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1,3,2-Diheterophosphacyclanes Containing a Hexacoordinate Phosphorus Atom

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Data are presented on the methods of synthesis, structure, and physical and chemical properties of cyclic compounds of hexacoordinate phosphorus-λ^6-1,3,2-diheterophosphacyclanes, in which the phosphorus atom is incorporated in one, two, and three heterocycles containing P-O or P-N bonds. The dynamic stereochemistry and equilibrium dissociative as well as tautomeric processes involving them are described. The role of phosphorus(VI)† intermediates in the reactions of organophosphorus compounds with tricoordinate, tetracoordinate, and pentacoordinate phosphorus is analysed. The bibliography includes 140 references.

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I. INTRODUCTION

Compounds of hexacoordinate phosphorus (phosphorates) began to be investigated vigorously only in the last decade, although the first description of substances of this type dates back to 1954 and is associated with the study of the adducts of PCl_5 with pyridine (see Dillon et al.[1,2] and the references quoted therein). Numerous inorganic "ate" complexes formed by compounds of pentacoordinate phosphorus and basic substances[3] as well as cyclic and acyclic organylhalogenophosphorates[4] are known. Cyclic phosphorates with six P–C bonds and aromatic substituents and finally λ^6-1,3,2-diheterophosphacyclanes with monocyclic, bicyclic, and tricyclic structures were later described. Individual aspects of the chemistry of compounds of hexacoordinate phosphorus have been dealt with in reviews.[5–8]

Numerous phosphorus(VI) compounds are now known and their number continues to grow, which undoubtedly indicates an appreciably greater role of these compounds in phosphorus chemistry than has been assumed hitherto. Hexacoordinate intermediates in the reactions of organophosphorus compounds containing a phosphorus atom with a lower coordination number are apparently important. Interesting data have been obtained on the steric structures of phosphorates and the equilibrium processes involving them.

Analysis of the literature data has shown that the stability of hexacoordinate phosphorus compounds increases sharply following the incorporation of the phosphorus atom in one or several rings, mainly five-membered rings. The acyclic alkoxyphosphorates known at the present time[9] are stable only in solution.

The first attempt has been made in the present review to give a systematic account of the available literature data on 1,3,2-diheterophosphoacyclanes containing a phosphorus-(VI) atom entering into the composition of one, two, or three rings, mainly four- or five-membered rings, and bound to several heteroatoms (O, N). Data on the methods of synthesis, structure, physicochemical, and chemical properties of these compounds, the dynamic and equilibrium processes involving them, and the role of phosphorus(VI) compounds as intermediates in the chemical reactions of organophosphorus compounds (OPC) were used in the review.

The data on the compounds of hexacoordinate phosphorus with the 1,3,2-diheterophosphacyclane structure, summarised in the present review, supplement the available information about the reactivities of similar heterocyclic compounds containing tricoordinate,[10] tetracoordinate,[11] and pentacoordinate[12] phosphorus atoms and in our view they provide at the same time an integral picture of the chemistry of 1,3,2-diheterophosphacyclanes.

II. SYNTHESIS AND REACTIONS

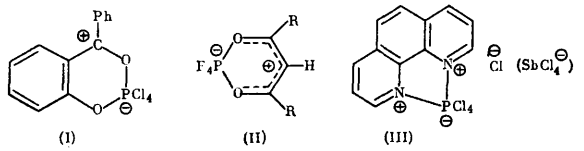
Phosphorates of two types are known: those with salt (ionic) structures, in which the phosphorus atom is part of the composition of a phosphorus(VI) anion or (more rarely) a phosphorus(VI) cation, and neutral molecules, which exist in the form of dipolar ions with an anionoid phosphorus atom. A convenient analytical criterion whereby it can be demonstrated that the phosphorus atom has a coordination number of six is the marked shielding of the ^{31}P(VI) nucleus; it is manifested by the fact that the signals in the NMR spectra are displaced to very strong fields (between −70 and −300 p.p.m.). As already stated, the cyclisation of phosphorus(VI) compounds tends to increase their stability; the acyclic organylphosphorates $(MeO)_6P^-$ and $(EtO)_6P^-$ have been identified by ^{31}P NMR in solutions. They decompose when an attempt is made to isolate them from solution.[9]

1. Monocyclic Phosphorates

The commonest method of synthesis of monocyclic phosphorates involves the reactions of phosphorus pentahalides with bifunctional nucleophiles in which one of the halogen atoms at the pentacoordinate phosphorus is substituted and

† [Roman numerals used in this way refer to coordination number and not to oxidation state in this review (Ed.of Translation)].

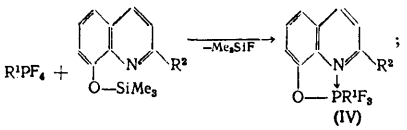
a sixth phosphorus–element bond is formed as a result of the donor–acceptor interaction of the electron-deficient P(V) atom with a second basic centre of the bidentate organic ligand. The reaction of *o*-hydroxybenzophenone with PCl_5 leads to a quantitative yield of the six-membered cyclic phosphorate (I), to which the structure of a dipolar ion has been attributed on the basis of the spectroscopic data and the high dipole moment (9.17 D):[13]



(I) (II) (III)

β-Dicarbonyl compounds evidently react in the enolic form, as in the formation of λ^5-1,3,2-dioxaphosphorinane (II).[14,15] Substitution by a neutral nitrogen-containing base is accompanied by the quaternisation of the donor centre [in structure(III)][16,17] and the strength of the donor–acceptor bond increases after the introduction of electron-accepting substituents at the phosphorus atom, for example, for $R^1 = F$ in the phosphorate (IV).[18,19]

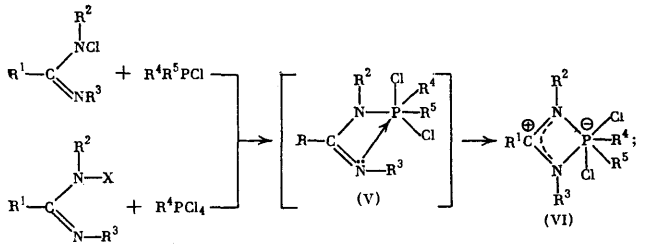
The formation of hexacoordinate structures in reactions involving nucleophilic substitution at a pentacoordinate phosphorus atom is frequently ensured by the presence of a donor centre in a suitable position within the substituting reagent:



(IV)

R^1=F, Me, Et, Ph; R^2=H, Me.

The intramolecular cyclisation of *NN'*-dialkyl-*N*-halogenophosphoranylamidines (V), formed in the reaction of *NN'*-disubstituted amidines with the chlorides of tricoordinate or pentacoordinate phosphorus made it possible to obtain a series of phosphorates (VI) containing the 1,3,2-diazaphosphetidine ring.[20–23] We may note that the reaction of *N*-chloroamidines constitutes in essence the 1,1-addition of the N–Cl fragment to the P(III) atom of the chlorophosphine:

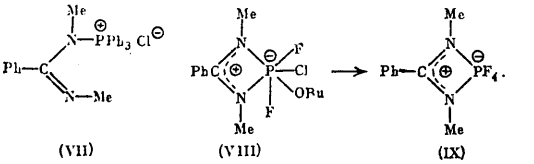


(V) (VI)

X = H, $SiMe_3$; R^1 = Ph, CCl_3, CF_3; R^2, R^3 = alkyl; R^4, R^5 = alkyl, aryl, halogen.

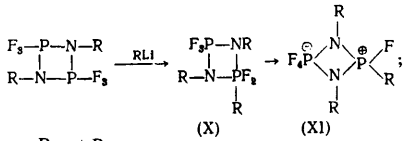
The reaction of *NN'*-dimethyl-*N*-trimethylsilylbenzamidine with bis(*o*-phenylenedioxy)chlorophosphorane results in the formation of tricyclic phosphorates.[20]

The stability of the four-membered monocyclic phosphorates (VI) depends greatly on the character of the substituents at the phosphorus atom and in the N–C–N triad. The benzamidinium derivative with four chlorine atoms at the phosphorus atom (VI, R^1 = Ph, $R^2 = R^3$ = Me, $R^4 = R^5$ = Cl) is the most stable. The replacement of the phenyl group at the amidinium carbon atom by the electron-accepting CCl_3 and CF_3 groups destabilises the P(VI) structure, inducing the reversible P → C migration of a chlorine atom[22] (see Section IV). An increase in the bulk of the substituent at the nitrogen atom and the introduction of two phenyl groups at the phosphorus atom lead to the same result. Three phenyl groups at the phosphorus atom stabilise only the phosphonium salt (VII),[23] while the butoxy-group induces the disproportionation of the alkoxyphosphorate (VIII) to the tetrafluoro-analogue (IX).[21]



(VII) (VIII) (IX)

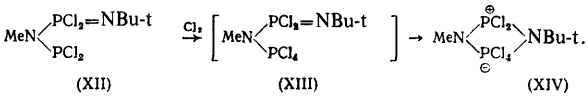
Hexacoordinate phosphorus compounds may prove to be more stable than the phosphoranes having the analogous structure. Thus the presence of bulky substituents in the diazadiphosphetidine ring induces the rearrangement of the phosphorane (X) to the corresponding phosphorate (XI):[24]



(X) (XI)

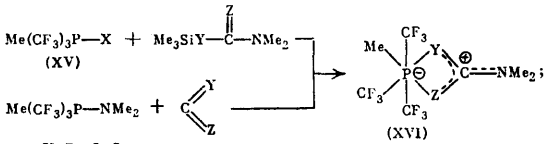
R = t-Bu.

The intramolecular addition of the nucleophilic iminonitrogen to the P(V) atom, inducing the formation of stable phosphorates, can occur so readily that, for example, in the chlorination of the aminophosphimine (XII) the resulting phosphorane (XIII) rearranges immediately to the phosphorate (XIV):[25]



(XII) (XIII) (XIV)

The reactions of halogenophosphoranes (XV) with silylcarbamates lead analogously to the phosphorate-carbamates (XVI) in a high yield.[26–28] The latter are also obtained when CO_2, COS, and CS_2 are inserted in the P–N bond in aminophosphoranes (XVII):



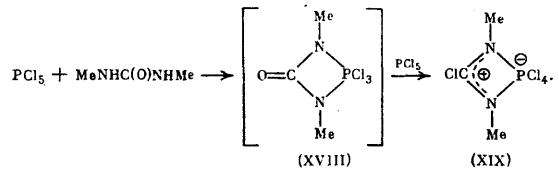
(XV) (XVI)

Y, Z = O, S.

The monothiocarbamates (XVI, Y = O, Z = S) are converted quantitatively into the dithio-derivatives on treatment with carbon disulphide. The resonance of the phosphorus atom in the phosphetidines (XVI) is characterised by a signal at very high field (between −251 and −298 p.p.m.).

Phosphorus(VI) compounds may be formed from phosphoranes also as a result of the addition to the electrophilic P(V) atom of "external" nucleophiles—the anions of proton-containing nucleophiles and neutral *n*-donor Lewis bases.

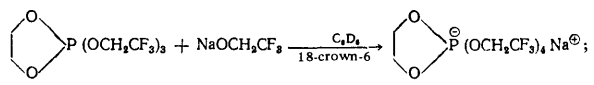
The interaction of *NN'*-dimethylurea with PCl_5 results in the formation of a phosphorate (XIX) with the diazaphosphetidine ring as a result of the chlorination of the phosphorane (XVIII) produced initially:[29–31]



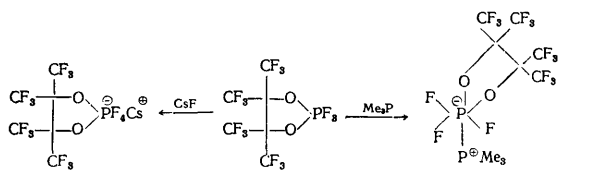
(XVIII) (XIX)

Further substitution of the chlorine atoms in compound (XIX) on treatment with dimethylurea leads to a phosphorate of the spiran type, which, however, cannot be isolated from solution.[32]

Monocyclic phosphoranes are characterised by a pronounced Lewis acidity and readily react with anions, being converted into stable phosphorates. Thus, in the presence of crown-ether, the phosphorane (XX) is converted by alkoxide into the corresponding sodium phosphorate,[33] while the perfluoropinacol trifluorophosphorane combines with both a fluoride anion and a neutral trimethylphosphine molecule, forming stable phosphorates with the characteristic chemical shifts of the P(VI) and P(IV) atoms in compound (XXI):[34,35]

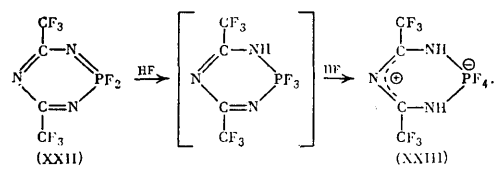


(XX) $\delta(^{31}P) = -128$ p.p.m.



$\delta(^{31}P) = -122.9$ p.p.m. (XXI) $\delta(^{31}P) = -130, +20$ p.p.m.

The formation of the six-membered monocyclic phosphorate (XXIII) as a result of the addition of hydrogen fluoride to the N–P=N triad of the cyclophosphazene (XXII) has been described:



(XXII) (XXIII)

The structure of the dipolar phosphorate (XXIII) was demonstrated by the IR, ^1H, ^{19}F, and ^{31}P NMR spectra [$\delta(^{31}P)$ = 162.7 p.p.m.] and mass-spectrometrically.[36]

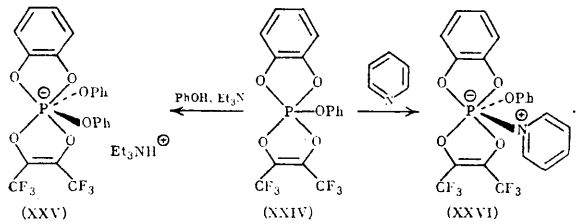
The thermal and hydrolytic stabilities of phosphorates are close to the corresponding properties of phosphoranes. Chlorine-containing phosphorates are usually very sensitive to moisture, while certain fluorine-containing compounds exhibit an appreciable hydrolytic stability.[37]

As already mentioned, the high-field position of the P(VI) signal in the ^{31}P NMR spectra, characteristic of phosphorates, can be conveniently used for the identification of the latter. The values of $\delta(^{31}P)$ for monocyclic phosphorates are in the range −100– −200 p.p.m., while for acyclic P(VI) compounds the $\delta(^{31}P)$ reach −300 p.p.m.;[38,39] the phosphorus atom in fluorine-containing phosphorates usually resonates in somewhat weaker fields.[40] The shielding of the phosphorus nucleus as a rule diminishes when the P(VI) atom is incorporated in one or more five-membered rings (see Section III).

2. Bicyclic Phosphorates

The incorporation of a phosphorus atom in one or two heterocycles is known to stabilise hypervalent structures.[12] This is equally valid also for P(VI) compounds: the stability of phosphorates increases on passing from acyclic to monocyclic and bicyclic and further to tricyclic λ^6-phosphacyclanes.

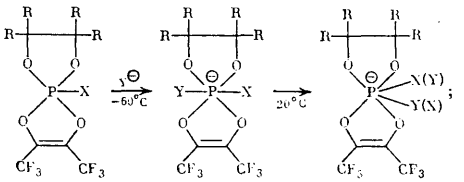
The commonest method of synthesis of bicyclic phosphorates involves the addition of ionic or neutral nucleophiles to the P(V) atom in the corresponding spirophosphoranes. The addition of the phenoxide ion or pyridine to the spirophosphorane (XXIV) leads to the spirophosphates (XXV) and (XXVI) respectively with two bidentate and two monodentate ligands:[41,42]



(XXV) (XXIV) (XXVI)

The ionic compound (XXV) is more stable than the dipolar ion (XXVI), which regenerates the initial phosphorane after prolonged heating.

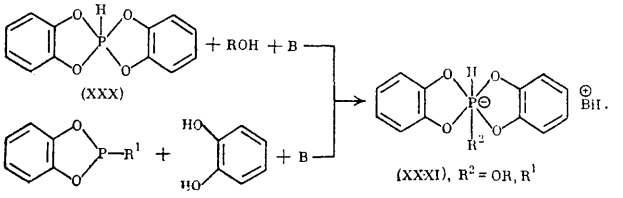
The addition of ionic nucleophiles to the phosphoranes (XXVII) results in the formation of the more stable *cis*-phosphorates (XXIX), which are the products of thermodynamically controlled reactions; under the conditions of kinetic control, the *trans*-isomers (XXVIII) arise and undergo the *trans–cis* isomerisation as the temperature is increased.[41,43–48]



(XXVII) (XXVIII) (XXIX)

X, Y = F, OC_6H_4F-p.

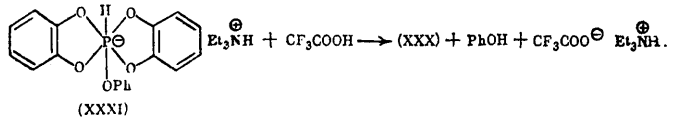
Compounds with a P–H bond, namely hydrophosphorates, constitute an interesting group of phosphorates. They can be synthesised from the hydrophosphoranes (XXX) by treatment with alcohols in a basic medium[49–55] or by the reaction of monocyclic phosphonites with catechol under the same conditions:[49,56–60]



(XXX) (XXXI), R^2 = OR, R^1

The hydrophosphorates (XXXI, R^2 = OPh) regenerate phosphoranes in many instances on treatment with acids via a reaction which is the opposite to that of the formation

reaction of the P(VI) compounds:[50]



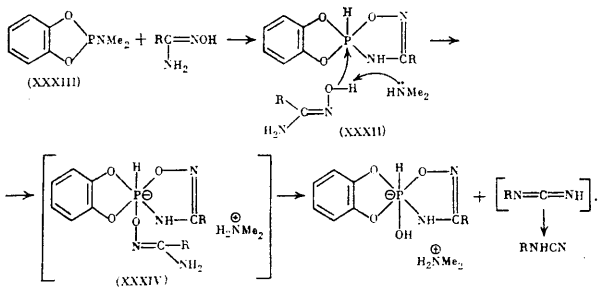
(XXXI)

Acetic acid does not induce this decomposition, i.e. the basicity of the phosphorate (XXXI) is intermediate between that of $MeCOO^-$ and CF_3COO^-.

The ease of formation of phosphoarates from spirophosphoranes and nucleophiles depends on the Lewis acidity of the P(V) atoms and increases as the cyclic substituents become more electron accepting.[54] The greatest tendency to be converted into P(VI) compounds is shown by spirophosphoranes containing 4,5-benzo-1,3,2-dioxaphospholan rings; spirophosphoranes with alkylenedioxy-substituents do not form hydrophosphorates on interaction with alcohols.[55]

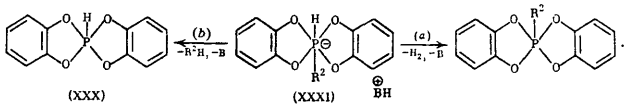
The spirophosphoranes (XXXII), which are derivatives of catechol and amidoximes, are sufficiently electrophilic to combine with the protic nucleophiles methanol, aminoalcohols, and amidoximes in non-polar solvents in the presence of bases, although the interaction with pyridine has not been observed under these conditions.[53] In polar solvents, phosphorates decompose to symmetrical phosphoranes.

The interaction of the phospholan (XXXIII) with amidoxime in solution in the benzene–ether mixture takes place in an unusual manner. Substitution of the dimethyl amino-group and subsequent reaction of the phosphorane (XXXII) with amidoxime proceed via the hydrophosphorate (XXXIV) stage, in which the N–O bond is broken. This leads to the phosphorate (XXXV), containing the P–OH and P–H groups, the first of the hydroxyphosphorates described:[53]



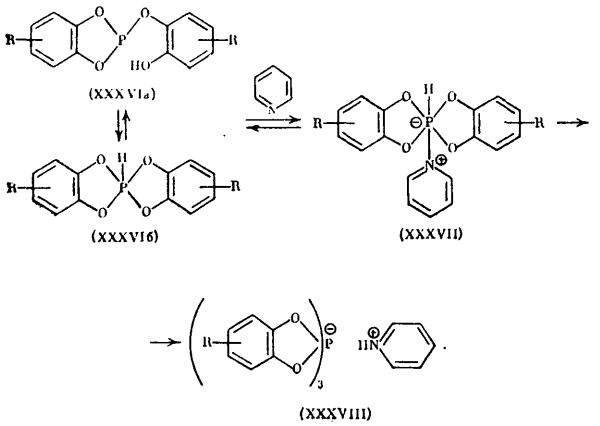
(XXXIII) (XXXII) (XXXIV)

At elevated temperatures, the hydrophosphorates (XXXI, B = Et_3N) decompose. The decomposition pathway depends on the nature of the exocyclic substituent R^2: for R^2 = Me, t-Bu, or Ph, hydrogen is evolved and alkyl(phenyl)spirophosphoranes are obtained (pathway *a*). The presence at the phosphorus atom of groups which can be eliminated more readily (R^2 = Ph or OMe) results in the regeneration of the amine and the hydrophosphorane (XXX) (pathway *b*):[56–60]



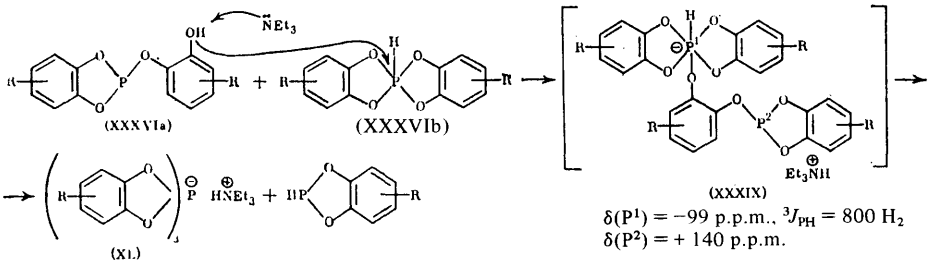
(XXX) (XXXI)

On dissolution in pyridine, the spirophosphoranes (XXXVI) interact with the solvent. The dynamics of this process has been investigated (see Section VI) and the very hygroscopic phosphorate (XXXVII) has been isolated.[42,61–63] In the course of 24 h, it is converted into the tricyclic phosphorate (XXXVIII):



(XXXVIa) (XXXVIб) (XXXVII) (XXXVIII)

In the presence of stronger bases (triethylamine, triethylenediamine, and di-isopropylamine), the reaction does not stop at the hydrophosphorate stage and a tricyclic phosphorate is formed immediately. It has been suggested[63] that stronger (harder) bases react with the tautomeric P(III) form of the hydrophosphorate (XXXVIa), which gives rise, with participation of the hydrophosphorane (XXXVIb) to the phosphite-phosphorate (XXXIX) and subsequently the phosphorate (XL):



(XXXVIa) (XXXVIб) (XXXIX) (XL)

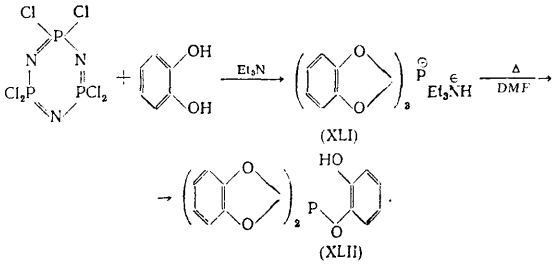
$\delta(P^1) = -99$ p.p.m., $^3J_{PH} = 800$ Hz
$\delta(P^2) = +140$ p.p.m.

An analogous process probably occurs also in the case of spirophosphoranes with a P–OH bond.[64]

3. Tricyclic Phosphorates

Among all the derivatives of hexacoordinate phosphorus known at the present time, tricyclic phosphorates together with halogenophosphorates constitute the most numerous group of compounds. The inclusion of the P(VI) atom in the octahedral structure of the spirotricyclophosphorate, especially one made up of three five-membered rings, increases sharply its thermodynamic stability (reduces the molecular energy). It is therefore not surprising that tricyclic phosphorates have been some of the first organic compounds with a hexacoordinate phosphorus atom to be synthesised and characterised.

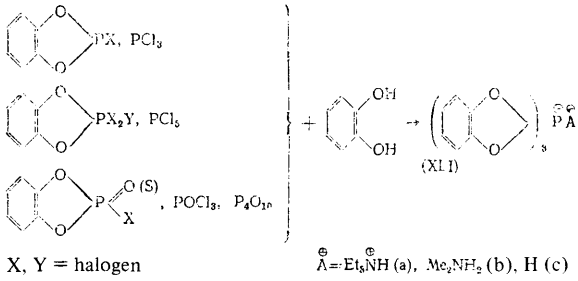
The first tricyclophosphorate was obtained as a result of the unexpected and interesting reaction of hexachlorocyclotriphosphazene with catechol in the presence of triethylamine.[65–70] *o*-Aminophenol reacts analogously:



(XLI) (XLII)

After the phosphorate (XLI) has been heated for a long time in anhydrous dimethylformamide (DMF), the phosphorate (XLII) is formed, while in the presence of moisture the product is tri(*o*-phenyl) phosphate. The latter is also obtained on hydrolysis of compound (XLI) with hot water and on acidolysis with inorganic acids.

The thermodynamic ease of formation of the tris(phenylenedioxy)phosphorate anion determines the course of many reactions of compounds of tricoordinate, tetracoordinate, and pentacoordinate phosphorus with catechol in the presence of bases[12,71–74] or with the dilithium salt of catechol:[75]



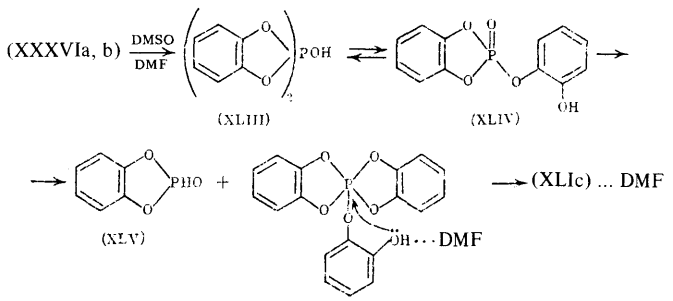
X, Y = halogen

$\overset{\oplus}{A}$ = $\overset{\oplus}{Et_3NH}$ (a), $\overset{\oplus}{Me_2NH_2}$ (b), H (c)

2,2′-Dihydroxybiphenyl reacts with PCl_5 to form a phosphorate with three seven-membered rings.[74]

The phosphorate (XLIc) is stable only in a basic medium (DMF, DMSO, amines) and apparently exists in solutions in the form of the free acid;[71] it has been suggested[64] that in weakly basic solvents this compound exists in the tautomeric P(V) form (XLII).

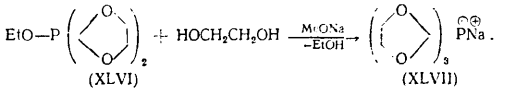
The tricyclophosphorate of type (XLIc) is formed as a result of the oxidation of the hydrophosphoranes (XXXVIa, b) with DMSO, sulphur, or iodine in DMF. The reaction evidently takes place via a stage involving the hydroxyphosphorane (XLIII), which interacts with its tautomeric phosphate form (XLIV), and is completed by the formation of the phosphite (XLV) and the phosphorates (XLIc) bound in a hydrogen-bonded complex with a solvent molecule:[64]



(XXXVIa, b) (XLIII) (XLIV) (XLV) (XLIc) ... DMF

Reactions involving the substitution of mobile ligands in phosphoranes by bifunctional compounds and reactions in which bidentate ligands add to tervalent phosphorus compounds have been fruitful for the purpose of the synthesis of phosphoranes.

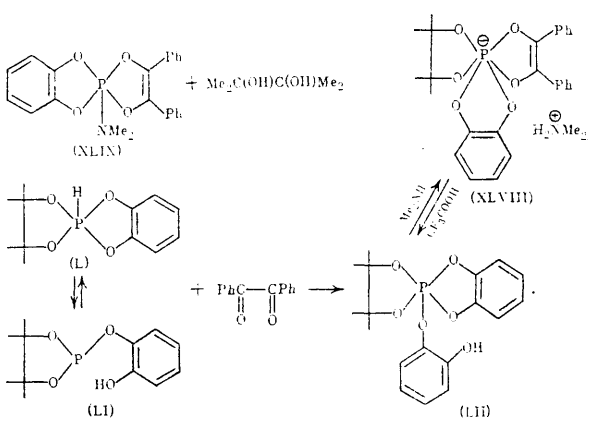
The first of these principles constituted the basis of the synthesis of the aliphatic tricyclic phosphorate (XLVII) by the reaction of ethylene glycol with the spirophosphorane (XLVI):[76]



(XLVI) (XLVII)

Compound (XLVII) does not melt before decomposition (300–310 °C). The attempts to obtain other aliphatic tricyclophosphoranes by this method were unsuccessful.

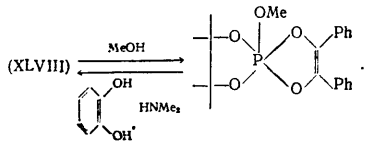
The phosphorate (XLVIII), made up of three different rings, arises analogously when the exocyclic dimethylamino-group in the spirophosphorane (XLIX) is substituted by a diol. The same λ^6-phosphacyclane (XLVIII) can be arrived at using the interaction of the hydrophosphorane (L) [which is apparently involved in the reaction in its tautomeric phosphite form (LI)] with benzil in the presence of dimethylamine:[77–82]



(XLIX) (XLVIII) (L) (LI) (LII)

Treatment of the phosphorate (XLVIII) with trifluoroacetic acid converts it into the phosphorane (LII). The methanolysis of compound (XLVIII) induces the elimination of catechol and leads to the phosphorane (LIII). Conversely, catechol

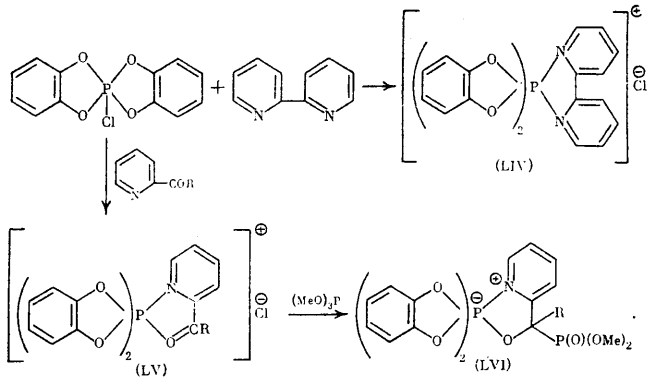
and dimethylamine readily convert the methoxyphospha(V)-cyclane (LIII) into the phosphorate (XLVIII) at room temperature:[78,81]



(LIII)

These reactions reflect the comparative ease of the interconversions P(V) ⇌ P(VI) in the presence of acids and bases (see Section IV).

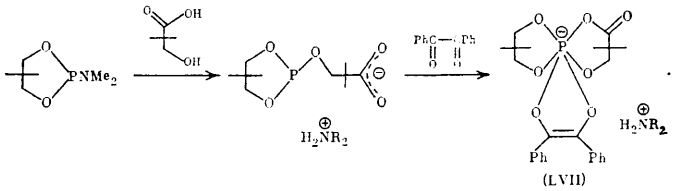
Substitution with subsequent intramolecular cyclisation via the formation of the N → P donor–acceptor bond made it possible to synthesise cationic compounds with hexacoordinate phosphorus from bipyridyl and pyridyl ketone:[43,83,84]



(LIV) (LV) (LVI)

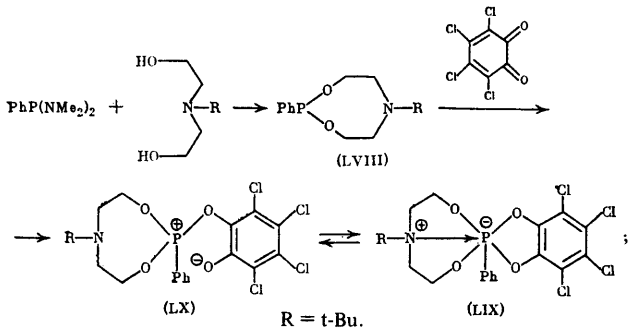
The anion exchange of the chlorine in the phosphorate (LIV) makes it possible to obtain other P(VI) compounds, including an exotic molecule in which the hexacoordinate phosphorus is present in both the anionic and cationic components.[43] The phosphorate (LV) enters into the Arbuzov reaction, forming the phosphonato-phosphorate (LVI) in the form of two spectroscopically different diastereoisomers[84] (see below).

The second principle governing the increase of the coordination number of the phosphorus atom to six with formation of tricyclic phosphorates involves the addition of bifunctional nucleophiles to the phosphorus atom in cyclic phosphites having in the exocyclic substituent a group capable of adding to the phosphorus centre.[85] Thus the reactions of cyclic phosphoramidites with hydroxy acids and further with α-diketones lead to the tricyclophosphorates (LVII):



(LVII)

The phosphite (LI) is converted analogously into the phosphorate (XLVIII), while 1,3,6,2-dioxazaphosphocane (LVIII), obtained from a phosphonamidite and *N*-t-butyldiethanolamine, reacts with chloranil to form the phosphorate (LIX), in which the coordination number of phosphorus, equal to six, is determined by the formation of the transannular N → P bond:[86]

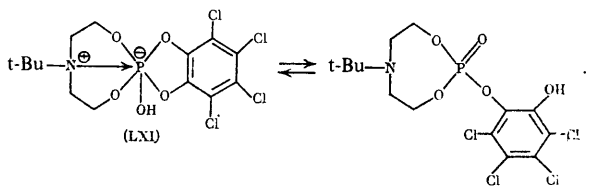


(LVIII) (LX) (LIX)

R = t-Bu.

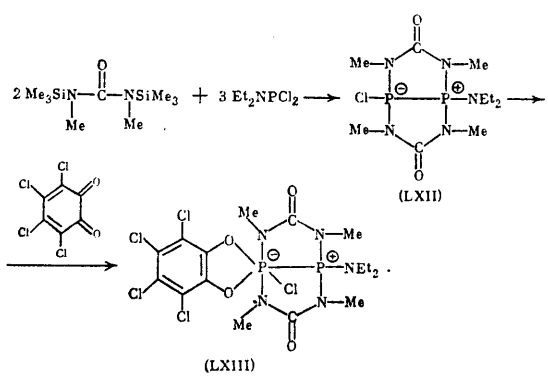
The authors[86] suggest that the equilibrium (LX) ⇌ (LIX) occurs in the system, as shown by the observation of two signals in the ^{31}P NMR spectra—at −14.5 p.p.m. for (LX) and at −96.2 p.p.m. for (LIX) in proportions of 2 : 3.

The interaction of *N*-t-butyldiethanolamine with the amide or chloride of phenylenephosphorous acid leads only to a phosphorate of type (LXI).[87] An equilibrium mixture of the phosphorate (LXI) with the P–OH fragment and the phosphate has been obtained in the reaction of phosphorous acid containing the 1,3,6,2-dioxazaphosphocane ring with tetrachloro-*o*-benzoquinone:[86]



(LXI)

In order to synthesise tricyclic phosphorates, dicarbonyl compounds have been made to interact not only with cyclic phosphites but also with cyclic phosphonium compounds. Thus the first phosphorate (LXIII) with a P–P bond has been obtained by adding chloranil to the anionoid phosphorus atom in the condensed bicyclic structure (LXII):

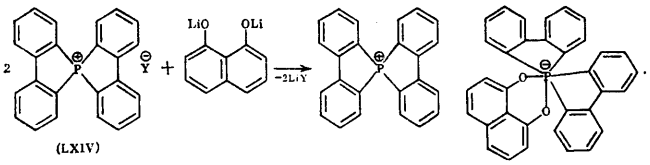


(LXII) (LXIII)

The chlorine atom at the phosphorus atom can be exchanged for fluorine by treatment with arsenic trifluoride (but not sodium fluoride).[88]

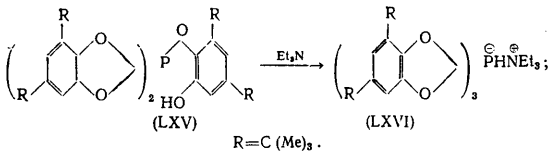
The spirocyclic phosphonium salt (LXIV) interacts with salts of catechol or naphthalene-1,8-diol, forming a phosphorate in which the P(VI) atom is part of two phospholan

rings and one 1,3,2-dioxaphosphorinane ring:[75]



(LXIV)

The phosphorane (LXV) has been obtained by the reaction of 3,5-di(t-butyl)-o-quinone with white phosphorus in the presence of 3,5-di(butyl)catechol as the reductant.[89] The addition of triethylamine to compound (LXV) induces the precipitation of the phosphorate (LXVI), which is also formed in the reaction of phospha(III)adamantane with the same *o*-quinone:[90]



(LXV) (LXVI)

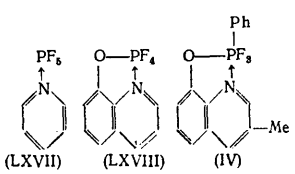
R=C (Me)$_3$.

The thermolysis of the dimer $(MeNPF_3)_2$, which results in the formation of complex polyhedral structures incorporating hexacoordinate phosphorus atoms, has been described.[91]

III. MOLECULAR STRUCTURE AND DYNAMIC STEREOCHEMISTRY

X-Ray diffraction analysis of acyclic,[92–94] monocyclic,[15,18,19,26–28,30,35] spirobicyclic,[45] and spirotricyclic[44,70] hexacoordinate phosphorus compounds made it possible to establish unambiguously their tetragonal-bipyramidal structure with a greater or smaller distortion of the octahedral skeleton, depending on the nature of the ligand bound to the central P(VI) atom.

The length of the N–P bond in the nitrogen-containing P(VI) complexes, formed via the intermolecular [as in compound (LXVII)] or intramolecular [as in compounds (LXVIII) and (IV)] binding of the nitrogen atom to phosphorus, is greater than the length of the usual single nitrogen–phosphorus bond (1.769 Å).[18,19,94]



(LXVII) (LXVIII) (IV)

An appreciable weakening of the N → P bond has been observed in the series of neutral P(VI) complexes (IV), (LXVII), and (LXVIII): 1.898 Å for (LXVII), 1.911 Å for (LXVIII), and 1.980 Å for (IV), owing to the decrease of the Lewis acidities of the groups in the sequence $PF_5 > POF_4 > POF_3Ph$. It is striking that the influence of other ligands is also reflected in the length of the P–F bond. Thus the length of the P–F bond in compound (LXVIII) diminishes with decrease of the electronegativity of the *trans*-ligand in the sequence F–P(F) > F–P(←N) > F–P(O).[18]

A significant distortion of the regular octahedral geometry, expressed by the deviation of the PF^1, PF^2, and PO bonds from the P–C bond, has been observed in the molecular structure (IV). This may be a consequence of the repulsion of the coplanar P–O and P–F bonds from the P–C bond, which is characterised by a high electron density in the latter.[19] A similar deviation of the fluorine atoms from the nitrogen atom has been observed in the complex (LXVII).[94]

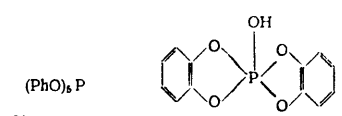
An increase in the length of the phosphorus–nitrogen bonds (1.91 and 1.85 Å) compared with the single bond has been found also in the four-membered ring of the zwitterionic complex (XIX).[30] On the other hand, the C–N bonds are much shorter (1.34 and 1.19 Å) than the usual bond (1.48 Å) and this suggests the delocalisation of the positive charge in the N–C–N triad and the partial double bond character of the C–N bonds. One of the causes of the formation of the "long" P–N bonds in compound (XIX) may be the angular strain in the four-membered phosphorus-containing heterocycle.

For the same reason, the P–O bonds in the complexes (XVI) are appreciably longer (1.82 and 1.89 Å) compared with the phosphorate (XLIa).[26,27] The electron density in these compounds is also delocalised in the carbamate unit, which is indicated by the smaller lengths of the C–O bonds (1.29 and 1.30 Å) compared with the usual bond (1.43 Å) and by the significant shortening of the C–N bond involving the bridgehead carbon atom (1.33 Å); the terminal C–N bonds are considerably longer (1.48 and 1.49 Å). The small difference between the lengths of the P–O bonds is associated with the *trans*-influence of the Me and CF_3 groups. The P–O bond in the *trans*-position with respect to the relatively small electron-accepting trifluoromethyl substituent is somewhat shorter than the O–P(Me) bond.

The fluorophosphorates $F_{4-n}(CF_3)_nPO_2CNMe_2$ have an analogous steric structure. The trifluorophosphorate (n = 1) has been isolated in the form of two structural isomers with "equatorial" and "axial" CF_3 groups. One isomer has been observed for each of the compounds with n = 2 and n = 3, X-ray diffraction of the monofluoro-derivatives demonstrating the "equatorial" disposition of the fluorine atom; the carbamate ring, the fluorine and phosphorus atoms, and the carbon atom of one of the CF_3 groups are coplanar. The length of the P–O(F-*cis*) bond (1.832 Å) exceeds somewhat the length of the other bond, namely P–O(F-*trans*) (1.788 Å).[28]

The difference between the lengths of the P–O bonds (1.706 and 1.723 Å) in the five-membered phenylenedioxy-rings of the *tris*(*o*-phenylenedioxy)phosphorate anion (XLIa) reflects some distortion of the octahedral structure of the phosphorate. The endocyclic OPO angles (91.4°) are close to the right angle, indicating the absence of angular strain.[70]

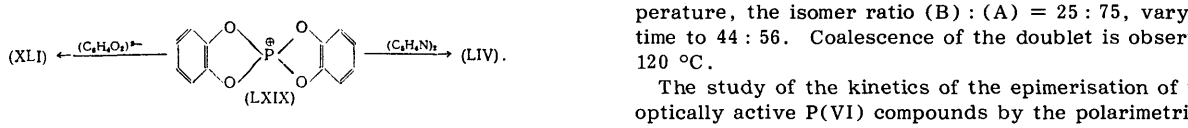
At the same time the increase of the length of the endocyclic ether bonds compared with the exocyclic bonds is evidently in general characteristic of small rings incorporating a phosphorus atom and heteroatoms with an unshared electron pair.[45] Thus the exocyclic P–O bonds in the phosphorate (XXV) are appreciably shorter (1.656 Å) than the endocyclic bonds (1.711 Å). According to the authors,[45] this may indicate a greater degree of $(p-d)_\pi$ binding of the unshared electron pairs of the exocyclic oxygen atoms to the phosphorus atom compared with the endocyclic atoms. This effect, which has also been established in phosphorane molecules, is called "steric inhibition of $(p-d)_\pi$ bonding".[45] It has been suggested[45] that this may entail a decrease of the shielding of the phosphorus nuclei by the electrons, which is reflected in a shift of the ^{31}P signal in the NMR spectra towards weaker magnetic fields, observed when one or several five-membered rings are introduced into hydroxyphosphorane molecules:



$\delta(^{31}P) = -88.7$ p.p.m. −30 p.p.m.

In phosphorate molecules a tendency has also been observed towards decreased shielding of phosphorus on passing from acyclic [$\delta(^{31}P)$ = −142 p.p.m. for $(MeO)_6P^-K^+$ [9] and −147 p.p.m. for $(EtO)_6P^-K^+$ [9]] to monocyclic [−128 p.p.m. for (XXI) [33]], bicyclic [−109.5 p.p.m. for (XXV) [41] and −98 p.p.m. for (XXXI, R^2 = OPh) [50]], and tricyclic [−82 p.p.m. for (XLI, A = Na) [75] and −89 p.p.m. for (XLVII) [70]] phosphorates.

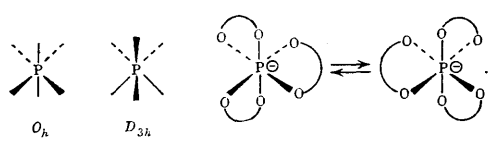
A distorted octahedral configuration has also been found in the cationic bipyridyl P(VI) complex (LIV).[44] The unusual features of its structure can be clearly revealed by comparing it with the structure of the phosphorate (XLI) and the hypothetical spirocyclic phosphonium cation (LXIX), from which compounds (XLI) and (LIV) can be produced formally by the addition of the bidentate phenylenedioxy- and bipyridyl ligands respectively:[44]



The P–O bonds in the cation (LIV) are shorter by 0.045 Å and the endocyclic OPO angles are greater by 1.6° than in compound (XLI). The OPO axis, which is almost straight in compound (XLI), bends in compound (LIV) towards the bipyridyl ligand (172.7°). The imaginary addition of the phenylenedioxy-dianion to the tetrahedral phosphorus in the cation (LXIX) yields a P(VI) configuration which is close to the octahedral P(VI) configuration in compound (XLI). An analogous change in the geometry of the molecular skeleton should also occur in the transition (LXIX) → (LIV), but, since the bipyridyl ligand is a weaker electron donor than the catechol dianion, the features of the "tetrahedral" configuration are retained in the structure (LIV).[44]

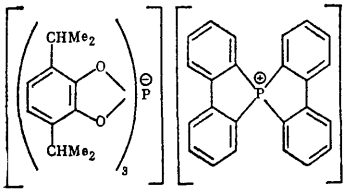
X-Ray diffraction data for the only cyclic six-membered λ^6-1,3,2-diheterophosphorinane investigated by this method, namely the acetylacetonate complex (II), indicate only small changes in the length of the P–O bond compared with those in compound (XLI), i.e. the P–O bonds in the dioxaphosphor(VI)inane ring are also of the σ-type. The ring has the boat conformation with the phosphorus and C(5) atoms deviating from the plane of the remaining atoms.[19]

Thus an octahedral O_h geometry is characteristic of phosphorate structures, as for many other molecules incorporating elements with a coordination number of six.[95] Recent calculations for the hypothetical PH_6^- molecule have shown[96] that this geometry is more stable than the alternative prismatic geometry with the D_{3h} symmetry:

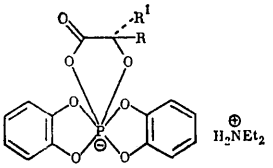


(1)

The tris-chelate hexacoordinate structures, including phosphorate anions, are chiral and exhibit the enantiomeric equilibrium (1) in solutions. The diastereotopic nature of the methyl groups in the isopropyl groups of compound (LXX) (two doublets with δ = 0.86 and 1.03 p.p.m., J^3_{hh} = 7 Hz) confirms this postulate.[97] The study of the ^1H and ^{31}P spectra of the phosphorates (LXXI) led to an analogous conclusion:[98]



(LXX)



(LXXI) a) R = Ph, R^1 = H;
b) R = R^1 = Me.

The phosphorus atom in compound (LXXIa) gives rise to two signals in the region of −90 p.p.m. and the difference between the chemical shifts is 0.5 p.p.m. The proton of the aliphatic ligand resonates in the form of two doublets with δ(A) = 5.33 p.p.m. and δ(B) = 5.19 p.p.m. At the instant of the synthesis of compound (LXXIa) at room temperature, the isomer ratio (B) : (A) = 25 : 75, varying with time to 44 : 56. Coalescence of the doublet is observed at 120 °C.

The study of the kinetics of the epimerisation of the optically active P(VI) compounds by the polarimetric and NMR method made it possible to determine the free energies of activation for the unimolecular epimerisation process $\Delta G^{\#}$ = 20.5 kcal mol^{-1} for (LXXIa) and 21.7 kcal mol^{-1} for (LXXIb), whose rate increases with increase of the concentration of the test substances.[98,99] The epimerisation of phosphorates is characterised by low activation entropies and, as noted for phosphorates of type (LXXI), is accelerated in the presence of acids.[100]

Two mechanisms of the enantiomeric isomerisation (and in general of polytopic processes) of octahedral structures has been discussed: the regular mechanism unaccompanied by the dissociation of the bond between the central atom and the ligand and the irregular mechanism which takes place with cleavage of the element–ligand bond. In the former case the ligand isomerisation process proceeds in accordance with the trigonal twist mechanism via a transition state having the pyramidal D_{3h} structure,[96,101] while in the second case the process proceeds via intermediates with a pentcoordinate central atom.

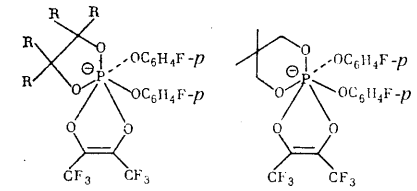
Calculation of the barriers to the topomerisation of simple molecules[95,96] demonstrated that the regular mechanism is energetically unfavourable. Thus the energy barriers to the trigonal twist E amount to −66 kcal mol^{-1} for PF_6^-, −56 kcal mol^{-1} for PCl_6^-, and −41 kcal mol^{-1} for PH_6^-, which indicates the stereochemical rigidity of the octahedral O_h structures for atoms of non-transition elements. It is difficult to say to what extent these calculated data are applicable to complex real systems containing oxygen and nitrogen atoms as well as chelated ligands, but one should note that the replacement of hydrogen atoms by more electronegative atoms or groups increases the activation barrier.[101]

The experimental results of the study of the kinetics of the epimerisation of phosphorates presented above led the authors[98–100] to the conclusion that the isomerisation has the irregular mechanism. The process proceeds with dissociation of one of the ether bonds in the aliphatic five-membered ring, pseudorotation in the phosphorane intermediate, and subsequent recyclisation leading to the formation of the second enantiomer. The free energies of epimerisation found fall within the range characteristic of ligand reorganisation processes involving phosphoranes (14–22 kcal mol^{-1}).[96,102] The low activation entropies agree with this conclusion and the concentration effects found are associated with the variation of the ionic strength of the solution, which influences the dissociation of the bonds and the charge separation.[98]

An analogous epimerisation mechanism has been proposed for neutral P(VI) chelates (LVI): the $\Delta G^{\#}$ for these processes fall within the range indicated above: 18.1 kcal mol^{-1} for (LVI, R = C_5H_4N) and 17.3 kcal mol^{-1} for (LVI, R = Ph).[47]

At the same time the irregular permutation process has been postulated for the *cis–trans* isomerisation of the phosphorates (XXVIII), investigated by ^{19}F NMR.[47] At room temperature these compounds are characterised by the energetically favourable *cis*-disposition of the aryloxy-ligands. However, at −101 °C the CF_3 groups in the phosphorate (XXVIIIb, R = Me) give rise to signals at −0.49 and −0.75 p.p.m., while *p*-FC_6H_4O generates signals at −60.2 and −61.7 p.p.m. The CF_3 signals coalesce reversibly at −77 °C ($\Delta G^{\#}$ = 9.7 kcal mol^{-1}), whereas for *p*-FC_6H_4O coalescence is observed at 34 °C ($\Delta G^{\#}$ = 14.5 kcal mol^{-1}). For the analogous *cis*-anion (XXVIIa, R = H), the free energy of activation determined from the coalescence of the signals of the trifluoromethyl group, is 17.2 kcal mol^{-1} (T_c = 80 °C). In the case of the 1,3,2-dioxaphosphor(VI)inane anion (LXXII), the signals of the CF_3 groups coalesce at 3 °C ($\Delta G^{\#}$ = 13.1 kcal mol^{-1}), whereas the signals of the *p*-FC_6H_4O groups remain separated up to 60 °C ($\Delta G^{\#}$ > 16 kcal mol^{-1}).

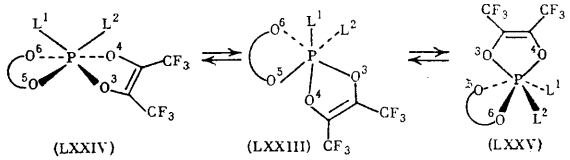
Thus the energy barriers to "equilibration" in the phosphorates (XXVIIIa, b) and (LXXII) are different for different magnetically non-equivalent groups—CF_3 and *p*-FC_6H_4O. This can be explained from the standpoint of the formation of different trigonally-prismatic intermediates in the above processes:



(XXVIII) (LXXII)

R = H (a); Me (b)

Scheme 1

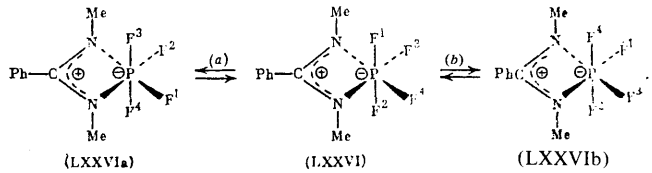


(LXXIV) (LXXIII) (LXXV)

In the structure (LXXIII, L = *p*-FC_6H_4O) the 60° clockwise rotation of the (2,4,3) trio relative to the (1,5,6) trio leads to the trigonal prism (LXXIV) in which the CF_3 groups are equivalent and there is no *p*-FC_6H_4O (Scheme 1). On the other hand, the 60° anticlockwise rotation of the (1,2,3) trio relative to the (4,5,6) trio generates the trigonal prism (LXXV) with the equivalent fluorophenoxy-groups and non-equivalent trifluoromethyl groups. Other possibilities involving a trigonal twist (there are eight in all—not shown in the Scheme) have an analogous effect on both types of F atoms. The observed experimental results are believed[47] to agree well with the regular permutation polymerisation process. The retention of the values of J_{PF} for structures (XXVIII) and (LXXII) confirms the intramolecular character of this topomerisation.

The permutation isomerisation of *NN*-dimethylbenzamidinium tetrafluorophosphorate (LXXVI), as a result of which the mutually non-equivalent F(1,2) and F(3,4) atoms change places in the tetragonal bipyramid according to ^{19}F NMR data, is also intramolecular.[103] This is indicated by the retention of the ^{31}P–^{19}F and ^{31}P–^{1}H spin–spin coupling and also by the absence of an influence of the concentration of the test substance in solution and by the nature of the solvent on the rate of isomerisation

Scheme 2



(LXXVIa) (LXXVI) (LXXVIb)

Two alternative isomerisation mechanisms were discussed in this instance also: irregular and regular. The irregular mechanism can in its turn include the dissociation of the phosphorus–nitrogen bond, which leads to structure (LXXVIa) (Scheme 2), in which all four fluorine atoms change places (pathway *a*) or the dissociation of the P–F bond with migration of, for example, the F^2 atom to the cationoid carbon. In this case (pathway *b*) the positions of three F atoms change and structure (LXXVIb) is formed (the intermediate structures are not shown in Scheme 2). For the regular mechanism, it is also possible to put forward several versions of the trigonal twist, but the exchange of all fluorine atoms is preferred to the greatest extent [pathway *a* leading to (LXXVIa)].

The fairly high free energy of activation for the permutation isomerisation of compound (LXXVI) (23.6 kcal mol^{-1} at 170 °C) exceeds the values characteristic of the polytopic rearrangements of phosphorates. In view of this and also the independence of the rate of isomerisation of the nature of the solvent the authors are inclined[103] to select the regular mechanism via pathway *a* (LXXVI) → (LXXVIa), although the available data are as yet insufficient for an unambiguous conclusion.

Thus one may decide that, on the basis of what are so far still few instances of the study of polytopic rearrangements of P(VI) compounds, it is impossible to arrive at reliable conclusions about their mechanism. However, one cannot rule out the possibility that the character of the ligand reorganisation in phospha(VI)cyclanes can depend greatly on their structure—the nature of the atoms attached to phosphorus and the number, size, and compositions of the phosphorus-containing heterocycles. One can only note that the irregular mechanism is believed to be preferred for spirotricyclic phosphorates, while the regular mechanism is preferred for spirobicyclic and monocyclic phosphorates.

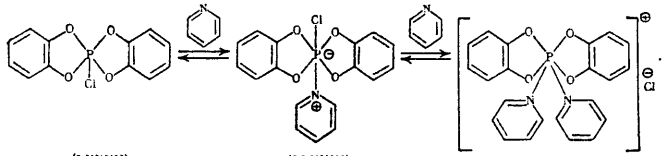
IV. P(VI) ⇌ P(V) EQUILIBRIUM PROCESSES

The capacity for the rupture of one of the P(VI)–ligand bonds, which is responsible for the possibility of the intramolecular or intermolecular P(V) ⇌ P(VI) equilibrium processes, is characteristic of certain hexacoordinate phosphorus compounds.

When the tautomeric mixture (XXXVIa, b) interacts with pyridine, a successive decrease of the intensity of the low-field NMR signal of the P(III) atom in the form (XXXVIa) and an increase of the peak intensity in strong fields, reflecting the content of the P(V) form (XXXVIb) and the P(VI) form (XXXVII), are observed as the mole fraction of the base increases and the temperature is reduced. An appreciable excess of the base at room temperature shifts the resonance peak to the "phosphorate" region (−93 p.p.m. for 8 moles of pyridine).[42,61,62]

The position of the P(III) ⇌ P(V) ⇌ P(VI) equilibrium is significantly affected also by the basicity of the amine. The weak base diphenylamine does not induce appreciable changes in the ^{31}P NMR spectrum, while in the presence of tertiary and secondary aliphatic amines the signals due to the P(III) and P(V) forms disappear and high-field doublets appear at −110 p.p.m. (J_{PH} = 800 Hz).[63]

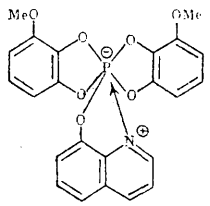
The addition of pyridine to the chlorophosphorane (LXXVII) is also accompanied by a shift of the (LXXVII) signal (−9.5 p.p.m.) to a strong field (−84.5 p.p.m.):



(LXXVII) (LXXVIII) (LXXIX)

It has been suggested[43] that the reversible addition of the base molecule [(LXXVII) ⇌ (LXXVIII)] takes place without a significant reorganisation of the (LXXVII) molecular skeleton and requires only a low activation barrier to be overcome. This is responsible for the lability of the above equilibrium and for this reason the average signal of both forms, (LXXVII) and (LXXVIII), is observed. However, after the addition of even the first portions of pyridine, the (LXXIX) signal is observed at −100 p.p.m., together with the −84.5 p.p.m. peak, its intensity increasing with increase of the mole fraction of pyridine on reaching a maximum in the presence of a twofold excess of the base. The (LXXVIII) → (LXXIX) transition represents a substitution reaction and requires a higher activation barrier to be overcome. In the presence of an excess of pyridine the cationic P(VI) compound (LXXIX) crystallises quantitatively.

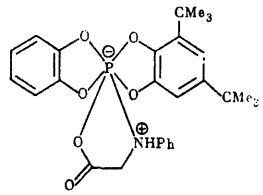
The capacity of phosphoranes to be converted into phosphorate structures is manifested most distinctly in the formation of the intramolecular P–N bond. Compound (LXXX) exist in the P(VI) form even at room temperature [$\delta(^{31}P)$ = 78 p.p.m.].[62]



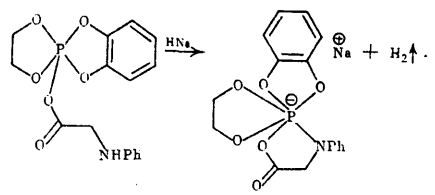
(LXXX)

The study of factors determining the capacity for intramolecular N → P complex formation in systems of type (LXXX) has demonstrated a strong influence of the nature of the ligands on the tendency towards the formation of phosphorates. The electron-accepting properties of the substituents at the phosphorus atom play a decisive role in this connection. Thus, when one fluorine atom is replaced by an alkyl group in the molecule of compound (IV), the N–P bond is not formed and the difluoro-derivative exists exclusively in the form of the difluorophosphorane, while tri- and tetrafluoro-analogues exist only in the P(VI) form.[18]

Two arylenedioxy-substituents have a strong positive influence on the phosphorus atom, so that compound (LXXXI) is characterised by a high-field signal [$\delta(^{31}P)$ = 89 p.p.m.]. The introduction of the aliphatic ethylenedioxy-group instead of the phenylenedioxy-ligand results in the existence of only the P(V) form—the phosphorus atom in the structure (LXXXII) is pentacoordinated. However, when compound (LXXXII) is acted upon by sodium hydride, it is converted into the phosphorate (LXXXIII).

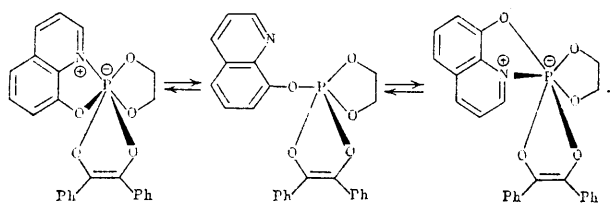


(LXXXI)



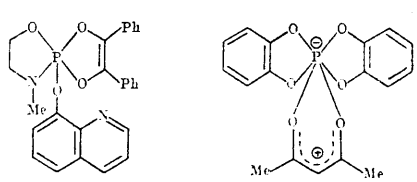
(LXXXII) $\delta(^{31}P)$ = −28 p.p.m. (LXXXIII) $\delta(^{31}P)$ = −83 p.p.m.

The high-field signal can reflect the P(V) ⇌ P(VI) equilibrium, which is as a rule established rapidly on the NMR time scale and for this reason both forms are manifested by a single average signal, whose increasingly upfield shift implies an increase in the content of the P(VI) compound in the equilibrium mixture. Thus the resonance peak for compound (LXXXIV) in the region of −85 p.p.m., recorded at 20 °C, is observed in weak fields (−75 p.p.m.) at 150 °C and, conversely, on reducing the temperature to −70 °C, the signal undergoes an upfield shift to −88.7 p.p.m., while at −90 °C an additional resonance line appears at −90.6 p.p.m. It has been suggested[85] that a decrease of temperature shifts the equilibrium towards the P(VI) isomer, which exists in the two diastereoisomeric forms (LXXXIVa) and (LXXXIVb), with corresponding doubling of the signal at −90 °C.



(LXXXIVa) (LXXXIV) (LXXXIVb)

It is striking that replacement of the endocyclic oxygen atom in the ethylenedioxy-fragment of compound (LXXXIV) by the more electron-donating NMe group lowers the Lewis acidity of the phosphorus atom and the oxazaphospha(VI)-cyclane (LXXXV) is a phosphorane [$\delta(^{31}P)$ = −43.7 p.p.m.]

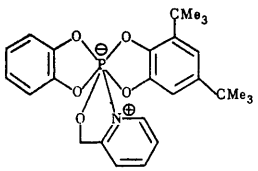


(LXXXV) (LXXXVI)

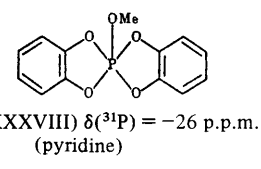
Comparison of the structures of compounds (LXXXII) and (LXXXIV) also indicates the importance of the effects of electron delocalisation in the stabilisation of hexacoordinate structures. The π-electron system of the hydroxyquinoline ligand, which promotes the delocalisation of electron density, favours the P(VI) form more than does the aliphatic structure of *N*-phenylglycine. The relative instability of the P(VI) acetylacetonate compound (LXXXVI) is explained

by the fact that the delocalisation of electron density is restricted to the region within the non-polar 1,3,2-dioxaphospholan ring.[85]

The influence of the entropy factor on the position of the P(V) ⇌ P(VI) equilibrium, which is more significant for intermolecular complex formation ($\Delta S_0 = -30$ e.u.) than for intramolecular complex formation (−10 e.u.), has been noted.[85] In particular, as a result of this complex formation is not observed in the pyridine–phosphorane (LXXXVIII) system if compound (LXXXVII) exists mainly in the P(VI) form.



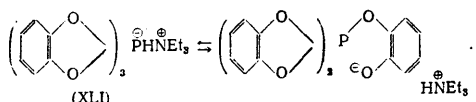
(LXXXVII) $\delta(^{31}P) = -86$ p.p.m.



(LXXXVIII) $\delta(^{31}P) = -26$ p.p.m. (pyridine)

Finally, mention must be made of the role of steric effects of the substituents in the ligand. Thus the introduction of a methyl substituent in the 2-position in the hydroxyquinoline fragment in compound (LXXX) shifts the equilibrium towards the P(V) form, which has been explained by the repulsion of the methyl group and one of the oxygen atoms of the benzodioxaphospholan rings. This hinders the closure of the oxazaphospholan ring (the formation of an N → P bond).[85]

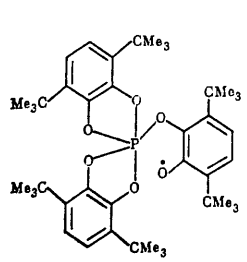
It has been suggested that the P(V) ⇌ P(VI) equilibrium obtains also in the tri(phenylenedioxy)phosphorate anion (XLI) and is displaced towards the phosphorane (XLIa) in solution and towards the phosphorate in the crystalline phase:[66]



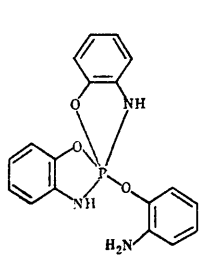
(XLI) (XLIa)

A sextuply degenerate rearrangement with "random wandering" of the charge over the aromatic ligands obtains in this instance.[95,104] However, the rate of such "random wandering" is low on the NMR time scale, so that the single average chemical shift due to the P(V) and P(VI) nuclei as well as the protons of the aromatic ring is observed in the spectra.

Such intramolecular degenerate tautomerism, associated with the "random wandering" of the free valence over the aromatic fragments, has been observed for the stable radicals having the octahedral P(VI) structures (LXXXIX).[104] On the other hand, the nitrogen compound (XC), having a analogous structure, exists in the phosphorane form, although the authors do not reject the possibility of formation of the corresponding phosphorates in the crystalline state.[68]



(LXXXIX)

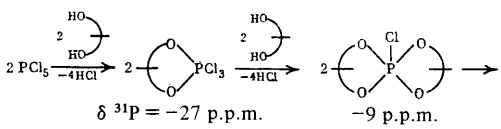


(XC) $\delta(^{31}P) = -46.3$ p.p.m.

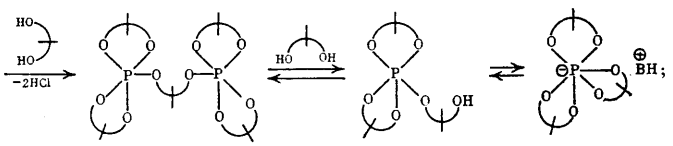
It has been established in many instances that the conjugate acid (XCIIa) of the anion (XCIa) and its analogues are intermediates in the synthesis of phosphorates from the corresponding phosphoranes and diols, usually catechol (see Section II). The transition (XCII) → phosphorate (XCIII) is a prototropic process associated with the intermolecular proton transfer to an "external" base, as in ring closure in hydroxyalkyl (aryl) phosphates.[12]

The study of the interaction of PCl_5 with catechol and 2,2′-dihydroxybiphenyl established the occurrence of the stepwise substitution of the chlorine atoms including the prototropic equilibrium P(V) ⇌ P(VI) [74] (Scheme 3)

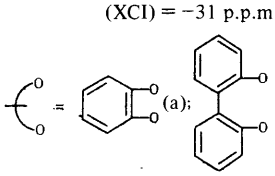
Scheme 3



$\delta\ ^{31}P = -27$ p.p.m. −9 p.p.m.

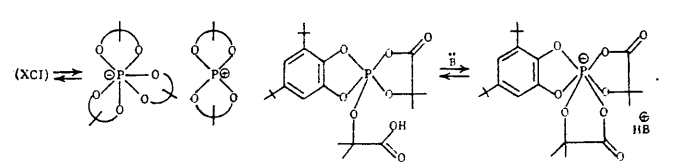


(XCI) = −31 p.p.m. (XCII) = −29 p.p.m. (XCIII) = −84 p.p.m.



When the PCl_5 : catechol ratio is 1 : 2.5, the deposition of a crystalline deposit of compound (XCI) is observed. The latter is redissolved by an excess of catechol. The existence of the equilibrium (XCI) ⇌ (XCII) (the ratio of the compounds involved was 8 : 2 in benzene) has been established by NMR. The addition of DMF to this mixture induces a gradual shift of the signal of compound (XCII) (−29 p.p.m.) to the region of −84 p.p.m. of compound (XCIII) and a decrease of intensity followed by the disappearance of the −31 p.p.m. signal of the compound (XCI). This corresponds to the process (XCI) ⇌ (XCII) ⇌ (XCIII), in which the equilibrium between the last two compounds is attained rapidly on the NMR time scale.

Koenig et al. [74] also did not rule out the existence in solutions of an equilibrium between compound (XCI) and the ion pair (XCIa), which has been confirmed by the ebullioscopic determination of the molecular weight of this compound:



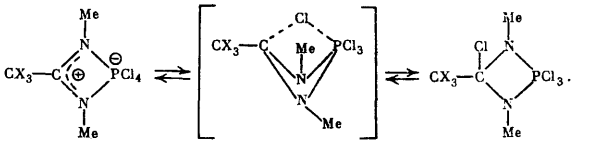
(XCIa) (XCIV) (XCV)

The conversion of the ω-hydroxyalkylphosphorane into a phosphorate has been observed in systems constructed with the aid of hydroxyacid ligands. In toluene the equilibrium (XCIV) ⇌ (XCV) is fully displaced towards the phosphorane (XCIV), while in DMF and DMSO it is displaced towards the spirophosphorate (XCV).[105]

The action of strong bases on the (XCI) ⇌ (XCII) equilibrium mixture leads to the formation of the insoluble phosphorates (XCIII). The use of the chiral base (−)-brucine in this reaction [74] made it possible to observe the signals of two diastereoisomeric brucinium phosphorates (−84.4 and

and −84.5 p.p.m.), which are in equilibrium. A kinetic study of the epimerisation of these diastereoisomers led the authors[74] to the conclusion that the P(VI) anion is obtained in the synthesis in a non-racemic form and that the P(V) → (VI) transformation is therefore stereospecific. The results obtained[74] agree well with the concept of the occurrence of degenerate tautomeric processes with participation of spirobicyclic and tricyclic anions of type (XLI).

The first example of chlorotropic tautomerism with participation of pentacoordinate and hexacoordinate phosphorus compounds has been described recently:[22]

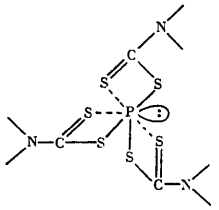


(XCVI) X = Cl (a); F (b) (XCVII)

The equilibrium (XCVIa) ⇌ (XCVIIa) is attained fairly slowly on the NMR time scale: the signals of both forms can be detected in the spectra. As the CX_3 group becomes more electron accepting (CF_3 > CCl_3), the solvent polarity decreases, the temperature rises, and the equilibrium is displaced towards phosphoranes. Thus at 30 °C the content of the P(V) form (XCVIIa) is 60% in CD_3CN, 84% in $C_6H_4Cl_2$-*o*, 87% in C_6H_6, and 97% in C_6D_{12}; at 50 °C the content of the P(V) tautomer in CD_3CN increases to 66%. The signals of the methyl protons coalesce at 120 °C. The independence of the rate of interconversion of the tautomeric forms of concentration indicates the intramolecular character of the tautomerism and suggests a structure with a bridging chlorine atom and a hexacoordinate phosphorus atom as the transition state or the intermediate.

The equilibrium processes with participation of pentacoordinate and hexacoordinate forms of organophosphorus molecules examined here model satisfactorily the first stage of the associative nucleophilic substitution of the pentacoordinate phosphorus, which presupposes the addition of the nucleophile to the P(V) atom of the substrate with formation of hexacoordinate intermediates and/or transition states.[12]

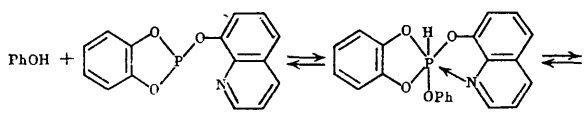
The question of the character of the intermediates or transition states in nucleophilic substitution reactions at a hexacoordinate phosphorus atom is therefore intriguing. The substitution of chlorine in compound (LXXVII) by a pyridine molecule with formation of the dipyridine P(VI) cation (LXXIX)[43] is one of the few examples of such reactions. The process is most likely to proceed via a dissociative mechanism with the preliminary elimination of the chloride anion. The associative mechanism appears unlikely: not a single example of the existence of structures with a phosphorus atom surrounded by seven ligands has so far been discovered. In the tris(dithiocarbamato)phosphines,[106,107] trisdithioacylates, and phosphinodithioyl derivatives of other group VB elements[108–110] described hitherto, a coordination number of seven of the central atom is attained by the formation of three sulphur–element coordinate bonds by virtue of the presence of a stereochemically active unshared electron pair of the element.



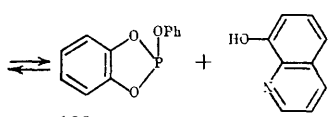
V. CYCLIC COMPOUNDS OF HEXACOORDINATE PHOSPHORUS AS INTERMEDIATES IN THE REACTIONS OF ORGANOPHOSPHORUS COMPOUNDS

It has been suggested and in many cases demonstrated that λ⁶-1,3,2-diheterophosphacyclanes can be intermediate in reactions of organophosphorus compounds containing the atoms of tricoordinate, tetracoordinate, or pentacoordinate phosphorus. The involvement of P(VI) intermediates in the reactions of tervalent phosphorus compounds has been demonstrated only in some instances and is more likely to be an exception rather than the rule.[10] The intermediate formation of hexacoordinate phosphorus compounds occurs only in specific cases—in reactions of bifunctional or polyfunctional reactants or substrates.

The formation of the intramolecular P(VI) complex (XCVIII) in the transesterification of the phosphite (XCIX) with phenol has been detected from ^{31}P NMR spectra: the signal of compound (XCVIII) with $\delta(^{31}P) = -100$ p.p.m. and $J_{Ph} = 860$ Hz, whose intensity is high at the beginning of the reaction and decreases as the latter is completed, has been detected at −70 °C in methylene chloride:[111]



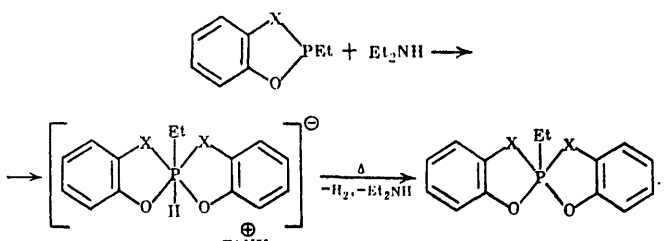
(XCIX) $\delta(^{31}P) = +126$ p.p.m. (XCVIII) = −100 p.p.m. $J_{PH} = 860$ Hz



128 p.p.m.

The stabilisation of compound (XCVIII) is achieved as a result of the presence of the 1,3,2-benzodioxaphospholan ring and the possibility of the formation of intramolecular P → N bonds.

The spirobicyclic phosphorate (Ca) has been isolated in 15% yield in the reaction of 2-ethyl-4,5-benzo-1,3,2-dioxaphospholane with diethylamine.[60] On heating, the salt (Ca) evolves a hydrogen molecule and is converted into the phosphorane (CIa). The same result has been obtained in the reaction of catechol with ethylphosphonous bis(diethylamide):



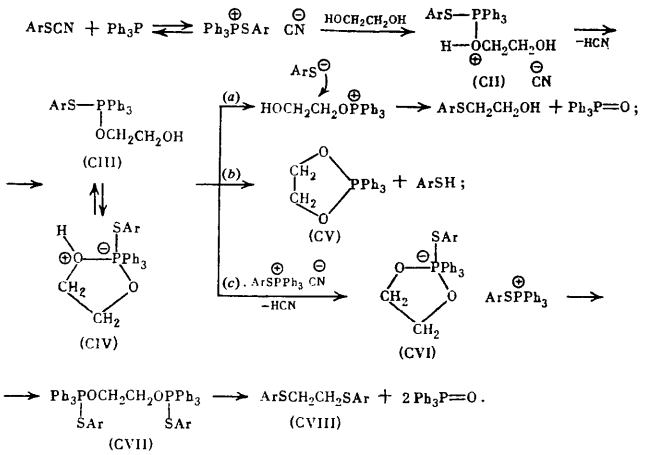
(C) (CI) a) X = O; b) X = NH

The interaction of *o*-aminophenol, leading to the phosphorane (CIb), can take place via the same pathway. However, the corresponding aminophosphorate could not be isolated owing to its smaller stability [see structure (XC)].

The results of the reactions of aryl thiocyanates with alcohols and diols in the presence of triphenylphosphine has been explained by the involvement of pentacoordinate and hexacoordinate phosphorus intermediates. The interaction of phenyl thiocyanate with triphenylphosphine and ethylene glycol takes place via pathway α (Scheme 4) and leads to 2-phenylthioethanol and triphenylphosphine oxide.[112]

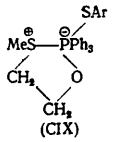
Aliphatic alcohols react analogously with formation of alkyl aryl sulphides.[113] On the other hand, another pathway (pathway *b*), leading to the isolation of *p*-methoxybenzenethiol and the cyclic phosphorane (CV), is also followed in the reaction with participation of *p*-methoxyphenyl thiocyanate. It has been suggested[112] that the oxonium–phosphorane adduct (CII) is a key intermediate in these processes.

Scheme 4



Its deprotonation by the cyanide ion affords the phosphorane (CIII); the decomposition of compounds of type (CIII) via pathway *a* is responsible for the formation of sulphides in the reactions of alcohols and of 2-phenylthioethanol in the reaction of ethylene glycol. The *p*-methoxyphenylthio-group is difficult to eliminate compared with the phenylthio-substituent and for this reason the attack by the terminal hydroxy-group on the pentacoordinate phosphorus atom competes with elimination of the arylthio-group from the phosphorane (CIII, Ar = *p*-$MeOC_6H_4$) (pathway *a*). This leads to the cyclic dipolar phosphorate (CIV); the fragmentation of the latter leads to the *p*-methoxybenzenethiol and the cyclic phosphorane (CV) (pathway *b*).

The possibility of the formation of the phosphorate (CIV) in these processes has been confirmed by the synthesis of aryl methyl sulphide in the reaction of *p*-methoxyphenyl thiocyanate with 2-methylthioethanol ($MeSCH_2CH_2OH$), which proceeds via the intermediate (CIX), which is analogous to the intermediate (CIV):



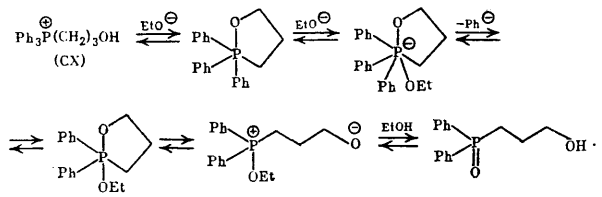
The involvement of *p*-nitrophenyl thiocyanate in this reaction does not lead to the formation of the sulphide, because the nucleophilicity of the arylthio-group is in this case insufficient for the demethylation of compound (CIX, Ar = *p*-$NO_2C_6H_4$) and the process proceeds in the "normal" way via pathway *a* to the bis-sulphide $MeSCH_2CH_2SC_6H_4NO_2$-*p*.

An essential condition for the formation of the phosphorate intermediate (CIV) from compound (CIII) is the presence of a free hydroxy-group, since glycol monoethers react only via pathway *a*, like primary alcohols.[112]

The *p*-nitro-substituent in the aryl group stabilises the negative charge on the phosphorus atom in the phosphorate (CIV) and the possibility of yet another competing pathway (pathway *c*) arises in this case; it is associated with the deprotonation of the phosphorate (CIV) by cyanide ion and the appearance of the ion pair (CVI). The interaction of the ions of the pair (CVI) leads to the bis-sulphide (CVIII) via the bisphosphorane (CVII) stage.

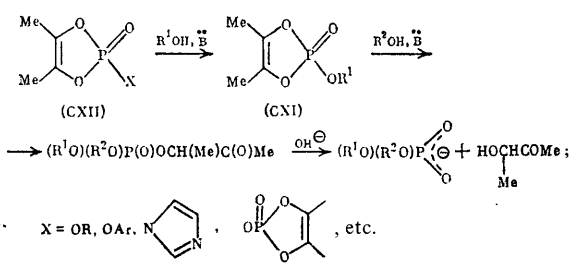
When the nitro-group is introduced in the *o*-position in the benzene ring, the formation of compound (CIV) is hindered for steric reasons and the process is therefore wholly directed via pathway *a*. The same results have been observed when 1,3- and 1,4-diols were used. Evidently the formation of phosphorates with a greater ring size than in compound (CIV) is energetically unfavourable.

An analogous intermediate formation of a five-membered ring in the P(V) and P(VI) intermediates ensures a sharp acceleration, induced by alkoxide ions, of the decomposition of 3-hydroxypropylphosphonium chloride (CX) (the rate constant at 60 °C is 7.3 litre mol^{-2} min^{-1}), compared with triphenyl-n-propylphosphonium chloride (the rate constant at 60 °C is 0.003 litre mol^{-2} min^{-1}):[114,115]



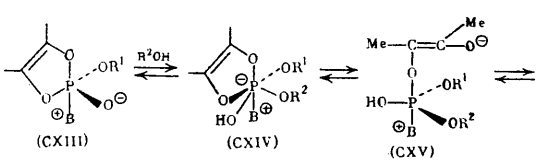
It has been suggested that tetracoordinate phosphorus compounds can give rise to P(VI) intermediates in chemical reactions involving base-catalysed nucleophilic substitution at a tetrahedral phosphorus atom.

In the presence of bases, the cyclic enediol phosphates (CXI) readily phosphorylate alcohols to form asymmetric diesters of phosphoric acid.[41,116] Effective catalysis by bases (amines,[117,118] phenoxides,[119,120] and the acetate ion[121]), which increases the rate of reaction by tens and hundreds of times, takes place in these reactions:



The mechanism of the catalytic action of bases is associated with the formation in the first stage of the hydroxyphosphorane (CXIII), which is obtained either by the reaction of the full phosphates (CXII, X = OR) with the catalyst or as a result of the addition of the alcohol to the enediol phosphate with a P–N bond (CXII, X=N⟨⟩N, N⟨⟩ etc.).[116]

The interaction with the substrate leads to an increase of the coordination number of the phosphorus atom in the rapidly formed intermediate phosphorate (CXIV):



The removal of one of the ligands in the intermediate (CXIV) converts the latter into the phosphorane (CXV) and then into the reaction products.

The essential feature of the catalytic action of bases apparently consists in increasing the rate of addition of nucleophiles to a phosphorane intermediate of type (CXIII) compared with the rate of reaction with the initial phosphate.

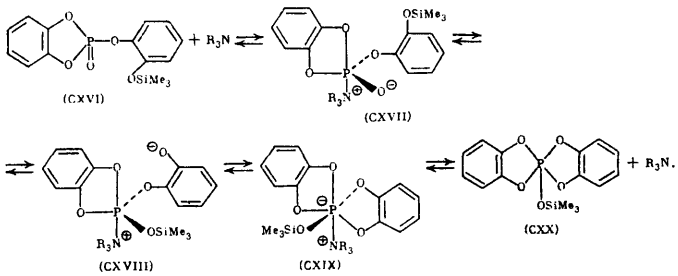
The phosphorylation of enediol phosphates by amide derivatives is accompanied by autocatalysis, because the interaction of, for example, the phosphimidazole (CXII, X = imidazolyl) with alcohol in the first stage is associated with the liberation of imidazole, which ensures effective catalysis of the phosphorylation reaction.[116-118,122]

The duration of the reaction of phosphoric acid triesters in the presence of imidazole is 2–30 min, while in its absence it is 8–12 h.[117] Triethylamine is just as effective in the reactions of primary alcohols and hardly affects the rate of phosphorylation of secondary alcohols. This is caused by the high steric requirements by the tertiary amine under the conditions involving the formation of a hexacoordinate intermediate. A definite role is also played by the basicity of the amine. Thus, in the base-catalysed opening of the ring in enediol phosphates by alcohols, the effectiveness of the catalysis is correlated with the basicity of the amines.[123]

The catalytic action of the *p*-nitrophenoxide ion in the trans-esterification of *p*-nitrophenyl diphenyl phosphate by alcohols has been explained by the formation of acyclic P(VI) intermediates.[116,124]

It has been noted[117,119] that the mechanism discussed here probably operates in the action of enzymes catalysing the reactions of phosphates and pyrophosphates in biological systems, because the presence of tyrosine, lysine, arginine, and histidine facilitates the addition of nucleophiles to a tetracoordinate phosphorus atom.

The base-catalysed cyclisation reactions of tetracoordinate phosphorus compounds containing an ω-hydroxyalkyl, *o*-hydroxy, or *o*-siloxyphenyl group [11,12] also take place with participation of P(VI) intermediates. Thus silyl transfer, which is responsible for the occurrence of the phosphate–phosphorane equilibrium (CXVI) (CXX), is accelerated by amines, the effectiveness of such catalysts diminishing as the steric requirements of the amines become more stringent.[125] The process includes the addition of the amine to the phosphate with formation of the monocyclic phosphorane (CXVII), in which the trimethylsilyl group is transferred from the phenoxy-oxygen to the equatorial oxy-anionic centre, so that the intermediate phosphorane (CXVIII) is produced. The addition of the anion to the phosphorane centre leads to the spirobicyclic zwitter-ionic phosphorate (CXIX), whose decomposition to the amine and siloxyphosphorane completes the isomerisation process:



The examples of the base catalysis of nucleophilic reactions of tetracoordinate phosphorus compounds presuppose the occurrence of two successive stages involving the addition of nucleophilic species to the tetrahedral phosphorus atom of the substrate and the phosphorane centre of the intermediate, which necessitates the participation of intermediates with the phosphorate structure in these processes. In this connection we may note that the formation of P(VI) intermediates, which may arise by the reaction of two hydroxide ions with the phosphoryl centre, has not been ruled out in the hydrolysis of five-membered cyclic phosphates either.[126,127] This hypothesis has been based on the experimental observation of a second-order dependence on hydroxide ion at high pH (in excess of 10) on the hydrolytic reaction.

However, the attempts to demonstrate the formation of phosphorate intermediates in the hydrolysis of ethyl ethylene phosphate using an isotope label and ^{31}P NMR (190.3 MHz) were not successful.[128] Nevertheless, the experimental data presented in this section make it necessary to consider the possibility of the formation of P(VI) structures and processes involving the interaction of tetracoordinate and even more so pentacoordinate phosphorus compounds with nucleophilies.[129] Furthermore, the data obtained in recent years leave no doubt that intermediates containing a P(VI) atom do in fact to a large extent determine the kinetic and synthetic results in many reactions of phosphoranes.[12]

It is known[12] that nucleophilic substitution at a pentacoordinate phosphorus atom can proceed via one or two mechanisms—dissociative, presupposing the unimolecular decomposition of the phosphorane to a phosphonium intermediate, and associative, in which nucleophilic species are added to or eliminated from the P(V) atom of the substrate. the formation of P(VI) intermediates in the second case has been established experimentally by isolating the products of the addition of ionic or neutral nucleophiles to phosphoranes.

Theoretical calculation for the minimum reaction energy pathway (MREP) in nucleophilic substitution at the P(V) involving the simple model reactions (2)–(4), i.e.

$$H^{\ominus} + PH_5 \rightleftarrows (PH_6)^{\ominus} \rightleftarrows PH_5 + H^{\ominus}, \quad (2)$$

$$H^{\ominus} + PH_4Me \rightleftarrows (PH_5Me)^{\ominus} \leftrightarrows PH_4Me + H^{\ominus}, \quad (3)$$

$$H^{\ominus} + PH_3Me_2 \rightleftarrows (PH_4Me_2)^{\ominus} \rightleftarrows PH_3Me_2 + H^{\ominus}, \quad (4)$$

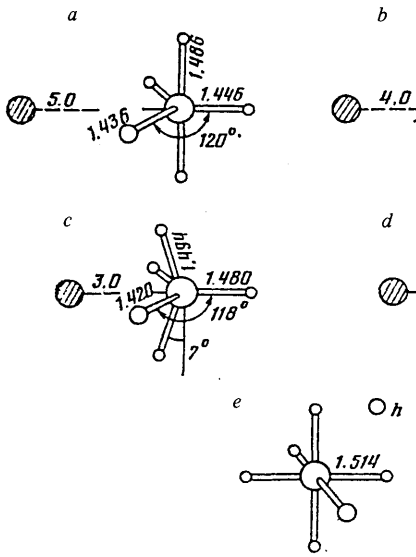
demonstrated that the attack by the hydride ion takes place rigorously in the equatorial plane of the trigonal bipyramid of the substrate.[95] The interaction leads to an octahedral intermediate and the main geometrical rearrangement of the system takes place in the reaction zone ($R \cong 2.0$–2.2 Å) with a gradual decrease of the total energy (see Figure). The *trans*-equatorial ligand begins to "sense" the approach of the nucleophile even over long distances and the *trans*-P–H bond gradually lengthens and, when the interaction is completed, reaches its equilibrium value. The lengths of the *cis*-P–H bonds increase monotonically.

Calculations for the less symmetrical RR^1PH_3 molecules have shown that the energetically most favourable direction of attack of a nucleophile involves movement along the bisector of the RPR^1 angle.

According to the data of Minaev and Minkin,[95] the addition of the nucleophile to the P(V) atom results in the preferential *cis*-disposition of the most electronegative group and the removal of the electronegative group being substituted takes place in the *cis*-conformation. #

The view has been expressed recently that equatorial attack by the nucleophile in the trigonal bipyramid of the phosphorane intermediate[130] and not only axial attack, as had been believed previously,[11] is possible also in reactions involving nucleophilic substitution at a tetrahedral phosphorus atom proceeding with retention of configuration.

At the same time, it has been shown[46,48] that, when the formation of P(VI) anions is subject to kinetic control, the addition of ionic nucleophiles to spirophosphoranes results in the initial formation of *trans*-phosphorates, which isomerise on raising the temperature to the thermodynamically favourable *cis*-phosphorates[12] (see also Section IV).



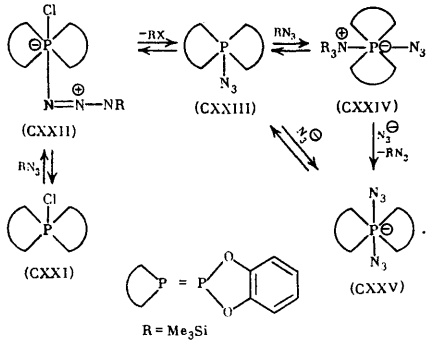
The minimum energy pathway in reaction (2);[95] the heats of formation of the supermolecule (ΔH_f, kcal mol^{-1}) are quoted for different distances R between the hydride ion and the attacked molecule: *a*) 120.5; *b*) 118.4; *c*) 115.4; *d*) 88.9; *e*) 78.6.

The formation of phosphorate intermediates in nucleophilic substitution at a pentacoordinate phosphorus atom has been detected in many instances by NMR.[12]

In the reaction of the chlorophosphorane (CXXI) with trimethylsilyl azide at −100 °C, the main product is the zwitter-ionic adduct (CXXII), which eliminates chlorotrimethylsilane at −60 °C and is converted into the azidophosphorane (CXXIII). However, the use of a twofold excess of the silyl azide yields as the main component of the reaction mixture the phosphorate (CXXIV), which is subsequently converted into compound (CXXV) (Scheme 5).

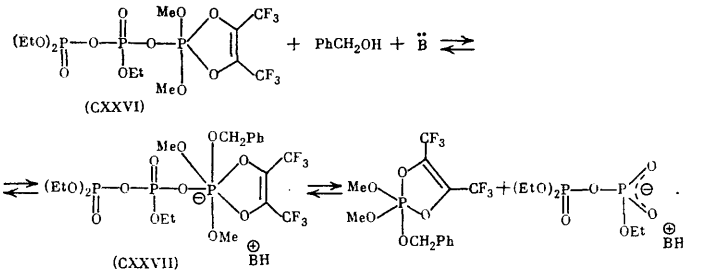
The equilibria (CXXIII) ⇌ (CXXIV) and (CXXIV) ⇌ (CXXV) are characteristic of the interaction of phosphoranes with nitrogen-containing nucleophiles (see Section IV). Phenylenedioxytrichlorophosphorane also combines with the azide molecule in the first stage and then exchanges in succession all the chlorine atoms for the azido-ligands

Scheme 5

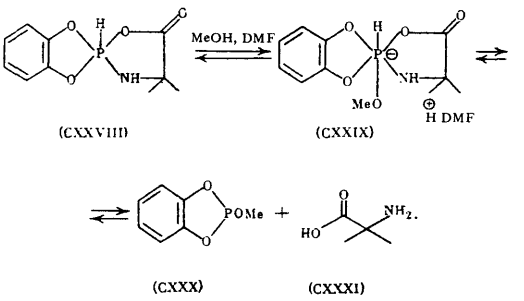


Thus reactions involving the nucleophilic substitution of chlorine atoms by azide ions proceed via a series of consecutively formed individual phosphorate intermediates.[131]

The interaction of hydroxyphosphoranes with alcohols, which takes place via transesterification[41,132,133] or alcoholysis[55] mechanisms, also involves the intermediate formation of phosphorates. Thus in the presence of γ-collidine, benzyl alcohol substitutes the pyrophosphate ligand in the phosphorane (CXXVI) in a relatively rapid and reversible reaction proceeding via the monocyclic phosphorate (CXXVII). The coordination of the phosphorus atoms is preserved in the reaction products.[41]

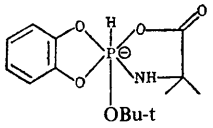


However, in alcoholysis reactions leading to products with a reduced coordination number of the phosphorus atom, the formation of phosphorate intermediates can be established spectroscopically in many instances.[55] The methanolysis of the hydrophosphorane (CXXVIII) in DMF leads to the cyclic phosphite (CXXX) and the aminoacid (CXXXI). At −60 °C a high-field signal [$\delta(^{31}P)$ = 110 p.p.m., J_{PH} = 760 Hz] was recorded in the NMR spectrum of the reaction mixture:



The signal was assigned to the intermediate (CXXIX) on the basis of a comparison with the similar spectroscopic characteristics of the phosphorate (CXXXII) obtained from

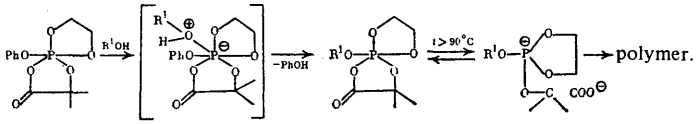
compound (CXXVIII) and t-BuOK.



(CXXII) $\delta(^{31}P) = -112$ p.p.m., $J_{PH} = 740$ Hz

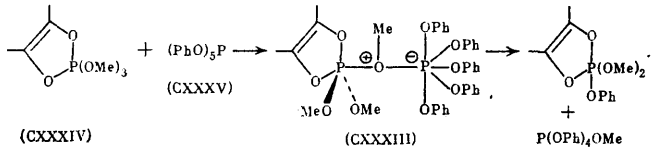
It is striking that the attack by the nucleophile is directed not to the alternative electrophilic centre of the molecule of compound (CXXVIII), namely the carbonyl carbon atom, but to the phosphorane phosphorus atom, which is known[12] to be characterised by a pronounced Lewis acidity. The replacement of the phenylenedioxy-substituent in compound (CXXVIII) by the less electron accepting ethylenedioxy-group precludes the detection of the P(VI) intermediate in the course of alcoholysis.[55]

It has been suggested that the transesterification of spirophosphoranes in neutral media and their subsequent polymerisation at an elevated temperature (>90 °C) proceed via a stage in which bicyclophosphorates (CXXXII) are formed:[134]



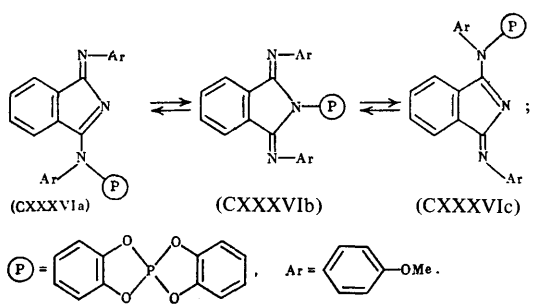
(CXXXII)

The formation of the oxonia-phosphorate intermediate (CXXXIII) probably ensures[135] intermolecular ligand exchange between the cyclic and acyclic phosphoranes (CXXXIV) and (CXXXV):



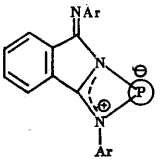
(CXXXIV) (CXXXV) (CXXXIII) $P(OPh)_4OMe$

Systems in which phosphotropic tautomerism occurs with participation of the phosphoranyl group have been discovered recently.[136] Two equal intensity singlets, at 3.63 p.p.m. (1) and 3.94 p.p.m. (2), as well as a singlet at 3.75 p.p.m. (3) with the intensity ratio (1 + 2) : (3) = 0.45 : 0.55, have been observed in the ^1H NMR spectrum of a solution of the phosphorane (CXXXVI) in *o*-dichlorobenzene at 25 ° C. The ^{31}P NMR spectra also contain two singlets with $\delta(^{31}P) = -26.8$ and -36.7 p.p.m. and the same intensity ratio. The proton signals coalesce at 120 °C. This spectral pattern was explained by the existence of a dynamic equilibrium between the forms (CXXXVIa), (CXXXVIb), and (CXXXVIc) owing to two consecutive 1,3-migrations of the phosphoranyl group in the N=C–N=C–N pentad of compound (CXXXVI):



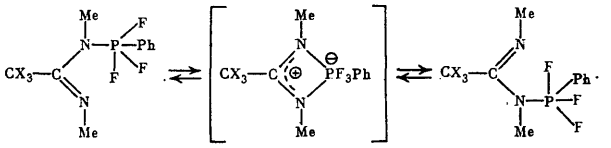
(CXXXVIa) (CXXXVIb) (CXXXVIc)

The free energy of activation for the process is 16.9 kcal mol^{-1}. The rate of these migrations is independent of concentration, which indicates an intramolecular mechanism of this phosphotropic process, involving the formation of the intermediate (CXXXVII) with a hexacoordinate phosphorus atom, which is short-lived on the NMR time scale and cannot therefore be detected spectroscopically.

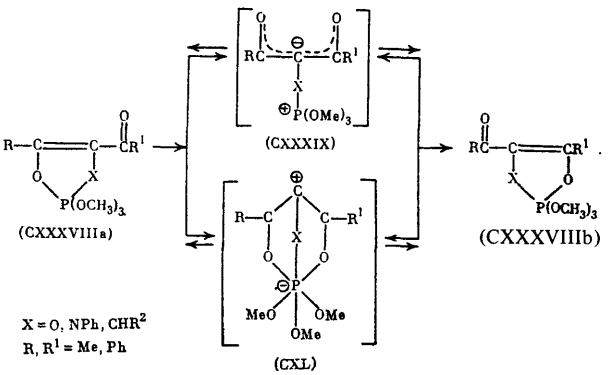


(CXXXVII)

A degenerate triad phosphotropism, associated with the migration of the PF_3Ph group, occurs in the phosphorane derivatives of trihalogenoacetamidinium. The intermediate phosphorate intermediate cannot be detected, because it is destabilised by the electron-accepting group at the cationoid carbon atom and the phenyl group at the phosphorate phosphorus atom:[137]



One cannot rule out the possibility that the phosphorotropic tautomerism (CXXXVIIIa) ⇌ (CXXXVIIIb), observed in monocyclic phosphoranes containing an acyl group at an endocyclic carbon atom,[138–140] can involve not only a dissociative mechanism via a betain intermediate (CXXXIX) with the phosphonium atom, but also via an associative mechanism with participation of a hexacoordinate intermediate or transition state (CXL). However, the experimental data are insufficient to make a choice between these variants.



(CXXXVIIIa) (CXXXIX) (CXXXVIIIb)

X = O, NPh, CHR^2
R, R^1 = Me, Ph

(CXL)

The present paper completes a series of reviews[10–12] devoted to the chemistry, mainly reactivity, of 1,3,2-diheterophosphacyclanes containing a phosphorus atom with different coordination numbers. Summarising briefly the literature data of the last decade, one must note that all the main current trends in the development of organophosphorus chemistry have been reflected in the chemistry of these phosphorus-containing heterocycles. The endeavour by investigators to establish a relation between the structure and reactivity of OPC and to express it quantitatively whenever possible must be included among them in the first place. Much attention has been devoted to the study of the fine

details of the reaction mechanisms and through their understanding to the development of new methods of synthesis of OPC, including those which are practically useful. The discovery of the character and role of the intermediates in the reactions of OPC is important for the development of the chemistry of phosphorus compounds at the present stage. It has led investigators to recognising the fact of the relative ease with which the coordination number of the phosphorus atom can change and to new views on the character of the driving forces in the reactions of OPC and has strongly stimulated progress in the chemistry of hypervalent compounds of phosphorus and other non-transition elements.

At the same time, many problems in the chemistry of 1,3,2-diheterophosphacyclanes, such as the character of the intramolecular electronic interactions, the manifestation of the stereochemistry of the phosphorus-containing heterocycle in the reactivity of OPC of this type, the quantitative characteristics of the electronic and steric effects of the alkylene(phenylene)dihetero-substituent or the entire phosphacyclane fragment, and many others still require a more far-reaching development. We are confident that studies in the near future will be marked by new successes in this rapidly developing field of organophosphorus chemistry.

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