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Advances in the Chemistry of Phosphorus(III) 1,3,2-Diheterophosphorinanes

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Studies on the synthesis and chemical reactions of 1,3,2-diheterophosphorinanes containing a tervalent phosphorus atom are examined for the first time within a single review. The influence of the heteroatoms surrounding the phosphorus atom on the properties of the phosphorinane system is analysed. The chemical features of mono- and poly-cyclic 1,3,2-diheterophosphorinane are compared and the ways of the practical utilisation of these substances are discussed.
The bibliography includes 338 references.

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I. INTRODUCTION

Phosphorus(III) 1,3,2-diheterophosphorinanes (DHP) constitute a large group of six-membered heterocycles whose molecules contain a tervalent phosphorus atom surrounded by other heteroatoms. Here one should include also the corresponding hydrophosphoryl, hydrothiophosphoryl, and hydroiminophosphoryl compounds, one of the tautomeric forms of which contains a tricoordinate phosphorus atom. The phosphorus–oxygen heterocycles, namely 1,3,2-dioxaphosphorinanes (DOP) have been investigated most thoroughly but in very recent years related systems have begun to be considered: diazaphosphorinanes (DAP), oxazaphosphorinanes (OAP), and dithiaphosphorinanes (DTP).

The first examples of DHP were synthesised in the Soviet Union[1] and in the United States[2] at the end of the 1940's. During this period, the reasons for the interest in these compounds were largely classified and the volume of work was therefore small. It was not until the 1970's that the chemistry of the DHP was sharply activated, in connection with the development of much interest during this period in the comparison of the stereochemistry and reactivity of cyclohexanes and saturated heterocycles. In addition, at this time realistic methods became available for the investigation of the electronic structure of the DHP and particularly the elucidation of the nature of the interaction of the electron pairs and orbitals of the triad $-\ddot{X}-\ddot{P}-\ddot{Y}-$, which is incorporated in six-membered rings with different degrees of rigidity. Finally, the development of the chemistry of DHP was stimulated by the publication of novel synthetic studies, including those leading to the solution of important applied problems. Ultimately the interests of specialists in organophosphorus synthesis, stereochemistry, spectroscopy, complex catalysis, bio-organic chemistry, and the chemistry of high-molecular-weight compounds coincided in the study of the DHP. Because of this, an extensive scientific field was established, the

principal achievements in which are discussed in the present review.

The chemical behaviour of DHP is mainly determined by two factors: the nature of the central functional group and the overall structure of the molecule. In dealing with the structure of the molecule, one must bear in mind whether the substance belongs to mono- or poly-cyclic systems, since the latter frequently have chemical properties which are not altogether usual. In this connection, we subdivided the entire contents of the review into two parts, devoted to the mono- and poly-cyclic systems.

In each section the synthesis and partly the stereochemistry are considered initially and then the chemical properties of the DHP.

Since the appendix to the Russian translation of the book of Purdela and Vilceanu[3] gives a list of publications on phosphorus-containing heterocycles covering the literature up to 1969, in the present review attention has been concentrated only on studies of the latest period.

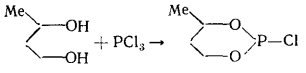
II. MONOCYCLIC 1,3,2-DIHETEROPHOSPHORINANES

1. Synthesis

DHP can be obtained using two approaches. The first combines the phosphocyclisation of 1,3-glycols and similar 1,3-bifunctional compounds, i.e. reactions leading to the formation of six-membered phosphorus-containing heterocycles from linear systems. Data on this problem are discussed in this section separately for DOP, DAP, and DTP. The system adopted is dictated by the non-uniformity of the studies on different DHP and also by the fact that they are not always produced by general methods. The second approach is based on the exchange reactions of the substituents at the phosphorus atom already incorporated in the phosphorinane ring. The corresponding data are considered in the next section which deals with the chemical reactions of DHP. This procedure eliminates the possibility of repetitions and makes it possible to relate the problem of the synthesis of individual classes of DHP to their general chemical characteristics.

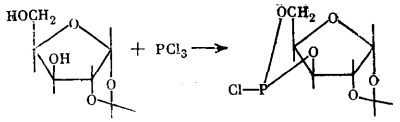
(a) 1,3,2-Dioxaphosphorinanes

When 1,3-diols react with phosphorylating agents having at least two leaving groups, it is possible to obtain different types of DOP. Phosphorus trichloride has been used as the phosphorylating agent in many investigations[1,2,4-8], for example:

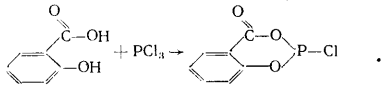


The reaction is usually carried out in a dry solvent. A tertiary amine is not always used to combine with the hydrogen chloride evolved. The hydrogen chloride is then removed from the reaction mixture by bubbling in a dry inert gas. This feature, apparently associated with the anomalously low basicity of cyclic phosphorochloridites, greatly simplifies the synthesis of chlorophosphorinanes and distinguishes it from the synthesis of dialkyl phosphorochloridites.

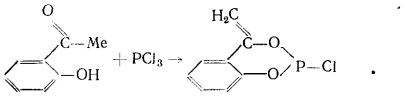
The condensation of phosphorus chloride has been widely investigated. A wide variety of halogenated glycols[9], the corresponding unsaturated systems[10], ethers[6,11,12], and nitro-compounds[13] have been made to undergo this condensation. In this case the possibility of a partial oxidation-reduction reaction, leading to nitrosoglycols and phosphoryl compounds, has been noted[13]. In addition, the cyclophosphorylation of the polyfunctional system of the antibiotic synthomycin[14] and 1,2-isopropylidenexylofuranose[15] has been achieved:



We shall consider the stereochemical aspect of the phosphorylation with phosphorus trichloride. A single stereoisomer, whose chlorine atom occupies an axial position, is as a rule formed in this case[15-20]. The reaction of phosphorus trichloride with 2-benzylglycerol, leading to a mixture of unequal amounts of two stereoisomers, is an exception[12]. Salicylic acid reacts with phosphorus trichloride similarly to β-glycols[21]:

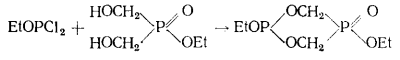


As regards the chemical aspect, the analogous phosphorylation of acetylacetone and 2-acetylphenol, leading to unsaturated DOP, is of great interest[22]:



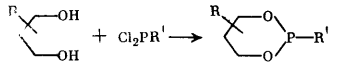
Unfortunately this synthesis has not yet been widely developed. Among other phosphorus trihalides, only phosphorus tribromide has been made to react with diols, 2-bromo-1,3,2-dioxaphosphorinane being obtained[18,23].

Numerous studies have been devoted to the cyclophosphorylation of 1,3-diols with tervalent phosphorus acid dichloride. In particular, a detailed study has been made of the interaction of glycols with Menshutkin acid chlorides in the presence of bases[6,7,15,24,25]. The cyclisation reaction[26]



is promising in many respects.

The dichloride of phosphorus acids react with 1,3-glycols similarly to the Menshutkin acid chlorides. This makes it possible to obtain interesting cyclic phosphonites albeit not always in high yields[24,27-30]:

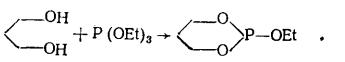


We may also note that the condensation reactions with phosphonous acid dichlorides are of less universal importance than the corresponding reactions with phosphorus trichloride owing to the occurrence of side reactions[31].

In its stereochemical aspect, the phosphocyclisation with acid dichlorides differs from the cyclisation with phosphorus trichloride. When asymmetric glycols are used, not one but two interconvertible stereoisomers are formed, in which the axial position is preferred for the alkoxy-group.

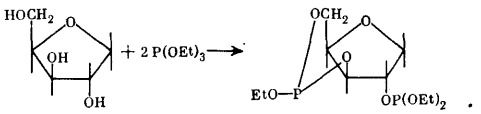
The reactions discussed above have attracted attention because of the outward simplicity of their mechanism and the availability of phosphorylating agents. Nevertheless, they do not always yield good results owing to the presence of hydrogen chloride, which is not completely bound by the acceptors employed. A significant factor for larger-scale syntheses is also the fact that many reactions involving

phosphorus chloride require the employment of large volumes of dry solvents. Bearing this in mind, alternative cyclophosphorylation methods have begun to be studied in many laboratories, including those dealing with applied problems. The transesterification method was the first to be studied in detail, for example:



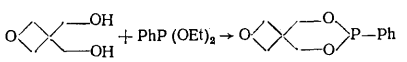
It has been shown that various forms of glycols[4,9,18,33,34] readily interact with the simplest neutral phosphorus acid esters. It has been suggested that this reaction be used to simplify industrial polymer stabilisers[32].

The reaction of xylitan, which is an asymmetric triol, with an excess of triethyl phosphite merits special attention. The β-glycol group in xylitan ensures the selective formation of the phosphorinane ring; the second of the *trans*-vicinal hydroxyls is more passive and is phosphorylated without cyclisation:



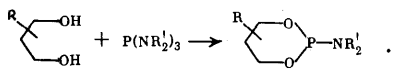
A similar regioselectivity has also been noted in the phosphorylation of 2,4-methylenexylitan[35].

Neutral phosphonites can also be transesterified with 1,3-glycols,[36,37] including those with other functional groups. As an illustration, we may quote the synthesis of the spirocyclo system[36]



Dialkyl phosphites are also involved in transesterification with various β-glycols. This results in the formation of DOP belonging to the class of hydrophosphoryl compounds[4,12,38–42]. A mixture of two geometrical isomers of DOP is usually obtained as the technical product. One of them, which has the phosphoryl group in the equatorial position, crystallises out[38–40,43].

In the latest studies the phosphorylation of 1,3-diols is usually carried out using the triamides of phosphorus acid[34,38,39,42,44–47]:



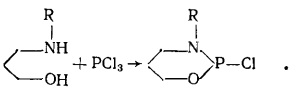
The reaction is carried out simply and under mild conditions in the absence of corrosive side products and is very productive. Because of this, it has found extensive preparative applications, particularly in a series of complex systems. Thus it has been used in the synthesis of aminophosphorinanomonoses[15,25,40] and nucleosides[47,48].

The problem of the configuration of the phosphorus centre in 2-amino-DOP has been discussed in the literature. From NMR data, it has been concluded that the position of the amino-group depends on the nature of the substituents at the nitrogen atoms[45,49–52]. The unusual equatorial disposition is probably promoted by the orbital interaction of the nitrogen and phosphorus; on the other hand, if the unshared electron pair of the nitrogen atom is delocalised over the structural elements of the amino-group, then the axial disposition of the substituent obtains more readily[52].

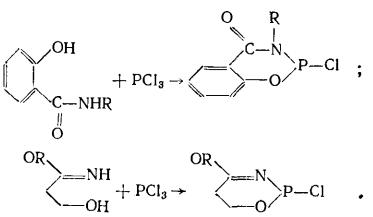
The diamides of alkylphosphorus[48,53], arylphosphorus[53], and phosphonous[54] acids are also effective phosphorylating agents. Many DOP, particularly those derived from sterically hindered phenols[53], sugars[25], and nucleosides[48], have been obtained on their basis.

(b) 1,3,2-Oxaphosphorinanes

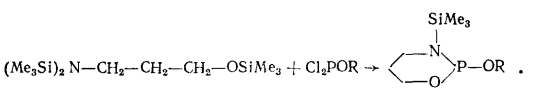
OAP have been vigorously investigated in the last ten years, mainly in connection with the requirements arising in the development of bio-organic chemistry. They are synthesised from β-aminoalcohols in different ways depending on the nature of the latter. *N*-Alkyl-[55–59] and *N*-aryl-propanolamines[55] react with phosphorus trichloride in the presence of triethylamine to form 2-chloro-oxazaphosphorinanes:



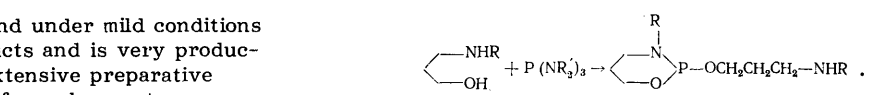
The amides of salicylic acid[60] and the iminoesters of β-hydroxypropionic acid[61] have been similarly condensed with phosphorus trichloride to form OAP with functional groups:



The phosphocyclisation is also carried out using the dichlorides of alkylphosphorous[57,60,62], phosphoramidous[57,63], and phosphonous[64] acids. The dichlorides of alkylphosphorous acid are condensed with *O*,*N*,*N*-tri(methylsilyl)propanolamine[65]:

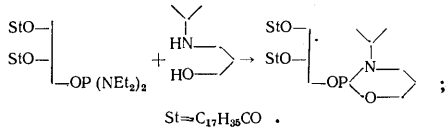


The most frequently employed method of synthesis of OAP involves the interaction of 1,3-aminoalcohols or their derivatives with a tervalent phosphorus acid amides, unexpected results being obtained. The simplest instance of such cyclisation is the interaction of secondary aminoalcohols with the triamides of phosphorous acid. It has been stated in a patent[55] that, for an equimolecular reactant ratio, 2-amino-OAP are obtained. However, it was shown later[57] that, for different ratios of reactants, different substances are formed, namely 2-γ-aminopropyl-OAP:



A similar type of phosphocyclisation has also been described for the phosphorylation of unsubstituted propanolamine with phosphorus acid triamides[66]. This result, i.e. double phosphorylation, is apparently associated with the higher reactivities of 2-amino-OAP, which are intermediates in this synthesis, than those of phosphorus acid triamides. Triamides of phosphorous acid readily phosphorylate *N*-acetylpropanolamine[67,68]. The absence of secondary phosphorylation is entirely logical, because the basicity of the phosphorus atom (the most important factor in reactivity) in 3-acetyl-2-amino-OAP is significantly reduced.

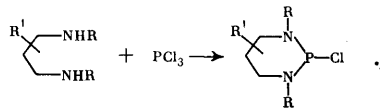
Phosphorodiamidites react with an equimolar amount of propanolamine[62,69,70], *N*-alkylpropanolamine[57,71,72], and *N*-acylpropanolamine[68] to form OAP of different types, including those which belong to the class of phospholipids as regards their structure, for example[72]:



St=$C_{17}H_{35}CO$.

(c) 1, 3, 2-Diazaphosphorinanes

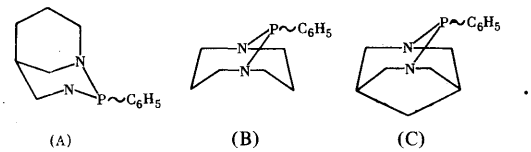
DAP began to be studied later than OAP but more extensively. Initially they were synthesised successfully by the reactions of secondary 1,3-diamines with tervalent phosphorus acid halides. Numerous studies have been devoted to phosphorylation with phosphorus dichlorides[73–78]:



A wide variety of chlorides of 1,3-alkylenephosphorodiamidic acid chlorides, which exist in the form of a single isomer in which the chlorine atom has the axial orientation, have been synthesised by the above methods[73,76,79]. 2-Chloro-4-methyl-1,3-diphenyl-DAP, which consists of two isomers, is an exception. Bearing in mind the results of Belov et al.[80], one may postulate that the chlorine atom in the systems considered occupies the axial position.

Experiments with secondary amides of β-alkylaminopropionic[81] and *N*-alkylanthranilic[82,83] acids have been described, but pure 2-chloro-4-oxo-DAP were not obtained. Nevertheless the technical products have been used successfully in further extremely complex reactions[83].

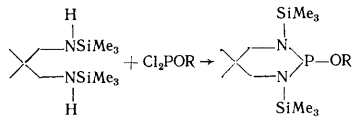
The dichlorides of alkylphosphorous[73,78], phosphoroamidous[73,76,78]†, and phosphonous[73,76] acids usually react with secondary 1,3-diamines to form various DAP. Together with linear diamines, their cyclic analogues began to be studied in the phosphorylation reaction, which makes it possible to synthesise "bulky" DAP of great stereochemical interest[73], for example:



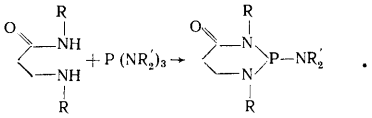
(A) (B) (C)

The chemical shifts of the phosphorus atom in these derivatives are determined by the geometry of the molecules to a significant extent : 94.3 p.p.m. for (A), 103.6 p.p.m. for (B), and 180.8 p.p.m. for (C).

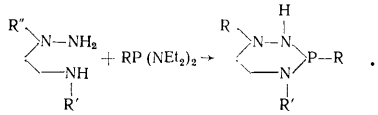
N-Silylated DAP are formed when Menshutkin acid chlorides react with bisdisilylated 1,3-diamines[84]:



The second method of synthesising the diazaphosphorinane ring is based on the transamidation of the amides of tervalent phosphorus acids. It is experimentally simple and is of great synthetic value. Thus the full amides of phosphorous acids phosphorylate extremely effectively secondary diamines[77] and aminoamides[81]:



We may note that the reaction of phosphorous acid triamides with secondary 1,3-diamines does not suffer from the limitation which we have considered for the reaction with propanolamines. This indicates some difference in the phosphorylation of related diamines and aminoalcohols and possibly amines and alcohols in general. The diamides of alkylphosphorous acid have been investigated in the reaction with primary 1,3-diamines, which made it possible to obtain the hitherto unavailable but very promising DAP without substituents at the nitrogen atoms[84]. The diamides of phosphonous acids have been made to react with aminohydrazines. Condensation resulted in the synthesis of the first representatives of 1,2,4,3-triazaphosphorinanes[85]:



It may be supposed that the proposed condensations will permit the synthesis in the immediate future of a large number of new DAP of interest for structural and synthetic research.

(d) 1, 3, 2-Dithiaphosphorinanes

This field of synthesis of DHP has been studied very much less than those already discussed, which reflects the overall picture showing that the thiol esters of tervalent phosphorus acids have been little investigated. Nevertheless, it has already been established that some of the simplest DTP are chemically very unusual; furthermore, they exhibit insecticidal and herbicidal activities[86].

1,3-Dithiols interact with phosphorus trichloride in the presence of tertiary amines to form 2-chloro-DTP.[86–88] The dichlorides of alkylphosphorous[89], alkylphosphorothious[88], phosphoroamidous[87], and phosphonous[88–93] acids, have also been used as phosphorylating agents. It has been noted[91] that DTP dimers are formed together with the DTP themselves. The problems of the stereochemistry of DTP have been examined in a number of studies[89,93–95]. Azathia- and oxathiaphosphorinanes have not so far been described in the literature.

2. Chemical Properties

In writing this section of the review, the authors had two aims: to carry out a subject survey of synthetic studies and to examine the characteristics of the chemical behaviour of DHP determined by their cyclic structure. The latter aim presupposes in its turn the analysis of the electronic structure and intramolecular dynamics of DHP, which is at present difficult to achieve in the required detail despite the progress made, for example, in the study of Arshinova[96]. However, it is possible to make introductory remarks which will draw the reader's attention to the problem and will help him to become acquainted with the factual data.

† The reaction has no general importance and is very unusual in its chemical aspect. Its analysis will be described in the section dealing with the chemical properties of DHP.

An ordered orientation of the unshared electron pairs of the heteroatoms, which is absent from the corresponding acyclic systems, is characteristic of DHP [97–99] and presumably the n_P–n_O interaction is blocked in DOP by virtue of such order. This is confirmed by a comparison of photoelectron spectroscopic data and the chemical properties of acyclic and cyclic compounds. The problem of the involvement of the electron pairs of the nitrogen atoms of OAP and DAP in the n_P–n_N interaction is more complex, since in this case their orientation can generally speaking depend on the influence of the substituents present.

The orientation of an exocyclic substituent at the phosphorus atom plays a significant role in the chemical characteristics of monocyclic DHP. If the substituent having n or π electrons is axial, its electrons are less effectively delocalised than those of a similar equatorial substituent. This difference is probably associated with the blocking of an interaction of the n_P–n_X type on the assumption of the axial position.

Another feature of the DHP consists in the somewhat small number of their conformational transitions[100]. The limited number of such transitions is thrown into particular relief when substituents are introduced into the hydrocarbon part of the ring or when an additional ring is condensed. Henceforth the possibility of synthesising in the series of DHP rigid systems in which the central and additional functional groups are located in space in such a way that they can ensure attack from unusual directions and hence also unusual types of reaction. Having outlined this situation, we formulated the principle of the stereochemical regulation of the reactivity in the series of cyclic derivatives of tervalent phosphorus acids. This principle has already been realised in the reactions of DHP.

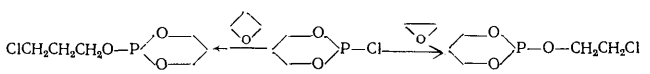
Since numerous scientific articles and patents have been devoted to the reactions of monocyclic DHP, the relevant data are discussed separately in terms of classes of compounds.

Within each section the data are further subdivided on the basis of the principal structural-chemical features. The following characteristics are discussed in succession for the usual DHP: (1) substitution reactions involving an exocyclic substituent at the phosphorus atom; (2) protonation and oxidation reactions; (3) Arbuzov alkylation and related syntheses; (4) other processes. After this, the chemical properties of DHP, which are prototropic systems (hydrophosphoryl and thiohydrophosphoryl substances), are discussed in separate subsections.

(a) 1, 3, 2-Dioxaphosphorinanes

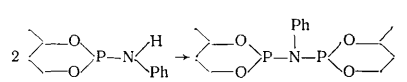
Substitution reactions at the phosphorus atom. The nucleophilic substitution of chlorine in 2-chloro-DOP has been studied in greatest detail. These compounds are readily converted into neutral phosphites in their reactions with alcohols[6,7,10,15,22,101–103], phenols[7,104,105], substituted glycerols[106,107], and sugars[15,107,108] in the presence of bases. The problems of the stereochemistry of the reaction and the characteristics of the steric organisation of the cyclic neutral phosphites obtained have been examined in a number of studies[101,102,107,109,110].

2-Chloro-DOP can be converted into the corresponding neutral phosphites even on treatment with oxirans and oxetans[111,112], for example:

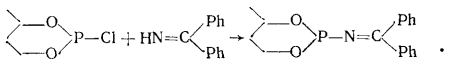


Six-membered cyclic phosphorochloridites react with mercaptans to form phosphorothioites (see, for example, Okruszek and Stec[113]).

Numerous communications contain data concerning the interaction of 2-chloro-DOP with nitrogen-containing bases of different types. Arbuzov and Zoroastrova showed for the first time[114] that 1,3-alkylene phosphorochloridites react with a simplest secondary amides to form 2-amino-DOP. Subsequently this reaction came to be widely employed[10,12,15,34,102,115,116]. It was shown that, when amines are phosphorylated by asymmetric cyclic chlorides, a mixture of two isomers is always formed[19,51,102,110]#. Primary amines in general behave in this reaction analogously to secondary amines[49,50,114,118], although they yield less satisfactory results on a preparative scale. This is associated with the disproportionation, first investigated in relation to the anilide of 1,3-butylenephosphorous acid[118]:

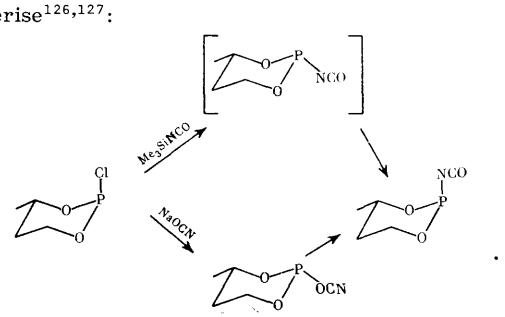


In the presence of bases, imines are also phosphorylated by 2-chloro-DOP in accordance with the general mechanism, for example[119]:



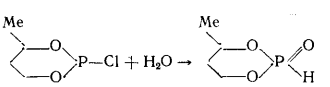
Instead of amines, it is possible to use their *N*-trimethylsilyl or magnesium derivatives.

2-Chloro-DOP exchange the chlorine atom for many groups on interaction with salts of acids or their trimethylsilyl derivatives. Thus the reaction with antimony trifluoride yields fluorides[8], that with carboxylic and alkylcarbonic acid salts gives rise to acylates[120,121], the reactions with cyanotrimethylsilane[122], silver cyanate[123], or hydrocyanic acid in the presence of triethylamine results in the formation of cyanides[124], and the reaction with isothiocyanatotrimethylsilane yields isothiocyanates[125]. The reaction with cyanic acid derivatives is of special interest. *N*-Trimethylsilyl derivatives leads to phosphoisocyanates, while salts of cyanic acid result in the initial formation of the *O*-isomers, which then isomerise[126,127]:



2-Chloro-DOP react with sodium dialkyl phosphites to form asymmetric pyrophosphites (*O*-phosphorylation of the ambident phosphite anion[128]), while their reaction with *N*-trimethylsilylacetamide gives rise to acid cyclic phosphites[129]. The latter reaction probably involves the *O*-phosphorylation of the silyl derivative with formation of the phosphiminoacetate, which then decomposes splitting off acetamide.

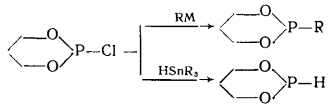
The hydrolysis of 2-chloro-DOP to cyclic hydrophosphoryl compounds has been studied in detail[7,10,12,15,33,117,130], for example:



This problem has been treated erroneously by Bodkin and Simpson[117].

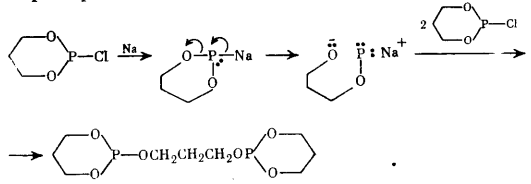
The hydrolysis of asymmetric phosphorochloridites results in the formation of two isomers, the stable isomer, with an equatorial phosphoryl group, crystallising out[43,117]. The sulphydrolysis of 2-chloro-DOP leads to cyclic hydrothiophosphoryl compounds[130,131]. The problems of the stereochemistry of this reaction have been studied[131].

The consideration of the substitution of chlorine in the series of DOP will be completed by examining reactions with organometallic compounds and metals. It has been suggested that the following reactions take place with Grignard and Norman reagents[132] and with tin hydrides[110,133]:



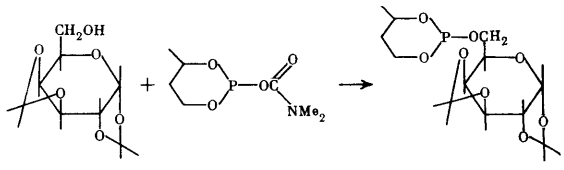
The cyclic esters of hypophosphorus acid obtained are of definite interest as the parent members of the series of DOP. Using them, it is possible to determine the stereochemistry of phosphorus in various DOP by comparative ^{1}H and ^{13}C NMR.[110]

The 2-chloro-DOP do not react with alkali metals in an altogether usual manner[134]§. The process probably begins with one-electron transfer and involves the stage in which P-metallated DOP are formed. The latter decomposes owing to the concerted donor–acceptor action of the geminal substituents at the phosphorus atom. The polar intermediate undergoes further reduction and phosphorylation with formation of diphosphites:



If 2-chloro-DOP is treated with other metallating and even silylating agents, for example, triphenyl-lithiosilane, then a diphosphite is also obtained[134].

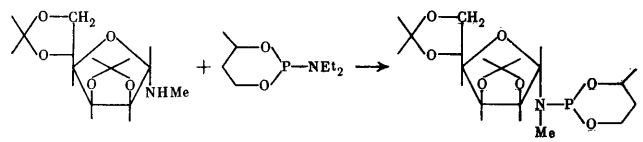
2-Acyloxy-DOP are similar to 2-chloro-DOP as regards reactivity. These compounds have found applications as phosphorylating agents and are used in the synthesis of certain cyclic phosphites[120,121]. Their advantage is that in the acylation of nucleophiles less corrosive carboxylic, alkylcarbonic, and carbamic acids are evolved instead of hydrochloric acid, as mentioned above. As an illustration of the foregoing, we may quote the following examples[136]:



The hydrolysis[128] and acidolysis[137] of the above cyclic acyl phosphites gives rise to hydrophosphoryl compounds. The same result has been noted in the decarboxylation of formyl phosphites[138].

Other popular reagents frequently used for the purposes of fine organophosphorus synthesis are the amides of 1,3-alkylenephosphorous acids. These compounds are readily available, convenient to work with, and exhibit the optimum reactivity in many reactions. When they are used in phosphorylation, the amine is evolved, but it does not as a rule complicate the process and is readily removed from the reaction mixture. 2-Amino-DOP readily phosphorylate alcohols[7,40,47,115,139–143], phenols[7,140,144], substituted glycerols[106,107], and sugars[15,107,108,145]. An important factor is the difference in the ease of interaction of the two geometrically isomeric amides with alcohols[139].

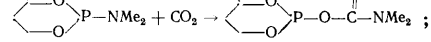
A series of studies has been devoted to the phosphorylation of amines by transamination[141,146]. Very recently transamination has been used to synthesise new systems—phosphoglycosylamines[147]:

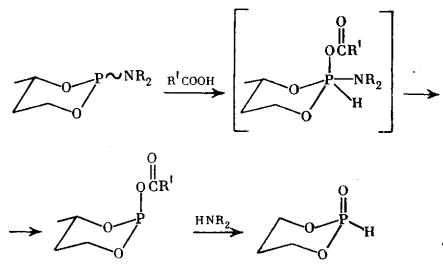


The interaction of 2-amino-DOP with carboxylic acids has been described in the literature. If two moles of acid are consumed per mole of the phosphoramide, substitution takes place with formation of acyl phosphites; the other reaction product is the amine, which combines with the excess acid[148]. If one mole of acid is used, then the substitution at the phosphorus atom is supplemented by the cleavage of the acyl phosphite by the amine and an acid cyclic phosphite is obtained[38,39,40,42,44]. A significant factor in the synthesis is its stereospecificity[38,39,44]—the formation of a labile isomer with an axial phosphoryl group. A mixture of cyclic acyloxyaminophosphoranes, capable of ready interconversion by pseudorotation, is apparently formed initially. The most stable conformer subsequently decomposes with formation of only one axial acyl phosphite. The process terminates with deacylation, which does not involve the configuration of phosphorus (see below).

The conversion of 2-amino-DOP into acid cyclic phosphites is also possible via hydrolysis accelerated by acid catalysts[7,12,114]. Sulphydrolysis takes place similarly[131].

2-Amino-DOP are also capable of insertion reactions. Thus they react with carbon dioxide to form carbamoyl phosphites, for example[136]:



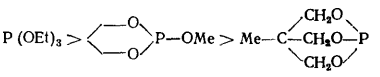


Fewer synthetic studies have been made on the conversion of neutral phosphite DOP into other compounds of this class. They can undergo selective hydrolysis[148,149] and alcoholysis[150] via the exocyclic substituent. 2-t-Butoxy-DOP [151] and its thio-analogue[152] undergo thermal decomposition to the corresponding hydrophosphoryl and hydrothiophosphoryl compounds and isobutene. According to NMR data, the equatorial substituent undergoes degradation at a higher rate than the axial substituent[151].

§ Erroneous results have been published[135].

Apart from the nucleophilic substitution at the phosphorus atom in the DOP system, radical substitution has also been described. In this case the geometrical isomers react at different rates and the process is accompanied by inversion at the phosphorus atom[153].

Addition reactions. An interesting feature of the chemical behaviour of DOP consists in the fact that the electron-donating capacity of the phosphorus atom is determined by the cyclic nature of the substances and the spatial orientation of the unshared electron pair of the phosphorus atom. At the beginning of this section we reported the characteristic features of the unshared electron pairs of the heteroatoms in DOP and in this connection one can conclude that the basicity of phosphites decreases in the sequence



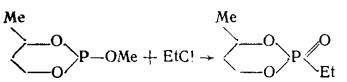
This conclusion has been confirmed experimentally. Thus the ionisation potential of the highest level of the phosphorus atom increases appreciably in this series (8.99, 9.37, 9.95 eV).[97,98] At the same time the basicity, determined both in the gas phase by ionic cyclotron resonance[154] and in the liquid phase at −50 °C from the $^1J_{P-H}$ constants of the protonated esters[155–156], decreases¶. The Lewis basicity of acyclic, monocyclic, and bicyclic phosphites varies similarly. This problem has been analysed by studying the stability of the borane[157,158] and nickel[160] complexes and by infrared spectroscopy. Advances in the investigation of the electronic structure of monocyclic DOP are also manifested by the fact that the theoretical conclusion that the basicities of differently oriented unshared electron pairs at the phosphorus atom are different has been proved experimentally: the axial pair is more basic than the equatorial pair[154,156,157,161]. Investigations demonstrating the marked influence of the exocyclic substituent on the electron-donating properties of the phosphorus atom are also of interest. Thus the amino-group significantly increases the electron-donating properties of the phosphorus atom relative to the alkoxy-group and the chlorine atom[97,98].

The study of the complex formation reactions between DOP and copper[1,162], boron[158,163], molybdenum[158,161,164], nickel[160, 165], cobalt[166,167], and palladium[168] derivatives has shown that the configuration at the phosphorus atom is retained in these reactions (X-ray diffraction has been used[158,160,161,163]). Complexes are synthesised in order to solve specific chemical problems. Adducts with the copper(I) salts are used for the identification of DOP.[1,114,162] The adducts with nickel salts[165] isomerise but-1-ene to a mixture of but-2-enes, while the corresponding rhodium[169,170] and palladium[168,171] derivatives are used as hydrogenation catalysts. In the latter case it has been shown that the configuration of the phosphorus ligand determines the activity and stereoselectivity of the catalysts. It has been stated that the formation of complexes of DOP increases their reactivity in organic synthesis[172]. Such studies are apparently very promising and merit vigorous development.

The electron-donating properties of the phosphorus atom in DOP are also manifested in their oxidation. This reaction has been widely used on a preparative scale and has involved cyclic hypophosphites[133], phosphites[7,46,48,106,145,173–179], phosphoramidites[15,48,50,158,273,180], phosphorimidites[119], phosphorocyanidites[123], phosphoroisocyanidites[126], phosphorochloridites[34], phosphorothioites[113], and phosphonites[27, 132]. The question of the stereochemistry of the oxidation reaction is being actively discussed in the literature, conflicting views being expressed. Under conditions excluding the interconversion of the different DOP formed, they are probably converted stereospecifically by the majority of oxidants into phosphoryl forms with retention of the configuration at the phosphorus atom. This is indicated by the conclusions reached in a series of studies[34,50,127,158,173,175,178, 181]. On the other hand, the possibility of the non-stereospecific oxidation has been indicated[113,176]. It has been suggested that the reactions of two geometrical isomers may not have completely identical mechanisms[182].

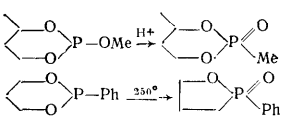
Sulphurisation†[7,25,53,106,107,113,126,133,145,175,179], selenisation[49,113,133,176,183,184], and imination[48,116,133] of DOP are carried out similarly to oxidation. Here too there is no complete unanimity in the stereochemical interpretation of the results. Both complete retention of the configuration at the phosphorus atom[127,158,179] and its partial inversion[113,176] have been noted.

Arbuzov alkylation and related syntheses. Neutral phosphite DOP undergo the usual Arbuzov alkylation[6,24,47,143,149, 162,175,187–189], for example:

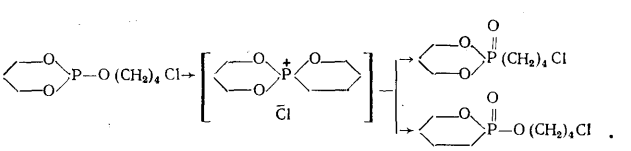


In the majority of cases the alkylation probably involves the retention of configuration at the phosphorus centre[158,162,175, 190] although its partial inversion can also occur[176]. However, one cannot rule out the possibility that the quaternisation of the DOP entails a partial inversion of the configuration of the initial substance, which in fact affects the final results. The reactivity of tripropyl phosphite has been compared with those of the corresponding dioxaphosphorinane and dioxaphospholan by differential thermal analysis. It has been shown that the reactivity diminishes in the above series[191].

The phosphite[192] and phosphonite[193] isomerisations, leading to phosphoryl compounds, are relevant to the data under discussion:



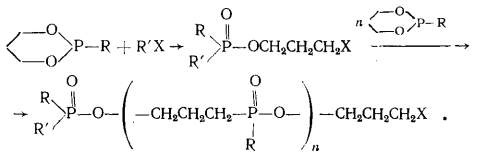
There exist data showing that the Arbuzov reaction can be accompanied by the opening of the dioxaphosphorinane system. This occurs when 2-methoxy-4,4,6,6-tetramethyl-DOP interacts with fluorosulphonic acid[194], when 2-butoxy-4-methyl-DOP interacts with bromotriphenylmethane[149], and in intramolecular interactions of the type[103,112,195]



¶ Mikolajczyk et al.[159] were the first to carry out a semi-quantitative comparison of cyclic and acyclic phosphates.

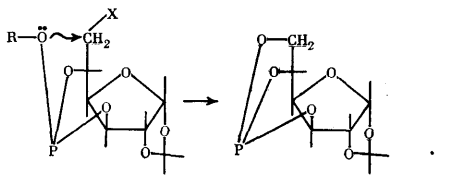
† Together with sulphurisation, other reactions involving the transfer of sulphur and occurring on treatment of elemental sulphur merit attention. Thus neutral cyclic phosphites of nucleosides are sulphurised with di-t-butyl disulphide[185] and 2-chloro-DOP is sulphurised by acetylsulphenyl chloride[156].

The competition between the endocyclic and exocyclic pathways in the decomposition of the quasi-phosphonium intermediates disappears on passing from phosphite to phosphonite derivatives. A fundamentally new method of synthesising polyphosphonates, which is impossible for acyclic systems, has been demonstrated in this instance. The method consists in treating the cyclic phosphonite with an insufficient amount of the alkylating agent. A γ-halogenopropyl phosphinate, which propagates the alkylation process via a relay mechanism, is formed in the first stage[27,196]:



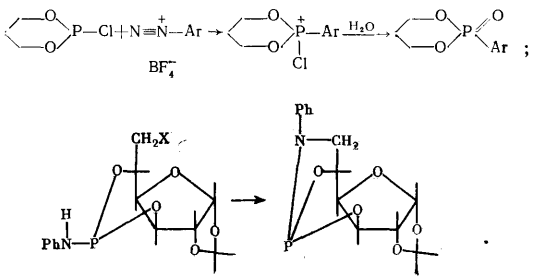
Japanese workers have reported an analogous polymerisation of cyclic phosphonites but in the presence of boron trifluoride[29].

It has recently been possible to show that the intramolecular alkylation of stereochemically rigid DOP, in which an electrophilic carbon atom and the oxygen atom of an exocyclic alkoxy-group are in close spatial proximity, can be achieved. Such spatial disposition led to a reaction which is an alternative to the Arbuzov reaction, which demonstrated the possibility of steric regulation in the alkylation of neutral phosphites#[197]:

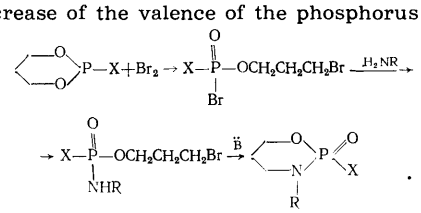


The intramolecular cyclisation of the anilide of the corresponding glycophosphorus acid takes place similarly. The possibility of the alkylation of the nitrogen atom in the amides of tervalent phosphorus acid was thereby demonstrated reliably for the first time[198] (see below).

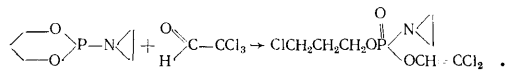
The arylation of certain DOP has also been described in the literature, for example[199]:



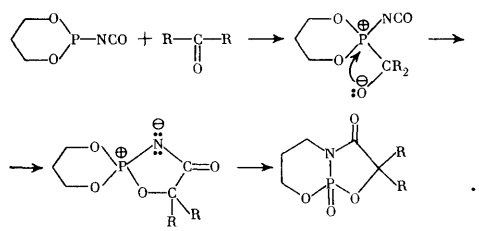
A series of reactions are related to the alkylation of DOP: interactions with hypochlorites[200], sulphenyl chlorides[188,201], and chloramines[102], which entails the formation of cyclic phosphates, phosphorothioates, and phosphoramidates. When account is taken of the stereoregularity of these reactions, conclusions can be reached concerning their preparative value. Data concerning the reactions of DOP with halogens have been published recently[111,202]. It has been established that, regardless of the type of substituent at the phosphorus atom, the reaction is accompanied by ring opening, which is unexpected. On treatment with primary amines, the acid halides formed give rise to amides, which readily cyclise. Thus here we have a transition from DOP to OAP with an increase of the valence of the phosphorus atom[202]:



The Perkow reaction also takes place with DOP, for example[203]:

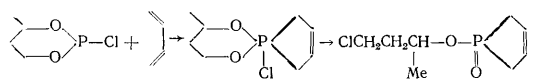


The interaction of 2-isocyano-DOP with electrophilic carbonyl compounds merits attention[204–206]:

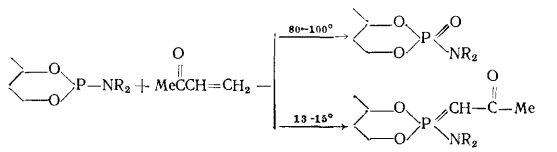


On the other hand, electrophilic carbonyl compounds with a halogen atom in the α-position react with 2-isocyano-DOP differently, namely via the Perkow mechanism, with opening of the phosphorinane ring and retention of the isocyano-group[207].

Other processes. The phosphorus atom in the dioxaphosphorinane ring is biphilic, as a result of which there is a possibility of the addition to DOP of dipolar or readily polarisable 1,3-homo- and 1,3-hetero-diene systems, for example[208]:



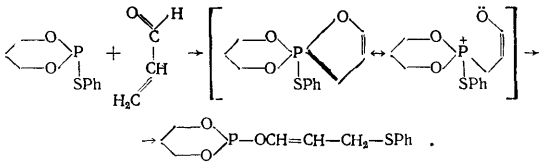
The substituent at the phosphorus atom influences the reaction significantly. Thus the amino-group prevents the addition of alkadienes. However, 2-amino-DOP can combine with polar substances, for example α,β-unsaturated ketones. Depending on temperature, different reactions take place in this instance[209]:



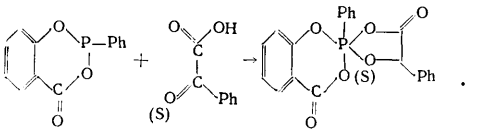
Next, the cyclic imide can react with the excess acrolein and be converted via the Wittig mechanism into 1,3-butylene phosphoramidate. It is of interest to note that 1,2-alkylene phosphoramidites react with methyl vinyl ketone to form only spiroisophospholen.

The cyclisation of the 3,5-cyclic phosphorochloridite of 6-tosyl-1,2-glucofuranose, which apparently takes place as a result of the mutual approach of the phosphorus and O(6) atoms, should also be noted[197].

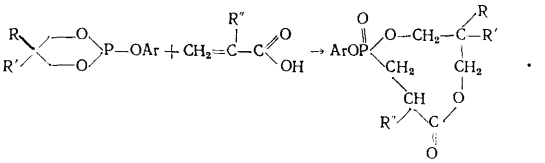
If there is an SR group at the phosphorus atom in the initial DOP, then the primary adduct reacts in an unusual manner[210]:



The cycloaddition may not be followed by a further chemical development when DOP containing the amino-group at the phosphorus atom§ or a hydrocarbon group are used, for example[212]:

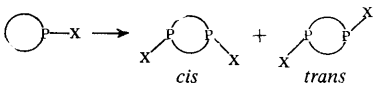


On the other hand, 2-aryloxy-DOP react with acrylic acids to form macrocyclic phosphonates[214]:



This outwardly unusual reaction has a rational explanation. The process begins with cycloaddition, after which the intermediate undergoes a reorganisation via the Arbuzov mechanism. Next, the acid cleaves the neutral phosphite to a hydrophosphoryl compound of the acyl phosphite type and the latter cyclises via a standard pathway with formation of a phosphorus–carbon atom.

An important feature of the chemical behaviour of DOP is their ability to undergo reversible condensation on storage. This process can lead to dimers, trimers, and in the general case oligomers. It is significant that the condensation leads at each stage to the appearance of pairs of isomers[215]:

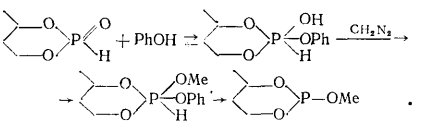


This interesting reaction was studied by NMR. According to the authors, such disproportionation is a catalytic process and is accelerated by admixtures of acid substances, frequently the hydrochlorides which usually contaminate DOP. If this is so, then disproportionation can be prevented by effective purification of the compound.

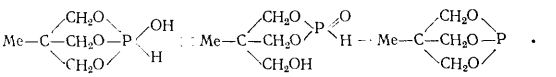
Reactions of hydrophosphoryl and hydrothiophosphoryl DOP. DOP containing the prototropic functional group $\rangle P(=X)H$ are being actively investigated, the research being accompanied by an acute controversy concerning the influence of the ring on chemical properties. Within the framework of this controversy, a special enhanced acidity has been attributed to these substances[216–219]. Reliable experiments on this subject have not been reported but it has been shown nevertheless that the hydrophosphoryl compounds in the series of DOP have certain characteristic features.

We shall consider initially the basic properties of the cyclic acid phosphites. Information on this question has been obtained in the study on the *p*-fluorophenol complexes. It has been shown that the axial orientation of the phosphoryl group ensures a higher basicity than the equatorial orientation, which is consistent with the general theoretical analysis of the systems considered at the beginning of this section. On the other hand, an approximate correspondence of the basicities of DOP and dialkyl phosphites has been established. Nevertheless the experiments performed have demonstrated a large difference between the cyclic and open-chain hydrophosphoryl compounds. The former, particularly those with an equatorial phosphoryl group, are significantly associated in solutions, while the latter are not[220]¶.

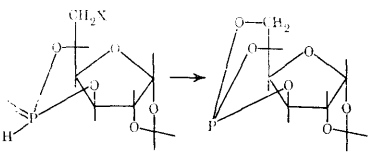
The interaction of hydrophosphoryl DOP with proton donors may apparently not consist solely in protonation. It has been shown that, after the addition of phenol or water, 1,3-butylene phosphite begins to react with diazomethane to form ultimately a cyclic neutral phosphite+[221]:



The above reaction is apparently related to the "anomalous" cyclisation of the monocyclic metriol phosphite[172,222]:



The spatial approach of the functional groups is probably an important factor in this case, since the benzyl ester of metriol phosphite also undergoes a similar cyclisation. The steric factor is undoubtedly manifested in the very easy intramolecular alkylation reactions, which are alternatives to the Michaelis–Becker synthesis[197,223]:



The reaction proceeds easily either in the presence of tertiary amines or when the substance is kept at a somewhat reduced pressure. Its chemistry resembles that of the intramolecular alkylation of bis(β-chloroethyl phosphite)[224] but takes place much more readily because the process is predetermined by steric factors owing to the rigidity of the initial system.

§ A similar final result has been noted in the case where two equivalents of electrophilic monocarbonyl compounds were used[213].

¶ The association may be accompanied by the condensation of these substances. Esters without substituents in the hydrocarbon part of the ring undergo oligomerisation particularly readily[42].

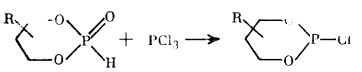
+ It has been stated that neopentylene phosphite reacts at 20–25 °C with diphenyldiazomethane to form diphenylmethyl-neopentylene phosphite, which immediately isomerises. The authors[218] attribute this observation to the anomalous acidity of the initial DOP. An alternative explanation of the experimental result is the scheme presented above.

Hydrophosphoryl DOP undergo intermolecular alkylation reactions (α-hydroxy- and α-amino-alkylation, etc.) which to a large extent correspond to the analogous reactions involving open-chain systems. We shall confine ourselves to quoting certain typical communications[225–227] and shall consider in greater detail the stereochemistry of these reactions. Soviet workers[228] were the first to show that the α-hydroxyalkylation takes place stereoselectively. Later Mosbo and Berkade supplemented this finding by data concerning the characteristics of the reaction in the presence of acids[226]. Finally, it has been shown quite recently[229] on the basis of the structure of the substances obtained that the reactions take place with retention of the configuration of the phosphorus centre. This conclusion leads to the possibility of the stereospecific synthesis of complex phosphorinanes. The kinetics of the reaction of isomeric forms of phosphorinanes with various carbonyl compounds have also been investigated and the dependence of the reaction rate on the configuration at the phosphorus atom in the initial substance has been established. This dependence is not constant for all aldehydes and ketones[229].

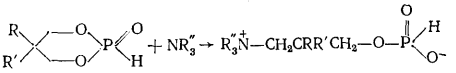
Like other acyclic analogues, hydrophosphoryl and hydrothiophosphoryl DOP can be modified oxidatively by the Todd–Atherton method as well as other procedures[5,12,110,133,230–234]. However, rigorous stereochemical features are characteristic of these substances. Thus they react stereoselectively with retention of the configuration at the phosphorus atom[117,228,235]. The problem has been discussed in greatest detail in a study[229] where both a difference between the reactivities of the geometrical isomeric forms of phosphites was demonstrated and the possible causes of the steric hindrance in the synthesis were analysed.

The report of the addition of sulphur to 1,3-alkylene phosphites[236], which takes place more readily than the corresponding reaction with dialkyl phosphites, is of undoubted interest.

Yet another valuable chemical feature of hydrophosphoryl DOP must be pointed out. It is known that, on reaction with phosphorus trichloride, dialkyl phosphites give rise to Menshutkin acid chlorides. In contrast to this, six-membered alkylene phosphites react with phosphorus trichloride retaining the fundamental molecular skeleton[237]:



Hydrophosphoryl DOP can also react with the opening of the six-membered phosphite ring. Thus, on reaction with tertiary amines, they give rise to betaines[238]:



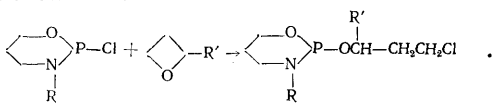
We may note that this alkylation proceeds under more severe conditions than the interaction of dialkyl phosphites with amines.

Among other reactions accompanied by a change in the six-membered ring, we shall mention cyclo-oligomerisation[42]. The presence of substituents in the hydrocarbon part of the ring prevents this process.

(b) 1,3,2-Oxaphosphorinanes

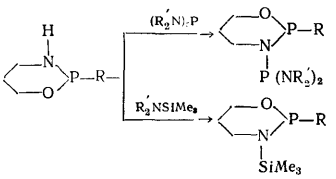
OAP have been less thoroughly investigated, but certain reactions of these compounds, which may be of interest to many specialists in the chemistry of organophosphorus compounds, have been achieved.

We shall consider initially the exchange of exocyclic substituents at the phosphorus atom. On reaction with secondary amines[57], carboxylic acid salts[60], tributyltin hydride[64], and water[239], 2-chloro-OAP exchange the chlorine atom for the corresponding groups in the usual way. The reaction with an equimolar amount of alcohol also takes place analogously[57,60,61,71,240]. We may note that the use of an excess of alcohol is inadmissible owing to the possibility of ring opening[62]. 2-Chloro-OAP are converted into esters also on treatment with oxetans[240]:



2-Amino-OAP can be made to exchange the amino-group for the hydroxy-group[239] or an alkoxy-group[57] by standard methods. In the reaction with 2-aminophenols the substitution is accompanied by addition[63].

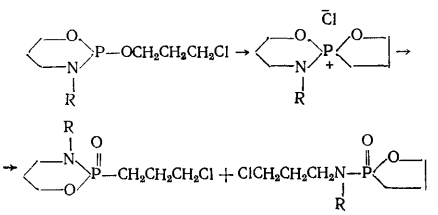
It has been shown that OAP with the endocyclic fragment $-NH-P\lessdot$ can be effectively phosphorylated[241] and silylated[70] at the nitrogen atom using mild reagents:



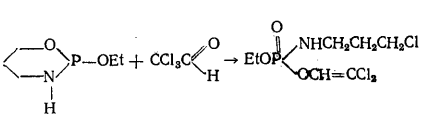
The ease of phosphorylation depends greatly on the chemical nature of the phosphoramide: the presence of electron-accepting groups at the phosphorus atom hinders the process, while the presence of electron-donating groups facilitates it[241].

OAP form complexes with transition metals, for example platinum, which are of interest for oncology[59]. OAP are oxidised[72,242] and sulphurised[67] in the usual way. The combination of the oxidation of glycerol-containing OAP with subsequent ring opening leads to a novel method of synthesis of phospholipids important for membranology[72].

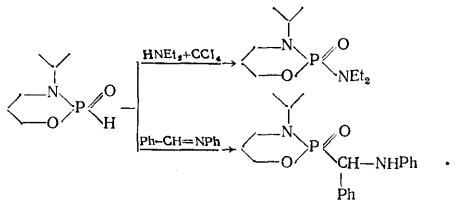
The alkylation of OAP and similar reactions have been little investigated. The intramolecular Arbuzov interaction of γ-chloroalkyl ethers of this series has been reported[240]:



The possibility of two pathways leading to the cleavage of the phosphoester bonds in the quasi-phosphonium intermediate was demonstrated in the above study. In another communication[69], devoted to the employment of the Perkow reaction for a series of OAP, only one version of the degradative stage is mentioned, which appears less probable:



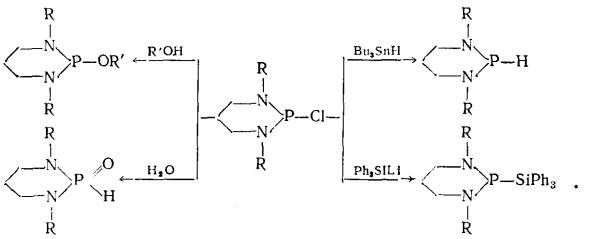
Hydrophosphoryl OAP enter into the usual oxidative phosphorylation and aminoalkylation reactions[239]:



(d) 1, 3, 2-Diazaphosphorinanes

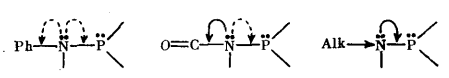
The reactions of DAP, like those of OAP, have still been little investigated, but the number of studies in this field is increasing and the scientific importance of the results obtained is growing.

A series of studies have been devoted to the substitution of the exocyclic groups at the phosphorus atom. On interaction with alcohols in the presence of bases, 2-chloro-DAP of different types give rise to ester-amides[73,75–78,81], the reaction with carboxylic acid salts produces mixed anhydrides[76,77], the reaction with tributyltin hydride affords cyclic amides of hypophosphorous acid[79,110,243], the reaction with triphenylsilyllithium leads to the formation of phosphoramidosilicides[134], and the reaction with water produces the corresponding hydrophosphoryl compounds[81,82,243]:

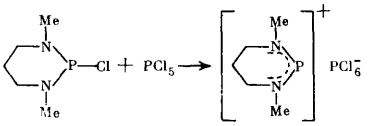


The reaction with secondary amines, which in the case of other DHP always leads to the usual results, proved to be more complex. 2-Chloro-1,3-diphenyl-DAP [78] and 2-chloro-1,3-dimethyl-4-oxo-DAP [81] react with secondary amines to give high yields of the full cyclic amides of phosphorous acid. On the other hand, 1,3-dialkyl-2-chloro-DAP behave differently in this reaction[75–77,141]. Thus the phosphorylation of aziridine and dimethylamine involves the expected nucleophilic substitution but the phosphorylation of diethylamine, which is only a little more basic, was unsuccessful. Furthermore, the attempt to synthesise the required cyclic triamide by another acid chloride method yielded an entirely unexpected result[76,77]#.

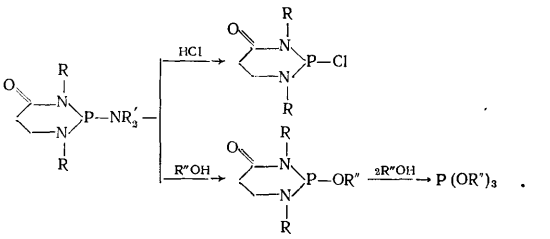
We believe that the observed difference in the phosphorylation reaction is associated with the different basicities of the expected reaction products. *N,N'*-Diphenyl derivatives and particularly compounds containing the carbonyl group are much weaker bases than the *N,N'*-dialkyl derivatives:



Compounds of the latter type therefore manifest relatively more basic properties than triethylamine and accept hydrogen chloride with the cleavage of the exocyclic P–N bond and the formation of 2-chloro-DAP. If this view is correct, then we may conclude that in the diazaphosphorinane ring there is a more pronounced electron-donating effect on the phosphorus atom than in the open-chain phosphorus tetraalkyldiamide systems. This hypothesis is confirmed to some extent by the results of a mass spectrometric study of 2-chloro-DAP and data for their interaction with phosphorus pentachloride[244]:

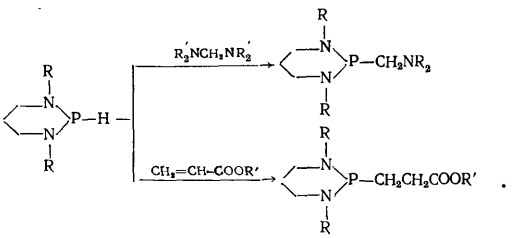


2-Amino-DAP have also been used in other substitution reactions, for example[78,81]:



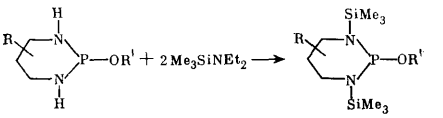
We may note that the reagents used must be measured in rigorously specified amounts, since degradation of endocyclic phosphoramide linkages is also observed in the presence of their excess.

Substitution reactions and similar processes have been described for 2-hydro-DAP:[245]



These reactions are of great interest for the synthesis of complex DAP and are apparently promising for synthetic purposes.

In conclusion of the consideration of the substitution reactions, we may point out the silylation of 1,3-dihydro-DAP at the nitrogen atom[84]:

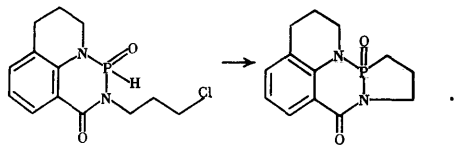


DAP tends to enter into reactions involving an increase of the valence of phosphorus: oxidation[75,77], sulphurisation[77,78], and quaternisation[244]. Unfortunately the complex-formation reactions of DAP have not yet been investigated, which impoverishes the field of the chemistry of transition metal complexes of organophosphorus ligands.

Hydrophosphoryl DAP have been relatively widely investigated. The simplest of these compounds have been made to undergo the Todd–Atherton oxidative phosphorylation[77,81,243] and aminoalkylation[77,81]. Novel possibilities for the Michaelis–Becker alkylation (including intramolecular alkylation) of

The required triamides are obtained successfully by non-acid chloride methods[77].

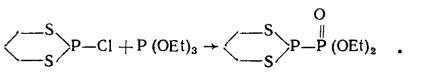
bicyclic and tricyclic DAP with formation of fairly complex systems have been recently demonstrated[83]:



(e) 1, 3, 2-Dithiaphosphorinane

DTP have been studied less thoroughly than other DHP, which, however, does not imply less chemical importance to these compounds.

Substitution reactions at the phosphorus atom have been studied mainly in relation to 2-chloro-DTP. Satisfactory results have been noted for the interactions with alcohols[86,87§], amines[87,246], mercaptans[88], and water[247]. The Arbuzov and Michaelis–Becker reactions have been carried out[248,249]:

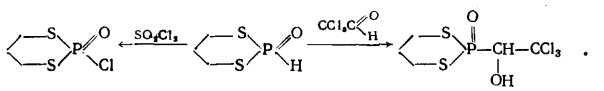


2-Amino-DTP react satisfactorily with dialkylphosphorodithioic acids to form mixed anhydrides[250]. However, they do not phosphorylate in the usual manner alcohols taken in equimolar amounts. In such cases a small amount of a secondary amine is produced and a trialkyl phosphite is obtained[87].

In contrast to other DHP, DTP are poorly oxidised and sulphurised[87,88,91,92,250]. Their complex formation reactions have not been studied.

The behaviour of hydrophosphoryl DTP merits special consideration[247]. Their physical and chemical properties differ sharply from those characteristic of other hydrophosphoryl DHP. Under the usual conditions, they are crystalline substances which are very sparingly soluble in the majority of solvents, apparently owing to their dimerisation due to their enhanced acidity.

It has been possible to achieve the chlorination and certain other reactions of these unusual hydrophosphoryl compounds, for example[247]:

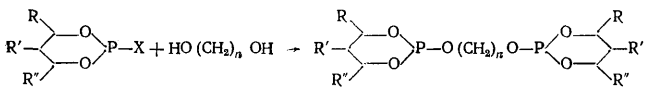


III. POLYCYCLIC DIHETEROPHOSPHORINANES

In terms of structural features, all the polycyclic DHP can be divided into three independent classes: systems with isolated rings, spirans, and condensed polycycles. Chemically, these classes are different from one another. In terms of their fundamental features, the first two resemble the monocyclic DHP and we shall therefore describe the problems of the chemistry of these substances only briefly. On the other hand, condensed polycycles are unusual systems and their synthesis and chemical properties are therefore analysed in detail in the present review.

1. Polydiheterophosphorinanes with Isolated Rings

This class of compounds has been studied only in relation to dioxaphosphorinanes. The six-membered cyclic diphosphites are of interest if only because they are more stable than their acyclic analogues. Alkylenebis-DOP have been obtained by the phosphorylation of diols with 1,3-alkylene phosphorochloridites[251], 1,3-alkylene, acyl phosphites[252], 1,3-alkylene phosphoramidites[253], or fluoroethyl phosphites[150]:



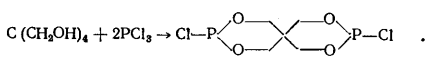
Together with the usual glycols, dihydric phenols[253] as well as systems with functional groups of substituents, for example dianhydrosorbitol[251], have been introduced into the reaction.

Among the phosphorylating agents enumerated above, amides are experimentally most convenient. These reagents have been used in the phosphorylation of novolac resins[254] and cellulose[255]. For this reason, high-molecular-weight poly-DOP have been obtained. The reactivities of di- and poly-DOP are very similar to those of the usual monocyclic compounds. They are readily oxidised and readily combine with sulphur[251,255] and are also alkylated via the Arbuzov and Perkow reactions[255].

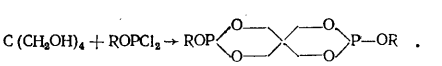
2. Spiran Bisdiheterophosphorinanes

Hitherto only dioxaphosphorinane examples of the above class of compounds have been described in the literature. Despite their structural limitations, the number of relevant studies has been fairly large. This is due to the practical importance of the spiran bis-DOP, among which polymer stabilisers[256–260] and modifiers[261], plasticisers and oils[262], antipyrenes[111], and pesticides[263] have been found.

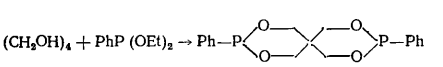
The synthesis of spiran bis-DOP is based on the employment of pentaerythritol. This readily available tetrol was made to react with phosphorus trichloride[264,265]:



Unfortunately in the published methods only a very brief description of the preparative aspect of the experiments is given and apparently they make it possible to obtain only an acid dichloride which is not altogether pure. The phosphorylation of pentaerythritol by Menshutkin acid chlorides has been described in the literature; in this case a tertiary amine must be used to bind hydrogen chloride[266]:



The second method of synthesis of a spirodiphosphite system involves the transesterification of neutral esters (usually triphenyl phosphite) by pentaerythritol for a molecular reactant ratio of 2 : 1.[18,256,257,266] Diethyl phenylphosphonite reacts similarly with pentaerythritol[37]:



The steric organisation of spiro-di-DOP has begun to be studied in a series of laboratories. By measuring the dipole moment and Kerr constants[37,267,268], NMR experiments[18],

§ The reaction with t-butyl alcohol yields a hydrophosphoryl compound and isobutene[87].

and X-ray diffraction[269], it has been shown that the molecules of these compounds contain two rings in the chair conformations, relative to which the alkoxy-group is in the axial position and the amino-group is in the equatorial position.

As regards chemical reactions, the chloride of pentaerythritol-diphosphorous acid has been studied in greatest detail. On treatment with alcohols[256,266], mercaptans[265], epoxides[211], sodium isocyanate[270], and amines[266], this compound exchanges the chlorine atom for the corresponding nucleophilic groups. The reaction with formic acid[138] or t-butyl alcohol[271] results in the formation of a bishydrophosphoryl compound, while the corresponding bisthiohydrophosphoryl compound has been synthesised by the sulphydrolysis of the corresponding acid dichloride[272].

The neutral phosphite spiro-bis-DOP and certain related compounds have been investigated in oxidation[266], sulphurisation[266,270], and Arbuzov alkylation[262,266] reactions. The last reaction has been recently proposed for the vulcanisation of fluororubbers[261].

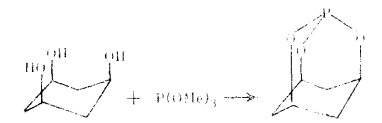
3. Condensed Polydiheterophosphorinanes

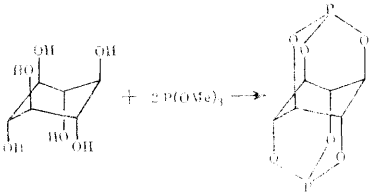
A large number of condensed poly-DHP, containing different as well as the identical structural elements, have been investigated at the present time. They can be usefully divided into four groups: 1-phospha-2,8,9-trioxa-adamantanes, 1-phospha-2,6,7-triheterobicyclo[2.2.2]octanes, and 1-phospha-2,7,8-heterobicyclo[3.2.1]octanes; the fourth group formally combines other systems which have so far been little investigated.

(a) 1-Phospha-2, 8, 9-trioxa-adamantanes

Two compounds of this group are known at the present time; phloroglucitol phosphite and scyllitol diphosphite. The molecules of these substances constitute systems bounded by dioxaphosphorinane rings in the chair conformation. This factor is responsible for the high stability of these substances and a number of their other features[273,274].

The transesterification method has been proposed to synthesise phloroglucitol phosphite and scyllitol diphosphite:





In the former case the yield is 93%[275] and in the latter only several per cent[276]. The low yield of scyllitol diphosphite is apparently due to the poor compatibility of the reactants in the phosphorylation reaction.

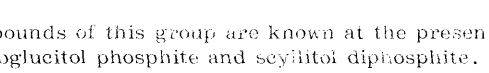
The chemical properties of the esters considered have been little investigated. It has been shown that phloroglucitol phosphite is protonated in the gas phase[154], forms complexes with palladium, platinum, nickel, copper, and silver[277], undergoes the Arbuzov reaction (it is possible to isolate the intermediate quasi-phosphonium compound),[275] and is oxidised by benzoyl peroxide to the corresponding phosphate[278]. The reaction of this phosphite with ozone has also been studied[274]. Finally, the hydrolysis of 1-phospha-2,8,9-trioxa-adamantane, consisting in the cleavage of one of the ester linkages with formation of a bicyclic hydrophosphoryl compound which forms metal complexes activating the phosphorus centre in nucleophilic reactions, has been considered in the literature[272].

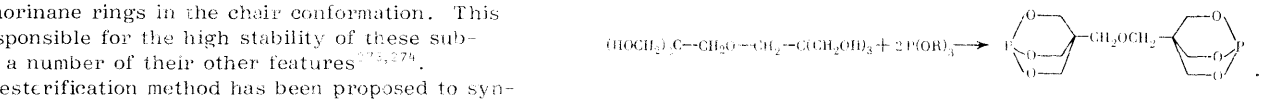
(b) 1-Phospha-2, 6, 7-triheterobicyclo[2. 2. 2]octanes

This is the most numerous and most thoroughly investigated group of compounds among all the condensed poly-DHP. It includes phosphite, phosphorothioite, and phosphoramidite systems, which have a number of characteristic features. Unfortunately the extent to which the above types of bicyclic compounds have been studied are different and so far it is difficult to achieve a thorough comparison of their properties.

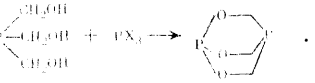
1-Phospha-2,6,7-triozabicyclo[2.2.2]octanes have been synthesised by the phosphorylation of 1,1,1-tris(hydroxymethyl)alkanes and related compounds. Phosphorus trichloride[279,280], the simplest neutral phosphites[281–283], phosphorous acid triamides[284], and acyl phosphites[252] have been used as phosphorylating agents. The simplicity of the methods of synthesis of these compounds and also the ready availability of the initial triols explain the interest of chemical engineers in 1-phospha-2,6,7-trioxabicyclo[2.2.2]octanes, particularly in the possibility of using them as stabilisers for different materials[281].

Pentaerythritol[266,285] and bispentaerythritol[285] are phosphorylated analogously, forming skeletal systems:

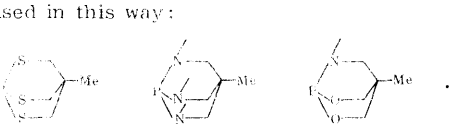




The above reactions have been extended in recent years to the phosphorylation of tris(hydroxymethyl)phosphine, which yielded the phosphinophosphite 1,4-diphospha-2,6,7-trioxabicyclo[2.2.2]octane[286]:



In addition, similar condensations have been achieved with tris(mercaptomethyl)ethane[287], tris(methylaminomethyl)ethane[183,288,289], and bis(hydroxymethyl)methylaminomethylethane[289]. Bicyclic phosphorinanes containing sulphur and nitrogen have been synthesised in this way:



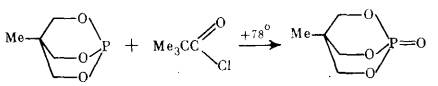
Finally, 2,3,5,6,7,8-hexazabicyclo[2.2.2]octane, which is based on an inorganic skeleton, has been obtained from 1,2-dimethylhydrazine[288].

Structurally, phosphatriheterobicyclo-octanes are in many respects analogous to the phosphatrioxa-adamantanes examined above—in each individual instance the bulky molecules of the substances are bounded by 1,3,2-diheterophosphorinane

rings, which differ from one another. Thus the bonds are significantly eclipsed in phosphatriheterobicyclo-octanes, which results in different mutual orientations of the bonds of the P–O–C–H vicinal system in their molecules[273]. The spectroscopic properties of the complexes of the above compounds have been compared[273]. We shall now consider the chemical behaviour of 1-phospha-2,6,7-triheterobicyclo[2.2.2]octanes. The corresponding 2,6,7-trioxa-derivatives have been studied in greatest detail. They are appreciably weaker based than the monocyclic DOP and phosphatrioxa-adamantane. This conclusion is based on the study of the ionisation potentials by photoelectron spectroscopy[97,99,290], the proton affinities in the gas phase (ion–cyclotron resonance)[154], the stability of the complexes with phenol[291], and the spectroscopic properties of protonation products[156,158,292] and the borate[155] and nickel[160] complexes. All these data indicate a relatively pronounced s character of the unshared electron pair of the phosphorus atom in 1-phospha-2,6,7-trioxabicyclo[2.2.2]-octanes. Nevertheless these phosphites form complexes readily with many metals: copper and silver[277,293], molybdenum[164], manganese[294], rhenium[295], cobalt[166,167,296,297], nickel[165,296,298], iron[296,299,300], and platinum and palladium[277, 301].

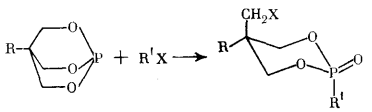
Some of the complexes enumerated above are of particular importance as stabilisers of olefins[164] or catalysts of the isomerisation and oligomerisation of unsaturated compounds[165, 302–304].

1-Phospha-2,6,7-trioxabicyclo[2.2.2]octanes are oxidised in the usual way to phosphates[266,278,279,305]. Several new observations have been made for this reaction, which has been thoroughly investigated in a series of neutral phosphites: it has been noted that hydrogen peroxide[279] and pivaloyl chloride[306] can be used as oxidants:

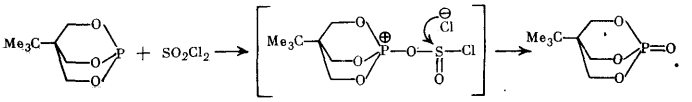


It has been established that metriol and etriol phosphites react with ozone to form stable ozonides, which decompose on heating with the corresponding bicyclic phosphates and singlet oxygen[274,305]. It was concluded that such ozonides are likely to be of preparative value[305]. Sulphurisation[266,307, 308], selenisation[308], and imination[286] have been studied together with oxidation.

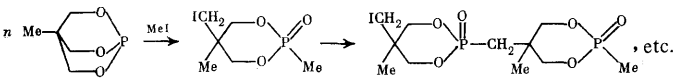
The above neutral phosphites exhibit stereoselectivity in alkylation by the Arbuzov reaction[275]:



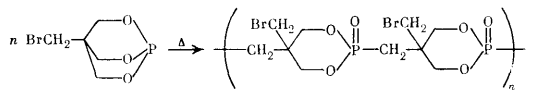
The reactions with sulphenyl chlorides[309], chloramines[309,310], bromine[172], chlorine, and sulphuryl chloride[172,309,310] proceed analogously. In the last case the possibility of a different reaction pathway was noted when a bicyclic phosphite with a tertiary butyl group in the C(4) position was used. This bulky group prevents the traditional attack by the anion on the key carbon atom and its attack is therefore directed to the sulphoxy-group with the ultimate formation of a neutral phosphite, i.e. oxidation takes place[311]:



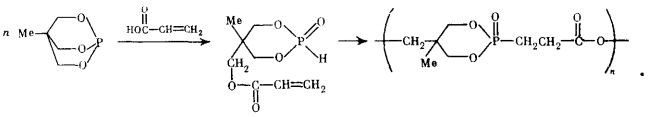
The Arbuzov and related reactions have been suggested for the synthesis of non-combustible phosphorus-containing polymers. Thus the reaction of metriol phosphite with a catalytic amount of methyl iodide results in the formation of a polyphosphonate[312]:



Another polyphosphonate has been obtained in the autoalkylation of bromometriol phosphite[280]:



Pentaerythritol phosphite polymerises similarly and the resulting polyphosphonate hydrolyses to β,β,β-tris(hydroxymethyl)ethylphosphonic acid[313]. The copolymerisation of metriol phosphite with acrylic acid is of interest[314]:



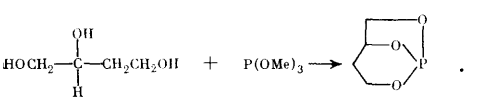
Much attention has been devoted in the literature to the hydrolysis of 1-phospha-2,6,7-trioxabicyclo[2.2.2]octanes and it has been shown that these substances are more resistant to hydrolysis and acidolysis than the usual neutral phosphites[41]. However, it has been possible to achieve the hydrolysis of metriol phosphite[172] and pentaerythritol phosphite[315]. In the former case the isolation of the hydrolysis products involves considerable difficulties and it has therefore been suggested that the reaction mixture be subjected to complete silylation with formation of two silyl phosphites[172]. Bicyclic phosphites are apparently not hydrolysed by the traditional Arbuzov mechanism, which emphasises yet again their unusual chemical behaviour.

Phosphabicyclo-octanes containing nitrogen instead of oxygen have so far been little investigated and data required for a reasoned comparison of their nature with that of the related systems are still being merely accumulated. Nevertheless we may point out that the results of an X-ray diffraction study[288], the dipole moments and NMR spectra[316], and photoelectron spectroscopic data[317] have been described. Oxidative[183], imination[318], and complex formation[319] reactions have been achieved.

(c) 1-Phospha-2, 7, 8-triheterobicyclo[3. 2. 1]octanes

The study of this series of compounds was begun with the simplest phosphite and was later extended to complex phosphorylated hydrocarbons.

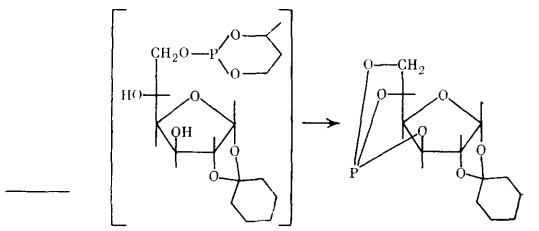
1,2,4-Trihydroxybutane and its 2,2-dimethyl derivatives are readily phosphorylated by phosphorus trichloride[320], trimethyl phosphite[320,321], or phosphorus hexaethyltriamide[284,320] with formation of 1-phospha-2,7,8-trioxabicyclo[3.2.1]-octanes, for example:



The structure and conformation of the phosphites have been investigated by ^{1}H NMR.[18,322]

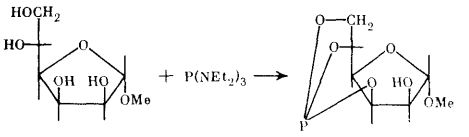
In later studies it was shown that 1,2-alkylideneglucofuranoses, whose molecules incorporate a 1,2,4-triol fragment are phosphorylated similarly to phosphorous triamides[284],

[323] and triphenyl phosphite[324]. The intramolecular transesterification



which takes place readily at 20 °C, constitutes a very novel synthesis[325]. The structure of such compounds has been demonstrated by X-ray diffraction[326], ^{1}H NMR, and ^{13}C NMR.[234]. An important outcome of this investigation was the establishment of a significant decrease of the OPO valence angles compared with the usual values.

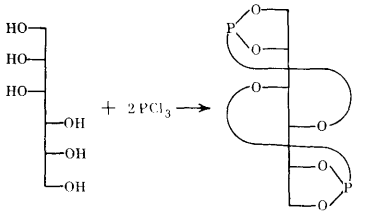
Apart from the carbohydrate triols mentioned above, a series of corresponding tetraols have been introduced into the reaction with phosphorus hexaethyltriamide and it was shown that, when the hexafuranose molecule contains hydroxyls in the C(3), C(5), and C(6) positions with the "glucose configuration", then these hydroxyls (and not the fourth hydroxyl) actually react[327]. This can be illustrated by the following synthesis:



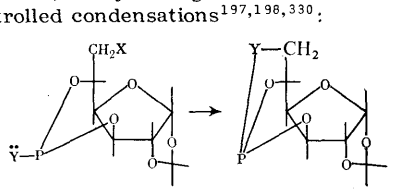
The data presented permit the conclusion that the 1-phospha-2,7,8-trioxabicyclo[3.2.1]octane system, adapted to the structure of hexafluranoses, exhibits a special stability.

6-Alkyl(aryl)amino-6-deoxy-1,2-isopropylideneglucofuranoses, 3-benzamido-3-deoxy-1,2-isopropylideneglucofuranoses[328], and the corresponding mercapto-derivatives[329, 330] are phosphorylated analogous to the sugars mentioned above. A series of 1,2-isopropylideneglucofuranose derivatives of bicyclicphosphoramidites and bicyclicphosphorothioites were synthesised.

A more complex case of phosphorylation was noted in the interaction of a hexaol (sorbitol) with phosphorus trichloride. A bisbicyclicphosphite, whose molecules contain two 1-phospha-2,7,8-trioxa[3.2.1]octane fragments, was isolated as one of the products[331]:

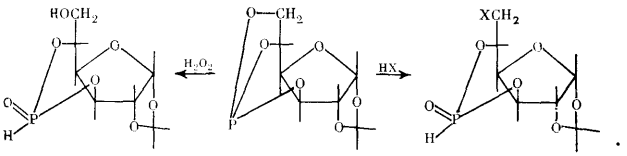


A second method of synthesising bicyclicphosphites, bicyclicphosphoramidites, and bicyclicphosphorothioites derived from 1,2-alkylideneglucofuranoses consists in stereocontrolled condensations[197,198,330]:



As regards chemical reactions, the 1-phospha-2,3,7-trioxabicyclo[3.2.1]octanes considered are characterised by important features determined by their molecular geometry, namely by the decrease of the OPO valence angles contrary to the usual behaviour. As a consequence of this decrease, the amount of *s* character of the unshared electron pair of the phosphorus atom greatly increases, which reduces in its turn the basicity and nucleophilicity of this atom. The foregoing has been confirmed experimentally by comparing the Lewis basicities[160] and by protonating in the gas and liquid phases[154,156] various neutral phosphites. It is noteworthy that 1-phospha-2,3,7-trioxabicyclo[3,2,1]octanes are not oxidised by powerful oxidants[320,323,325], do not combine with sulphur[323], and undergo the Arbuzov alkylation with much difficulty[320,324,325]. On the other hand, they are very readily halogenated by chlorine and bromine[323]. The reaction proceeds via a stage involving the formation of an adduct with a pentacovalent phosphorus atom[323]. The very mild interaction with chloramines apparently proceeds in the same manner[320].

The bicyclic phosphites considered do not react with the usual strong acids, but readily undergo ring opening on treatment with hydrogen chloride and particularly hydrogen bromide in a non-polar medium and also on treatment with hydrogen peroxide[197]:

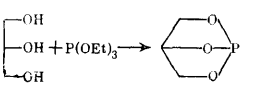


We may point out that other types of DHP are oxidised by hydrogen peroxide without ring opening, i.e. we may note instances of a significant influence of the geometry of the phosphite on its reactivity.

1,2-Alkylideneglucofuranose cyclicphosphoramidites and cyclicphosphorothioites have been little investigated. It has been shown that they readily undergo methanolysis with formation of trimethyl phosphite and the corresponding sugar [328,329,330]. The chlorination of phosphorothioites is of interest[329,330].

(d) Other Condensed Polydiheterophosphorinanes

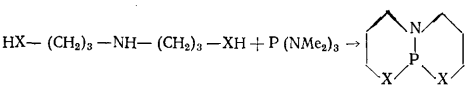
It was shown that the transition from 1-phospha-2,6,7-trioxabicyclo[2.2.2]octanes to 1-phospha-2,7,8-trioxabicyclo-[3.2.1]octanes entails a decrease of the OPO valence angles and hence a significant alteration of the chemical properties of the substances. An even greater deformation of the phosphite valence angle should occur in 1-phospha-2,6,7-trioxabicyclo[2.2.1]heptanes. The simplest compound of this series has been synthesised by phosphorylating glycerol with triethyl phosphite[332]:



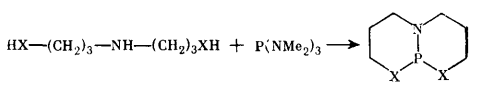
The structure of this substance has been recently confirmed by electron diffraction and it was shown that the C–O and P–O bonds in the bridged structure are longer than in the phosphorinane structure[333]. From this follows the conclusion that the bridge fragment is chemically more labile in reactions involving the opening of the cyclic system. However, this conclusion conflicts with data present in a communication[334] where the opposite opening of the bicyclic compound in the reaction with phosphorus trichloride is reported.

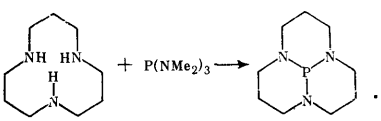
The OPO valence angles in the bicyclic glycerol phosphite are contracted compared with the angles in the bicyclic compounds examined above[333]. As a result of this, the bicyclic glycerol phosphite is a very weak nucleophile[278].

Unusual structural motifs may be manifested in the formation of condensed DHP whose molecules contain tervalent nitrogen atoms. The linear secondary aminodiols[335] and triamines[336] give rise to unusual bicyclic DHP on interaction with phosphorus triamides:



Tris(1,3-propylene)triamine is phosphorylated analogously[337]:





This reaction has been extended also to cyclic triamides[336,338].

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Summarising, we may note two principal conclusions. The first concerns the availability of the substances considered and consists in the fact that at the present time simple methods have been proposed for the synthesis of various types and classes of DHP. This has led to a significant expansion of the synthetic and structural possibilities in the chemistry of tervalent phosphorus and a firm base has been created for the solution of problems of practical importance.

The second conclusion concerns the reactivity of DHP. The high synthetic value of DHP has been demonstrated and the fundamental differences between them and the corresponding acyclic derivatives have been established. It is known that dialkyl phosphorochloridites and phosphoramidites, as well as compounds of a similar type tend to disproportionate and satisfactory results have not therefore been obtained in all the reactions. The above factor as well as the unusual conformational features of DHP facilitate more promising quantitative studies of the reactivities of these compounds compared with their acyclic analogues. DHP can apparently be more correctly employed in the study of the electronic effect of substituents linked to the tervalent phosphorus atom and of other urgent problems of physical organophosphorus chemistry.

REFERENCES

1. A.E.Arbuzov, V.M.Zoroastrova, and N.I.Rizpolozhenskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1948(2), 208.
2. H.J.Lucas, F.W.Mitchell, and C.N.Scully, J.Amer. Chem.Soc., 1950, **72**, 5491.
3. D.Purdela and R.Vilceanu, "Chemistry of Organophosphorus Compounds and Their Acid Derivatives" (Translated into Russian), Izd.Khimiya, Moscow, 1972, 630 pp.
4. A.A.Oswald, Canad.J.Chem., 1959, **37**, 1498.
5. R.S.Edmundson, Chem.Ind., 1965, 1220.
6. A.V.Bogatskii, A.A.Kolesnik, and Yu.D.Samitov, Zhur.Obshch.Khim., 1967, **37**, 1105.
7. E.E.Nifant'ev, E.E.Milliaresi, and N.G.Ruchkina, Zhur.Obshch.Khim., 1981, **51**, 1528.
8. N.A.Razumova, Zh.L.Evtikhov, and A.A.Petrov, Zhur.Obshch.Khim., 1968, **38**, 1117.
9. B.A.Arbuzov, V.E.Kataev, and R.P.Arshinova, Izv. Akad.Nauk SSSR, Ser.Khim., 1978, 2450.
10. B.Costisella and H.Gross, J.prakt.Chem., 1972, **314**, 532.
11. A.V.Bogatskii, T.D.Butova, A.A.Kolesnik, and R.A.Sabirova, Khim.Geterotsikl.Soed., 1965, 474.
12. D.A.Predvoditelev, T.G.Chukbar, T.P.Zeleneva, and E.E.Nifant'ev, Zhur.Org.Khim., 1981, **17**, 1305.
13. J.Neda and R.Vilceanu, Rev.Chim., 1980, **31**, 1053.
14. E.P.Taylor, J.Pharm.and Pharmacol., 1953, **5**, 254.
15. E.E.Nifant'ev, M.P.Koroteev, and N.M.Pugashova, Zhur.Obshch.Khim., 1981, **51**, 1900.
16. C.L.Bodkin and P.Simpson, J.Chem.Soc.B, 1971, 1136.
17. N.M.Zaripova and V.A.Naumov, Zhur.Strukt.Khim., 1973, **14**, 588.
18. D.W.White, R.D.Bertrand, G.K.McEwen, and J.G.Verkade, J.Amer.Chem.Soc., 1970, **92**, 7125.
19. E.E.Nifant'ev, A.A.Borisenko, and N.M.Sergeev, Dokl.Akad.Nauk SSSR, 1973, **208**(3), 651.
20. B.A.Arbusov, R.P.Arshinova, and S.G.Vulfson, Phosphorus, 1974, 626.
21. R.A.Sabirova and L.V.Nesterov, Zhur.Obshch.Khim., 1961, **31**, 897.
22. G.Cragg, B.Davidowitz, R.Giles, and R.Haines, Chem.Comm., 1977, 569.
23. A.Kh.Voznesenskaya and N.A.Razumova, Zhur.Obshch. Khim., 1969, **39**, 387.
24. B.A.Arbuzov, R.P.Arshinova, and T.A.Guseeva, Zhur.Obshch.Khim., 1975, **45**, 1432.
25. E.B.Nifant'ev, M.P.Koroteev, and N.M.Pugashova, Zhur.Obshch.Khim., 1977, **47**, 2633.
26. E.E.Nifant'ev, G.Ya.Legin, S.F.Sorokina, and A.A.Borisenko, Zhur.Obshch.Khim., 1979, **49**, 2627.
27. K.A.Petrov, Z.E.Nifant'ev, and I.I.Sopikova, Vysokomol.Soed., 1960, **2**, 685.
28. W.Bentrude, Han-Wan Tan, and K.Yee, J.Amer. Chem.Soc., 1975, **97**, 573.
29. T.Makaijame, T.Fujisawa, Y.Tamura, and Y.Yokota, J.Org.Chem., 1964, **29**, 2572.
30. W.Bentrude, K.Yee, R.Bertrand, and D.Grant, J.Amer.Chem.Soc., 1971, **93**, 797.
31. G.M.Cragg, B.Davidowitz, G.V.Fazakerley, and L.R.Nassimbeni, Chem.Comm., 1978, 510.
32. US P.3 205 250, 1965.
33. M.Mikolajczyk, Chem.Comm., 1969, 1221.
34. J.A.Mosbo and J.G.Verkade, J.Amer.Chem.Soc., 1973, **95**(14), 4659.
35. N.A.Makarova, E.T.Mukmenev, and B.A.Arbuzov, Izv.Akad.Nauk SSSR, Ser.Khim., 1974(8), 1849.
36. R.P.Arshinova, R.N.Gubaidullin, and E.T.Mukmenev, Zhur.Obshch.Khim., 1979, **49**, 2661.
37. R.P.Arshinova and R.N.Gubaidullin, Izv.Akad.Nauk SSSR, Ser.Khim., 1979(7), 1518.
38. E.E.Nifant'ev, A.A.Borisenko, and I.S.Nasonovskii, Dokl.Akad.Nauk SSSR, 1971, **196**, 121.
39. E.E.Nifant'ev, I.S.Nasonovskii, and A.A.Borisenko, Zhur.Obshch.Khim., 1971, **41**, 2368.
40. E.E.Nifant'ev, L.T.Elepina, A.A.Borisenko, M.P.Koroteev, and L.A.Aslanov, Phosphorus, 1979, **5**, 315.
41. I.M.Petrova, N.V.Zyk, and E.E.Nifant'ev, Vestnik Moskov.Univ., Ser.Khim., 1971(4), 433.

42. E.E.Nifant'ev and I.S.Nasonovskii, Zhur.Org.Khim., 1975, **11**, 2206.
43. W.Saenger and M.Mikolajczyk, Chem.Ber., 1873, **106**, 3519.
44. I.S.Nasonovskii, A.A.Kryuchkov, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1975, **45**, 724.
45. W.G.Bentrude and Han-Wan Tan, J.Amer.Chem.Soc., 1972, **94**, 8222.
46. D.A.Predvoditelev, T.G.Chukbar, and E.E.Nifant'ev, Zhur.Org.Khim., 1981, **17**, 1547.
47. G.S.Bajwa and W.G.Bentrude, Tetrahedron Letters, 1978, 421.
48. G.Baschung and V.Kvita, Angew.Chem., 1973, **85**, 44.
49. T.J.Bartczak, A.Christensen, R.Kinas, and W.J.Stec, Tetrahedron Letters, 1975, 3243.
50. W.J.Stec and A.Okruszek, J.Chem.Soc., Perkin I, 1975, 1828.
51. A.Cogne, A.Guimaraes, and J.Martin, Org.Magn.Res., 1974, **6**, 629.
52. E.E.Nifant'ev and A.A.Borisenko, Zhur.Obshch.Khim., 1977, **47**, 482.
53. E.E.Nifant'ev, D.A.Predvoditelev, A.P.Tuseev, M.K.Grachev, and M.A.Zolotov, Zhur.Obshch.Khim., 1980, **50**, 1702.
54. I.P.Andrianova and E.E.Nifant'ev, USSR P.483 397, 1975; Byul.Izobret., 1975, No.33, 50.
55. US P.3 175 250, 1965.
56. E.E.Nifant'ev, D.A.Predvoditelev, and M.K.Grachev, USSR P.469 710, 1973; Byul.Izobret., 1975, No.17, 69.
57. E.E.Nifant'ev, D.A.Predvoditelev, and M.K.Grachev, Zhur.Obshch.Khim., 1976, **46**, 477.
58. I.A.Nuretdinov, O.N.Nuretdinova, and I.A.Safin, Izv. Akad.Nauk SSSR, Ser.Khim., 1978(4), 950.
59. A.Okruszek and J.G.Verkade, Phosphorus, 1979, **7**, 235.
60. R.A.Sabirova and L.V.Nesterov, Zhur.Obshch.Khim., 1967, **37**, 732.
61. V.E.Shishkin, G.V.Sitanova, and Yu.M.Yukhno, Zhur.Obshch.Khim., 1977, **47**, 225.
62. M.A.Pudovik, O.S.Shulyndina, and L.K.Ivanova, Zhur.Obshch.Khim., 1974, **44**, 501.
63. A.Munoz, B.Garriques, and R.Wolf, Phosphorus, 1978, **4**, 47.
64. E.E.Nifant'ev, A.A.Borisenko, S.F.Sorokina, and M.K.Grachev, Zhur.Obshch.Khim., 1977, **47**, 2474.
65. V.V.Kurochkin, A.I.Zavalishina, S.F.Sorokina, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1979, **49**, 711.
66. N.P.Grechkin, R.R.Shagidullin, and G.S.Gubanova, Izv.Akad.Nauk SSSR, Ser.Khim., 1968(8), 1797.
67. L.I.Mizrakh, L.Yu.Polonskaya, and L.N.Kozlova, Zhur.Obshch.Khim., 1975, **45**, 1469.
68. M.A.Pudovik, S.A.Terent'eva, M.D.Medvedeva, and A.N.Pudovik, Zhur.Obshch.Khim., 1973, **43**, 679.
69. A.N.Pudovik, M.A.Pudovik, and L.K.Ivanova, Zhur. Obshch.Khim., 1971, **41**, 2180.
70. M.A.Pudovik, N.P.Morozova, M.D.Medvedeva, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1978(7), 1637.
71. M.K.Grachev, D.A.Predvoditelev, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1976, **46**, 1677.
72. E.E.Nifant'ev, D.A.Predvoditelev, and M.K.Grachev, Bioorg.Khim., 1977, **3**, 68.
73. R.O.Hutchins, B.E.Marjanoff, and J.P.Albrand, J.Amer.Chem.Soc., 1972, **94**, 9151.
74. I.V.Komlev, A.I.Zavalishina, and I.P.Chernikevich, Zhur.Obshch.Khim., 1972, **42**, 802.
75. J.A.Mosbo, Tetrahedron Letters, 1976, 4789.
76. E.E.Nifant'ev, A.I.Zavalishina, and S.F.Sorokina, Zhur.Obshch.Khim., 1977, **47**, 1960.
77. E.E.Nifant'ev, A.I.Zavalishina, A.A.Borisenko, and E.I.Smirnova, Zhur.Obshch.Khim., 1979, **49**, 64.
78. E.I.Smirnova, A.I.Zavalishina, and A.A.Borisenko, Zhur.Obshch.Khim., 1981, **51**, 1956.
79. E.E.Nifant'ev, A.A.Borisenko, A.I.Zavalishina, and S.F.Sorokina, Dokl.Akad.Nauk SSSR, 1974, **219**, 881.
80. N.V.Belov, V.V.Ilyukhin, V.R.Kalinin, and A.I.Zavalishina, Dokl.Akad.Nauk SSSR, 1981, **258**, 344.
81. E.E.Nifantiev, A.I.Zavalishina, and E.I.Smirnova, Phosphorus, 1981, **10**, 261.
82. G.M.Coppola and R.L.Mansukhani, J.Heterocyclic Chem., 1978, **15**, 1169.
83. G.M.Coppola, J.Heterocyclic Chem., 1979, **16**, 897.
84. E.E.Nifant'ev, A.I.Zavalishina, and V.V.Kurochkin, Zhur.Obshch.Khim., 1981, **51**, 474.
85. G.S.Gol'din, S.G.Fedorov, G.S.Nikitina, and N.A.Smirnova, Zhur.Obshch.Khim., 1974, **44**, 2668.
86. US P.4 140 514, 1979.
87. E.E.Nifant'ev, A.I.Zavalishina, S.F.Sorokina, and V.S.Blagoveshchenskii, Zhur.Obshch.Khim., 1974, **44**, 1694.
88. V.S.Blagoveshchenskii, E.E.Nifant'ev, and O.P.Yakovleva, Vestnik Moskov.Univ., Ser.Khim., 1975(2), 227.
89. R.O.Hutchins and B.E.Marjanoff, J.Amer.Chem.Soc., 1972, **94**, 3266.
90. K.Bergesen, Acta Chem.Scand.A, 1975, **29**, 567.
91. J.P.Dutasta, J.Martin, and J.B.Robert, J.Org. Chem., 1977, **42**, 1662.
92. B.E.Marjanoff and R.O.Hutchins, J.Org.Chem., 1977, **42**, 1022.
93. B.E.Marjanoff, A.T.McPhail, and R.O.Hutchins, J.Amer.Chem.Soc., 1981, **103**, 4432.
94. J.Martin and J.B.Robert, Org.Magn.Res., 1975, **7**, 76.
95. A.A.Borisenko, S.F.Sorokina, and A.I.Zavalishina, Zhur.Obshch.Khim., 1978, **48**, 1251.
96. R.P.Arshinova, Zhur.Obshch.Khim., 1981, **51**, 1007.
97. R.F.Hudson and J.G.Verkade, Tetrahedron Letters, 1975, 3231.
98. V.V.Zverev, Ya.Ya.Villem, and R.P.Arshinova, Dokl. Akad.Nauk SSSR, 1981, **256**, 1412.
99. R.P.Arshinova, V.V.Zverev, Ya.Ya.Villem, and N.V.Villem, Zhur.Obshch.Khim., 1981, **51**, 1757.
100. R.P.Arshinova, Dokl.Akad.Nauk SSSR, 1978, **238**, 859.
101. G.Aksnes, R.Eriksen, and K.Mellingen, Acta Chem. Scand., 1967, **21**, 1028.
102. L.L.Chang and D.Z.Denney, J.Org.Chem., 1977, **42**, 782.
103. O.N.Nuretdinova and N.P.Anoshina, Izv.Akad.Nauk SSSR, Ser.Khim., 1978(10), 2382.
104. B.A.Arbuzov, R.P.Arshinova, T.D.Sorokina, and A.B.Rezimov, Izv.Akad.Nauk SSSR, Ser.Khim., 1977(9), 2006.
105. US P.4 195 016, 1980.
106. E.E.Nifant'ev, D.A.Predvoditelev, and Kh.Kh.Alarkon, Zhur.Org.Khim., 1978, **14**, 63.
107. D.A.Predvoditelev, M.K.Grachev, M.V.Galakhov, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1979, **49**, 285.
108. E.E.Nifant'ev, D.A.Predvoditelev, M.K.Grachev, and V.A.Shin, Dokl.Akad.Nauk SSSR, 1977, **235**, 595.
109. D.Z.Denney and D.B.Denney, J.Amer.Chem.Soc., 1966, **88**, 1830.
110. E.E.Nifantiev, S.F.Sorokina, A.A.Borisenko, A.Zavalishina, and L.A.Vorobjeva, Tetrahedron, 1981, **37**, 3183.
111. Japanese P.549 178, 1979; Ref.Zhur.Khim., 1980, 8N83.

112. B.A.Arbuzov, L.Z.Nikonova, O.N.Nuretdinova, and N.P.Anoshina, Izv.Akad.Nauk SSSR, Ser.Khim., 1975(2), 473.
113. A.Okruszek and W.J.Stek, Z.Naturforsch., **30**, 430.
114. A.E.Arbuzov and V.M.Zoroastrova, Izv.Akad.Nauk SSSR, Ser.Khim., 1952(5), 789.
115. E.E.Nifant'ev, N.L.Ivanova, and D.A.Predvoditelev, Dokl.Akad.Nauk SSSR, 1976, **228**, 357.
116. V.A.Gilyarov, M.A.Tikhonova, T.M.Shcherbak, and M.I.Kabachnik, Zhur.Obshch.Khim., 1980, **50**, 1438.
117. C.L.Bodkin and P.Simpson, J.Chem.Soc., Perkin II, 1973(5), 676.
118. E.E.Nifant'ev, G.F.Bebikh, and T.P.Sakodynskaya, Zhur.Obshch.Khim., 1971, **41**, 2011.
119. E.V.Borisov, A.K.Akhlebinin, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1981, **51**, 473.
120. K.A.Petrov, E.E.Nifant'ev, and I.I.Sopikova, Dokl. Akad.Nauk SSSR, 1963, **151**, 859.
121. E.E.Nifant'ev and I.V.Fursenko, Zhur.Obshch.Khim., 1967, **37**, 1134.
122. A.N.Pudovik, G.V.Romanov, E.N.Ofitserov, and V.P.Kukhar', USSR P.771 107, 1980; Byul.Izobret., 1980, No.38, 140.
123. W.J.Stek, T.Sudol, and B.Uznanski, Chem.Comm., 1975, 467.
124. B.Uznansu and W.J.Stec, Synthesis, 1975, 735.
125. E.N.Ofitserov, T.A.Zyablikova, E.S.Batyeva, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1976(6), 1380.
126. Zh.M.Ivanova, E.A.Stukalo, N.S.Tishchishina, and G.I.Derkach, Zhur.Obshch.Khim., 1970, **40**, 1942.
127. E.E.Ishmaeva, E.N.Ofitserov, and T.A.Faskhutdinova, Zhur.Obshch.Khim., 1980, **50**, 30.
128. B.A.Arbuzov, K.V.Nikonorov, O.N.Fedorova, G.M.Vinokurova, and Z.G.Shishova, Dokl.Akad.Nauk SSSR, 1953, **93**, 817.
129. A.N.Pudovik, M.A.Pudovik, L.K.Kabardin, and T.A.Pesteva, USSR P.585 169, 1977; Byul.Izobret., 1977, No.47, 82.
130. A.Zwierzak, Canad.J.Chem., 1967, **45**, 2501.
131. D.A.Predvoditelev, D.N.Afanas'eva, Yu.B.Filippovich, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1973, **43**, 73.
132. W.Chodkiewica and D.Cuillerm, Compt.rend., Ser.C, 1979, **289**, 61.
133. W.J.Stec, B.Uznansu, and J.Michalski, Phosphorus, 1973, **2**, 239.
134. E.E.Nifant'ev, S.F.Sorokina, A.A.Borisenko, and L.A.Vorob'eva, Dokl.Akad.Nauk SSSR, 1982, **262**, 900.
135. E.E.Nifant'ev, A.I.Zavalishina, and I.V.Komlev, Zhur.Obshch.Khim., 1971, **41**, 1451.
136. N.K.Kochetkov, E.E.Nifant'ev, I.P.Gudkova, and M.P.Koroteev, Zhur.Obshch.Khim., 1970, **40**, 2199.
137. E.E.Nifant'ev and I.V.Fursenko, Zhur.Obshch.Khim., 1967, **37**, 511.
138. US P.408 605, 1978.
139. E.E.Nifant'ev, N.L.Ivanova, and A.A.Borisenko, Zhur.Obshch.Khim., 1970, **40**, 1420.
140. E.E.Nifant'ev and N.L.Ivanova, Zhur.Obshch.Khim., 1971, **41**, 2192.
141. J.A.Mosbo, Phosphorus, 1978, **4**, 273.
142. E.V.Borisov, N.L.Ivanova, and E.E.Nifant'ev, Zhur. Fiz.Khim., 1979, **53**, 2803 [Russ.J.Phys.Chem., 1979(11)].
143. A.E.Sopchik and W.G.Bentrude, Tetrahedron Letters, 1980, 4679.
144. V.P.Evdakov, V.P.Beketov, and B.I.Bryantsev, Zhur.Obshch.Khim., 1977, **47**, 1726.
145. I.P.Gudkova, I.K.Golovnikova, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1968, **38**, 1340.
146. E.E.Nifant'ev, A.I.Zavalishina, and M.R.Ter-Ovanesyan, Zhur.Obshch.Khim., 1969, **39**, 360.
147. E.E.Nifant'ev, S.A.Rumyantseva, M.P.Koroteev, K.Sisneiros, and N.K.Kochetkov, Zhur.Obshch.Khim., 1981, **51**, 2806.
148. E.E.Nifant'ev, A.M.Sokurenko, and I.V.Fursenko, Zhur.Obshch.Khim., 1968, **38**, 1909.
149. A.E.Arbuzov and V.M.Zoroastrova, Izv.Akad.Nauk SSSR, Ser.Khim., 1952(5), 779.
150. E.E.Nifant'ev and I.V.Fursenko, Zhur.Obshch.Khim., 1965, **35**, 1882.
151. A.A.Borisenko and E.E.Nifant'ev, Zhur.Obshch.Khim., 1970, **40**, 2765.
152. N.K.Bliznyuk, R.S.Klopkova, and L.D.Protasova, USSR P.578 315, 1977; Byul.Izobret., 1977, No.40, 73.
153. W.G.Bentrude, W.A.Khan, M.Murakami, and Han-Wan Tan, J.Amer.Chem.Soc., 1974, **96**, 5566.
154. R.N.Hodges, F.A.Houle, J.L.Beauchamp, R.A.Montag, and J.G.Verkade, J.Amer.Chem.Soc., 1980, **102**, 932.
155. D.W.White and J.G.Verkade, Phosphorus, 1973, **3**, 9.
156. L.J.Griend, J.G.Verkade, J.F.Pennings, and H.M.Buck, J.Amer.Chem.Soc., 1977, **99**, 2459.
157. D.W.White and J.G.Verkade, Phosphorus, 1973, **3**, 15.
158. J.G.Verkade, Phosphorus, 1976, **2**, 251.
159. M.Mikolajczyk, J.Michalski, and A.Zwierzak, Chem. Comm., 1971, 1257.
160. J.O.Albright, F.L.Tanzella, and J.G.Verkade, J.Coord. Chem., 1976, **6**, 225.
161. R.A.Jacobson, B.A.Karcher, and R.A.Montag, Phosphorus, 1981, **11**, 27.
162. B.A.Arbuzov, R.P.Arshinova, Yu.M.Mareev, and V.S.Vinogradov, Dokl.Akad.Nauk SSSR, 1973, **208**, 849.
163. J.Rodgers, D.W.White, and J.G.Verkade, J.Chem. Soc.A, 1971, 77.
164. US P.4 012 399, 1977.
165. C.L.Rix and J.G.Verkade, Coord.Chem.Revs., 1975, **16**, 129.
166. R.Weiss and J.G.Verkade, Inorg.Chem., 1979, **18**, 529.
167. K.Yasufuku, A.Hamada, K.Aoki, and H.Yamazaki, J.Amer.Chem.Soc., 1980, **102**, 4363.
168. T.S.Kukhareva, I.V.Medova, and E.E.Nifant'ev, Dokl.Akad.Nauk SSSR, 1977, **233**, 870.
169. G.M.Grishina, A.T.Teleshev, and E.E.Nifant'ev, Zhur. Obshch.Khim., 1982, **52**, 1307.
170. A.T.Teleshev, G.M.Grishina, and E.E.Nifant'ev, Zhur. Obshch.Khim., 1982, **52**, 583.
171. E.E.Nifant'ev, T.S.Kukhareva, and E.I.Klabunovskii, Dokl.Akad.Nauk SSSR, **253**, 1389.
172. R.D.Bertrand, H.J.Berwin, G.K.McEwen, and J.G.Verkade, Phosphorus, 1974, **4**, 81.
173. J.A.Mosbo and J.G.Verkade, J.Amer.Chem.Soc., 1972, **94**, 8224.
174. W.G.Bentrude and K.C.Yee, Tetrahedron Letters, 1970, 3999.
175. B.A.Arbuzov and R.P.Arshinova, Izv.Akad.Nauk SSSR, Ser.Khim., 1974(3), 665.
176. W.J.Stec, K.Lesiak, D.Mielczarek, and B.Stec, Z.Naturforsch., 1975, **30**, 710.
177. W.G.Bentrude, H.J.Hargis, and N.A.Johnson, J.Amer. Chem.Soc., 1976, **98**, 5348.
178. M.Mikolajczyk and J.Luczak, J.Org.Chem., 1978, **43**, 2132.
179. R.P.Arshinova, G.D.Sorokina, A.B.Remizov, G.E.Korolev, and B.A.Arbuzov, Izv.Akad.Nauk SSSR, Ser.Khim., 1979(10), 2242.
180. E.E.Nifantiev, S.A.Rumyantseva, M.P.Koroteev, and E.H.Abbasav, Phosp.Sulf., 1981, **12**, 27.

181. A.Nakanishi, K.Nishikida, and W.G.Bentrude, J.Amer. Chem.Soc., 1978, **100**, 6398.
182. D.B.Denney, D.Z.Denney, and S.G.Schutezbank, Phosphorus, 1980, **8**, 369.
183. R.D.Krachefsky, R.Weiss, and J.G.Verkade, Inorg. Chem., 1979, **18**, 469.
184. US P.3 180 793, 1965.
185. A.E.Sopchik and W.G.Bentrude, Tetrahedron Letters, 1981, 307.
186. M.Mikolajczyk, I.Krzywanski, and B.Liemnicka, Tetrahedron Letters, 1975, 1607.
187. W.G.Bentrude and J.H.Hargis, J.Amer.Chem.Soc., 1970, **92**, 7136.
188. N.K.Bliznyuk, Z.N.Kvasha, and G.I.Chistova, USSR P.433 156, 1974; Byul.Izobret., 1975(23), 64.
189. G.S.Bajwa and W.G.Bentrude, Tetrahedron Letters, 1980, 4683.
190. M.G.B.Drew, J.Rodgers, D.W.White, and J.G.Verkade, Chem.Comm., 1971, 227.
191. V.V.Ovchinnikov, V.M.Valitova, R.A.Cherkasov, and A.N.Pudovik, Zhur.Obshch.Khim., 1979, **49**, 2434.
192. V.A.Al'fonsov, Yu.N.Girfanova, G.U.Zamaletdinova, E.S.Batyeva, and A.N.Pudovik, Dokl.Akad.Nauk SSSR, 1980, **251**, 105.
193. F.Matheg and D.Thavard, J.Organometal.Chem., 1976, **117**, 377.
194. R.Weiss, L.Griend Vande, and J.G.Verkade, J.Org. Chem., 1979, **44**, 1860.
195. O.N.Nuretdinova and B.A.Arbuzov, Izv.Akad.Nauk SSSR, Ser.Khim., 1974(6), 1364.
196. G.Singh, J.Org.Chem., 1979, **44**, 1060.
197. M.P.Koroteev and E.E.Nifant'ev, Dokl.Akad.Nauk SSSR, 1980, **250**, 1395.
198. E.E.Nifant'ev, M.P.Koroteev, and A.V.Vasil'ev, Zhur. Obshch.Khim., 1982, **52**, 1691.
199. Z.E.Golubski and Z.Skrowaczewska, Synthesis, 1979, 21.
200. J.Finley and D.Denney, J.Amer.Chem.Soc., 1970, **92**, 362.
201. M.Mikolajczyk, J.Krzywanski, and B.Ziemnicka, J.Org. Chem., 1977, **42**, 190.
202. J.E.Brault and P.Savignac, J.Organomet.Chem., 1974, **66**, 71.
203. N.P.Grechkin, R.R.Shagidullin, and L.N.Grishina, Izv.Akad.Nauk SSSR, Ser.Khim., 1968(4), 854.
204. A.N.Pudovik, I.V.Konovalova, V.P.Kakurina, and L.A.Burnaeva, Zhur.Obshch.Khim., 1973, **43**, 553.
205. I.V.Konovalova, L.A.Burnaeva, and A.N.Pudovik, Zhur.Obshch.Khim., 1974, **44**, 261.
206. I.V.Konovalova, T.A.Faskhudtinova, and L.A.Burnaeva, Zhur.Obshch.Khim., 1979, **49**, 739.
207. I.V.Konovalova, L.A.Burnaeva, and N.K.Novikova, Zhur.Obshch.Khim., 1978, **48**, 746.
208. N.A.Razumova, Abstract of Doctoral Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1971.
209. A.Kh.Voznesenskaya and N.A.Razumora, Zhur.Obshch. Khim., 1975, **45**, 1235.
210. V.V.Ragulin, N.A.Razumova, V.I.Zakharov, and A.A.Petrov, Zhur.Obshch.Khim., **50**, 462.
211. F.Ramirez, M.Nagabmeshanam, and C.P.Smith, Tetrahedron, 1968, **24**, 1785.
212. S.Kobayashi, T.Kobayashi, and T.Saegusa, Chem. Letters, 1979, **4**, 393; Chem.inform., 1980(6), 141.
213. I.V.Konovalova, E.Kh.Ofitserova, T.V.Yudina, and A.N.Pudovik, Zhur.Obshch.Khim., 1977, **47**, 476.
214. US P.3 812 219, 1974.
215. J.P.Albrand, J.P.Dutasta, and J.B.Robert, J.Amer. Chem.Soc., 1974, **96**, 4584.
216. V.V.Ovchinnikov, V.I.Galkin, E.G.Yarkova, R.A.Cherkasov, and A.N.Pudovik, Dokl.Akad.Nauk SSSR, 1977, **235**, 118.
217. V.V.Ovchinnikov, O.A.Cherkasova, and E.G.Yarkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1978(3), 689.
218. V.V.Ovchinnikov, V.I.Galkin, R.A.Cherkasov, and A.N.Pudovik, Dokl.Akad.Nauk SSSR, 1979, **249**, 128.
219. V.V.Ovchinnikov, R.A.Cherkasov, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1980(4), 934.
220. E.I.Matrosov, E.E.Nifant'ev, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Ser.Khim., 1976(3), 530.
221. E.E.Nifant'ev, I.S.Nasonovskii, and E.I.Matrosov, Zhur.Obshch.Khim., 1969, **39**, 1891.
222. E.E.Nifant'ev and I.M.Petrova, Zhur.Obshch.Khim., 1968, **38**, 2341.
223. E.E.Nifantiev, M.P.Koroteev, S.A.Lisenko, S.A.Rumjancheva, and N.K.Koshetkov, Carbohydrate Res., 1982, **101**, 125.
224. V.G.Pesin and A.M.Khaletskii, Zhur.Obshch.Khim., 1961, **31**, 2515.
225. A.N.Pudovik and G.A.Golitsyna, Zhur.Obshch.Khim., 1964, **34**, 876.
226. J.Mosbo and J.Verkade, J.Amer.Chem.Soc., 1973, **95**, 204.
227. D.A.Predvoditelev, D.N.Afanas'eva, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1974, **44**, 1697.
228. E.E.Nifant'ev and I.S.Nasonovskii, Dokl.Akad.Nauk SSSR, 1972, **203**, 841.
229. E.E.Nifant'ev and A.A.Kryuchkov, Zhur.Obshch.Khim., 1981, **51**, 2428.
230. A.Zwierzak, Tetrahedron, 1969, **25**, 5177.
231. D.A.Predvoditelev, D.N.Afanas'eva, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1974, **44**, 748.
232. D.A.Predvoditelev, D.N.Afanas'eva, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1974, **44**, 2629.
233. N.P.Grechkin, L.N.Grishina, and I.D.Neklesova, USSR P.433 152, 1974; Byul.Izobret., 1974, No.23, 64.
234. D.A.Predvoditelev, D.N.Afanas'eva, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1976, **46**, 40.
235. W.J.Stec and M.Mikolajczyk, Tetrahedron, 1973, **29**, 535.
236. V.V.Ovchinnikov, V.I.Galkin, R.A.Cherkasov, and A.N.Pudovik, Zhur.Obshch.Khim., 1977, **47**, 290.
237. O.N.Nuretdinova and L.Z.Nikonova, Izv.Akad.Nauk SSSR, Ser.Khim., 1975(3), 694.
238. Swedish P.573 440, 1976.
239. E.E.Nifant'ev, D.A.Predvoditelev, and M.K.Grachev, Zhur.Obshch.Khim., 1974, **44**, 2779.
240. O.N.Nuretdinova and L.Z.Nikonova, Zhur.Obshch. Khim., 1980, **50**, 533.
241. M.A.Pudovik, S.A.Terent'eva, and A.N.Pudovik, Zhur.Obshch.Khim., 1975, **45**, 518.
242. M.K.Grachev, V.A.Sukhanov, and D.A.Predvoditelev, Zhur.Org.Khim., 1977, **13**, 1830.
243. E.E.Nifant'ev, A.I.Zavalishina, and S.F.Sorokina, Zhur.Obshch.Khim., 1978, **48**, 1419.
244. B.E.Marjanoff and R.O.Hutchins, J.Org.Chem., 1972, **37**, 3475.
245. E.E.Nifant'ev, A.I.Zavalishina, S.F.Sorokina, A.A.Borisenko, and L.A.Vorob'eva, Zhur.Obshch. Khim., 1976, **46**, 1184.
246. J.Martin, J.B.Robert, and C.Taieb, J.Phys.Chem., 1976, **80**, 2417.
247. E.E.Nifant'ev, A.I.Zavalishina, and S.F.Sorokina, Dokl.Akad.Nauk SSSR, 1972, **203**, 593.
248. V.S.Blagoveshchenskii, O.P.Yakovleva, and A.A.Borisenko, Dokl.Akad.Nauk SSSR, 1976, **230**, 845.

249. L.V.Ermansan, V.S.Blagoveshchenskii, and N.N.Godovikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1980(12), 2788.
250. O.P.Yakovleva, V.S.Blagoveshchenskii, and A.A.Borisenko, Izv.Akad.Nauk SSSR, 1975(9), 2060.
251. E.E.Nifant'ev, M.P.Koroteev, and S.A.Lysenko, Zhur.Obshch.Khim., 1976, **46**, 937.
252. I.V.Fursenko, G.T.Bakhvalov, and E.E.Nifant'ev, Zhur.Obshch.Khim., 1968, **38**, 2528.
253. V.I.Kodolov, N.R.Dol'nik, and E.E.Nifant'ev, USSR P.504 779, 1975; Byul.Izobret., 1976, No.8, 45.
254. S.G.Fedorov and E.E.Nifant'ev, Zhur.Prikl.Khim., 1966, **39**, 1881.
255. D.A.Predvoditelev, E.E.Nifant'ev, and Z.A.Rogovin, Cell.Chem.Technol., 1967, **1**, 179.
256. R.N.Gubaidullin, V.F.Eganov, R.P.Arshinova, and E.T.Mukmenev, Izv.Akad.Nauk SSSR, Ser.Khim., 1973(5), 1116.
257. US P.4 096 114, 1978.
258. B.P.1 505 049, 1978.
259. Japanese P.5 387 381, 1978; Ref.Zhur.Khim., 1979, 10N106.
260. US P.4 180 498, 1979.
261. L.P.Karasev, V.P.Bukalov, A.M.Ogrel', A.P.Tuseev, and E.E.Nifant'ev, Vysokomol.Soed., 1970, **22A**, 1404.
262. US P.3 141 032, 1964.
263. US P.3 355 523, 1967.
264. US P.3 192 243, 1965.
265. N.K.Bliznyuk, Z.M.Kvasha, and G.A.Madzhara, USSR P.374 324, 1973; Byul.Izobret., 1973, No.15, 52.
266. E.T.Mukmenev and G.I.Kamai, Dokl.Akad.Nauk SSSR, 1963, **153**, 605.
267. B.A.Arbuzov, R.P.Arshinova, S.G.Vul'fson, and E.T.Mukmenev, Izv.Akad.Nauk SSSR, Ser.Khim., 1973(11), 2426.
268. B.A.Arbuzov, R.P.Arshinova, and E.T.Mukmenev, Izv.Akad.Nauk SSSR, 1974(11), 2485.
269. L.E.Carpenter, R.A.Jacobson, and J.G.Verkade, Phosphorus, 1979, **6**, 475.
270. P.M.Pivawer, A.D.Bliss, and R.Rätz, J.Heterocyclic Chem., 1967, **4**, 599.
271. N.K.Bliznyuk, L.D.Protasova, and R.S.Klopkova, USSR P.476 267, 1976; Byul.Izobret., 1975, No.25, 74.
272. R.Rätz and A.D.Bliss, J.Heterocyclic Chem., 1966, **3**, 14.
273. R.D.Bertrand, R.D.Compton, and J.G.Verkade, J.Amer.Chem.Soc., 1970, **92**, 2702.
274. A.P.Schaap, K.Kees, and A.L.Thayer, J.Org.Chem., 1975, **40**, 1185.
275. J.G.Verkade, T.J.Huttemann, M.K.Fung, and R.W.Ring, Inorg.Chem., 1965, **4**, 83.
276. O.Vogl, B.C.Anderson, and A.M.Simons, J.Org. Chem., 1969, **34**, 204.
277. R.Keiter and J.G.Verkade, Inorg.Chem., 1970, **9**, 404.
278. D.B.Denney, D.Z.Denney, S.Schutezbank, and S.L.Varga, Phosphorus, 1973, **3**, 99.
279. J.G.Verkade and L.T.Reynolds, J.Org.Chem., 1960, **25**, 663.
280. French P.2 387 239, 1978.
281. US P.3 155 703, 1964.
282. US P.3 845 168, 1974.
283. N.K.Ovchinnikova, M.K.Berzilina, and E.E.Nifant'ev, Zhur.Org.Khim., 1975, **11**, 1839.
284. E.E.Nifant'ev and I.M.Petrova, Zhur.Obshch.Khim., 1970, **40**, 2196.
285. US P.3 310 609, 1967.
286. E.S.Kozlov, Zhur.Obshch.Khim., 1980, **50**, 2425.
287. E.I.Matrosov, G.M.Petov, and M.I.Kabachnik, Zhur. Strukt.Khim., 1974, **15**, 250.
288. J.C.Clardy, R.L.Kolpa, and J.G.Verkade, Phosphorus, 1974, **4**, 133.
289. G.H.Cooper, I.W.Lawston, R.L.Rickard, and T.D.Inch, J.Medicin.Chem., 1978, **13**, 207.
290. L.W.Yarbrough and M.B.Hall, Chem.Comm., 1978, 161.
291. L.J.Griend, D.W.White, and J.G.Verkade, Phosphorus, 1973, **3**, 5.
292. L.J.Griend and J.G.Verkade, Phosphorus, 1973, **3**, 13.
293. J.G.Verkade and T.S.Piper, Inorg.Chem., 1962, **1**, 453.
294. M.Green, R.I.Hancock, and D.C.Wood, J.Chem.Soc.A, 1968, 2718.
295. N.P.Johnson and M.E.Pickford, J.Chem.Soc.A, Dalton Trans., 1976, 950.
296. C.A.Tolman, L.W.Yarbrough, and J.G.Verkade, Inorg.Chem., 1977, **16**, 479.
297. J.O.Albright, J.C.Clardy, and J.G.Verkade, Inorg. Chem., 1977, **16**, 1575.
298. J.H.Meiners, C.J.Ris, J.C.Clardy, and J.G.Verkade, Inorg.Chem., 1975, **14**, 705.
299. S.Aime, G.Gervazio, and P.Stanghellini, Inorg. Chem.Acta, 1980, **40**, 131.
300. M.Rosenblum and P.Waterman, J.Organomet.Chem., 1981, **206**, 197.
301. J.M.Jenkins and J.G.Verkade, Inorg.Chem., 1967, **6**, 2250.
302. Japanese P.539 745, 1978; Ref.Zhur.Khim., 1979, 3N128.
303. Japanese P.5 331 144, 1978; Ref.Zhur.Khim., 1979, 17N99.
304. Japanese P.5 331 145, 1978; Ref.Zhur.Khim., 1979, 21N134.
305. M.E.Brennan, Chem.Comm., 1970, 956.
306. D.B.Denney and J.Hanifin, Tetrahedron Letters, 1963, 2177.
307. US P.3 038 001, 1962.
308. C.Wen-Hsuan, J.Org.Chem., 1964, **29**, 3711.
309. W.S.Wadsworth, S.Larsen, and H.L.Horten, J.Org. Chem., **38**, 256.
310. W.S.Wadsworth and H.L.Horten, J.Amer.Chem.Soc., 1970, **92**, 3785.
311. R.S.Edmundson and C.I.Forth, Phosphorus, 1980, **8**, 315.
312. Japanese P.6273, 1967; Ref.Zhur.Khim., 1969, 11S304.
313. US P.4 089 893, 1978.
314. US P.3 755 270, 1973.
315. French P.2 380 287, 1978.
316. J.A.Mosbo, J.T.Pipal, and J.G.Verkade, J.Magn. Res., 1972, **8**, 243.
317. A.H.Cowley, D.W.Goodman, N.A.Kuebler, M.Sanchez, and J.G.Verkade, Inorg.Chem., 1977, **16**, 854.
318. R.D.Kroshefsky and J.G.Verkade, Inorg.Chem., 1975, **14**, 3090.
319. R.D.Kroshefsky, J.G.Verkade, and J.R.Pipal, Phosphorus, 1979, **6**, 377.
320. R.S.Edmundson and E.W.Mitchell, J.Chem.Soc.C, 1971, 3179.
321. R.S.Edmundson and E.W.Mitchell, Chem.Comm., 1966, 482.
322. M.Kainosho and A.Nakamura, Tetrahedron, 1969, **25**, 4071.
323. N.K.Kotchetkov, E.E.Nifantiev, M.P.Koroteev, Z.K.Zhane, and A.A.Borisenko, Carb.Res., 1976, **47**, 221.
324. S.Tuokava, K.See, H.Yashida, and T.Ogata, Bull. Chem.Soc.Jap., 1971, **41**, 143.
325. Z.G.Nifant'ev, I.P.Gudkova, and Ting-Tang Ch'ang, Zhur.Obshch.Khim., 1972, **42**, 506.

326. L.A.Aslanov, S.S.Sotman, and V.B.Rybakov, Zhur. Strukt.Khim., 1979, **20**, 1125.
327. E.E.Nifantiev, M.P.Koroteev, Z.K.Zhane, A.A.Borisenko, and N.K.Kochetkov, Tetrahedron Letters, 1977, 4125.
328. S.A.Rumyantseva, M.P.Koroteev, and S.A.Lysenko, Zhur.Obshch.Khim., 1982, **52**, 418.
329. E.E.Nifant'ev, M.P.Koroteev, and S.A.Ermishkina, Zhur.Obshch.Khim., 1978, **48**, 1904.
330. E.E.Nifant'ev, M.P.Koroteev, S.A.Lysenko, and N.K.Kochetkov, Izv.Akad.Nauk SSSR, Ser.Khim., 1980(6), 1441.
331. L.I.Gurarii, A.Kh.Plyamovatyi, R.C.Arshinova, Z.T.Mukmenev, and B.A.Arbuzov, Dokl.Akad.Nauk SSSR, 1977, **232**, 1304.
332. D.B.Denney and S.L.Varga, Phosphorus, 1973, **2**, 245.
333. S.A.Shaidulin, V.A.Naumov, and N.A.Makarova, Zhur.Strukt.Khim., 1978, **19**, 942.
334. N.A.Makarova, E.T.Mukmenev, and B.A.Arbuzov, Dokl.Akad.Nauk SSSR, 1973, **213**, 1331.
335. D.B.Denney, D.Z.Denney, P.J.Hammond, and C.Haung, J.Amer.Chem.Soc., 1980, **102**, 5073.
336. D.B.Denney, D.Z.Denney, and P.J.Hammond, J.Amer. Chem.Soc., 1981, **103**, 2054.
337. T.J.Atkins, Tetrahedron Letters, 1978, 4331.
338. T.J.Atkins and J.E.Richman, Tetrahedron Letters, 1978, 5149.

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