CHEMISTRY OF OXAPHOSPHORANES (REVIEW)

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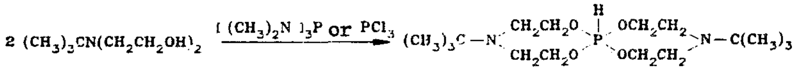
The research of recent years on the synthesis of new types of phosphoranes with P–O bonds (oxaphosphoranes) is examined. Particular attention is directed to the problems of the thermodynamic stabilities of oxaphosphoranes and the homolytic reactions of hydrooxaphosphoranes.

The interest in organophosphorus compounds with a pentacoordinated phosphorus atom is associated with the solution of problems such as pseudorotation in the trigonal biopyramid, the structures of the intermediates in the Arbuzov rearrangement, nucleophilic substitution of tri- and tetracoordinated phosphorus atoms, the ratios of the thermodynamic stabilities of organophosphorus compounds with different coordinations, etc.

Oxaphosphoranes occupy a special place in the chemistry of phosphoranes because of their accessibility, their relative stabilities, and the promising character of their use as effective stabilizers for a number of polymeric materials. In a previously published review [1] principal attention was directed to the heterolytic reactions of oxaphosphoranes; at the same time, the volume of information regarding new methods of synthesis of these compounds, the synthesis of structures with fundamentally new properties, and the homolytic transformations of hydrospirophosphoranes has increased sharply in the last several years. For example, the homolytic reactions of hydrospirooxaphosphoranes make it possible to synthesize compounds of the 1,2,3-dioxaphospholane series that play an important role in biochemical transformations and, in particular, are encountered as products of the enzymatic hydrolysis of ribonucleic acids and are also intermediates in the alkaline hydrolysis of lecithins, nephalins, etc. [2] and find extensive practical application as pesticides and additives that impart thermal stability to polymers, etc. [3-10].

METHODS OF SYNTHESIS

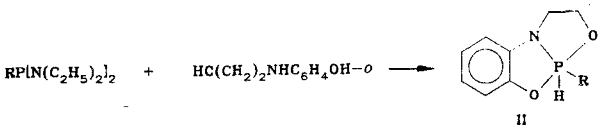
The reaction of the corresponding phosphorus compounds that contain P–Cl and P–N bonds with OH or NH acids is the traditional method for the synthesis of hydrotetraoxaphosphoranes. This method continues to be widely used to obtain previously undescribed hydrooxaphosphoranes and, which is more interesting, to obtain new types of compounds of this class. Thus the first representatives of tetraoxaphosphoranes I with a phosphorus atom included in an eight-membered ring were obtained in [11]:



$$2\,(CH_3)_3CN(CH_2CH_2OH)_2 \xrightarrow{[(CH_3)_2N]_3P \text{ or } PCl_3} (CH_3)_3C{-}N\begin{matrix} CH_2CH_2O \\ CH_2CH_2O \end{matrix}\overset{H}{P}\begin{matrix} OCH_2CH_2 \\ OCH_2CH_2 \end{matrix}N{-}C(CH_3)_3$$

I

The same reaction proved to be applicable for obtaining bicyclic oxaphosphoranes II [12, 13], as well as tricyclic oxaphosphoranes [14] of the IV type in the process of the unusual acidolysis of amidophosphite III:



II

Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1155-1171, September, 1989. Original article submitted February 16, 1988; revision submitted December 5, 1988.

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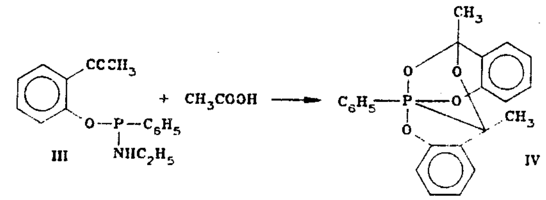
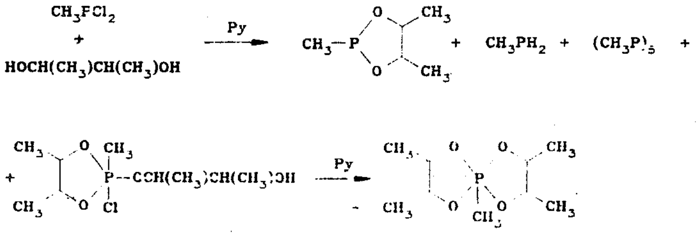
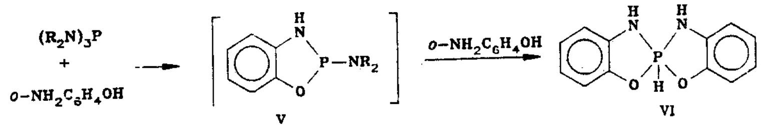


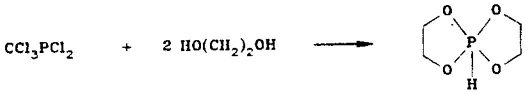
When trivalent phosphorus chlorides are used as the starting compounds, the reaction is carried out in the presence of a base and, consequently, may be complicated by the formation of a phosphorus analog of carbene. In fact, pentamethylphosphorus is formed as a side product [15, 16]:



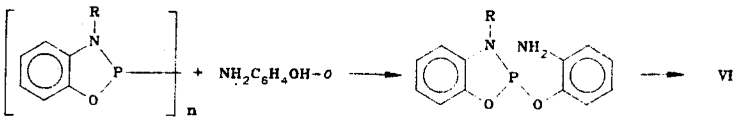
Because of the greater thermodynamic stabilities of some phosphoranes as compared with phosphites, phosphite V cannot be isolated at any ratio of the starting reagents [17]:



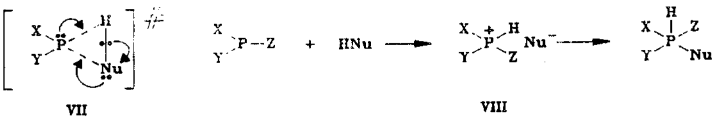
Cases of facile cleavage under the influence of glycols of not only the P–O, P–N, and P–Cl bonds but also the P–C bond have been found. This process is realized if the substituent attached to the phosphorus atom has a high negative inductive effect [18]:



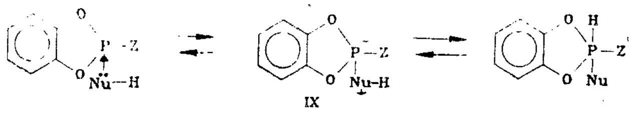
Phenols and aminophenols are traditionally used as OH and NH acids for the cleavage of the P–N bonds in amidophosphites [19]. The 1,3,2-benzoxazaphosphole oligomer can be used as the amidophosphite [20]:



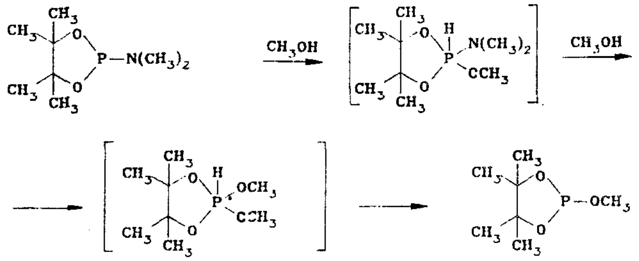
Data indicating that PH-phosphoranes are formed intermediately in nucleophilic substitution reactions at the tricoordinated phosphrous atom with, for example, alcohols have recently appeared with increasing frequency [21-24]. These intermediates may be formed via 1,1 addition of the nucleophile at the trivalent phosphorus atom or in one step – through three-center transition state VII – or in two steps – through ionic intermediate VIII [25]:

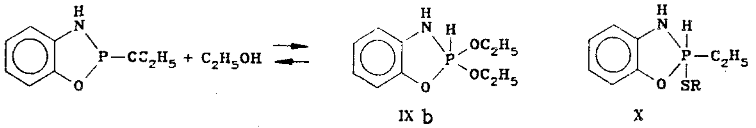


In the case of high electrophilicity of the phosphorus atom and the possibility of effective delocalization of the negative charge (for example, in benzodioxaphospholanes) nucleophilic attack on the phosphorus atom may precede proton transfer [26]:



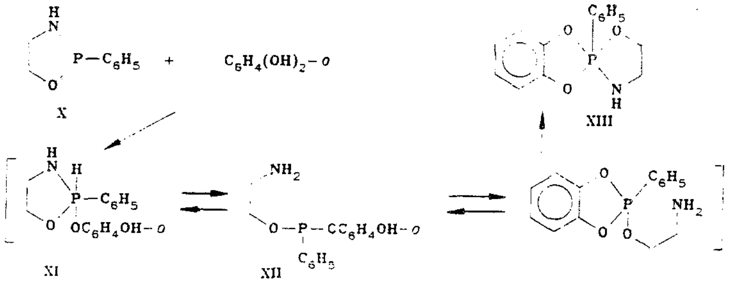
Intermediates of the IX type were detected by ^{31}P NMR spectroscopy [26-28]:



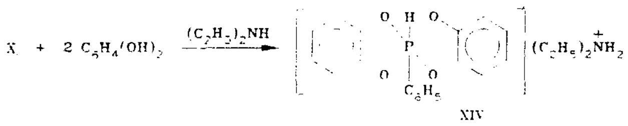


In some cases mercaptans also react similarly to give stable phosphorane X [29].

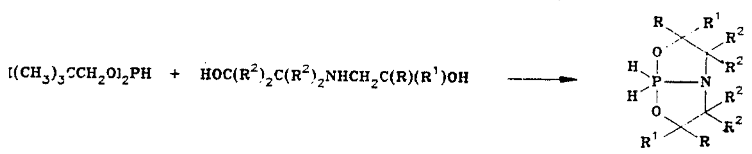
The reactions with diatomic phenols include several of the steps described above: thus, for example, an interesting and extremely unusual example of the synthesis of trioxaphosphorane XIII has been found [30]; the reaction evidently includes the addition of the phenol (with respect to one phenol fragment) to the cyclic phosphite with the formation of monocyclic phosphorane XI; the latter, as expected, exists in tautomeric equilibrium with open form XII, which is stabilized additionally by coordination of the amino group with the phosphorus atom, and unusual cyclization with the splitting out of hydrogen then follows; the structure of XIII was proved reliably by the usual methods; however, considering the unusual character of the process, data from x-ray diffraction analysis would be extremely useful.



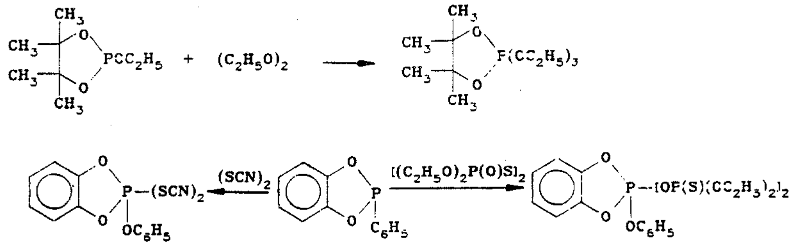
If the reaction of the oxazaphospholane with pyrocatechol is carried out in the presence of amines, an ethanolamine residue is replaced by a pyrocatechol residue, and the amine converts the PH-phosphorane to phosphorate XIV:



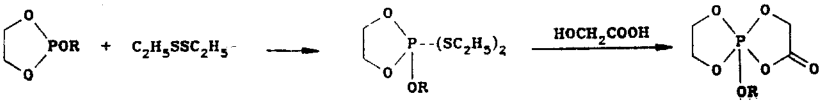
Dioxaphosphoranes of a previously unknown type – with two P–H bonds in the molecule – were obtained by oxidative addition to dialkoxyphosphines [31], as shown below [32]:



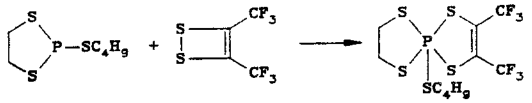
It is known that the stabiliities of oxaphosphoranes increase markedly when two dioxaphospholane rings are present in the structure; the monocyclic dioxa- and monooxaphosphoranes and, subsequently, noncyclic analogs are less stable (for example, see [33]). It is also known that tricoordinated organophosphorus compounds display biphilic reactivities in reactions with, for example, peroxides, thioperoxides, dithiaperoxides, etc.; as in the above-examined reactions with alcohols, phenols, and mercaptans, the corresponding heterophosphoranes are initially formed. If the heterophosphoranes are stable, these reactions can serve as convenient methods for their synthesis. Quite stable oxaphosphoranes that are stabilized by a dioxaphospholane ring are obtained via this method [35, 36]:



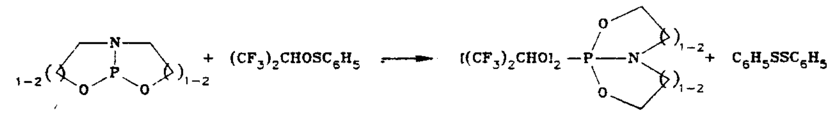
Unsymmetrical oxathiaphosphoranes are stable for a short time at low temperature and are readily converted to more stable pentaoxaphosphoranes [37, 38]:



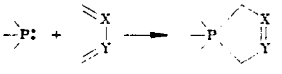
Symmetrical pentathiaphosphoranes are stable when electron-acceptor trifluoromethyl groups are introduced into at least one ring [39, 40]:



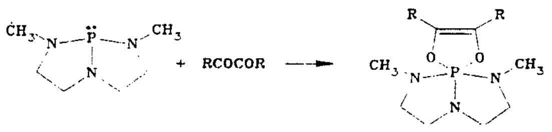
The tendency for the formation of a P–O bond rather than a P–S bond can be demonstrated distinctly in the case of the widely used method for the synthesis of pentaoxaphosphoranes from thioperoxides [17, 41, 42]:

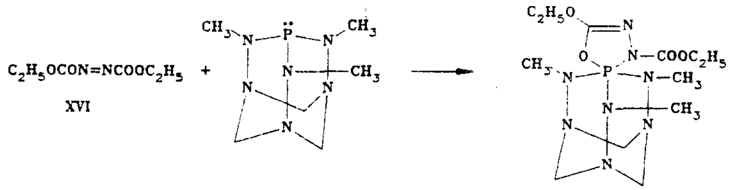


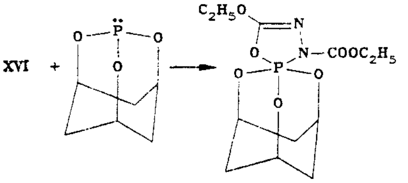
The well-known oxidative cycloaddition reaction has been widely used in recent years for the synthesis of new types of oxaphosphoranes. These processes may take place either in two steps or synchronously via a diene condensation mechanism (for example, see [39, 43, 44]). The most diverse compounds of the XV type have been introduced into this reaction as oxidizing agents [45-58]:

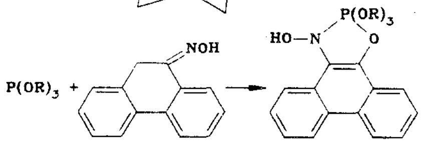


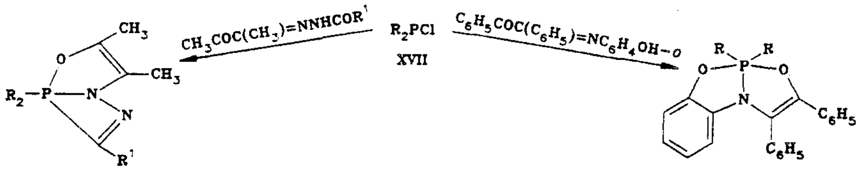
XV



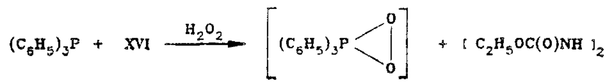




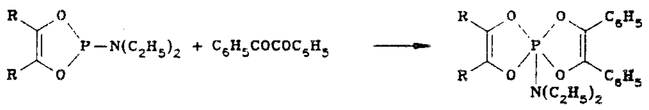




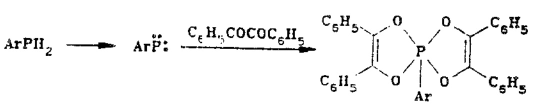
It has been demonstrated that a dioxaphosphorane is an intermediate in the reaction of triphenylphosphine with diethyl azodicarboxylate in the presence of hydrogen peroxide [59]:



Tetraoxaphosphoranes of a previously unknown type with two dioxaphospholene rings can be obtained from cyclic vinyl esters of amidophosphorous acid via the same scheme [60]:

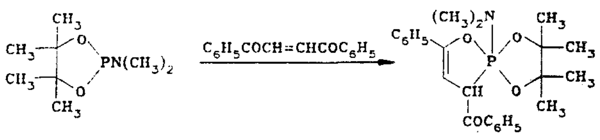


These structures were later obtained from an intermediate generated phosphinidene [61]:

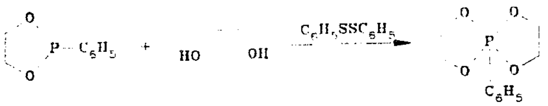


Ar= 2,4,b-tri-tert-butylphenyl

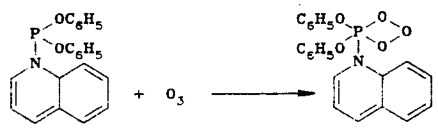
A reaction involving cyclization to spiro structures also proceeds with compounds with a system of conjugated O═C─C═C bonds [62]:

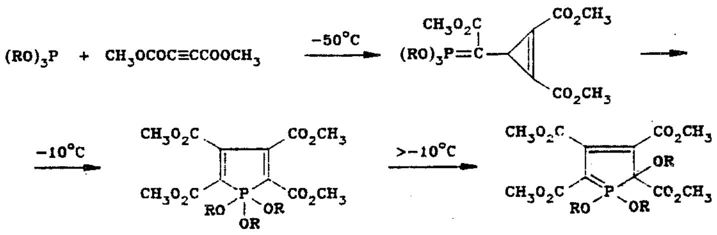


The reaction of phosphites with alcohols in the presence of a hydrogen acceptor essentially models the reaction with diketones [63]:



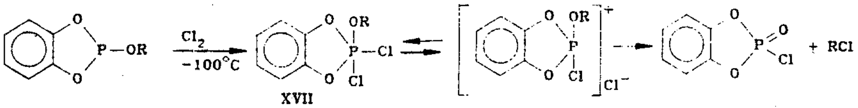
The oxidation of amidophosphites to tetraoxaphosphoranes [63] or the reaction of dimethyl acetylenedicarboxylate with trialkyl phosphites [64] can be regarded as formally similar to it:





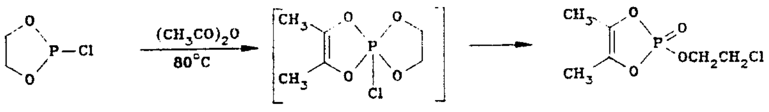
In the case of triketones only two keto groups participate in the reaction [65]:

It is known that compounds of tricoordinated phosphorus are readily oxidized by halogens; in the case of organophosphorus compounds that contain at least one P—OAlk bond this is followed by an Arbuzov rearrangement. Phosphoranes XVII which contain a P—O group and a halogen atom attached to the phosphorus atom, are, as a rule, unstable and readily dissociate at the P—Hal bond to give phosphonium salts and then undergo rearrangement [66]:

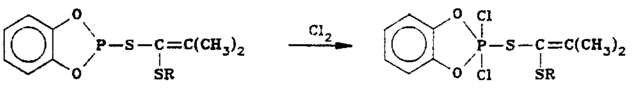


XVII

An intermediate of the XVII type can be obtained via a different pathway — by oxidative additive to chlorophosphites [67]:

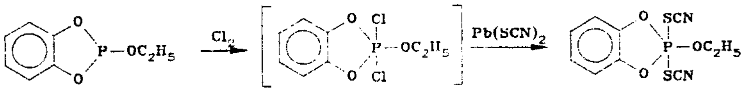


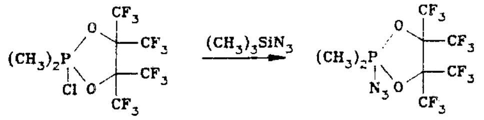
It is known that the Arbuzov rearrangment is not realized for P-alkenylthiophosphoranes; this is confirmed by the stability of phosphorane XVIII [68]:

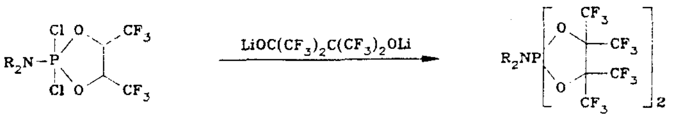


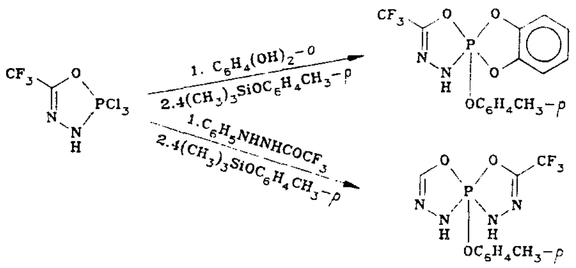
XVIII

Phosphoranes with an alkoxy group and a chlorine atom can be detected at low temperatures; in addition, at low temperatures one can carry out their reaction with various nucleophiles with retention of the phosphorane structure; in a number of cases this proved to be a preparative method for the synthesis of new oxaphosphoranes [69-73]:

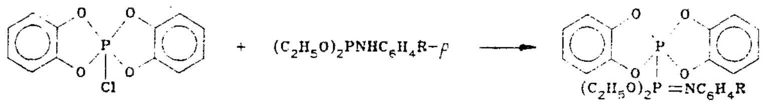


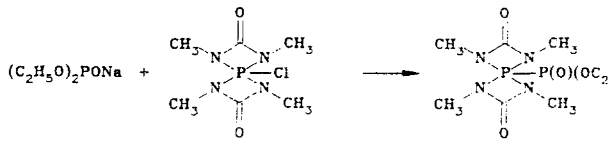


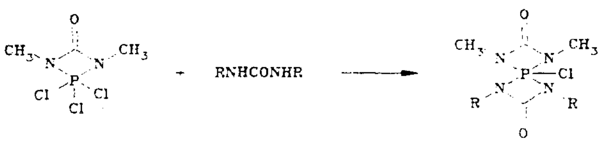


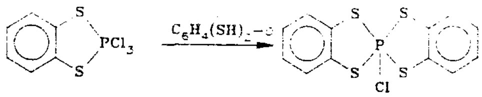


If amidophosphites, in which the nucleophilic center is located at the phosphorus atom, or the ambident diethyl phosphonite anion acts as the nucleophile, phosphoranes of a new type with a P—P bond between the 4- and 5-coordinated phosphorus atoms are formed [74, 75]:



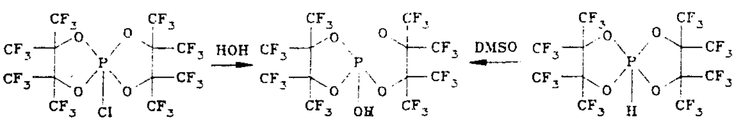






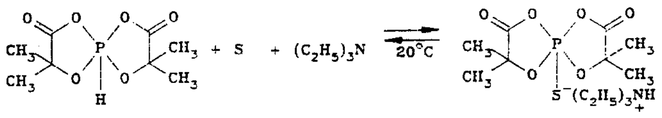
The hydrolysis of chlorotetraoxaphosphoranes can occur without cleavage of the P—O bonds when strong electron-acceptor substituents are present at the oxygen atom [76]. The hydrolysis proceeds in a neutral or alkaline medium, and the resulting hydroxyphosphoranes are resistant to hydrolysis and are not decomposed even by concentrated sulfuric acid.

Thus one can obtain phosphoranes of a new type with P—OH groups. These phosphoranes have an additional reaction center (the OH group); as will be demonstrated below, this gives additional possibilities for organophosphorus synthesis. Such phosphoranes can also be obtained by oxidation of PH-phosphoranes with dimethyl sulfoxide at 20°C [77].

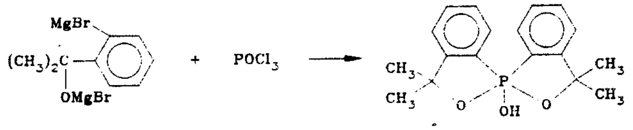


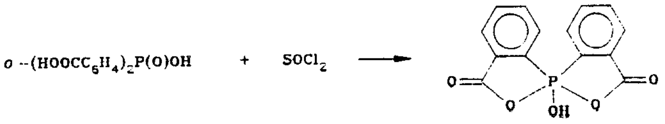
XIX

The production of phosphoranes with an SH group attached to the phosphorus atom is evidently also possible; this is confirmed by the following transformations [78]:



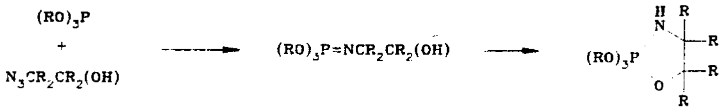
The formation of hydroxyphosphoranes models the reactions that are used for the synthesis of PH-phosphoranes, such as the following processes [79, 80]:



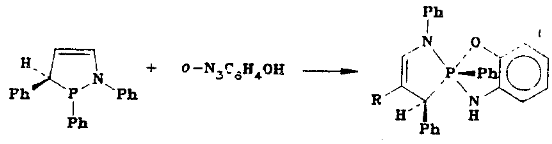


Ring-chain tautomerism between isomers with tetra- and pentacoordinated phosphorus atoms in series of imino compounds was first detected in [81]:

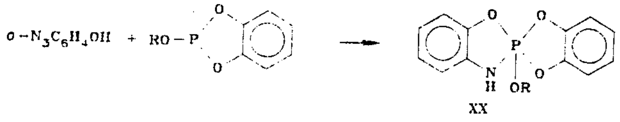
In this connection the reaction of phosphites with the corresponding azides can be used to obtain oxazaphosphoranes (the Cadogan reaction) [82, 83]:



This method for the synthesis of phosphoranes is particularly attractive in that the process is stereoselective [84]:

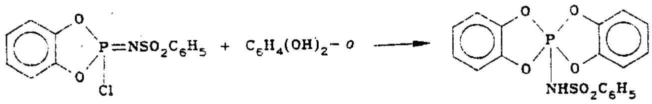


The introduction of an oxaphospholane ring stabilizes $\mathrm{P^V}$ isomer XX, for which the existence of a valence tautomer with a tricoordinated phosphorus atom has not been detected [85, 86]:



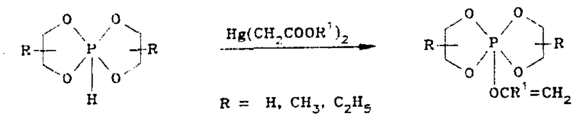
XX

Tautomeric equilibrium also cannot be detected for phosphorane XXI and for its analogs obtained on the basis of phenylenediamine and aminophenol [39]:



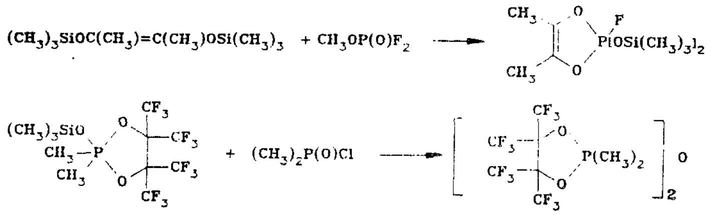
XXI

The reaction of mercurated oxa compounds with readily accessible tetraoxahydrospirophosphoranes is a preparative method for the synthesis of alkenyloxytetraoxaspirophosphoranes (in ~70% yields):

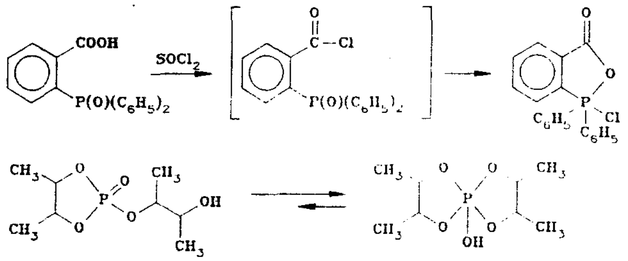


The reaction with mercurated ketones takes place in the presence of tert-butyl peroxide and upon UV irradiation; this, in conjunction with other data, makes it possible to assume that this process takes place through phosphoranyl radicals [87, 88].

Oxaphosphoranes can be synthesized starting from compounds of not only tri- and pentacoordinated phosphorus but also from tetracoordinated phosphorus; the type of reaction may be the very same. Thus the general principle of the easy removal of trimethylsilyl halides can be extended to halophosphoranyl compounds [88-92]:



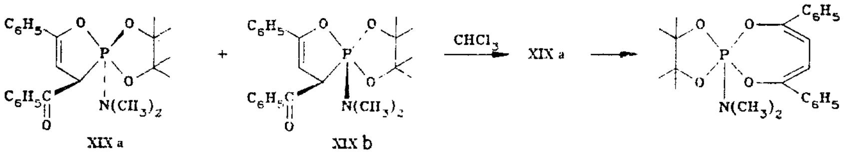
Examples in which phosphoryl compounds undergo complete rearrangement to oxaphosphoranes [93] or the tautomeric equilibrium is shifted to favor the oxaphosphorane structure [94] are also known:



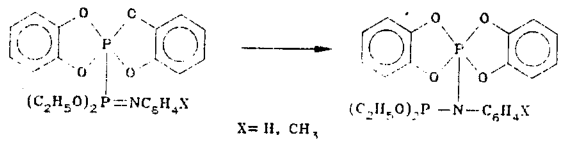
REACTIVITIES

As we have already mentioned above, the principal factor that determines the stabilities of pentacoordinated phosphorus compounds is the presence in the phosphorane molecule of a dioxaphospholane fragment [94]. This was demonstrated convincingly in the case of oxahalophosphoranes [95], pentaoxaphosphoranes [94], and phosphoranes that contain P—C, P—S, and P—N bonds [96-98]. A series of studies by Markovskii and co-workers, in which the stabilizing effect of a substituent with a bicyclooctane structure on, for example, the pentacoordination state of the phosphorus atom, have been published in recent years [99, 100].

In the general case an increase in the number of P—O bonds in the oxaphosphorane structure stabilizes the compound: this is well illustrated by a rearrangement in which the stabilizing effect of the five-membered ring becomes less significant as compared with the formation of a new P—O bond [63]:

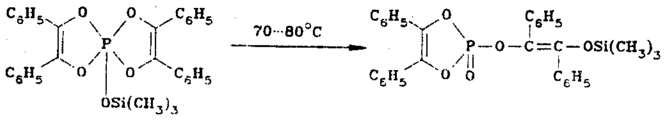


Examples of the facile rearrangement of an oxaphosphorane with one P—P bond to an oxaphosphorane with a P—N bond are known [74]:

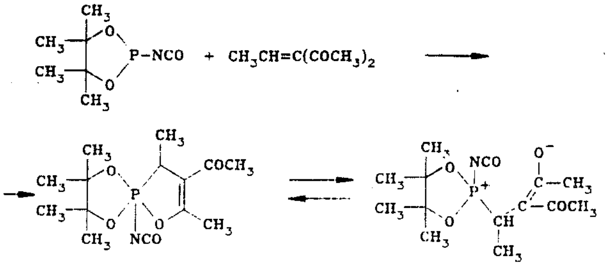


When X = NO_2, the starting phosphorane is completely stable, since electron-acceptor substituents stabilize imino oxides of tricoordinated phosphorus compounds.

Numerous examples of tautomeric equilibria between compounds with a phosphorane structure and phosphoryl and phosphonium, compounds and tricoordinated phosphorus compounds are known; there are, of course, cases in which the equilibrium is shifted completely to one or the other side, which is determined by the character of the substituent attached to the phosphorus atom and the conditions under which the rearrangement is carried out. Thus in the example presented below the structure with a phosphoryl group is energetically more favorable [101]

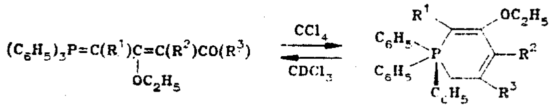


The presence of a dioxaphospholane ring in the phosphorane structure is not always a guarantee of its stability; phosphorane XXII exists in equilibrium with phosphonium structure XXIII, which is logically explained by the requirements of apicophilicity; the apicophilicity of the isocyanato group is equal to the apicophilicity of the chlorine atom, and three oxygen atoms in two rings also tend to occupy an apical orientation [102]:

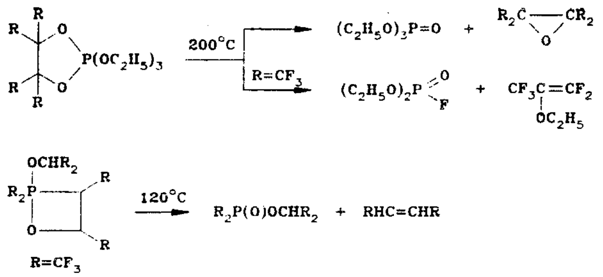


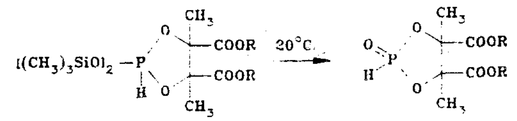
XXII XXIII

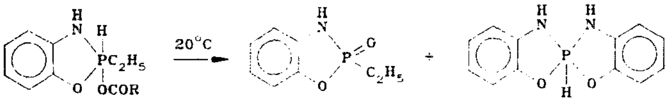
Examples of tautomeric equilibria in the $R_3P{=}A \rightleftarrows R_3\overset{\frown}{P\,A}$ system are known [103]:

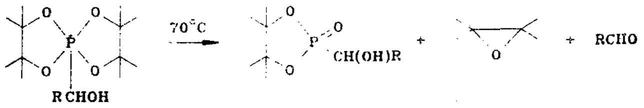


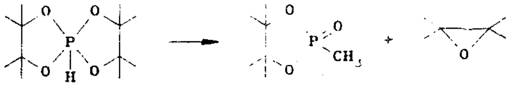
The pathways of the decomposition of oxaphosphoranes are also extremely different. If the structure of the phosphorane permits the formation of a phosphoryl group, the decomposition proceeds precisely via the following pathway [104-110]:

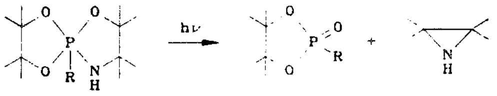


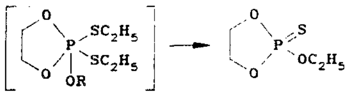




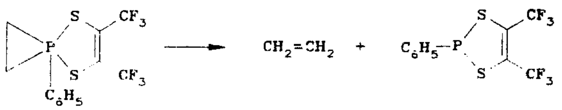








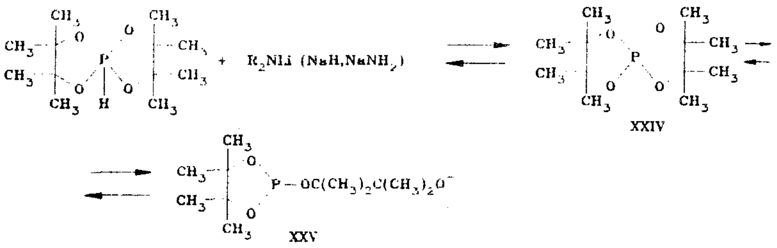
The thermodynamic stabilities of phosphoranes sometimes prove to be lower than the stabilities of tricoordinated phosphorus compounds. A decomposition process with the formation of the latter most often proceeds in cases in which the starting phosphorane does not contain P—O bonds, i.e., fragmentation with the formation of a phosphoryl group is impossible [111]:



In some cases the stabilities of compounds with a pentacoordinated phosphorus atom and the stabilities of compounds with a phosphorus atom with a different coordination become comparable or very close; in these cases an equilibrium is established, as is often observed for the reactions of phosphonites with dienes. Tautomeric equilibrium has long been known for hydrospirotetraoxaphosphoranes and the corresponding hydroxyphosphites [112].

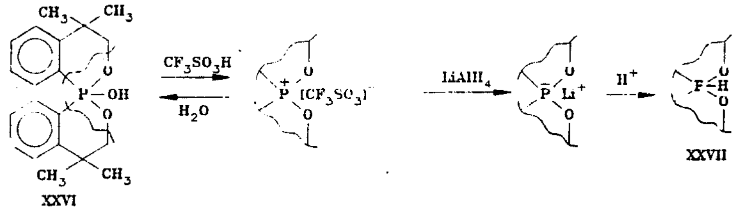
The P—H bond in tetraoxaspirophosphoranes is readily metallated with the formation of anion XXIV. The production of such anions is of fundamental significance for understanding the little-investigated bimolecular nucleophilic substitution reactions at tricoordinated phosphorus atom [113-115], since anion XXIV has the structure of the proposed intermediate of these processes:

$$R_3P + Y^- \longrightarrow [R_3P{-}Y^-] \longrightarrow R_2PY + R^-$$

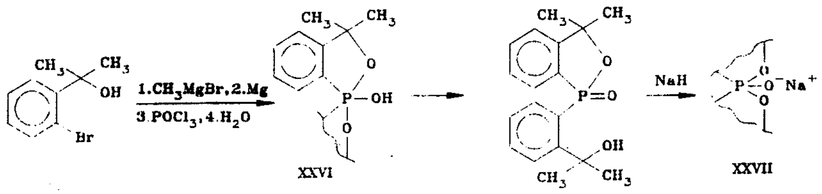


According to ^{31}P NMR data, a fast equilibrium is established between anions XXIV and XXV. Alkylation with methyl iodide and silylation with trimethylchlorosilane take place at the oxygen atom, but the reaction with methyl bromide, ethyl iodide, butyl iodide, and allyl bromide, as well as with aromatic aldehydes, proceeds at the phosphorus atom with retention of the phosphorane structure.

An anion of the XXIV type can be obtained from hydroxyspirophosphoranes (XXVI, for example), which react with trifluoromethanesulfonic acid to give a stable spirobicyclic dioxaphosphonium triflate; the latter is reduced by lithium aluminum hydride to the corresponding conjugate base of the PH-phosphorane [114]:



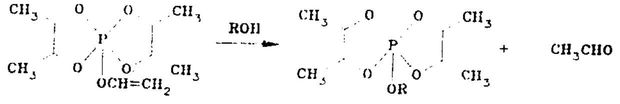
Hydroxydioxaphosphoranes of the XXVI type are not oxidized by oxidizing agents such as hydrogen peroxide in chloroform; this indicates the absence in these compounds of a tautomer with a tricoordinated phosphorus atom [114]. Hydroxydioxaphosphorane XXVI is formed via the scheme presented below [114] and is also readily metallated wtih the formation of sodium trioxaphosphorane oxide XXVII [115, 116]:



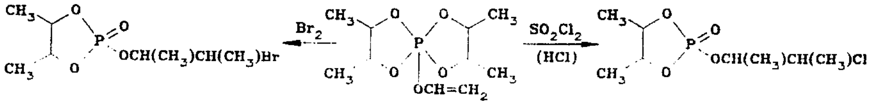
Anions of the XXVII type can also be further used in organophosphorus synthesis [117] and serve as models for the investigation of nucleophilic substitution reactions at the tetracoordinated phosphorus atom [40].

The synthesis of phosphoranes with P—P bonds between two pentacoordinated phosphorus atoms was accomplished through phosphoranide anions [118].

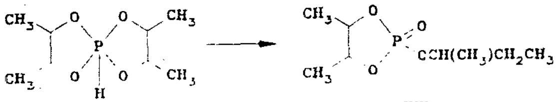
Nucleophilic substitution reactions at the pentacoordinated phosphorus atom (alcoholysis, for example) proceed with retention of the phosphorane structure through octahedral intermediates or through a transition state with a hexacoordinated phosphoruus atom. This reaction is reversible — the liberated alcohol again undergoes re-esterification [119]. Vinyloxyspirophosphoranes undergo irreversible alcoholysis under exceptionally mild conditions (30-40°C, basic or acidic catalysis); this transformation is a preparative method for the synthesis (in quantitative yields) of 5-alkoxytetraoxaspirophosphoranes [120]. Electrophilic addition to vinyloxyspirophosphoranes proceeds as concerted 1,6 addition with the formation of the corresponding phosphates [87]:



R= alkyl, allyl, propargyl, β-hydroxyalkyl



Radical reactions have been studied to the greatest extent in series of hydrotetraoxaspirophosphoranes. Homolysis of the P—H bond in these compounds is possible under the influence of light in the absence of specially added sources of radicals; however, photolysis in the presence of di-tert-butyl peroxide or an alkyl nitrite is usually employed [121]; the formation of spirophosphoranyl radicals that do not undergo β fragmentation was detected by EPR spectroscopy. At the same time, it is known that phosphoranyl radical $[(CH_3)_3CO]_4\dot{P}$, which contains dioxaphospholane rings, undergoes extremely fast β-cleavage at low temperatures [122]. However, it was shown in recent years that a β-cleavage process is also realized for spirophosphoranyl radicals under more severe conditions (in the presence of tert-butyl peroxide at 130°C). Thus hydrospirophosphorane XXVIII is isomerized under these conditions to dioxaphospholane XXIX [123]:



XXVIII XIX

The reaction has general character and is realized for both unsubstituted and substituted hydrospirophosphoranes [124, 125], proceeding via a chain mechanism, and the rate of the process is determined by the number and nature of substituents in the dioxaphospholane rings.

Thus at the present time the chemistry of oxaphosphoranes is no less a vast area of the chemistry of organophosphorus compounds than the chemistry of, for example, phosphites. The high reactivities of oxaphosphoranes are responsible for their extensive use as reagents in fine organic synthesis and in various branches of the national economy.

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REACTION OF $\alpha,\beta,\alpha',\beta'$-DIEPOXYKETONES WITH METHANOL IN THE PRESENCE OF BORON TRIFLUORIDE ETHERATE

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The reaction of trans-diepoxyketones with methanol in the presence of boron trifluoride etherate leads to tetrahydropyran-4-ones and/or tetrahydrofuran-3-ones. The size of the heterocycle forming depends on the direction in which the alkylsubstituted epoxide ring opens and is determined by the relative configuration of the chiral centers of the epoxide rings.

It is known that the reaction of keto-epoxides with alcohols in an acidic medium occurs ambiguously and, depending on the structure of the substrate, leads to products of alcoholysis or isomerization [1-4]. Alcoholysis takes place primarily with the β-opening of the hydroxypyrane ring [1-4]. Moreover, we have shown previously that the generation of α- or β-hydroxypropionyl groups in the sidechain of a small ring (aziridine or oxirane) leads to intramolecular cyclization with formation of five or six-membered, oxygen-containing heterocycles [5, 6]. In order to study the stereochemical laws of the heterocyclization of diepoxyketones and the synthesis of functionally substituted compounds in the tetrahydropyran-4-one and tetrahydrofuran-3-one series, we have recently studied the reaction of arylaliphatic diepoxyketones with methanol in the presence of boron trifluoride etherate.

As objects of study, we chose $\alpha,\beta,\alpha',\beta'$-diepoxyketones Ia,b-IIIa,b, IVa, Vb, and VIb, prepared by the alkaline epoxidation of the β-arylacryloyloxiranes [5]. The a-group compounds differ from the b-group diastereometers in the relative configuration of the α-carbon atom of the alkylsubstituted epoxide ring in relation to the chiral centers of the trans-arylsubstituted ring.*

The reaction of diepoxyketones I-IVa with methanol in the presence of an equimolar amount of boron trifluoride etherate leads to a mixture of 3-hydroxy-5-methoxy-2-aryltetrahydropyran-

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*Comparison of the results obtained with the data in [5, 6] assigns the diastereomers of the diepoxides and azirinylepoxyketones with the relative configurations RRR(SSS) to the a-group and the diastereometers with the relative configuration SRR(RSS), to the b-group.

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