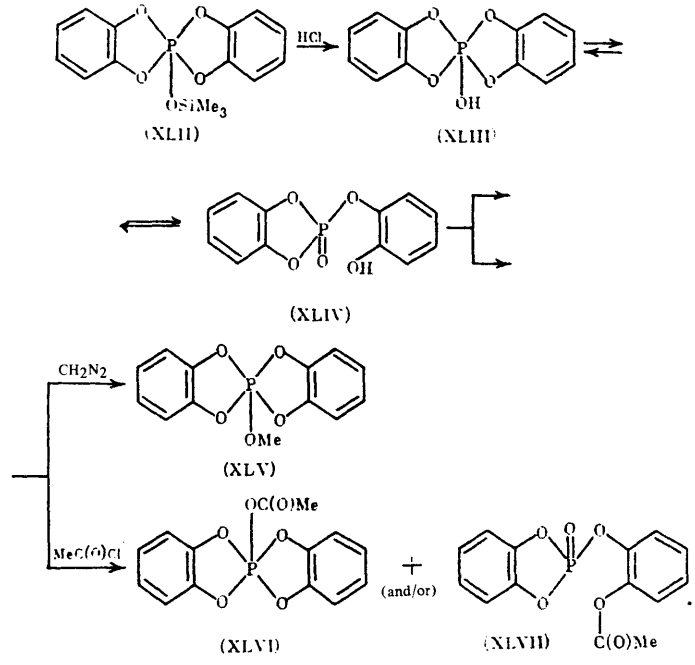


(XL) (XLI)

The formation of hydroxyphosphoranes has been postulated also in other reactions of γ-hydroxyalkyl(aryl) esters of phosphorus(IV) acids.[2]

These results indicate the possibility of the existence of a fairly mobile phosphate–phosphorane equilibrium involving hydroxyphosphoranes, which has been demonstrated for the first time by Ramirez et al.[64] and by Chang Bui Cong et al.[65] The product of the desilylation of bis(phenylenedioxy)siloxyphosphorane (XLII) has the structure of the phosphate (XLIV) in the crystalline state[66] [cf. the hydrolysis of the siloxyphosphorane (XXXV) to the phosphinate (XXXVII) [63]]. However, in acetonitrile at −48 °C the ^{31}P NMR spectrum showed two signals due to the phosphorus nucleus: the hydroxyphosphorane (XLIII) [$\delta(^{31}P) = 27.0$] was found together with the phosphate (XLIV) [$\delta(^{31}P) = +6.7$] in equilibrium with the latter and its amount was greater than that of the phosphate—the ratio P(IV) : P(V) = 1 : 1.5. The content of the phosphorus(V) form increases in the more basic acetone (3 : 1 at −48 °C):

Scheme 2



(XLII) (XLIII) (XLIV) (XLV) (XLVI) (XLVII)

Treatment of the (XLIII) ⇌ (XLIV) mixture with diazomethane affords a qualitative yield of the methoxyphosphorane (XLV); acetylation leads to a mixture of the acetyl derivatives of the phosphorane (XLVI) (20%) and the phosphate (XLVII) (80%) (Scheme 2). However, one should note that the synthetic result of the acetylation of compound (XXXV) or the (XLIII) ⇌ (XLIV) mixtures does not reflect the contents of the phosphorus(IV) and phosphorus(V) forms in the solutions: the reactions can proceed with transfer of the reaction centre [this has been confirmed

particularly strikingly by the reaction (XXXVII) + (XXXVIII) → (XXXIX) or may be subject to thermodynamic control. It has been established that the acetoxyphosphorane (XLVI) can be partly isomerised to the phosphate (XLVII) under the influence of the HCl evolved in the reaction.[66]

In the general case an increase in the content of the phosphorus(V) form in the hydroxyphosphorane–phosphate equilibrium is promoted by a decrease of temperature, by an increase of the basicity of the medium, and by the enhancement of the electron-accepting properties of the dioxyalkylene(arylene) substituent.

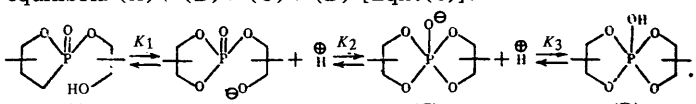
The intensity of the hydroxyphosphorane signal in the ^{31}P NMR spectra of the P(V) ⇌ P(IV) mixture begins to increase with decrease of temperature in those cases where individual lines correspond to each of the two forms P(V) and P(IV) [slow, in terms of the NMR time scale, equilibria of the type (XLIII) ⇌ (XLIV) and (LVI) ⇌ (LVIa) (Table 1)]. The averaged signal of the two equilibrium structures appears in rapid equilibria [hydroxyphsophorane (XLVIII) ⇌ (LI)]. A decrease of temperature entails a successive upfield shift of the resonance peak until the attainment of a fixed position in the region characteristic of hydroxyphosphoranes[67] (Fig.1).

The opening of the five-membered ring and the formation of phosphtate isomers are catalysed by acids. On the other hand, the introduction of bases into the P(V) ⇌ P(IV) mixture favours the hydroxyphosphorane structure up to formation of stable hydrogen-bonded complexes or salts of hydroxyphosphoranes, which can be isolated.[65–68]

However, the structure of the cyclic skeleton of the molecules of hydroxyphosphoranes is of decisive importance for the increase of their stability. Hitherto stable hydroxyphosphoranes have been identified only for a series of spirocyclic phosphoranes made up of five-membered oxa- and dioxa-phospholan rings (the effect of the five-membered ring).[12,69] NMR evidence has been adduced for the formation of relatively unstable acyclic,[70] monocyclic,[71] and condensed bicyclic hydroxyphosphoranes[72] (Table 1).

The stability of hydroxyphosphoranes increases sharply up to the formation of the sole P(V) form in solutions after the introduction of electron-accepting oxo-groups [compounds (LII), (LIII), (LV), and (LVIII)] or trifluoromethyl groups [compounds (LVII) and (LIX)]. A significant stabilisation of hydroxyphosphoranes is ensured by the presence of geminal dimethyl, bis(trifluoromethyl), and diphenyl fragments in rings (the Ingold–Thorpe effect[2]).

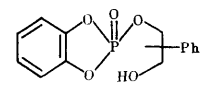
The estimation of the factors controlling the relative amounts of the forms involved in the hydroxyphosphorane ⇌ γ-hydroxyalkyl(aryl) phosphate equilibrium reduces, other conditions being equal, to the analysis of the sequence of equilibria (A) ⇌ (B) ⇌ (C) ⇌ (D) [Eqn.(3)]:[67]



(3)

The position of the hydroxyphosphorane–phosphate equilibrium is largely determined by two equilibrium constants—the dissociation constant K_1 and the cyclisation constant proper K_2, i.e. $K = K_1K_2$.[67] The determination of the thermodynamic parameters of the ring closure stage (B) ⇌ (C) (K_2) for compounds (XLVIII)–(L) with hydroxyacid ligands showed that the P(IV) form is slightly preferable for the cyclic oxo-compound (XLVIII) (ΔG^0 = +0.08, Table 2), whereas the spiran forms are more stable for the monosubstituted homologues (XLIX) and (L) under these conditions. The parameters obtained are close to those for other P(III) ⇌ P(V)[67] and P(V) ⇌ P(VI)[80] spirocyclisation processes.

The derivatives of the *gem*-disubstituted hydroxyacids (LII) and (LIII) and the phosphorane (LIV), synthesised with participation of benzohydroxamic acid, exist in the phosphorane forms over a wide temperature range (Fig.1). It is striking that the cyclic derivative of phenylethanediol (LX), whose structure is close to that of the spirophosphorane (LIV), does not pass to the spirophosphorane form under any of the conditions investigated. This has been attributed to the much lower dissociation constants K_1 of the phosphate (LX) compared with the phosphorylated derivative of benzohydroxamic acid (LIV):[67]



(LX)

The hydroxyphosphoranes (LVI)–(LVIII) containing endocyclic P–C bonds are exceptionally stable. These compounds have been isolated and exist as hydroxyphosphoranes in the crystalline state; the equilibrium with the phosphinate isomer is observed only in solutions of the tetrasubstituted hydroxyphosphorane (LVI).[69,76] The perfluoropinacone derivative (LIX) is so stable under the usual conditions that it can be easily recrystallised in the presence of moisture; the five-membered rings are not ruptured by sulphuric acid and potassium hydroxide.[79] In the latter case the poassium hydroxyphosphoranide is formed readily.

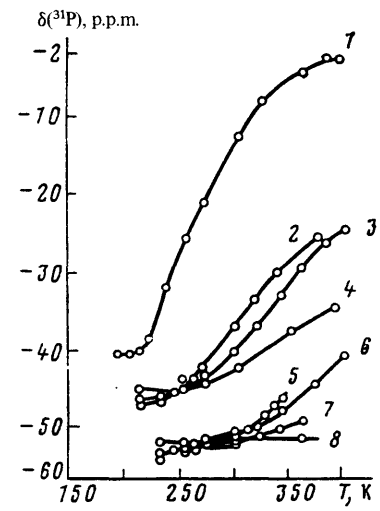


Figure 1. The influence of temperature on $\delta(^{31}P)$ for hydroxyphosphoranes:[67] 1) (XLVIII) (DMF); 2) (XLIX) (DMF); 3) (L) (DMF); 4) (LI) (DMF); 5) (LII) (CD_3CN); 6) (LII) (PhCN); 7) (LII) (DMF); 8) (LIII) (DMF); the numbering of the compounds is the same as in Table 1.

The XRD data for the triethylammonium salt of the hydroxyphosphorane (LIII)[74] and the salts of oligomeric hydroxyphosphoranes[75] confirmed that they have the TBP structure with five-membered rings in the *a* and *e* positions and the oxy-anion in the *e* position. The exocyclic P–O^- bond in these compounds is shortened, which reflects its double bond character.[73] This is caused in its turn by the influence of the oxo-group, as a result of which the phosphorus atom acquires a significant positive charge and the hydroxyphosphorane acquires fairly pronounced acid properties (Table 1).

Table 1. Stable hydroxyphosphoranes*.

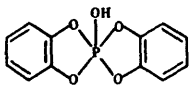
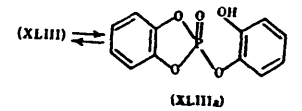
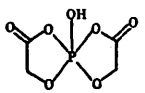
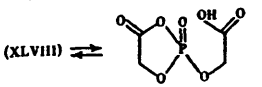
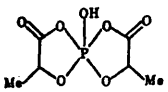
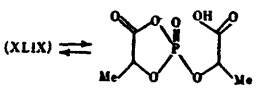
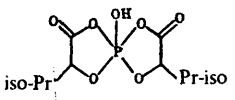
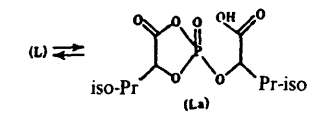
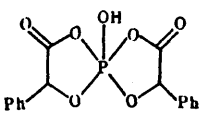
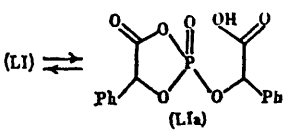
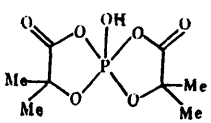
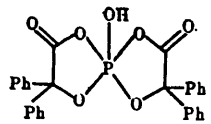
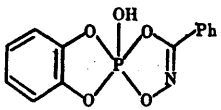
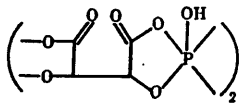
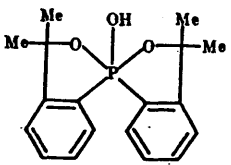
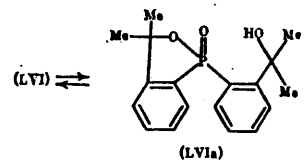
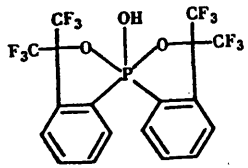
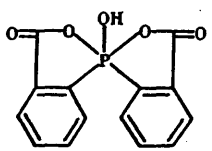
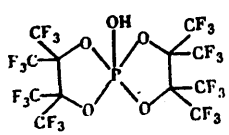
Hydroxyphosphorane	M.P. °C	pK_a(solvent)	$\delta(^{31}P)$, p.p.m. (solvent)	State in solution at room temperature	Refs.
 (XLIII)	—	9—10**	—27 (CD_3CN, —48° C)	 (XLIII) ⇌ (XLIIIa)	[64, 66]
 (XLVIII)	—	<3.5**	−13 (DMF)	 (XLVIII) ⇌ (XLVIIIa)	[67]
 (XLIX)	—	<3.5**	−37.4 (DMF)	 (XLIX) ⇌ (XLIXa)	[67]
 (L)	—	<3.5**	—43.5 (CD_3CN)	 (L) ⇌ (La)	[67]
 (LI)	—	3.5**	−42.8 (DMF)	 (LI) ⇌ (LIa)	[67]
 (LII)	—	2.5 (DMSO) 4.0 (DMF)	−52 (DMF)	[LII]	[67, 73, 74]

Table (cont'd).

Hydroxyphosphorane	M.P., °C	pK_a(solvent)	$\delta(^{31}P)$, p.p.m. (solvent	State in solution at room temperature	Refs.
 (LIII)	—	−0.6 (DMSO) 1.7 (DMF)	−52 (DMF)	(LIII)	[67, 73, 74]
 (LIV)	—	—	−23 (DMF)	(LIV)	[67]
 (LV)	—	−0.5 (DMSO)	−44 (DMF)***	(LV)	[73—75]
 (LVI)	181	10—11**	—26.3 (CH_3OD, —10° C)		[69, 76]
 (LVII)	168	5.3	−17.8 (THF)	(LVII)	[76, 77]
 (LVIII)	266—269	5.3**	—38.5 ($CDCl_3$)	(LVIII)	[77, 78]
 (LIX)	72	2.0	—34.5	(LIX)	[79]

*The Table includes data up to 1984 for hydroxyphosphoranes isolated in a pure state or identified in solution by ^{31}P NMR.
**Approximate estimate.
***$\delta(^{31}P)$ for oligomers: −45 for the complex of the trimer with DMSO; −42.5 for the complex of the pentamer with trimethylamine.[75]

Note. Numbers in square brackets denote references (Ed. of Translation).

The fact that XRD data[63,66] for the hydroxyphosphinate (XXXVII) and the hydroxyphosphate (XLIV) confirm the favourable entropy of the hydroxyphosphorane ring closure is striking. The hydroxy-group in the 2-position in the alkylene (arylene) ether group is in direct proximity (~3 Å) to the P(IV) atom.

Table 2. Thermodynamic parameters of the equilibrium P(IV) ⇌ P(V)–O⁻.[67]

Compound	ΔH^0, kcal mol^{-1}	ΔS^0, e.u.	ΔG^{0*}, kcal mol^{-1}
(XLVIIIa)	−3.9	−13	+0.08
(XLIXa)	−5	−13	−1
(La)	−4.8	−11	−1.3

* 30° C.

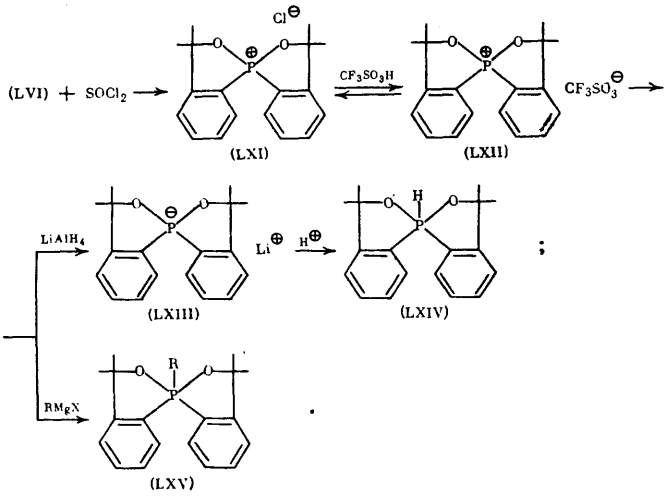
The isolation of stable hydroxyphosphoranes permitted well-founded inferences about their acid properties. This problem is of fundamental importance because hydroxyphosphoranes are partial esters of the hypothetical pentacoordinate phosphorus acid $P(OH)_5$.[81] At different stages of the investigation of hydroxyphosphoranes, their acid properties were estimated within wide limits—from pK_a = 10–11 [64,66] to claims that the strength of these acids is fairly high.[65] The latter were based on the ability of hydroxyphosphoranes to form stable hydrogen-bonded complexes with dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) and ammonium salts with tertiary amines.[65,67,68]

Indeed direct determination of the pK_a (Table 1) demonstrated their fairly marked dependence on the character of the substituents. It was found that the dissociation constants of the oxo-substituted hydroxyphosphoranes (LIII) and (LV) are higher than those of the strong dichloroacetic and diphenylphosphoric acids.[73–75] As expected, in the general case the acid properties of the hydroxyphosphoranes increase sharply after the introduction of electron-accepting substituents into the five-membered rings (Table 1).

The study of the comparative reactivities of the hydroxyphosphoranes (LVI)–(LVIII) also demonstrated a significant role of the nature of the substituents in the ring. Whereas the methylated derivatives (LVI) is readily converted into the quasi-phosphonium compound (LXI) on treatment with thionyl chloride, the analogous salts are not formed from compounds (LVII) and (LVIII). In these cases the electron-accepting ring substituents apparently destabilise the positive charge on the phosphorus atom. On the other hand, the difference between the acid strengths is such that the sodium salt of the acid (LVII) can be formed on treatment with alkali, whereas compound (LVI) is deprotonated only with sodium hydride. The oxo-analogue (LVIII) is converted into a phosphorus(IV) derivative in aqueous alkaline solutions.[69]

The anion exchange between compound (LXI) and trifluoromethanesulphonic acid leads to the triflate (LXII); the latter is reduced to the phosphoranide anion (LXIII), which gives rise to the hydroxyspirophosphoranes (XLIV) on acidification. It is of interest that the first representatives of hydroxyphosphoranes have been obtained by oxidising hydrophosphoranes.[65,67] Alkylation (arylation) of the cations (LXII) with Grignard reagents affords the alkyl(aryl)spirophosphoranes (LXV).[69]

The description of the TBP structure of hydroxyphosphoranes is based on the concept of hypervalent bonds: the apical and central atoms of the TBP are linked by a three-centre four-electron delocalised bond, which consists of one unoccupied and two occupied MO made up of a single *p* orbital of each atom involved in the hypervalent bond.[69,82] Such a structure presupposes the presence of long bonds between the electronegative *a*-atoms and the central atom carrying a partial positive charge.



The stability of the TBP increases after the introduction of electron-accepting substituents at the *a*-atoms and is increased by the five-membered ring and Ingold–Thorpe effects. It is believed[69,82] that a significant difference between the electronegativities of the *a*- and *e*-atoms, which is achieved by introducing σ-donor carbon-centred or p_π-donor heteroatomic equatorial ligands, is an important factor stabilising hypervalent structures. It has also been suggested[79] that steric shielding by bulky substituents, for example trifluoromethyl substituents in the structure of compound (LVII), can also promote an increase of the stability of such systems. This is evidently likewise true of hypervalent compounds of other elements (S, Si, I).[82]

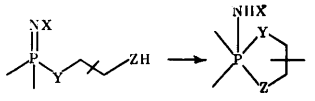
The importance of the synthesis and study of the structure and properties of hydroxyphosphoranes goes beyond the framework of the investigation of this new class of OPC alone. After the isolation and identification of hydroxyphosphoranes, the hydroxyphosphorane concept and the hypothesis of the role of phosphorus(V) intermediates in the nucleophilic substitution reactions at P(IV) received powerful experimental support. Data for the new type of phosphorus(V) acids combined with data for the strong acids of tetracoordinate phosphorus and weak acids of tricoordinate phosphorus constitute an integral picture of the complex problem of the relation between the structure and acidity of organophosphorus acids. It is extremely significant that the pathways leading to the approach to hydroxyphosphoranes presupposes the "opening" of the very strong (120–150 kcal mol^{-1} [83]) P=O bond (in essence addition to the P=O bond). Apparently energy is then gained as a result of the spirocyclisation of the reaction products.[2,69,76] This makes it necessary to look again at the character of the driving forces in many reactions of OPC: it may be that the formation of strong P=O bonds (or their analogues), as, for example, in the Arbuzov or Wittig reactions, is not the only factor which

determines the energy relations of chemical processes involving OPC and that account must be taken also of other factors, for example, the spirocyclisation and the effects accompanying it (see above).

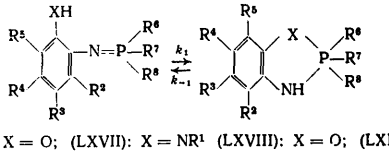
IV. AMINOPHOSPHORANES. THE PHOSPHIMIDE–PHOSPHORANE TAUTOMERISM

As stated above, the P=O double bond can participate in the addition reactions of H-containing nucleophiles with formation of hydroxyphosphoranes. In intermolecular addition reactions [Eqn.(1)] the latter are not detected—the interaction models the first stage of the nucleophilic substitution process at the tetrahedral phosphorus atom [$S_N2P(IV)$] which proceeds via an addition-elimination mechanism. Intramolecular addition to the P=O bond, particularly when it is accompanied by spirocyclisation, in some cases leads to stable hydroxyphosphoranes and this principle can evidently serve as the basis of the synthesis of stable cyclic phosphoranes.

Indeed the intramolecular addition of the γ-ZH functional group in alkoxy- or aryloxy-substituents to the P=N bond of phosphorus imides makes it possible to obtain stable aminophosphoranes (see Cherkasov et al.[2] and the literature quoted therein):



The intramolecular addition reactions involving the phosphimino-group and leading to spirocyclic aminophosphoranes are as a rule irreversible (see, however, Dahl et al.[84]), whereas in the series of monocyclic λ^5-diaza- and λ^5-oxazabenzophospholans it is possible to observe the ring–chain phosphimide–phosphorane tautomerism [Eqn.(4)] after the appropriate selection of substituents at the phosphorus and nitrogen atoms and in the benzene ring:



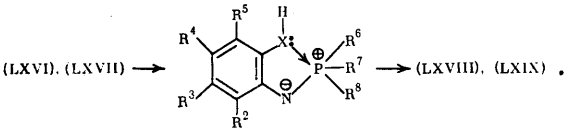
(4)

(LXVI): X = O; (LXVII): X = NR^1 (LXVIII): X = O; (LXIX); X = NR^1.

The study of the thermodynamics of equilibrium (4) in several reaction series[85–87] demonstrated the appreciable influence of temperature and of the nature of the solvent on the ratio of the tautomeric forms. Thus in nitrobenzene more than 90% of the acyclic phosphorus(IV) is present in the equilibrium mixture, whereas in tripropylamine the degree of cyclisation reaches 100%. With decrease of temperature, the equilibrium constant $K = k_1/k_{-1}$ increases [the content of the cyclanes (LXVIII) and (LXIX) increases].

The electronic influence of substituents is clearly shown when the groups in the phosphorus and imine components of the molecules are varied. Hydrogen atoms at the phosphorus atom fully displace the equilibrium towards aminophosphoranes. Electron-donating substituents in the imine fragment (R^3 = t-Bu) favour the phosphorus(V) form, while electron-accepting substituents ($R^3 = Ph_3C$) increase the content of the phosphimides (LXVI) in the tautomeric mixture.[85]

Thus the enhancement of the electron-donating properties of the atom X (O and N) to which a mobile hydrogen atom is attached and of the electron-accepting properties of the phosphorus atom promotes cyclisation. This is seen particularly clearly in the diazaphospholan series:[87] the NMR spectra of *N*-unsubstituted acyclic phosphimides (LXVII), R^1 = H, show only the phosphorus(IV) signal. These results are satisfactorily consistent with the mechanism involving the nucleophilic addition of the heteroatom X to the phosphorus atom in the cyclisation process.[85]



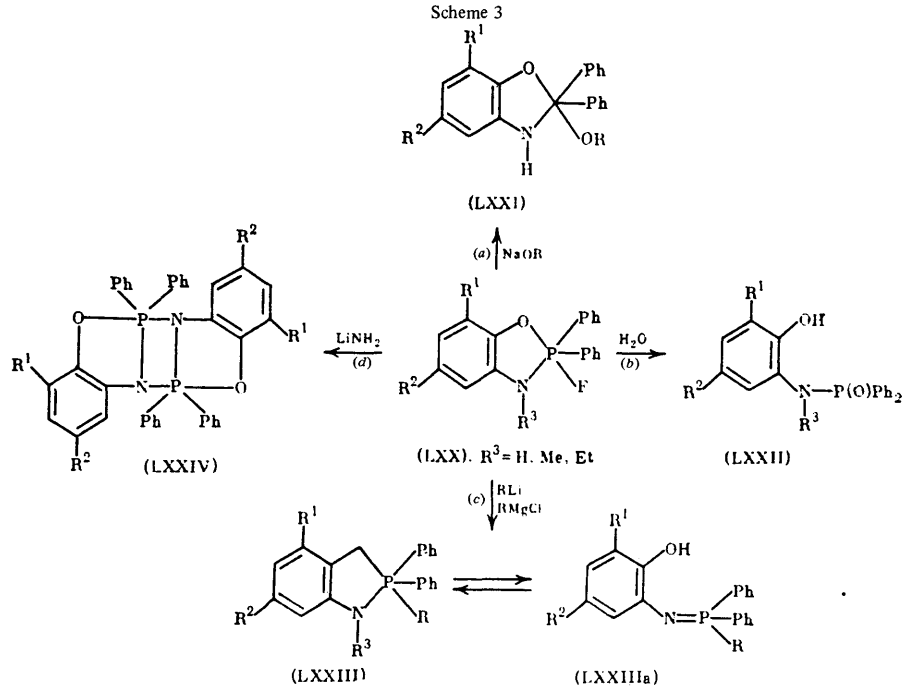
However, the steric characteristics of the substituents play a decisive role. In the series of oxaza-derivatives the equilibrium (LXVI) ⇌ (LXVIII) is displaced towards λ^5-oxazaphospholans only for R^4 = t-Bu.[85,86] Appreciable amounts of the phosphoranes (LXIX) appear in the mixture when the free rotation of the phosphimino-group in phosphimides is hindered (R^2 = t-Bu).[87]

This reaction series also illustrates the spirocyclisation effect which stabilises the phosphorus(V) form. The inclusion of phosphorus atoms in the five-membered ring, as in compound (LXVII, $R^7 = R^8$ = 2,2′-biphenylene), makes it possible to detect appreciable amounts of λ^5-diazaphospholans in the mixture even in those cases where the nitrogen atom is unsubstituted (R^1 = H).[87]

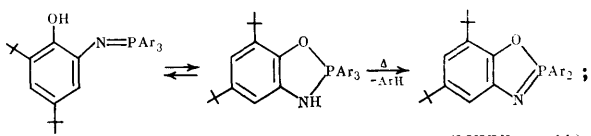
The observed features of the interconversions of phosphimides and aminophosphoranes are also manifested in the synthetic results of certain reactions of λ^5-oxazaphospholans.[88] Thus the ligand exchange of fluorine in the aminofluorophosphorane (LXX) for an alkoxy-group (Scheme 3, reaction *a*) does not alter the coordination of the phosphorus—the phosphorane (LXXI) is obtained, while hydrolysis (reaction *b*) leads to the phosphinamidate (LXXII) and not to an aminohydroxyphosphorane. The substitution of the fluorine atom by carbon-centred nucleophiles (reaction *c*) for R^3 = H induces the appearance of a mixture of products [(LXXIII, R^3 = H) ⇌ (LXXIIIa)]; when R^3 = alkyl, such tautomerism is naturally impossible and the only reaction product is the λ^5-oxazaphospholan (LXXIII, R^3 = Me or Et). The interaction of compound (LXX) with lithium amides (reaction *d*) leads to diazadiphosphetidines (LXXIV), evidently via the stage involving the formation of the phosphimine (LXXVI) with an endocyclic P=N bond:[88]†

† For information about the ease of dimerisation of cyclic phosphimides, see Dahl et al.[84] and Sheldrick et al.[89] and the literature quoted therein.

Scheme 3



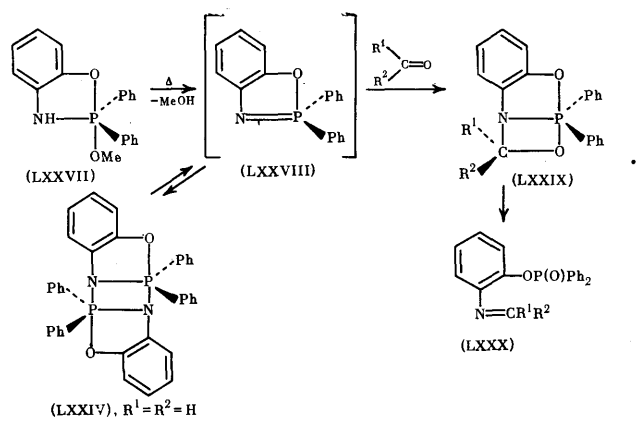
The phosphimides (LXXVI, a and b) are also formed when the phosphimides (LXXV, a and b) are heated above the melting point, which is accompanied by the evolution of the corresponding hydrocarbons:[90]



(LXXV, a and b) (LXXVI, a and b)

Ar = Ph (a), *n*-MeC_6H_4 (b)

The ability of cyclic aminophosphoranes to be converted into phosphimides has found a synthetic application in the reactions with carbonyl compounds.[91] The interaction of phosphorane (LXXVII) with aldehydes, ketones, and formamides proceeds via a stage involving the formation of the phosphimide (LXXVIII), which is converted into the phosphinates (LXXX) via a mechanism analogous to that of the Wittig reaction:

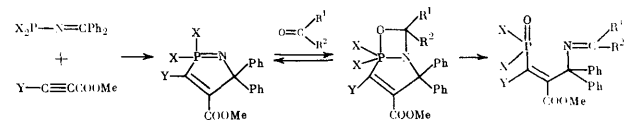


(LXXVII) (LXXVIII) (LXXIX) (LXXX)

(LXXIV), $R^1 = R^2 = H$

The formation of the phosphimide (LXXVIII) has been confirmed by the isolation of its dimer (LXXIV, R^1, R^2 = H) on thermolysis of compound (LXXVII) in solution or in the liquid state. The formation of the same final products (LXXX) as a result of the reaction of diazaodiphosphetidine (LXXIV) with carbonyl compounds indicates the reversibility of the dimerisation reaction (LXXVIII) ⇌ (LXXIV).

The transition state (LXXIX) (or the intermediate) in these reactions is modelled by the stable adducts (LXXXII, R^1 = Me or CF_3; R^2 = Me, CF_3 or Ph), obtained and isolated as a result of the consecutive [2 + 2]-cycloaddition reactions,[89,92] accompanied by a change in the coordination number of the phosphorus atom [P(III) → P(IV) in compound (LXXXI) and P(III) → P(V) in compound (LXXXII)]:



(LXXXI) (LXXXII) (LXXXIII)

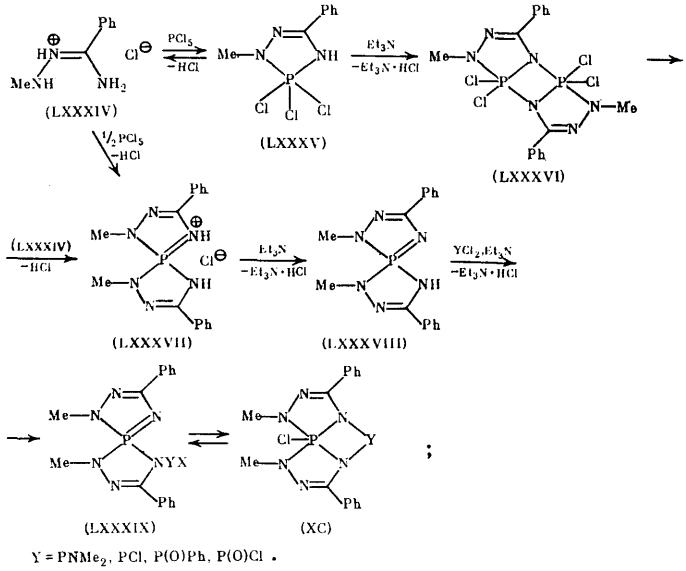
The stability of the cyclic adducts (LXXXII) with an aminophosphorane structure increases with decrease of temperature and with increase of solvent polarity. Acyclic phosphimides do not give rise to stable aminophosphoranes in their reactions with carbonyl compounds.[89]# The influence of the electron-accepting properties of the substituents in the carbonyl partner must also be optimal: the equilibrium in the reaction with acetone is wholly displaced towards the initial compounds. The adducts (LXXXII, $R^1 = CCl_3$, R^2 = H) with chloral and (LXXXII, $R^1 = C_6H_4NO_2$-*p*, R^2 = H) with *p*-nitrobenzaldehyde are converted into the aldiminophosphine oxides (LXXXIII, R = CCl_3 or $C_6H_4NO_2$-*p*, R^2 = H) with rupture of the phosphimide bond even at room temperature.

A version of the [2 + 2]-cycloaddition of hexafluoroacetone to an unstable phosphimide with an exocyclic P=N bond has been discussed by Storzer et al.[93]

The driving force of the cycloaddition reaction is the reduction of the angular strain in the TBP of the phosphorane (LXXXII) compared with the phosphimide (LXXXI). According to XRD data,[89] the structure of the phosphorane (LXXXII) deviates only slightly from the ideal TBP, whereas the initial compound (LXXXI), in which the endocyclic CPN angle differs greatly from the tetrahedral value, is destabilised by an appreciable steric strain.[92]

Interesting P(IV) ⇌ P(V) interconversions have been observed in the series of spirocyclic tetraaminophosphoranes.[94] The thermal condensation of equimolecular amounts of *N*-methylbenzamidrazone hydrochloride (LXXXIV) with phosphorus pentachloride leads to diaminotrichlorophosphorane (LXXXV), which is converted into the diazadiphosphetidine (LXXXVI) on treatment with bases. The same reaction with a twofold excess of compound (LXXXIV) is completed by the formation of the immonium chloride (LXXXVII); the latter is dehydrochlorinated by a tertiary amine to the spirocyclic phosphazene (LXXXVIII). The same compound can be arrived at by treating the dimer (LXXXVI) with the initial compound (LXXXIV) (Scheme 4):[94,95]

Scheme 4



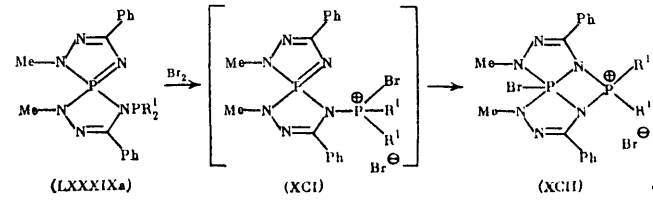
On passing from compounds (LXXXV) and (LXXXVI) to the spirocyclanes (LXXXVII) and (LXXXVIII), the phosphorus atom becomes a weaker electron acceptor (replacement of two chlorine atoms by amino-groups), so that the triaminophosphazene (LXXXVII) has an ionic structure, in contrast to the diamine analogue (LXXXV), and its dehydrochlorination product is monomeric [cf. the transition (LXXXV) → (LXXXVI)].

Phosphorylation of the phosphazene (LXXXVIII) by dichlorophosphines and dichlorophosphine oxides enabled Schmidpeter et al.[94] to observe a new type of reversible P(VI) ⇌ P(V) transitions—the phosphazene–diazadiphosphetidine rearrangement, involving the migration of chlorine (and not of a proton as in the previous examples) between the P(III) and P(IV) atoms in compound (LXXXIX) and an increase of the coordination number of one of the phosphorus atoms in compound (XC). This is accompanied by a pronounced shift of the $\delta(^{31}P)$ signal from ~50 p.p.m. for the P(IV) atoms in compound (LXXXIX) to −10 to −40 p.p.m. for the phosphorane phosphorus in compound (XC), the P(V) chemical shift depending significantly on the structure of the fragment Y.

The position of the tautomeric equilibrium is also determined by the nature of the P substituent in the fragment Y: the stronger the electron-accepting properties of the P(III) in the tricyclic tautomer (XC), the greater the shift of the equilibrium towards this tautomer. For the group Y = PPh, the tautomer (XC) is not detected and the introduction of the dimethylamino-group at P(III) lowers appreciably the content of the phosphorane: at room temperature in chloroform the ratio (LXXXIX) : (XC) is 73 : 27 for Y = $PNMe_2$.

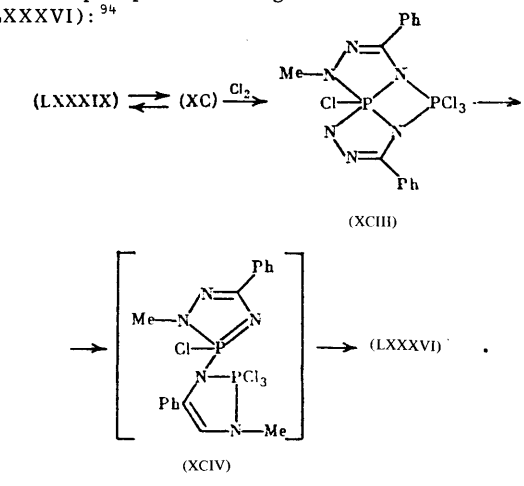
Each of the tautomeric forms (LXXXIX) and (XC) is chiral and can exist as two diastereoisomers and therefore in the general case four isomers may be present in the equilibrium mixture.[94] Thus, when crystalline compound (XC, Y = PCl) (one stereoisomer) is dissolved in chloroform, only a mixture of the diastereoisomers of compound (XC) in proportions of 92 : 8 is initially observed but after a week a mixture of three isomers is detected in the solution—one isomer of compound (LXXXIX) and two isomers of compound (XC) (32 : 63 : 5). The equilibrium mixture of the four isomers of compounds (LXXXIX) and (XC) with Y = POPh in benzene (17 : 30 : 27 : 26) is converted into a single crystalline isomer (XC, Y = POPh) after the removal of the solvent.[94]

It is of interest that the isomerisation described above takes place not only as a rsult of the transfer of a halogen between the P(III) and P(IV) atoms but also in the phosphazene–phosphonium system:[94]

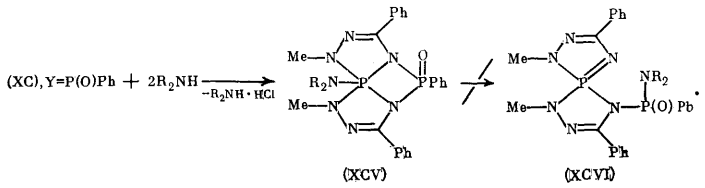


Bromination of the phosphazenes (LXXXIXa, R^1 = Ph or NMe_2) leads to tricyclic phosphorane–phosphonium isomers (XCII) and not to the expected spirophosphorane phosphazene–phosphonium isomers (XCI).

An even more complex reorganisation of the molecules takes place as a result of the bromination of the mixture of compounds (LXXXIX) and (XC, Y = PCl). The diphosphorane (XCIII), which exists only for a short time in solutions, undergoes in succession two types of isomerisation—the skeletal rearrangement to the hypothetical phosphazene (XCIV) as a result of the opening of the four-membered ring with transfer of the hydrazone group and subsequent closure of a new diazadiphosphetidine ring with formation of the dimer (LXXXVI):[94]



The amination of the halogenophosphoranes (XC) with ammonia, primary or secondary amines, and hydrazine leads to stable pentaaminophosphoranes (XCV) which are incapable of the P(V), P(IV)⇌P(IV), P(IV) tautomerism:



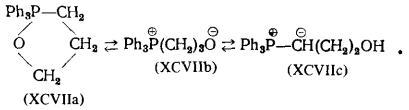
(XCV) (XCVI)

On reaction with aldehydes and ketones, the hydrazide [XCV, R_2N = N(He)NH_2] is converted into the corresponding hydrazones. It has been noted[94] that compounds of pentacoordinate phosphorus linked to five N-ligands as a rule tend to be converted into phosphorus(IV) derivatives. For example, the substitution of the halogen atoms in the dimer (LXXXVI) by amino-groups induces its conversion into the monomeric form.[95] In this sens compounds (XCV), which are not converted into the isomeric phosphonatophosphimides (XCVI), constitute a fairly rare example of stable pentaaminophosphoranes. §

V. OTHER TAUTOMERIC TRANSFORMATIONS OF PHOSPHORANES. PHOSPHOROTROPIC PROCESSES

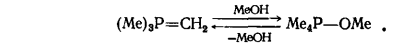
Various types of tautomeric transformations into compounds of tricoordinate, tetracoordinate, pentacoordinate, and hexacoordinate phosphorus have been observed for compounds of pentacoordinate phosphorus. Equilibrium transitions between compounds of pentacoordinate and dicoordinate phosphorus are so far unknown. The discovery and investigation of the phosphite–phosphorane and phosphimide–phosphorane tautomerism indicates the relative ease of the dissociation of the P=O and P=N bonds and the stability of the phosphoranes arising in such a process. All these equilibrium processes are characteristic only of cyclic, mainly λ^5-1,3,2-diheterophospholan, systems; in this case there is no analogy with acyclic compounds.

The dissociation of the P=C bond with formation of a phosphonium centre also proceeds fairly readily but the phosphorane–ylide equilibrium could not be observed for a long time, although some examples of the dual (both as a phosphorane and as an ylide) behaviour of phosphorane systems have been noted. Thus the λ^5-1,2-oxaphospholan (XCVII) has the structure of a compound with a pentacoordinate phosphorus atom (XCVIIa), but in some reactions it behaves as the betaine (XCVIIb), while in reactions with aldehydes and ketones it also reacts as a phosphonium ylide (XCVIIc):[97,98]

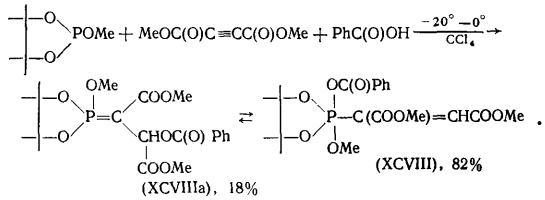


(XCVIIa) (XCVIIb) (XCVIIc)

The equilibrium between an ylide and a phosphorane has been reported but it is associated with the addition-elimination of the methanol molecule:[99]



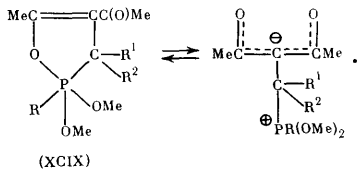
The first piece of evidence for the existence of the ylide–phosphorane equilibrium has been obtained[100] in a study of the interaction of cyclic phosphites with acetylenedicarboxylate ester in the presence of benzoic acid:



(XCVIIIa), 18% (XCVIII), 82%

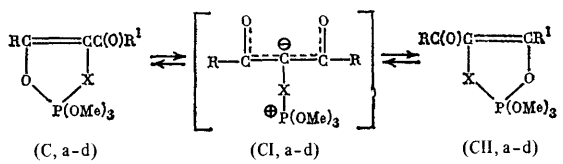
In methylene chloride the fraction of compound (XCVIIIa) increases to 37%, but, after the removal of this solvent and dissolution in CCl_4, the previous ratio is restored.

The phosphorane–phosphonium betaine tautomerism has been postulated for the monocyclic λ^5-1,2-oxaphospholens (XCIX) on the basis of the exchange of the methyl groups of the acetylacetonate system observed from ^{1}H NMR spectra.[3,4,10,101] An analogous phenomenon was believed[102,103] to be characteristic also of spirophosphorane systems:



(XCIX) (5)

The existence of the two tautomeric forms (Ca) and (CIIa), observed in solutions at room temperature [the ratio (Ca) : (CIIa) = 1 : 2 and is independent of the nature of the solvent], is apparently associated with the appearance of an intermediate dipolar ion (CI), which, however, is not detected in the spectra owing to its short life span:[104–106]



(C, a-d) (CI, a-d) (CII, a-d) (6)

(a) R=Ph; R^1 = Me; X = CHPh, $CHC_6H_4NMe_2$-*p*, $CHC_6H_4NO_2$-*p*;
(b) R = Me; R^1 = Me; X = CHMe, CHPh, $CHC_6H_4NMe_2$-*p*, $CHC_6H_4NO_2$-*p*;
(c) R = R^1 = Ph; X = O; (d) R = R^1 = Ph; X = NPh

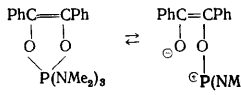
Detailed studies of the ^{1}H, ^{13}C, and ^{31}P NMR spectra of the (C, a–d)–(CII, a–d) systems as a function of temperature showed than an intramolecular transfer of the phosphorus-containing group takes place in such systems between two oxygen atoms;[107,108] the tautomeric process is degenerate for the phosphoranes (C, b–d)–(CII, b–d).

The chemical shifts of the phosphorus nuclei in all the solvents[107,108] remain unchanged over a wide temperature range (from −35° to +125 °C) and are observed in the regions characteristic of the resonance of the nuclei of pentacoordinate phosphorus(−27 to −51 p.p.m.). Thus the phosphonium structure is not an equilibrium component of these systems—the equilibrium is between two phosphorane forms

§ The synthesis of other aminophosphoranes containing two phosphorus atoms with different types of coordination has been described.[96]

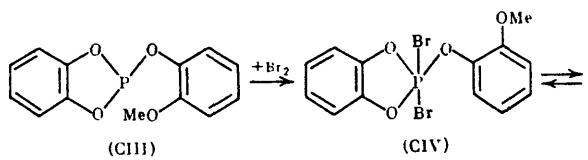
Eqn.(6) and the phosphorane–phosphonium tautomerism [Eqn.(5)] is not observed for compounds of this kind. The temperature-induced changes in the NMR spectra of phosphoranes described in other investigations[3,4,101–103] should apparently be interpreted analogously.

For exactly the same region, it is impossible to give an unambiguous answer concerning the possibility of the phosphorane–phosphonium equilibrium in aminophosphoranes:[101,109,110]

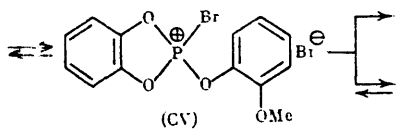


Detailed study of these systems by ^{1}H, ^{13}C, and ^{31}P NMR over a wide temperature range in solvents of different polarity led the authors[111,112] to the conclusion that the observed spectral changes are associated with the different polarities of the P–O bond, which depend on the dielectric constant of the medium.

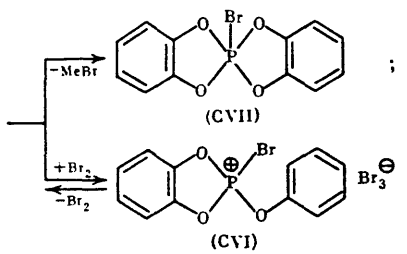
The existence of the equilibrium between the phosphorane and phosphonium structures has been demonstrated by low-temperature ^{13}C NMR in a study of the halogenation of the cyclic phosphite (CIII):[113]



(CIII) (CIV)



(CV)

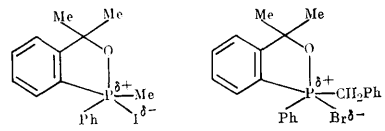


(CVII) (CVI)

At low temperatures (−100 °C) the dibromophosphorane (CIV) [$\delta(^{31}P)$ = 110 p.p.m.] and the phosphonium tribromide (CVI) (35 p.p.m.) were detected. The intermediate bromide (CV) ultimately symmetrises to form bromospirodiphenylenetetroxyphosphorane (CVII) (−28 p.p.m.); in essence this is an unusual version of the Arbuzov reaction, the second stage involving the dealkylation of the alkoxy-group separated from the phosphorus atom by the phenoxy-bridge. The driving force of this version of the Arbuzov reaction is spirocyclisation to compound (CVII) (see Section III) and not the formation of the thermodynamically favourable P=O bond as in the classical Arbuzov reaction.

The phosphorane–phosphonium equilibrium is characteristic also of acyclic phosphoranes. In acyclic systems this equilibrium is as a rule displaced towards the phosphonium form, while in cyclic systems it is displaced towards the phosphorane form, owing to the pronounced ring strain arising in cyclic, specially spirocyclic, phosphonium cations. Thus only the product with pentacoordinate phosphorus has been detected on chlorination of ethylene phosphorochloridite.[114]

The structure of the monocyclic phosphoranes (CVIII) and (CIX) is intermediate between the halogenophosphorane and phosphonium halide structures:[115,116]

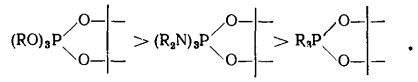


(CVIII) (CIX)

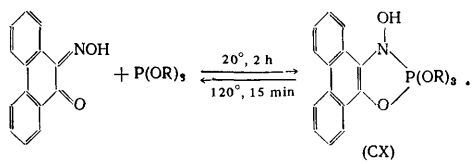
The appreciably ionic character of the phosphorus–halogen bond shifts the $\delta(^{31}P)$ signals of these compounds to the region characteristic of phosphonium structures, while the *ortho*-protons of the aromatic ring and the diastereotopic benzyl protons in compound (CIX) are manifested in the "phosphorane" region. By varying the substituents at the phosphorus atom, it is possible to alter the polarity of the phosphorus–halogen bond, whereupon the ^{1}H NMR spectra of such structures become characteristic in many cases of ionic compounds. This behaviour is very close to that observed for the NMR spectra of the adducts of α-dicarbonyl compounds with tris(amino)phosphines.[111,112]

VI. THERMOLYSIS OF PHOSPHORANES

It has already been stated that the stability of λ^5-1,3,2-diheterophosphacyclanes increases in the sequence acyclic < monocyclic < spirocyclic. This is valid also for their thermal stabilities. The series based on the influence of exocyclic groups at the phosphorus(V) atom on the thermal stabilities of monocyclic phosphoranes has been established:[117]



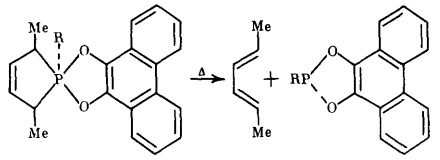
Many cyclic phosphoranes have such high thermal stabilities that they can be vacuum distilled, but some phosphoranes, obtained from phosphites or their analogues and α-dicarbonyl or αβ-unsaturated carbonyl compounds, decompose on heating intot the initial reactants, which indicates the reversibility of their formation reactions.[118–121] The phosphoranes formed after prolonged heating (50–60 °C) of trimethyl phosphite with dibenzylideneacetone, benzylideneacetophenone, and benzylidene-α-tetralone dissociate into the starting materials at a higher temperature (>90 °C).[122,123] The thermolysis of λ^5-1,3,2-oxaphospholans (CX) also leads to the ready elimination of trialkyl phosphites and the regeneration of the initial *o*-quinone monoxime:[124]



(CX)

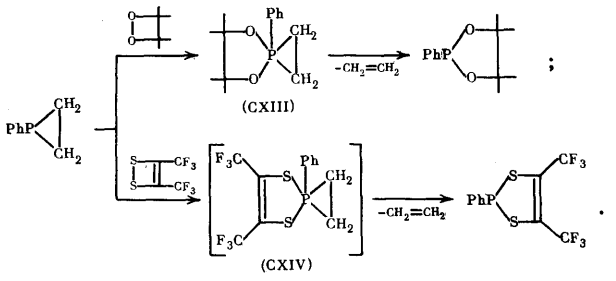
The rate of decomposition of λ^5-1,3,2-diheterophospholans is determined to some extent by the stereochemistry of the cyclic molecular skeleton.[125–128] Thus the study of the thermal decomposition of the stereoisomeric spirophosphoranes (CXI) established that steric factors exert a decisive influence on the rate of stereospecific fragmentation with formation of a diene and phosphonite (CXII): for the *cis*-disposition of the substituents R and Me in the phospholen ring, the decomposition proceeds much more readily; the bulky phenyl group at the phosphorus atom also accelerates the

fragmentation. The influence of electronic factors on this process is insignificant:[128]



(CXI) (CXII)

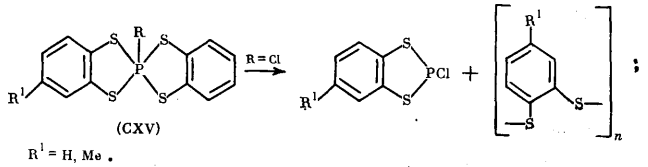
The thermal stability of λ^5-1,3,2-diheterophosphacyclanes varies within very wide limits depending on the structure of the rings and the nature of the substituents at the phosphorus atom (see Arbuzov and Polezhaeva[10] and the references quoted therein). As an example of extremely low stability, one may quote the spirophosphorane formed on interaction of phenylphosphiran with dioxetan.[129] The λ^5-dioxaphospholan (CXIII), containing a three-membered ring, is stable only at −80 °C; at room temperature it decomposes with elimination of ethylene. An analogous behaviour evidently obtains also in the case of the dithiaphospholen (CXIV):[130]



(CXIII) (CXIV)

These reactions involve a kind of "transcyclisation" of the phosphorus(III) derivatives.

Phosphoranes containing sulphur atoms linked directly to the phosphorus atom have been investigated much less than their oxygen analogues. The stability of the spiro-phosphoranes with four sulphur atoms (CXV) depends greatly on the exocyclic substituent R and decreases in the sequence Me > Ph ≫ Cl:

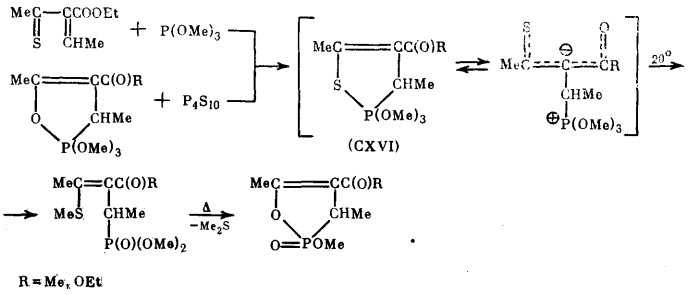


(CXV)

R^1 = H, Me.

Although in the latter case (R = Cl) the compound does form, it decomposes immediately with formation of oligomeric sulphides. The authors explain this instability by the unfavourable position of the chlorine atom in the e-position in the TBP or in the apical position of a square pyramid.[131]

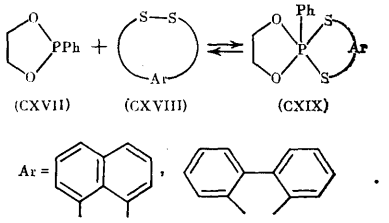
The monocyclic phosphoranes (CXVI) containing the 1,2-thiaphospholen ring cannot be isolated. They readily isomerise already in the course of their synthesis with migration of the methyl group to the nucleophilic sulphur atom:[132,133]



(CXVI)

R = Me, OEt

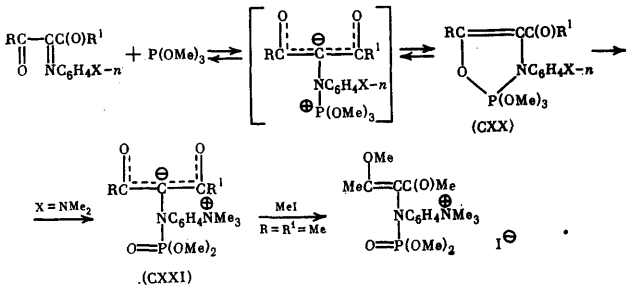
The first instance of reversible insertion in the disulphide linkage has been described.[134] The mode of the reaction of the cyclic phosphonite (CXVII) with the cyclic aromatic disulphides (CXVIII) depends on the nature of the solvent employed:



(CXVII) (CXVIII) (CXIX)

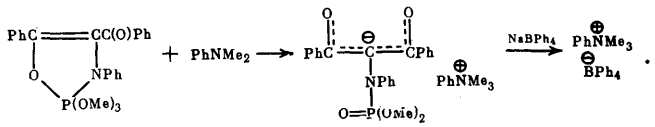
In acetonitrile the spirophosphoranes (CXIX) are formed readily and can be obtained in a crystalline state. In other media (CH_2Cl_2, $CHCl_3$) the reverse reaction predominates. Both processes proceed quantitatively without the formation of side products and are specific to the (CXVII) + (CXVIII) pair only.

The influence of the nature of the solvent on the stability of phosphoranes has been noted fairly frequently. The reversible formation reaction of the phosphoranes (CXX) has been observed for the interaction of 2-monoanils of 1,2,3-tricarbonyl compounds with trialkyl phosphites.[135–137] For X = H, the phosphorane (CXX) was isolated in a crystalline form. For X = NMe_2, the formation of phosphoranes in solution has been detected by ^{31}P NMR at room temperature. The attempts to isolate them in a crystalline state were unsuccessful: either the initial compounds are recovered (in ether) or the betaines (CXXI) are formed (in methylene chloride or in an excess of the phosphite). The betaines (CXXI), which are ammonium inner salts, are formed as a result of the O → N migration of the methyl group. The rearrangement of the phosphoranes into the stable betaine system, observed for the first time in Refs.135–137, shows that phosphoranes have the capacity to alkylate tertiary amines.

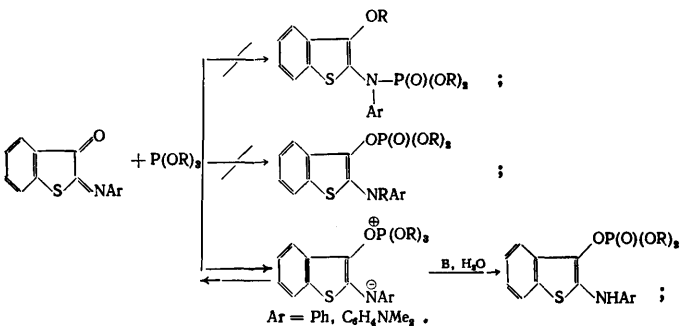


(CXXI)

This was also confirmed by the model reaction[138]

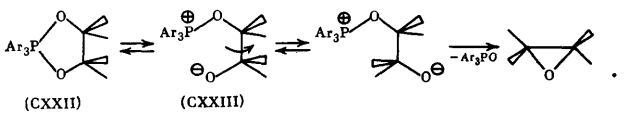


The monoanil of benzothiophen-2,3-dione does not react with trialkyl phosphites in a dry solvent; in the presence of moisture, the reaction proceeds via a protonation, but not alkylation, mechanism:[139]



Ar = Ph, $C_6H_4NMe_2$.

The thermolysis of λ^5-1,3,2-dioxaphospholans (CXXII) leads to the formation of epoxides with inversion of the configuration at the carbon atom[140-143] (see Arbuzov and Polezhaeva[10] and the references quoted therein). The mechanism of this reaction involves the heterolytic dissociation of the P–O bond, rotation about the C–C bond, and irreversible intramolecular substitution of the sp^3-carbon atom with formation of an epoxide:

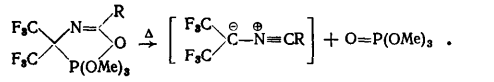


(CXXII) (CXXIII)

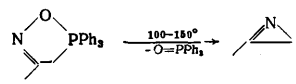
The study of the kinetics of these reactions by NMR [145] showed that they are of first order with respect to the phosphorane and that the thermolysis rate constants vary linearly with the σ constants of the substituents in the exocyclic aromatic groups (ρ = –3.5). The negative sign of ρ indicates the acceleration of the decomposition process with enhancement of the electron-donating properties of the varied groups, which facilitate the dissociation of the P–O bond and evidently stabilise the phosphonium centre in the intermediate (CXXIII).

At the same time the introduction of electron-donating groups should hinder the nucleophilic substitution reaction at the irreversible epoxide elimination stage, so that, when account is taken of effects which compensate one another, a fairly large absolute value of ρ is somehwat unexpected. The activation energy for the decomposition process (~20 kcal mol^{-1}) is close to that for the reactions of phosphoranes involving the rupture of the endocyclic P–O bond,[144] and the heterolytic dissociation reaction (CXXII) → (CXXIII) is therefore most important.[145]

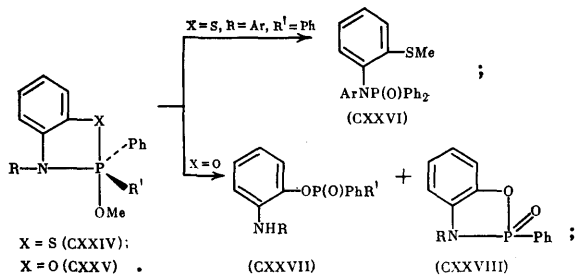
The thermal and photolytic decomposition of λ^5-1,4,2-oxazaphospholens leads to the formation of nitrile ylides[146] (see Arbuzov and Polezhaeva[10] and the literature quoted therein). Their formation was detected with the aid of dipolarophiles. The reaction with these substances leads to products of [3 + 2]- and [3 + 1]-cycloaddition:[147,148]



The pyrolysis of λ^5-1,5,2-oxazaphospholens is accompanied by the formation of azirines in high yields.[149] Bearing in mind the ready availability of such initial phosphoranes, which are obtained from α-bromoketones or ketoylides and triphenylphosphine, and also the possibility of carrying out all the stages without isolating the intermediates, the above method of synthesis of azirines can be regarded as fairly general and suitable for preparative purposes:



The formation of phosphoryl compounds on thermal decomposition of cyclic oxaphosphoranes has been frequently observed. The formation of compounds of tetracoordinate phosphorus as a result of thermal rearrangements of phosphoranes is rarer. Thus, on heating, the 1,3,2-thiazaphospholane (CXXIV) is converted into the phosphinamidate (CXXVI). On the other hand, the corresponding λ^5,1,3,2-oxazaphospholans (CXXV) are thermally very stable.[152] Their thermolysis in the gas phase[153] leads to the formation of products with retention [compound CXXVII)] or cleavage [compound (CXXVII)] of the oxazaphospholan ring depending on the character of the exocyclic substituents at the phosphorus atom: for R^1 = OMe, the main product is compound (CXXVIII), which has a cyclic structure:



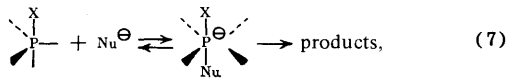
X = S (CXXIV); X = O (CXXV). (CXXVII) (CXXVIII)

VII. NUCLEOPHILIC SUBSTITUTION AT A PENTACOORDINATE PHOSPHORUS ATOM

The mechanism of nucleophilic substitution reactions at a pentacoordinate phosphorus atom [S_N2P(V)] has not been studied in quite such detail as the mechanism of substitution reactions at a phosphorus(IV) atom. To some extent this is associated with the fact that the chemistry of phosphoranes has developed mainly during the last two decades. However, the main difficulty consists in the exceptionally high rates of hydrolysis (solvolysis) of phosphorus(V) compounds.

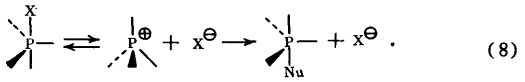
The kinetic study of these processes is complicated by the presence of a large number of stages—the reaction rarely stops after the rupture of one of the two bonds between phosphorus(V) and the heteroatom and usually develops further.

Two probable mechanisms of the $S_N2P(V)$ reactions have been discussed:[154–156] an associative mechanism involving hexacoordinate transition states and (or) intermediates:



(7)

and a dissociative mechanism with intermediate formation of phosphonium ions:



(8)

The study of the kinetics of the hydrolysis of pentaaryloxyphosphoranes demonstrated the exceptional sensitivity of the rate of reaction to the electronic and especially steric effects of the substituents at the benzene ring in neutral and alkaline media (Table 3).[154] The rate of reaction increases with enhancement of the electron-accepting properties of the substituent and is sharply retarded after the introduction of *ortho*-groups. This influence of the substituent X, the magnitude of the kinetic isotope effects (KIE) (k_{H_2O}/k_{D_2O} = 3 in hydrolysis by water and approximately unity in acid hydrolysis), and the absence of a salt effect are not characteristic of a dissociative process [Eqn.(8)] but agree well with the rate-determining attack by the water molecule or the hydroxide anion on the pentacoordinate phosphorus atom in pentaaryloxyphosphoranes:[154]

$$(ArO)_5P + H_2O \xrightarrow{slow} (ArO)_5\overset{\ominus}{P}OH + \overset{\oplus}{H};$$

$$(ArO)_5\overset{\ominus}{P}OH \xrightarrow{fast} (ArO)_3P{=}O + ArOH + ArO^{\ominus}.$$

The acid-catalysed reaction proceeds with protonation of the phosphoranes and the subsequent rate-determining substitution of the phenol by water:

$$(ArO)_5P + H^{\oplus} \underset{}{\overset{fast}{\rightleftharpoons}} (ArO)_4\overset{\oplus}{P}OAr \xrightarrow[H_2O]{slow} \text{products}. \quad (9)$$

The acid hydrolysis reaction is less sensitive to the influence of substituents but in this case too the steric effect of the group X is manifested distinctly by a decrease of k_{H^+} (Table 3). The rate of reaction varies linearly with the concentrations of H^+ and OH^- in the strongly acid and strongly alkaline media respectively (Fig.2).

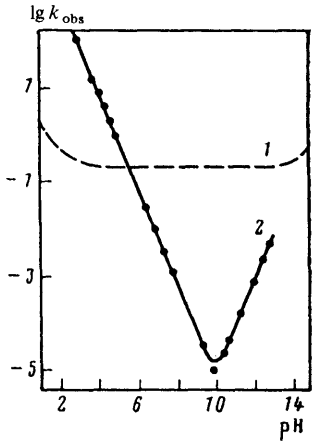


Figure 2. Dependence of the rate of hydrolysis of phosphorane (k_{obs}) on the pH of the medium: 1) penta-aryloxyphosphoranes; 2) spirophosphoranes (CXXIX).[154,155]

Table 3. Kinetics of the hydrolysis of pentaaryloxyphosphoranes $(XC_6H_4O)_5P$ at 25 °C in 25% dimethoxyethane.[154]

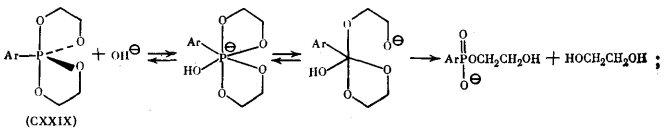
Reaction rate constant	X				
	H	*o*-Me	*p*-Me	*o*-Cl	*p*-Cl
k_{H_2O}, s^{-1}	0.202	$1.1\cdot10^{-5}$	0.0197	0.106	390
k_{H^+}, mol litre^{-1}s^{-1}	16.4	1.3	79	—	—
k_{OH^-}, mol litre^{-1}s^{-1}	11.4	$7.5\cdot10^{-4}$	3.4	—	—

Notation: k_{H_2O} is the rate constant for neutral hydrolysis ("plateau" on curve *2* in Fig.2), k_{H^+} the rate constant for acid hydrolysis (left-hand branch of curve *2*), and k_{OH^-} the rate constant for base hydrolysis (the right-hand branch of curve *2*).

An increase of the steric hindrance by the ligands destabilises the octahedral intermediate (or the transition state). By imparting a positive charge to the phosphorus atom, electron-accepting substituents accelerate the slow stage of the reaction, namely the attack by the nucleophile on the phosphorus(V) atom.

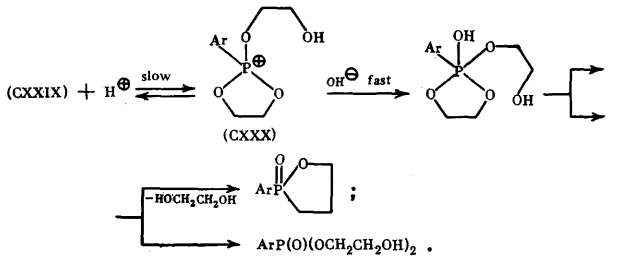
Another type of influence of the pH on the rate was established in a study of the kinetics of the hydrolysis of spirocyclic phosphoranes.[155] The alkaline reaction (in the pH range pH > 10, Fig.2) of the phosphoranes (CXXIX) is also described satisfactorily within the framework of the associative mechanism. In these reactions, involving the opening of the rings in λ^5-1,3,2-dioxaphospholans, and also in exocyclic substitution reactions involving alkoxy(aryloxy)-spiro-phosphoranes,[156] an increase of the reactivity of the organophosphorus substrates is observed after the introduction of electron-accepting substituents into the ligands.

However, in the range pH < 9 the hydrolysis of compound (CXXIX) resembles very closely the analogous reactions of dioxolan orthoesters, for which a dissociative carbonium mechanism has been established. It has been suggested[155] that the experimental results agree best with the acid-catalysed rate-determining dissociation reaction (CXXIX) ⇌ (CXXX) and the rapid cleavage of one or both rings:



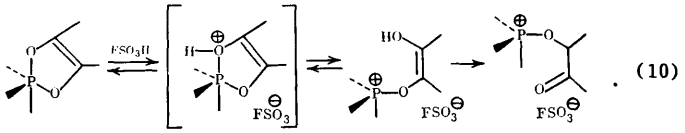
(CXXIX)

Ar = C_6H_4Me-*p*, Ph, C_6H_4Cl-*p*.



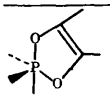
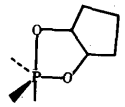
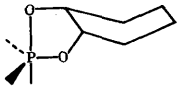
The pre-equilibrium protonation of the neutral oxaphosphorane (CXXIX) takes place with the simultaneous rupture of the P–O bond, so that the existence of the protonated phosphorane [Eqn.(9)] as an intermediate in cyclic systems is not obligatory.[155] This may be associated with the considerable ring strain in the protonated cyclic phosphorane. In this sense the acid hydrolysis of the phosphoranes (CXXIX) resembles the nucleophilic substitution reactions of five-membered cyclic phosphates.[2,157] It is believed[156] that in the general case the contribution of the dissociative mechanism should increase with enhancement of the electron-accepting properties of the ligands in the phosphorane.

Little is known about the existence of protonated phosphoranes. The formation of the protonated structure of a spirobicyclic phosphorane in the reversible acid catalysed hydroxyphosphorane–phosphate reaction (XLIII) ⇌ (XLIV) has been reported.[64] The study of the temperature variation of the ^1H, ^{13}C, and ^{31}P NMR spectra of certain monocyclic phosphoranes in the presence of small amounts of HSO_3F showed[158,159] that the protonated hydroxyphosphoranes are real intermediates in the reversible transition between dihydroxyphospholens and the isomeric enolphosphonium ions:



(10)

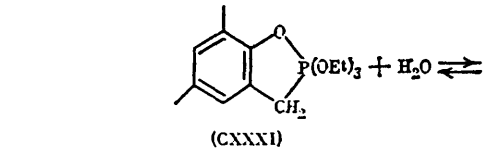
Table 4. Activation parameters for the phosphorane–dipolar ion equilibrium [Eqn.(10)].

Phosphorane	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	$\Delta G^{\neq}$, kcal mol^{-1}	Refs.
	2.8	−37	12.0	[159]
	3.0	−40	13.0	[160]
	2.6	−44	13.5	[160]

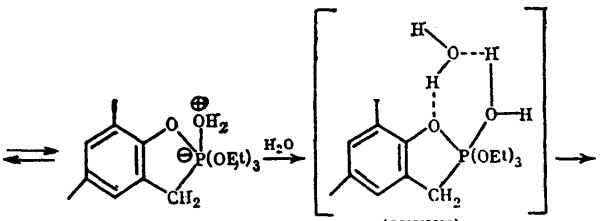
The rate of this process, which can be regarded as a model of intramolecular phosphorylation, is limited by structural factors and is entropy-controlled (Table 4). The equilibrium [Eqn.(10)] involves the bimolecular proton transfer between the protonated and neutral λ^5-1,3,2-dioxaphospholens. Equilibration is rapid when the ring contains a double bond and slow for saturated rings. It follows from the activation parameters for the phosphorane–phosphonium ion equilibrium[160,161] that the rigidity of the five-membered ring facilitates the ring closure to form the bicyclic phospholan structure, while in the case of a six-membered ring the process is less effective (Table 4).

The equilibria described here [Eqn.(10)] play an important role in the mechanism of the intramolecular phosphorylation of the 2-OH group in RNA, which is facilitated by the ribose ring.[160] It has also been noted that phosphorane–betaine interconversions of this kind are responsible for the ligand reorganisation processes involving spirocyclic arylphosphoranes, which are promoted by methyltrifluoromethanesulphonate.[162]

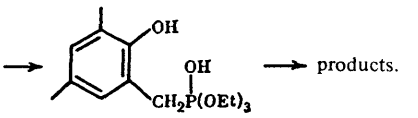
The associative mechanism has been demonstrated for the hydrolysis of the monocyclic phosphoranes (CXXXI) and (CXXXIII) in aqueous organic media.[163,164] The high values of the KIE (greater than 3), the large negative activation entropies, data concerning the influence of solvent polarity on the reaction rates, and the second (or higher) order of the reaction with respect to water suggest the formation of octahedral intermediates with phosphorus(VI). The subsequent involvement of a second water molecule in the process leads to ring opening products. The phosphorane (CXXXI) can form under these conditions the trimolecular complex (CXXXII):[163]



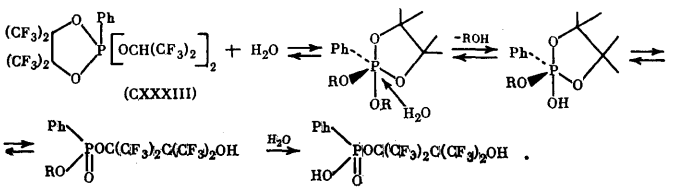
(CXXXI)



(CXXXII)



The hydrolysis of compound (CXXXIII) includes two pre-equilibrium stages—the formation of a hexacoordinate intermediate and exothermic opening of the λ^5-dioxaphospholan ring:[164]

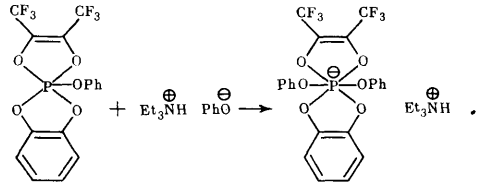


The formation of intermediate hexacoordinate phosphorate anions in the base hydrolysis of phosphoranes is especially probable in the series of λ^5,1,3,2-diheterophospholans. This

has been confirmed by numerous examples of the isolation or identification in solutions of phosphorus(VI) anions[166–169] (see Sarma et al.[165] and the literature quoted therein).

It has also been suggested that hexacoordinate intermediates can arise in the hydrolysis of ethylene methyl phosphate in highly alkaline media.[170,171] However, recent NMR studies of this process failed to confirm such a possibility.[172]

The stereochemical relations in the process involving an increase of the coordination number [P(V) → P(VI)] are clearly demonstrated by the comparison of the molecular structures of the phosphorane (CXXXIV) and the phosphate anion (CXXXV) (Fig.3), formed as a result of the addition of the phenoxide ion to the phosphorus atom in compound (CXXXIV).[165] It is usually suggested that the attack by the nucleophile on the central atom takes place in the equatorial plane of the TBP:[167,173]



(CXXXIV) (CXXXV)

The approach of the phenoxide anion to the O(3) atom from the rear (Fig.3*a*) should lead to a "phosphorate" with the *trans*-disposition of the PhO groups; the *cis*-configuration is a result of the addition of PhO^- to O(2) and O(4) from the rear. It has been established[165] that the most favourable steric disposition of the ligands in the "phosphorate" (CXXXV) (Fig.3*b*) is obtained following the attack on O(4) from the rear in the last sbustituted region of the phosphorane (CXXXIV). The alternative attack on O(3) from the rear gives rise to the sterically less favourable "phosphorate".

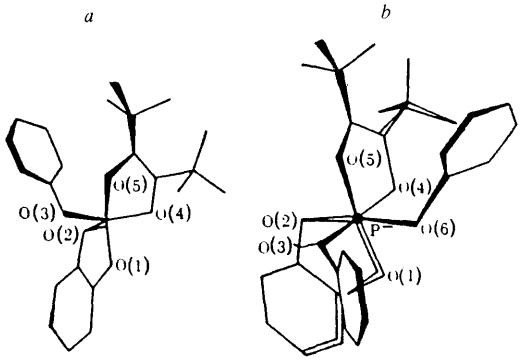


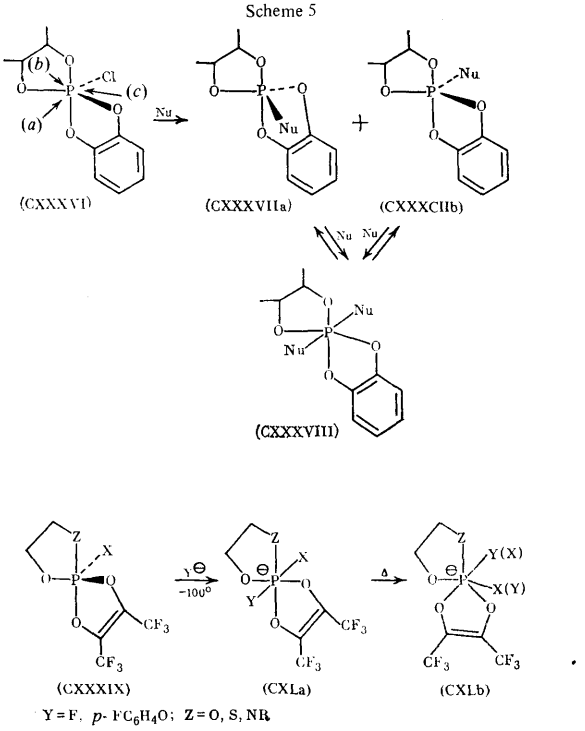
Figure 3. Molecular structures: *a*) phosphorane (CXXXIV); *b*) "phosphorate" (CXXXV).[165]

The stereochemical result of the $S_N2P(V)$ reactions depends to some extent on the nature of the nucleophile added to phosphorus(V) and on the leaving group.[173] The attack by the nucleophile on the phosphorus atom in exocyclic substitution reactions involving the phosphorane (CXXXVI) can proceed in principle via one of three pathways in the equatorial plane of the TBP (pathways *a*–*c*, Scheme 5). The *trans*-substitution via pathway *a* leads to the inversion of the configuration of the phosphorus atom, while *syn*-attack (pathways *b* and *c*) affords a product with retention of the configuration. Determination of the ratio of the stereoisomers (CXXXVIIa) and (CXXXVIIb) (7 : 1) by low-temperature ^{31}P NMR showed that the reactions of compound (CXXXVI) with dimethylamine and lithium dimethylamide proceed with the preferential inversion of configuration: $k_a = 7(k_b + k_c)$.

On substitution of PhO^- at −78 °C, the stereoisomeric composition corresponds to (CXXXVIIa) : (CXXXVIIb) = 1 : 1, while at room temperature the composition changes in favour of the isomer (CXXXVIIb) (0.64 : 1). Methyllithium gives rise to a mixture of equal amounts of the isomeric phosphoranes. The equilibration of the stereoisomers can be achieved via the hexacoordinate intermediate (CXXXVIII).

These results might have been interpreted on the assumption that the nucleophilic substitution at P(V) does not require the attack by the nucleophile of the leaving group.[173] However, it was later established for the interaction of phosphoranes of type (CXXXIX) with ionic nucleophiles at low temperatures (between −60° and −100 °C) that only the less stable *trans*-anions (CXLa), which isomerise to the "*cis*-phosphorates" (CXLb) on heating, are formed initially:

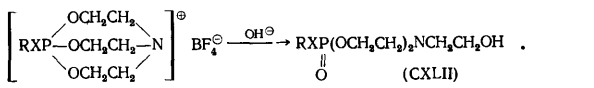
Scheme 5



The ease of the *trans*-attack, which is a kinetically controlled process, is due to the stereoelectronic effect of the LEP of the heteroatoms adjoining the P–Nu bond.[2,173] The *trans*-attack on spirocyclic phosphoranes of the type (CXXXIV) and (CXXXIX) is facilitated by the appropriate orientation of the LEP orbitals of the four heteroatoms, while the *cis*-attack is facilitated by only two of these orbitals.[174] The formation of the more stable *cis*-isomers (CXXXV) and (CXLb) is a thermodynamically controlled process, determined by the steric situation at the phosphorus(VI) atom [see the above remarks concerning the "phosphorate" (CXXXV)]. It has been noted[173] that the dissociative mechanism of the exocyclic nucleophilic substitution in spirocyclic phosphoranes is apparently impossible due

to the pronounced angular strain in the intermediate spirocyclic phosphonium cation. An analogous *cis–trans* isomerisation has been established also in a study of the interaction of the fluoride anion and the *p*-fluorophenoxide anion with λ^5-oxathia- and λ^5-oxaza-phospholens.[175]

As a consequence of the highly electrophilic properties of the phosphorus(V) atom, the attack by the nucleophile in the S_N 2P(V) processes is almost always directed at the phosphorus centre, in contrast to the nucleophilic substitution reactions at P(IV), where both the tetracoordinate phosphorus atom and the endo- or exo-cyclic carbon atoms can serve as centres for the nucleophilic interaction.[2] However, an instance of the selective pseudoequatorial attack by nucleophiles on the carbon atom in the TBP structure of the tricyclic phosphatranes (CXLI) has been observed recently:[176]



The transannular N → P bond in these compounds ensures quinary coordination of the phosphorus atom. In all cases (X = O or S) the products of the alkaline hydrolysis are the phosphates (CXLII) and nucleophilic attack is directed selectively to the pseudoequatorial carbon atom. It is believed[176] that such interaction is a consequence of the internal properties of the electronic configuration of the TBP: as a consequence of the dative transfer of electron density from the pseudoequatorial oxygen atom to the phosphorus atom, in the initial structure there is already some predisposition towards the formation of the P=O π-bond, which arises as a result of the reaction. A deficiency of electron density is therefore produced at the pseudoequatorial carbon atom, which renders this centre most sensitive to nucleophilic attack.

---o0o---

The data presented in this review demonstrate the multiplicity of the chemical properties of λ^5-1,3,2-diheterophosphacyclanes. The discovery of the role of cyclic phosphoranes and related structures with a phosphorus atom in the heterocycle (phosphonium cations, phosphoranide and hydroxyphosphoranide anions, "phosphorate" anions, and phosphorane–base complexes) as intermediates in many reactions of OPC, including those which have become classical, is of fundamental importance in this connection. This permits well-founded conclusions about the mechanisms of the reactions of OPC and indicates the usefulness of their investigation, particularly in relation to cyclic OPC. Various tautomeric processes and the relative ease with which the coordination number of the phosphorus atom can change in chemical reactions of OPC [P(III)–P(IV)–P(V)–P(VI)], which are particularly clearly manifested in the chemistry of cyclic phosphoranes, to a large extent predetermine the unity and wide variety in the phosphorus chemistry.

At the same time numerous questions concerning the reactivity of λ^5-1,3,2-diheterophosphacyclanes, such as the influence of the size of the heterocycle, of endocyclic heteroatoms, and of exocyclic functional groups and the quantitative estimation of the electronic and steric characteristics of phosphorus(V)-containing groups still await a more far reaching elucidation.

REFERENCES

1. M.A.Pudovik, V.V.Ovchinnikov, R.A.Cherkasov and A.N.Pudovik, Uspekhi Khim., 1983, **52**, 640 [Russ. Chem.Rev., 1983(4)].
2. R.A.Cherkasov, V.V.Ovchinnikov, M.A.Pudovik, and A.N.Pudovik, Uspekhi Khim., 1982, **51**, 1305 [Russ. Chem.Rev., 1982(8)].
3. R.Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", G.Thieme, Stuttgart, 1973.
4. R.R.Holmes, "Pentacoordinated Phosphorus Structure and Spectroscopy", Amer.Chem.Soc., Washington, 1980, Vol.1.
5. R.R.Holmes, Acc.Chem.Res., 1979, **12**, 257.
6. D.J.H.Smith, in "Comprehensive Organic Chemistry" (Edited by D.Barton and W.D.Ollis) (Translated into Russian), Izd.Khimiya, Moscow, 1983, Vol.5, p.16.
7. D.Hellwinkel, in "Organic Phosphorus Compounds", (Edited by G.M.Kosolapoff and L.Maier), Wiley-Intersci., New York, 1972, Vol.3, p.185.
8. F.Ramirez, H.Okuzaki, and J.F.Marecek, Heterocyles, 1978, **11**, 631.
9. R.Holmes, "Pentacoordinated Phosphorus, Reaction Mechanism", Amer.Chem.Soc., Washington, 1980, Vol.2.
10. B.A.Arbuzov and N.A.Polezhaeva, Uspekhi Khim., 1974, **43**, 933 [Russ.Chem.Rev., 1974(5)].
11. K.Burger, in "Organophosphorus Reagents in Organic Synthesis" (Edited by J.I.Y.Cadogan), Acad.Press, London, 1979, Ch.11.
12. F.Ramirex and I.Ugi, Bull.Soc.chim.France, 1974, 453.
13. R.Burgada, in "Khimiya i Primenenie Fosfororganicheskikh Soedinenii" (The Chemistry and Applications of Organophosphorus Compounds), Izd.Nauka, Moscow, 1974, p.232.
14. R.Burgada, Bull.Soc.chim.France, 1975, 407.
15. R.Burgada, Phosphorus Sulfur, 1976, **2**, 237.
16. A.Munoz, M.Sanchez, M.Koenig, and R.Wolf, Bull. Soc.chim.France, 1974, 2193.
17. D.Bernard, C.Laurenco, and R.Burgada, J.Organomet.Chem., 1973, **43**, 113.
18. C.Malavand and J.Barrans, Tetrahedron Letters, 1975, 3077.
19. S.D.Harper and A.J.Arduengo, J.Amer.Chem.Soc., 1982, **104**, 2497.
20. V.V.Ovchinnikov, M.A.Pudovik, V.I.Galkin, R.A.Cherkasov, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, p.434.
21. P.Savignac, B.Richard, Y.Leroux, and R.Burgada, J.Organomet.Chem., 1975, **93**, 331.
22. M.Koenig, A.Munoz, B.Gerrigues, and R.Wolf, Phosphorus Sulfur, 1979, **6**, 435.
23. C.Laurenco and R.Burgada, Tetrahedron, 1976, **32**, 2089.
24. L.I.Mizrakh and L.Yu.Polonskaya, Zhur.Obshch.Khim., 1979, **49**, 1168.
25. R.Burgada and H.Germa, Compt.rend., 1968, **267C**, 270.
26. H.Germa and R.Burgada, Bull.Soc.chim.France, 1975, 607.
27. N.P.Grechkin and G.S.Gubanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 2803.
28. C.Laurenco, D.Bernard, and R.Burgada, Compt. rend., 1974, **278C**, 1301.
29. C.Laurenco and R.Burgada, Tetrahedron, 1976, **32**, 2253.
30. H.Fauduet and R.Burgada, Compt.rend., 1980, **291C**, 81.
31. M.Sanchez, J.F.Brazier, D.Houalla, A.Munoz, and R.Wolf, Chem.Comm., 1976, 730.
32. R.Burgada, Compt.rend., 1976, **282C**, 849.
33. R.Burgada and A.Mohri, Phosphorus Sulfur, 1982, **13**, 85.

34. R.Burgada and A.Mohri, Phosphorus Sulfur, 1981, **9**, 285.
35. A.Munoz, M.Koenig, G.Gence, and R.Wolf, Compt. rend., 1974, **278C**, 1355.
36. A.Munoz, G.Gence, M.Koenig, and R.Wolf, Compt. rend., 1975, **280C**, 395.
37. A.Munoz, G.Gence, M.Koenig, and R.Wolf, Compt. rend., 1975, **280C**, 485.
38. D.Houalla, J.F.Brazier, M.Sanchez, and R.Wolf, Tetrahedron Letters, 1972, 2969.
39. D.Houalla, T.Monheich, M.Sanchez, and R.Wolf, Phosphorus, 1975, **5**, 229.
40. C.Bonninque, J.F.Brazier, D.Houalla, and F.H.Osman, Phosphorus Sulfur, 1979, **5**, 291.
41. D.Houalla, M.Sanchez, D.Goubeau, and G.Guillouzo Pfister, Nouv.J.Chem., 1979, **3**, 509.
42. R.Contreras, D.Houalla, A.Klaeve, and R.Wolf, Tetrahedron Letters, 1981, **22**, 3953.
43. D.Bondoux, I.Tkachenko, D.Houalla, R.Wolf, and I.Riess, Chem.Comm., 1978, 1022.
44. C.Pradat, J.G.Riess, D.Bondoux, B.F.Mentzen, I.Tkachenko, and D.Houalla, J.Amer.Chem.Soc., 1979, **101**, 2234.
45. D.Bondoux, B.F.Mentzen, and I.Tkachenko, Inorg. Chem., 1981, **20**, 839.
46. J.Wachter, F.Yeanneaux, and J.G.Riess, Inorg.Chem., 1980, **19**, 2169.
47. B.Garrigues, M.Koenig, and A.Munoz, Tetrahedron Letters, 1979, 4205.
48. D.Schonberg, W.Storzer, R.Bohlen, W.Kuko, and G.V.Röschentnaler, Chem.Ber., 1983, **116**, 3301.
49. I.Granoth and J.C.Martin, J.Amer.Chem.Soc., 1978, **100**, 7434.
50. I.Granoth and J.C.Martin, J.Amer.Chem.Soc., 1979, **101**, 4623.
51. M.R.Ross and J.C.Martin, J.Amer.Chem.Soc., 1981, **103**, 1234.
52. B.Garrigues and A.Munoz, Compt.rend., 1981, **293B**, 677.
53. J.Emsley and D.Hall, "The Chemistry of Phosphorus", Harper and Row, London, 1976, p.145.
54. Ch.B.Cong, G.Gence, B.Garriguer, M.Koenig, and A.Munoz, Tetrahedron, 1979, **35**, 1825.
55. Ch.B.Cong, A.Munoz, M.Koenig, and R.Wolf, Tetrahedron Letters, 1977, 2297.
56. J.M.Dupart, A.Grand, S.Pace, and J.G.Riess, J.Amer.Chem.Soc., 1982, **104**, 2316.
57. J.E.Richman, R.O.Day, and R.R.Holmes, J.Amer. Chem.Soc., 1980, **102**, 3955.
58. G.Bettermann, H.Buhl, R.Schmutzler, D.Schomburg, and U.Wermuth, Phosphorus Sulfur, 1983, **18**, 77.
59. F.H.Westheimer, Acc.Chem.Res., 1972, **5**, 204.
60. F.H.Westheimer, Pure Appl.Chem., 1977, **49**, 1059.
61. G.Kemp and S.Trippett, J.Chem.Soc., Perkin Trans. II, 1979, 879.
62. G.A.Kutyrev, R.A.Cherkasov, and A.N.Pudovik, Phosphorus Sulfur, 1982, **13**, 135.
63. D.Schomburg, O.Stelzer, N.Weferling, R.Schmutzler, and W.S.Sheldrick, Chem.Ber., 1980, **113**, 1566.
64. F.Ramirez, M.Nowakowski, and F.Marecek, J.Amer. Chem.Soc., 1977, **99**, 4515.
65. Ch.B.Cong, A.Munoz, M.Sanchez, and A.Klaebe, Tetrahedron Letters, 1977, 1589.
66. R.Barma, F.Ramirez, B.McKeever, M.Nowakowski, and J.F.Mareck, J.Amer.Chem.Soc., 1978, **100**, 5301.
67. A.Munoz, B.Garrigues, and M.Koenig, Tetrahedron, 1980, **36**, 2467.
68. A.Munoz, B.Garrigues, and M.Koenig, Chem.Comm., 1978, 219.
69. I.Granoth and J.C.Martin, J.Amer.Chem.Soc., 1979, **101**, 4618.
70. I.Granoth, Y.Segall, D.Waysbort, E.Shirin, and H.Leader, J.Amer.Chem.Soc., 1980, **102**, 4523.
71. I.Granoth, R.Alkabets, and E.Shirin, Chem.Comm., 1981, 981.
72. D.Houalla, M.Sanchez, R.Wolf, and F.H.Osman, Tetrahedron Letters, 1978, 4675.
73. A.Munoz, L.Lamande, D.Bayer, B.Garrigues, and R.Wolf, Phosphorus Sulfur, 1983, **18**, 85.
74. A.Dubourg, R.Roques, G.Gerwain, J.-P.Declercq, B.Garrigues, D.Bayer, A.Munoz, A.Klaeve, and M.Comtat, J.Chem.Res., S, 1982, 180.
75. A.Munoz, L.Lamande, D.Bayer, B.Garrigues, and R.Wolf, Phosphorus Sulfur, 1981, **15**, 71.
76. I.Granoth and J.C.Martin, J.Amer.Chem.Soc., 1978, **100**, 7434.
77. Y.Segall and I.Granoth, J.Amer.Chem.Soc., 1978, **100**, 5130.
78. Y.Segall and I.Granoth, J.Amer.Chem.Soc., 1979, **101**, 3687.
79. G.-V.Roschenthaler and W.Storzen, Angew.Chem., 1982, **94**, 212.
80. Ch.B.Cong, G.Gence, B.Garriuges, M.Koenig, and A.Munoz, Tetrahedron, 1979, **15**, 1825.
81. J.P.Guthrie, J.Amer.Chem.Soc., 1977, **99**, 3991.
82. J.C.Martin and W.H.Stevenson, Phosphorus Sulfur, 1983, **18**, 81.
83. D.E.C.Cobridge, "Phosphorus, an Outline of Its Chemistry, Biochemistry and Technology", Elsevier, Amsterdam, 1980.
84. B.M.Dahl, O.Dahl, and S.Trippett, J.Chem.Soc., Perkin Trans.I, 1981, 2239.
85. H.B.Stegmann, R.Haller, and K.Scheffler, Chem.Ber., 1977, **110**, 3817.
86. H.B.Stegmann, R.Haller, A.Burmester, and K.Scheffler, Chem.Ber., 1981, **114**, 14.
87. H.B.Stegmann, G.Wax, S.Peinelt, and K.Scheffler, Phosphorus Sulfur, 1983, **16**, 277.
88. H.B.Stegmann, H.V.Dumm, A.Burmester, and K.Scheffler, Phosphorus Sulfur, 1980, **8**, 59.
89. W.S.Sheldrick, D.Schomburg, A.Schmidpeter, and T.Crigern, Chem.Ber., 1980, **113**, 55.
90. H.B.Stegman, G.Bauer, E.Breitmaier, E.Herrmann, and K.Scheffler, Phosphorus, 1975, **5**, 207.
91. J.I.G.Cadogan, J.B.Husband, and H.M.Nab, Chem. Comm., 1981, 1054.
92. A.Schmidpeter, W.Zeiss, D.Schomburg, and W.S.Sheldrick, Angew.Chem., 1980, **92**, 860.
93. W.Storzer, G.-V.Roschenthaler, R.Schmutzler, and W.S.Sheldrick, Chem.Ber., 1981, **114**, 3609.
94. A.Schmidpeter, M.Nayibi, P.Mayer, and H.Tautz, Chem.Ber., 1983, **116**, 1468.
95. A.Schmidpeter, H.Tautz, and F.Schreiber, Z.anorg. Chem., 1981, **475**, 211.
96. G.Bettermann, H.Buhl, R.Schmutzler, D.Schomburg, and U.Wermuth, Phosphorus Sulfur, 1983, **18**, 77.
97. A.R.Hands and A.J.H.Mercer, J.Chem.Soc.C, 1967, 1099.
98. A.R.Hands and A.J.H.Mercer, J.Chem.Soc.C, 1968, 2448.
99. R.Burgada, Y.Leroux, and Y.O.El Khoshnich, Tetrahedron Letters, 1980, **21**, 925.
100. R.Burgada, Y.Leroux, and Y.O.El Khoshnich, Phosphorus Sulfur, 1981, **10**, 181.
101. F.Ramirez, Acc.Chem.Res., 1968, **1**, 168.
102. A.A.Petrov, V.V.Ragulin, V.I.Zakharov, M.S.Esakov, and N.A.Razumova, Dokl.Akad.Nauk SSSR, 1981, **259**, 379.

103. V.V.Ragulin, V.I.Zakharov, A.A.Petrov, and N.A.Razumova, Zhur.Obshch.Khim., 1981, **51**, 34.
104. B.A.Arbuzov, N.A.Polezhaeva, V.S.Vinogradova, G.I.Polozova, and A.A.Musina, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 2071.
105. B.A.Arbuzov, A.A.Musina, A.V.Aganov, R.M.Aminova, N.A.Polezhaeva, and Yu.Yu.Samitov, Dokl.Akad.Nauk SSSR, 1976, **228**, 805.
106. B.A.Arbuzov, N.A.Polezhaeva, R.T.Galiaskarova, A.V.Aganov, and A.I.Khayarov, Zhur.Obshch.Khim., 1982, **52**, 1025.
107. N.A.Polezhaeva, A.V.Aganov, A.I.Khayarov, and B.A.Arbuzov, Dokl.Akad.Nauk SSSR, 1981, **261**, 376.
108. B.A.Arbuzov, N.A.Polezhaeva, A.V.Aganov, and A.I.Khayarov, Phosphorus Sulfur, 1983, **18**, 49.
109. F.Ramirez, Pure Appl.Chem., 1964, **9**. 337.
110. R.Ramirez, A.V.Patwardan, H.J.Kugler, and C.P.Smith, Tetrahedron, 1968, **24**, 2275.
111. D.B.Denney, D.Z.Denney, P.J.Hammond, and Tseng Kuo-Sho, J.Amer.Chem.Soc., 1981, **103**, 2054.
112. D.B.Denney and S.D.Pastor, Phosphorus Sulfur, 1983, **16**, 239.
113. J.Gloede, H.Gross, J.Michalski, M.Pakulski, and A.A.Skowronska, Phosphorus Sulfur, 1982, **13**, 157.
114. J.Gloede, M.Pakulskii, A.Skowronska, H.Gross, and J.Michalski, Phosphorus Sulfur, 1982, 13, 163.
115. I.Granoth and J.C.Martin, J.Amer.Chem.Soc., 1981, **103**. 2711.
116. G.W.Astrologes and J.C.Martin, J.Amer.Chem.Soc., 1977, **99**, 4390.
117. F.Ramirez, C.P.Smith, J.F.Pilot, and A.S.Culati, J.Org.Chem., 1968, **33**, 3787.
118. V.A.Kukhtin, K.M.Kirillova, R.R.Shagidullin, Yu.Yu.Samitov, N.A.Lyazina, and N.F.Rakova, Zhur.Obshch.Khim., 1962, **32**, 2039.
119. B.A.Arbuzov, Yu.V.Belkin, and N.A.Polezhaeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1107.
120. B.A.Arbuzov, N.A.Polezhaeva, and V.S.Vinogradova, Izd.Akad.Nauk SSSR, Ser.Khim., 1967, 2281.
121. V.A.Kukhtin and K.M.Kirillova, Dokl.Akad.Nauk SSSR, 1961, **140**, 835.
122. B.A.Arbuzov, V.M.Zoroastrova, G.A.Tudrii, and A.V.Fuzhenkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 2581.
123. B.A.Arbuzov, A.V.Fuzhenkova, and G.A.Tudrii, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 2369.
124. M.M.Sidky, M.F.Zayed, A.A.El-Kateb, and I.T.Hennawy, Phosphorus Sulfur, 1981, **9**, 343.
125. V.V.Ragulin, A.A.Petrov, V.I.Zakharov, and N.A.Razumova, Zhur.Obshch.Khim., 1983, **53**, 741.
126. V.V Ragulin, A.A.Petrov, V.I.Zakharov, and N.A.Razumova, Zhur.Obshch.Khim., 1982, **52**, 239.
127. G.Scott, P.J.Hammond, C.D.Hall, and J.D.Bramblett, J.Chem.Soc., Perkin Trans.II, 1977, 882.
128. P.J.Hammond, J.R.Lloyd, and C.D.Hall, Phosphorus Sulfur, 1981, **10**, 47.
129. B.C.Campbell, D.B.Denney, D.Z.Denney, and L.S.Shih, Chem.Comm., 1978, 854.
130. D.B.Denney and L.S.Shih, J.Amer.Chem.Soc., 1974, **96**, 317.
131. D.B.Denney, D.Z.Denney, and Lun-Tsu Liu, Phosphorus Sulfur, 1982, **13**. 243.
132. B.A.Arbuzov, N.A.Polezhaeva, and V.V.Smirnov, Izv. Akad.Nauk SSSR, Ser.Khim., 1975, 688.
133. B.A.Arbuzov, N.A.Polezhaeva, and V.V.Smirnov, Izv. Akad.Nauk SSSR, Ser.Khim., 1975, 686.
134. Y.Kimrira, T.Kokura, and T.Soegusa, J.Org.Chem., 1983, **48**, 3815.
135. B.A.Arbuzov, N.A.Polezhaeva, and M.N.Agafonov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 436.
136. B.A.Arbuzov and N.A.Polezhaeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 445.
137. B.A.Arbuzov, N.A.Polezhaeva, and M.N.Agafonov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 608.
138. B.A.Arbuzov and N.A.Polezhaeva, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1631.
139. M.M.Sidky, W.M.Abdou, N.M.Ald-el Rahman, Phosphorus Sulfur, 1983, **16**, 331.
140. P.D.Bartlett, A.L.Baumstark, and M.E.Landis, J.Amer.Chem.Soc., 1973, **95**, 6486.
141. P.D.Bartlett, M.E.Landis, and M.J.Shapiro, J.Org. Chem., 1977, **42**, 1661.
142. Y.-Y.Koo and G.B.Schuster, J.Amer.Chem.Soc., 1977, **99**, 5403.
143. A.L.Baumstark, M.Barrett, and K.M.Kral, J.Heterocycl.Chem., 1982, **19**, 201.
144. D.Gorenstein, J.Amer.Chem.Soc., 1970, **92**, 644.
145. A.L.Baumstark, C.J.McCloskey, T.E.Williams, and D.R.Chrisope, J.Org.Chem., 1980, **45**, 3593.
146. K.Burger, J.Albanbauer, and F.Manz, Chem.Ber., 1974, **107**, 1823.
147. K.Burger and W.-D.Roth, Synthesis, 1975, 731.
148. K.Burger, S.Tremmal, W.D.Roth, and H.Gath, J.Heterocycl.Chem., 1981, 18, 247.
149. A.Hassner and V.Alexaman, J.Org.Chem., 1979, **44**, 3861.
150. J.I.C.Cadogan and B.S.Tait, J.Chem.Soc., Perkin Trans.I, 1975, 2396.
151. J.I.G.Cadogan and N.J.Tweddle, J.Chem.Soc., Perkin Trans.I, 1979, 1278.
152. J.I.G.Cadogan, D.S.B.Grace, P.K.K.Lim, and B.S.Tait, J.Chem.Soc., Perkin Trans.I, 1975, 2376.
153. J.I.C.Cadogan, J.B.Husband, and H.McNab, J.Chem. Soc., Perkin Trans.I, 1983, 1489.
154. W.C.Archie and F.H.Westheimer, J.Amer.Chem.Soc., 1973, **95**, 5955.
155. R.McCleland, G.Patel, and C.Cirinna, J.Amer.Chem. Soc., 1981, **103**, 6432.
156. S.Kobayashi, Y.Narukawa, T.Hashimoto, and T.Saeugusa, Chem.Lett., 1980, 1599.
157. I.S.Sigal and F.H.Westheimer, J.Amer.Chem.Soc., 1979, **101**, 5329.
158. M.M.C.F.Castelijns, P.Schipper, and H.M.Buck, Chem.Comm., 1978, 382.
159. M.M.C.D.Castelijns, P.Schipper, and H.M.Buck, J.Org.Chem., 1981, **46**, 47.
160. D.Van Aken, L.M.C.Paulissen, and H.M.Buck, J.Org.Chem., 1981, **46**, 3189.
161. D.B.Denney, D.Z.Denney, and Chi-Tei Ling, J.Amer. Chem.Soc., 1976, **98**, 6755.
162. C.L.Lerman and F.H.Westheimer, J.Amer.Chem.Soc., 1976, **98**, 179.
163. V.E.Bel'skii, L.A.Khismatullina, T.G.Bykova, A.V.Burykina, and B.E.Ivanov, Zhur.Obshch.Khim., 1979, **49**, 344.
164. A.Queen, A.E.Lemire, and A.F.Janzen, Int.J.Chem. Kinet., 1981, **13**, 411.
165. R.Sarma, F.Ramirez, B.McKeever, J.F.Marecek, and V.A.V.Prasad, Phosphorus Sulfur, 1979, **5**, 323.
166. A.Skowronska, M.Pakulski, and J.Mikhalski, J.Amer. Chem.Soc., 1979, **101**, 7412.
167. B.Garrigues, A.Munoz, and M.Millier, Phosphorus Sulfur, 1980, **9**, 183.
168. M.Koenig, A.Klaebe, A.Munoz, and R.Wolf, J.Chem. Soc., Perkin Trans.II, 1979, 40.
169. D.B.Denney et al., J.Amer.Chem.Soc., 1981, **103**, 1785.

170. R.Kluger et al., J.Amer.Chem.Soc., 1969, **91**, 6066.
171. P.Gillespie et al., Angew.Chem., 1971, **83**, 691.
172. D.G.Gorenstein and K.Taira, J.Amer.Chem.Soc., 1982, **104**, 6130.
173. S.Trippett and R.E.L.Waddling, Tetrahedron Letters, 1979, 193.
174. J.J.H.M.Font Freide and S.Trippett, Chem.Comm., 1980, 157.
175. J.J.H.M.Font Freide and S.Trippett, J.Chem.Res., S, 1981, 218.
176. D.Van Aken, I.I.Merkelbach, A.S.Koster, and H.M.Buck, Chem.Comm., 1980, 1045.

Ul'yanov-Lenin Kazan State University

Butlerov Research Institute