Amides of Trivalent Phosphorus Acids as Phosphorylating Reagents for Proton-Donating Nucleophiles

Edward E. Nifantiev,* Mikhail K. Grachev,† and Sergei Yu. Burmistrov‡

V. I. Lenin Moscow State Pedagocical University, Chemistry Department, Nesvizhskii per., 3, 119021 Moscow, Russian Federation

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I. Introduction

Phosphorylation, i.e., substitution of a phosphorus-containing function for hydrogen atoms in a molecule of an organic compound (normally a nucleophile), is a significant problem in organophosphorus chemistry. This is usually attained by virtue of reagents containing penta- or trivalent phosphorus atoms. The former have attracted more attention in early studies, whereas the latter have been studied more extensively in the subsequent period. This shift of interest is due to the fact that the use of reagents containing trivalent phosphorus ensures the highest phosphorylation rates and permits one to avoid many side processes. The advisability of using these reagents is also associated with the development of the modern strategy for the synthesis of complex organophosphorus compounds. According to this strategy, in the first step of a synthetic scheme, a reagent containing trivalent phosphorus reacts with a nucleophile to give a key compound to be used in subsequent transformations. If required, in the second step, the key

* To whom correspondence should be addressed. Fax: (7-095) 248 0162. E-mail: chemdept@mtu-net.ru.
† E-mail: chemdept@mtu-net.ru.
‡ E-mail: sergeib@zmail.ru, burmistr_s@yahoo.com.

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Edward E. Nifantiev, Soros Professor, was born in July 1933, Krasnoyarsk, Russia. He graduated from M.V. Lomonosov Moscow State University where he was awarded his Ph.D. (1959) and Doctor (1967) degrees in Chemistry. From 1971 he has worked as Head of the Department of Organic Chemistry, Chemistry Faculty of Moscow State Pedagogical University, where he has organized a laboratory on complex organophosphorus compounds. In 1987 he was awarded the Butlerov Prize, the highest award of the Russian Academy of Sciences in Organic Chemistry. He is a member of the Editorial Board of an international journal *Phosphorus, Sulfur and Silicon*. His research interests include adjacent fields which unite the chemistry of trivalent phosphorus with the chemistry of natural compounds and bioregulators, with coordination chemistry and metallocomplex catalysis, with stereochemistry and the chemistry of high molecular compounds. At present he is engaged in investigations of the synthesis and properties of macrocyclic phospho-containing cavity systems.

Mikhail K. Gratchev was born in July 1945, in Saratov, Russia. He graduated from D.I. Mendeleev Russian Chemical Technological University of Moscow with his Masters degree in 1969. He earned his Ph.D. (1976) and Doctor (1996) degrees in Chemistry at Moscow State Pedagogical University (M.S.P.U.), where he studied the synthesis of new phospholipids and phosphorylation of alcohols and amines by amides of trivalent phosphorus acids. In 1993 he worked in the Chemistry Department of the University of Texas at Austin in Professor Stephen F. Martin's laboratory. He is now Professor of Chemistry at the Department of Organic Chemistry, Chemistry Faculty of M.S.P.U. His research interests include the study of the phosphorylation of complex natural hydroxyl-containing compounds, synthesis and properties of phosphorylated cyclodextrins, and supramolecular chemistry.

compound can be oxidized, iminated, and alkylated; it can isomerize, add sulfur, selenium, or chlorine, be coordinated to a metal, etc. This ensures the synthesis of a broad range of compounds including those that cannot be prepared within the framework of classical preparative methods based on the use of pentavalent phosphorus derivatives.

Among the phosphorylating reagents that have been actively used in the last 10−15 years, amides

Sergei Yu. Burmistrov was born in March 1962, in Moscow, Russia. He graduated from D.I. Mendeleev Russian Chemical Technological University of Moscow with his Masters degree in 1985. He earned his Ph.D. degree in 1991 at Moscow State Pedagogical University (M.S.P.U.), where he studied the phosphorylation of alcohols and amines by amides of trivalent phosphorus acids. In 1996 he worked in the laboratory of Professor R. Schmutzler in Braunschweig, Germany. He is now Senior Research Worker at the Department of Organic Chemistry, Chemistry Faculty of M.S.P.U. His research interests include fine organic synthesis and the study of the phosphorylation of complex protonodonor nucleophiles, acid catalysis, stereoselectivity, and supramolecular chemistry.

of acids of trivalent phosphorus (ATPA) should be mentioned first. The advantages of these reagents include accessibility, high reactivity, and, what is especially important, the possibility of performing reactions under mild conditions. It is significant that these reagents can be appreciably activated by the addition of amine or azole hydrohalides. Owing to the above-listed features, ATPA are now widely employed for solving numerous synthetic problems, for example, for the preparation of important phosphorus-containing natural products (including biopolymers) and their analogues.

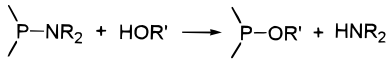
The studies describing particular cases of phosphorylation by phosphamides run into the thousands. Meanwhile, some fundamental problems associated with their reactivity have not yet been solved. Thus, the mechanism of phosphorylation is known only in the general outline, the relationship between the structure and the reactivity of reagents has not been elucidated, and little is known about the possibility of solvation. Thus, the width and the depth of investigations do not obviously correspond to each other. In our opinion, further progress in the study of phosphorylation of proton-donating nucleophiles by ATPA would be promoted by a publication presenting an analytical generalization of the published data with primary attention being focused on the recent achievements. This task stimulated writing of this review. The review includes, apart from the Introduction and the Conclusion, eight sections devoted to phosphorylation of alcohols and phenols, amines, amides, thiols, organic and organoelement acids, simple inorganic compounds, and, finally, hydride metal complexes. The authors have attempted to demonstrate that the use of phosphamides can be beneficial not only for the development of the potential of organic synthesis, but also for the solution of particular scientific problems. This approach is consistent with the modern trend for creation of border fields of knowledge; the interests

and capacities of the chemistry of trivalent phosphorus (including that of amides of trivalent phosphorus acids) can be connected with the chemistry of nucleic acids, phospholipids, molecular cages and cavities, polymers, coordination systems, etc.

II. Phosphorylatyion of Alcohols and Phenols

The reaction of ATPA with alcohols and phenols was discovered in the very late 1950s by three groups of researchers working independently (Scheme 1).[1−3]

Scheme 1

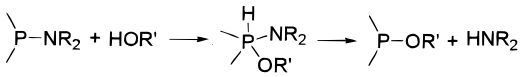


This is an unusual phosphorylation method. The unusual character of the alcoholysis of ATPA is also due to the fact that this reaction had actually been described twice[4,5] prior to its official discovery but had not been appreciated as an original and promising phosphorylation method even by the authors themselves. Indeed, no obvious analogies of this method had existed before it was discovered. In fact, amides of pentavalent phosphorus phosphorylate alcohols and phenols with low efficiency and only at high temperatures while carboxamides (and even amides of sulfenic acids[6]) do not react with alcohols at all (the corresponding esters, on the contrary, are smoothly converted into amides on treatment with ammonia or primary or secondary amines). In addition, the new method had remained unclaimed for some period because the synthetic problems in which it could demonstrate its opportunities neither had been formulated nor had become a concern of researchers engaged in organophosphorus chemistry. Meanwhile, the initial "induction period" was not wasted. During this period, the catalytic character of this reaction has been established and its main features have been elucidated. Finally, ATPA have occupied a fitting place in the arsenal of organophosphorus chemistry and related fields of science.

1. Phosphorylatyion Mechanism: Catalysis

Even in the first study dealing with the alcoholysis and phenolysis of simple ATPA,[3] an "addition−elimination" mechanism was proposed for this reaction (Scheme 2). Later, the possibility of the forma-

Scheme 2



tion of hydrophosphoranes has been confirmed experimentally in studies dealing with some cyclic systems.[7−14] Simultaneously, a mechanism based on the formation of a four-membered transition state has been proposed for the alcoholysis of ATPA,[15] but this has not been confirmed experimentally.

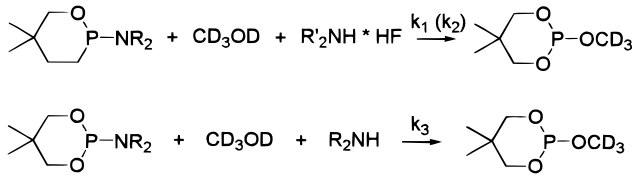
It should be noted that in the early stage of the investigation of alcoholysis of phosphamides, several useful observations concerning the effects of the medium[10,14−20] and temperature[21] on the reaction route have been made. In addition, it was found that phosphorylation slows down as amine resulting from the substitution is accumulated in the reaction mixture; apparently, this is due to complexation of the amine with the alcohol, which retards the main reaction.[10,18,20,22,23]

a. Catalysis of Phosphorylation by Amine Hydrohalides

The study of the rates of alcoholysis of ATPA showed that many reactions of this type are catalytic. This was found for the first time when the rates of phosphorylation of the simplest alcohols by phosph(III)amides thoroughly freed from possible impurities were compared with those by phosph(III)amides obtained by conventional methods and, hence, contaminated by some amine hydrochlorides (AHC).[24−26] Later, the discovered catalytic effect has been confirmed by many other researchers.[10,17,18,27−34]

The chemical essence of the catalysis had been the object of prolonged debates, the results of which were summarized.[35] Two hypotheses were discussed. According to one of them, acidic compounds protonate phosphamide at the phosphorus or nitrogen atom. Due to protonation, the phosphorus atom in the onium compound becomes more electrophilic and reacts more readily with an alcohol. According to the second hypothesis, phosphamide is protonated only at the nitrogen atom. The phosphammonium cation thus obtained is attacked by an anion (chloride, when AHC are used), being thus converted into phosphorus halide, which acts as the phosphorylating agent. The latter hypothesis has raised doubt,[3136−39] and later, it was critically reviewed. For instance, it was found experimentally that cleavage of the phosphamide bond in ATPA by amine hydrohalides is not a general reaction, for example, phosphoric hexaethyltriamide cleaves much less efficiently than hexamethyltriamide and higher amides do not react with amine hydrohalides on the preparative scale. Meanwhile, the efficiency of catalysis is high for all the abovementioned amides.[35] An even more interesting result was obtained by comparing the rates of deuteriomethanolysis of neopentylenediyl imidazolido (k_1) and *N*-ethylanilido (k_2) phosphites in the presence of amine hydrofluorides with the rates of deuteriomethanolysis of the fluoride of the same acid (k_3) (Scheme 3). It was shown that k_1 and k_2 are much

Scheme 3



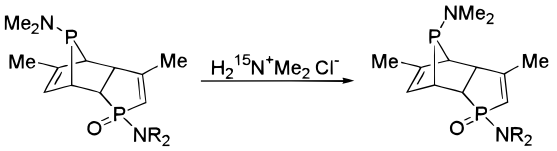
greater than k_3.[40,41] Subsequently, it was found that phosphorus amidofluorides can phosphorylate hydroxy groups due to the rupture of the phosphamide bond with retention of the fluorine−phosphorus bond.[42]

It is also significant that the catalytic activities of the diethylamine hydrofluoride and other corresponding hydrohalides (hydrohalides of secondary amines) in standard reactions are comparable.[40,41]

This would be impossible if the reaction pathway included the steps of formation and alcoholysis of phosphorus halides. To conclude the analysis of this hypothesis, we present the data of J. Szewczyk and L. D. Quin,[43] who studied the inversion of a phosphorus atom in the presence of ^{15}N-enriched dimethylamine hydrochloride. The complete inversion of a phosph(III)amide center was observed only in the presence of the above-mentioned catalyst. In addition, the ^{15}N label did not appear in the phosphamide studied. Thus, the activation of the phosphamide was associated with some interaction that does not involve the step of formation of acid chloride. Otherwise, ^{15}N-labeled dimethylamine would appear in the system and would react with the chloride to give ^{15}N-phosphodimethylamide.

The hypothesis assuming protonation of ATPA to onium compounds as a route of their activation toward the subsequent reaction with alcohols and other nucleophiles has been actively discussed in the literature. This possibility has been worked out in detail; initially N-protonation was considered to be more likely.[15,29,30,44] However, no convincing evidence for the protonation in ATPA−AHC−alcohol systems was obtained. Meanwhile, a successful experiment on the N-protonation of a metal complex derivative of a bicyclic ATPA was reported (Scheme 4).[45]

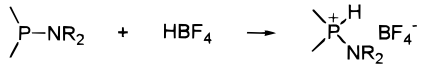
Scheme 4



The lone electron pair of phosphorus in the initial complex is involved in the formation of the phosphorus−molybdenum bond, and this determines the protonation of nitrogen.

Later, most of the authors pointed out that P- and N-protonation might occur in parallel[46−49] or that selective P-protonation takes place.[19,26,50] Some publications presented evidence supporting this reaction pathway, which was followed, according to IR[50,51] or NMR,[48,52−56] by studies of reaction mixtures or by X-ray diffraction analysis of the salts formed with anhydrous hydrogen tetrafluoroborate (Scheme 5).[57−59]

Scheme 5



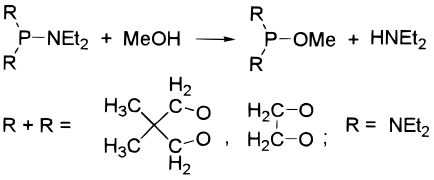
Later, other methods for preparing P-protonated ATPA were described; the structures of these compounds were determined by X-ray diffraction analysis, for example, see ref 60.

The series of works considered above was concluded by experiments on the alcoholysis of phosphonium salts. It was found that these salts do not react with alcohols.[58,59] Thus, the hypothesis that the ATPA protonation products act as intermediates in the alcoholysis of phosphamides also does not reflect the real situation. It has been of interest to compare the susceptibility for alcoholysis of the products of ATPA protonation and alkylation, because these salt-like substances are isoelectronic. None of them was found to change on treatment with alcohols.[59]

Further research on the chemistry of ATPA alcoholysis was concerned with the variation of the reaction rates as functions of the concentrations of various catalysts. For precision kinetic studies of acid-catalyzed transformations of ATPA, a purification method based on phase-transfer principles was developed; the method makes it possible to reach a residual concentration of the chloride ions equal to 1.1×10^{-4} g-ion/L.[58]

First, the quantitative features of the influence of amine salts on the rate of methanolysis of the following amines were elucidated (Scheme 6).[61] The

Scheme 6



rate constants for the first step of methanolysis were measured as functions of the diethylammonium chloride concentration, which varied within the range corresponding to the contents of this compound in phosph(III)amides purified by various methods. The pseudo-first-order rate constants (k_I^{Ψ}) were found from the decrease in the concentration of the initial amide using linearization in the coordinates $-\ln([>PNEt_2]/[PNEt_2]_0) = f(\tau)$, where $[>PNEt_2]_0$ is the initial amide concentration. The k_I^{Ψ} values thus obtained were used to calculate the second-order rate constant using the following equation: $k_{II} = k_I^{\Psi}/[MeOH]$.

The data of kinetic measurements can be represented by eqs[18] 1 and 2

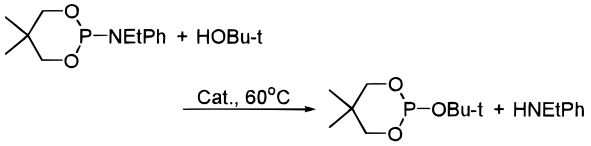
$$-d[>P-NEt_2]/d\tau = k_{II}[>P-NEt_2][MeOH] \quad (1)$$

$$k_{II} = k_0 + k_c[Et_2N^+H_2] \quad (2)$$

where k_0 is the rate constant for the noncatalyzed reaction, k_c is the catalytic factor taking into account the activating effect of diethylamine hydrochloride, and $[Et_2N^+H_2]$ and [MeOH] are the salt and methanol concentrations, which remain constant during the reaction. The linear variation of k_{II} versus the salt concentration indicates the first order with respect to the catalyst.

The influence of the type of AHC used on its catalytic activity in the alcoholysis of ATPA has also been studied. The experiment was carried out in the neopentylenediyl *N*-ethylanilidophosphite (**1**)−tertiary butyl alcohol system (Scheme 7).[58,62] Hydrochlo-

Scheme 7



rides of secondary and tertiary amines were used as catalysts.

The graphical processing of the results in conformity with eqs 1 and 2 showed the presence of a linear correlation between lg k_c and the acidity of the salts used as catalysts. These correlations for secondary and tertiary amine salts are represented by two independent straight lines. The introduction of the statistics factor *s* (the number of protons attached to nitrogen in the ammonium salt) combines these two lines into one.[56] The results were analyzed in terms of the Brønsted equation (3); for the process in question, this equation has the form[63]

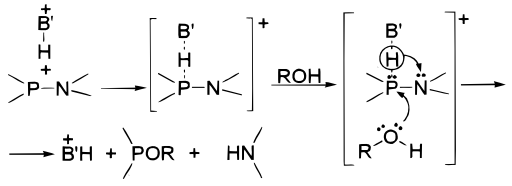
$$\lg(k_c/s) = \lg G_A - \alpha p K_a \qquad (3)$$

where G_A and α are the constants characterizing the reaction series. The slope (α) measures the sensitivity of the reaction to the strength of the acid catalyst. The α value proved to be much less than unity, which points to a general acid catalysis of phosphorylation. In this case, the parameter α is best interpreted as an approximate measure of the change in the charge of the proton-donor or proton-acceptor atom in the transition state.[63] Thus, the pathway of the catalyzed process includes the formation of a catalytic H-complex incorporating the whole substrate and catalyst rather than protonation of the phosphamide substrate (the formation of phosphonium or phosphammonium salt), as suggested previously. Unlike onium salts, this H-complex is a proton-labile system; apparently, this accounts for its susceptibility for alcoholysis.

The kinetic features of the *tert*-butyl alcoholysis considered above have been supplemented by data on methanolysis. The results obtained were generally similar; however, the replacement of *tert*-butyl alcohol by more polar methanol was found to result in a greater degree of proton transfer from the acid catalyst to the phosphamide substrate.[64]

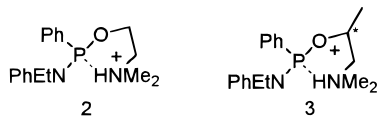
The foregoing can be summarized by concluding that alcoholysis of ATPA in the presence of AHC includes the formation of a catalytic H-complex, in which the proton performs two functions: first, it activates the phosphorus atom toward an electrophilic reaction, e.g., with an alcohol, and second, it migrates from phosphorus to nitrogen during the reaction of the adduct with the alcohol and thus facilitates rupture of the P−N bond (Scheme 8).[58,59,64]

Scheme 8



The above-outlined views have an important stereochemical consequence. If a chiral catalyst is used, the catalytic H-complex will also be a chiral species. Therefore, the use of chiral catalysts might result in stereoselective phosphorylation. In view of this assumption, racemic butylenediyl *N*-ethylanilidophosphite was made to react with 1,2:5,6-diisopropylidene-α-D-glucofuranose (molar ratio of the reactants 2:1) in the presence of the hydrochloride of racemic α-phenylethylamine and the corresponding (+)- and (−)-enantiomers. ^{31}P NMR analysis showed that the reaction with the racemic catalyst affords approximately equal amounts of two diastereomers. When the hydrochloride of the levorotatory amine was used, the yield of one diastereomer was greater by 10%. The use of the dextrorotatory amine hydrochloride ensures an approximately equal predominance of the other diastereomer. Thus, it was found that the use of optically active catalysts could induce stereoselective phosphorylation of ATPA.[58,62] Subsequently, this fundamental finding was used in a more efficient "contacting" of a phosphamide and a hydrochloride. For this purpose, the latter was incorporated into the molecule of model (**2**) and optically active (**3**) phosphamides, which resulted in efficient intramolecular catalysis. It is significant that the catalyst ensured substantial stereoselectivity of the reaction with the chiral substrate **3** (Scheme 9).[65]

Scheme 9



b. Phosphorylation in the Presence of Carboxylic Acids, Azoles, and Other Activators

The discovery of the catalytic influence of AHC on the alcoholysis of ATPA brought about the problem of the search for new ways of accelerating this type of phosphorylation. The acidic properties of phenols are known to be comparable with those of AHC. Therefore, successful experiments on the phosphorylation of ATPA in the presence of phenol were carried out.[66] Note that phenolysis of phosphamides does not require activation by AHC; apparently, phenol acts simultaneously as the reagent and the catalyst.

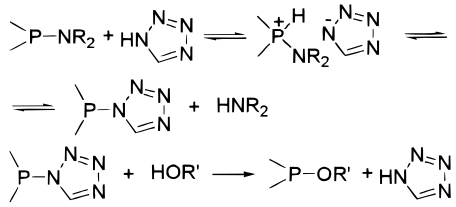
Recently, it was briefly reported that alcoholysis of ATPA is accelerated by chlorosilanes.[67] The possibility of using carboxylic acids, in particular, acetic acid, as phosphorylation catalysts has been studied in greater detail.[15,68] ATPA alcoholysis can also be catalyzed by other acids, for example, amidothiocarbaminic acids and their ammonium salts.[69]

The search for new versions of phosphorylation resulted in an attempt to activate alcoholysis by free azoles, which are N−H acids. 1-Tetrazole (pK_a ∼4.8) (see, for example, refs 70−73) is used most often; 1,2,4-triazole (p*K*a ∼10)[74,75] and azoles whose acidity has been enhanced by introduction of electronegative substituents into the azole ring (4,5-dichloroimidazole, 3-chloro-1,2,4-triazole,[74,76] 5-*para*-nitrophenyltetrazole, 5-mercaptotetrazole,[77] and some others[78]) are used less frequently. Azole salts, mainly diisopropylammonium tetrazolide, are also used for this purpose.[79−86] Very good results have been achieved in the phosphorylation of more complicated compounds under optimized conditions: complete phosphorylation occurs over a period of 2−3 min at 20 °C. Owing to these results, the azolide version has found espe-

cially wide use, in particular, in automated sequencers used to prepare oligonuceotides (see section II.4.b). Tetrazolide activation of phosphamides can eliminate some side processes, which occur under conventional conditions. Thus, alcoholysis of amido phosphorodithioites under ordinary conditions involves both P−N and P−S bonds,[87] whereas in the case of reaction of amido phosphorothioites and phosphorodithioites[88] with equimolar amounts of alcohols in the presence of tetrazole, only the phosphamide route of phosphorylation is observed.

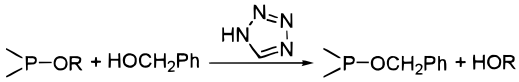
The matters with understanding of the chemistry of the azolide version of phosphorylation stand worse. It is significant that in the above-described experiments azoles were taken in equimolar or even in larger amounts with respect to ATPA rather than in catalytic amounts. Thus, these reactions can hardly be classified as catalyzed reactions. In this connection, note that ^{31}P NMR spectra of the reaction mixtures containing excess tetrazole exhibit a signal due to the transamidation product, namely, P(III)-tetrazolide, which is considered to be an intermediate product.[88−92] The possible formation of P(III)-tetrazolides has served as the subject of special studies emphasizing the role of the acidity of activators, which are able, in the opinion of the authors cited, to protonate the initial ATPA.[74,89,91,92] The researchers were able to perform kinetic measurements in the ATPA−tetrazole system and proposed a scheme for the phosphorylation of alcohols (Scheme 10).[92]

Scheme 10



Unfortunately, no thorough analysis of this scheme was carried out. Two critical remarks can be made concerning this point. First, the authors of this scheme only postulated but did not prove the ATPA protonation by a tetrazole. Second, they did not come to an understanding of the possible parallel processes. This remark is especially significant in view of the fact that tranesterification of neutral phosphites in the presence of tetrazole[93,94] and 1,2,4-triazole[95] has been reported (Scheme 11).

Scheme 11



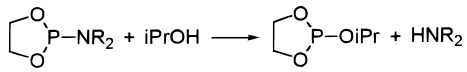
This process is related to the reaction discussed here because it also consists of nucleophilic substitution at trivalent phosphorus in the presence of azoles. However, in this case, transformation of alkyl phosphite into tri- or tetrazolide can hardly be postulated as a necessary reaction step. Indeed, reactions of this type are unknown whereas back reactions are well-known. Therefore, not only the above-presented methods of activation but also other activation methods should be analyzed. We believe that the most probable type of activation of alcoholysis of alkyl phosphites is the formation of a complex of this ester with azoles. In this case, general acid catalysis can be involved, as in the case of transformation of dialkylamides in either the target esters or azolides. If azolides prove to form as intermediates in the synthesis of esters, they also will need acid assistance from azoles. The formation and transformation of the corresponding azole complexes might be a crucial point of catalysis in all these cases. Unfortunately, kinetic studies using catalytic amounts of azoles are only at the beginning.[75]

2. General Features of Phosphorylation of Alcohols and Phenols

Kinetic studies of ATPA alcoholysis are few in number; therefore, no reliable correlations relating the reactivity of phosphamides to their structure have been identified so far. Nevertheless, it can be stated that some qualitative regularities have been elucidated to date. Thus, branched alcohols are normally less susceptible to phosphorylation than linear ones and secondary alcohols are inferior to primary ones.[10,17,66] High reactivity of ATPA toward phosphorylation of acidic alcohols[66] and especially phenols[10,14,15,17,66] has been reported. A distinctive feature of the latter compounds is that their reactivity depends appreciably on the solvent used.[15,96,97] It should be noted that intramolecular hydrogen bonds hamper phosphorylation of functionalized phenols.[98] ATPA are capable of phosphorylating enolizable carbonyl compounds, for instance, anthrone[99] and acetylacetone.[100]

The influence of the ATPA structure on the phosphorylation route follows more complex patterns. It has been found for numerous cases that the amido groups in phosphorus triamides can be replaced stepwise by alkoxy[101,102] or aryloxy[96,97] groups. Thus, triamides prove to be more reactive than diamides while diamides are more reactive than monoamides. The reactivity of ATPA bearing various substituents at the nitrogen atom has been considered in detail. For instance, in relation to the reaction shown in Scheme 12, it was demonstrated that the phospho-

Scheme 12

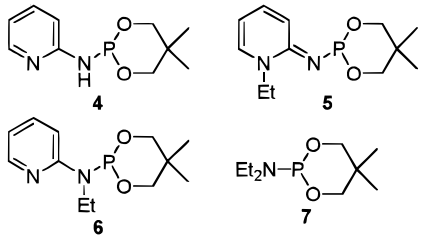


rylating activity of the amide increases in the following order of substituents at the phosphorus atom: $N(Pr^i)_2 < NMe_2 < NMePh < NPh_2$.[17] Attention is attracted by the high reactivity of mono- and diphenylamides, which has also been noted for other cases.[104] Phosphopyrrolides, which possess an enhanced stability against alcoholysis, are unpromising reagents.[10,50,104,105] Apparently, this is due to the exceptional inertness of the lone electron pair in pyrrole derivatives with regard to the formation of a hydrogen bond. Conversely, vinylamides of trivalent phosphorus acids (TPA) possess high phosphorylating capacity.[45] To summarize the foregoing, we can conclude that for the majority of systems the ten-

dency of the amido group to leave the phosphorus atom follows an inverse dependence on its basicity. Note that according to a study,[15] phenolysis of ATPA does not obey these regularities; these results seem to need reinvestigation rather then revision.

The discovered high reactivity of anilides in the alcoholysis prompted the researchers to extend the studies to the related heterocyclic phosphamides.[106,107] Phosphorylated 2-aminopyridine **4** and its two derivatives **5** and **6**, ethylated at different phosphorus atoms**,** have been involved in methanolysis (Scheme 13),[108,109]

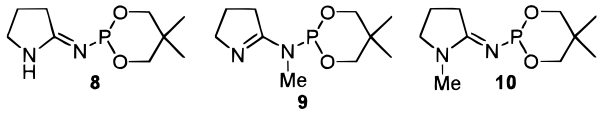
Scheme 13



The study of the rates of methanolysis of these compounds led to several important conclusions: (1) phosphamides **4** and **6** are more reactive than their aliphatic analogue **7**; the early observation of high reactivity of phosphanilides was thus reliably confirmed; (2) phosphamides **4** and **6** are more reactive than phosphoimide **5**; hence, electron distribution in the P−N−C−N moiety is a significant factor for the alcoholysis of a P−N bond; (3) phosphamide **4**, whose molecule contains secondary hydrogen atoms, proved to be much more reactive than the *N*-ethyl derivatives **5** and **6**. Moreover, reagent **4** does not need catalysts to undergo alcoholysis, whereas **5** and **6** do need a catalyst. Apparently, compound **4** acts simultaneously as the substrate and the activator in this reaction.[109]

Thus, the data presented here demonstrate that the susceptibility of ATPA for alcoholysis can depend crucially on structural features of these compounds. An even more interesting picture of this dependence is found in the case of alcoholysis of 2-aminopyrrolines.[108,110,111] The rates of methanolysis of three related compounds (**8**−**10**) were compared to demonstrate that compound **8** is the most reactive toward substitution (Scheme 14).

Scheme 14



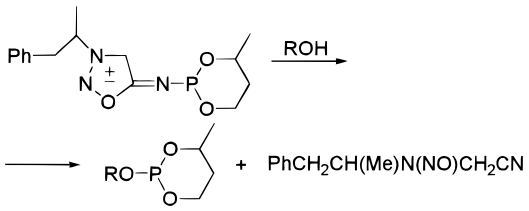
A specific feature of the structure of this compound is the presence of an active hydrogen atom. In view of the foregoing, note that pyrroline derivative **8** is more reactive than pyridine derivative **4**. This fact suggests that prototropy, which is more likely for phosphopyrroline **8** than for phosphopyridine **4**, plays an important role in phosphorylation.

The attention to phosphorylated derivatives of heterocycles as phosphorylation agents for fine organic synthesis has now become especially acute regarding investigations of phosphoazolides and related systems. The series of these works started with two publications[112,113] and continued in other studies,[114−118] in which phosphoimidazolides were noted as the most reactive compounds. In recent years, the tendency for expanding the search front and for systematization of the results has taken shape. In this connection, several studies dealing with the synthesis of various phosphoazolides and their phosphorylation capacity are worth noting.[119−123]

It was found that the reactivity of P(III) azolides depends on the type of phosphorus residue; more precisely, it substantially decreases in the sequence azolidophosphorus diesters > azolidophosphorus diamides > azolidophosphinites. The reactivity also depends on the nature of the azole, namely, it decreases in the sequence imidazolide > pyrazolide > triazolide > benzimidazolide.[95] Note that the solvent polarity also appreciably affects the phosphorylation capacity of P(III)-azolides.[95] In recent years, the use of nitrotriazolides, which are convenient reagents for fine organic synthesis, as phosphorylating reagents has been proposed.[124]

To continue the discussion of alcoholysis of heterocyclic phosph(III)amides and imides, we would like to mention the results of phosphorylation of alcohols with phosphosydnonimine (Scheme 15).[125]

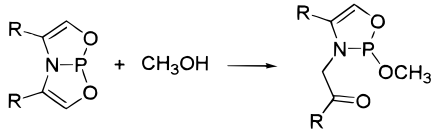
Scheme 15



This reaction is of interest due to the fact that it is not accompanied by accumulation of a nitrogen base, because the sydnoneimine being evolved isomerizes immediately to give *N*-nitroso-1-phenylisopropylaminoacetonitrile. At present, data on the alcoholysis of hydrazides,[126] hydroxylamides,[127] acylamides,[128] guanidides,[131] and azides[132] of some trivalent phosphorus acids have been reported. All these compounds possess good phosphorylating capacity, which is enhanced in the presence of acid catalysts; however, no specific features that would make these derivatives especially valuable have been noted. The corresponding isocyanates also possess phosphorylating capacity. In this case, the process is stepwise; first, phosphorylating carbamates are formed and then their P−N bonds are cleaved in the usual fashion.[133]

An unusual example of methanolysis of bicyclic divinyl phosphoramidites is worth noting. The reaction involves rupture of the vinyl phosphite rather than the amide bond (Scheme 16).[134] This outcome

Scheme 16

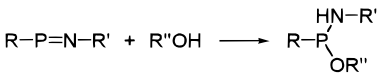


may be due to electromorphism of the initial compounds.[135]

The advantages of the phosphamide phosphorylation method, namely, mild reaction conditions and the absence of side processes, have been noted above. There are a few exceptions to this general rule which should be mentioned here. It was found that phosphorylation of triarylcarbinols by phosphorus imidazolide yields triarylimidazolylmethanes instead of the expected products.[136] The unpredictability of the outcome of reactions of some heteroorganic derivatives of ATPA is also a drawback of the phosph(III)-amide method. For example, systems containing C−Si[137] and O−Si[19,138] bonds can undergo mainly cleavage of these bonds rather than the P−N bonds during alcoholysis and phenolysis. An acid catalyst (tetrazole) can, however, switch the reaction to the cleavage of the P−N bond.[139] Similar complications have been noted for systems with P−N and P−S bonds.[140]

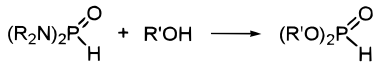
The above data refer to the transformations of amides of phosphorus, phosphonous, and phosphinous acids, which are traditional objects of investigation in organophosphorus chemistry. In recent years, it has been shown that the process in question is more general. Thus, hypophosphorus amides undergo alcoholysis.[141−143] Interestingly, phosphimine derivatives also react with alcohols and phenols[144,145] (Scheme 17).

Scheme 17



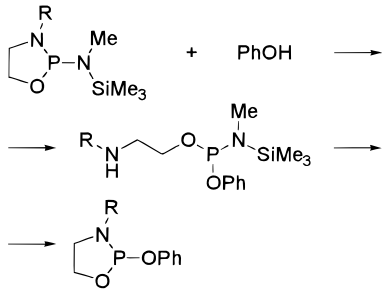
In the case where excess alcohol is used, further alcoholysis is possible, which involves the P−N σ-bond. Finally, the data on the transformations of hydrophosphoryl (hydrogen phosphonate) amides are noteworthy. These prototropic systems also easily react with alcohols[146,147] (Scheme 18).

Scheme 18



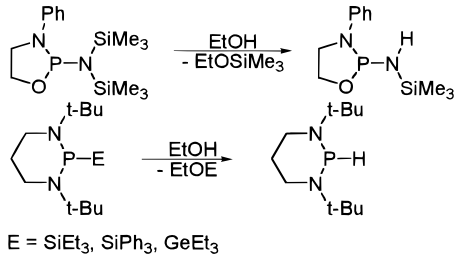
Let us consider the influence of structural factors on the route of alcoholysis and phenolysis of ring systems whose molecules contain both *exo*- and *endo*-phosphamide bonds. Data on the reactions of alcohols and phenols with equimolar amounts of 2-alkylamino-1,3,2-oxazaphospholanes and -diazaphospholanes[11,148−150] and phosphorinanes[150−153] can be found in the literature. These reactions mainly result in the cleavage of exocyclic bonds. Oxazaphospholanes containing an exocyclic P−C bond are much more reactive toward alcoholysis of an endocyclic P−N bond than the corresponding 2-alkoxy derivatives; the introduction of an alkyl substituent at position 5 of the oxazaphospholane ring markedly increases the stability of the P−N bond.[154] However, alcoholysis of oxazaphospholanes containing an exocyclic *N*-methyl-*N*-trimethylsilylamino group starts with the cleavage of the endocyclic P−N bond, the exocyclic bond being the second to react. In the case of phenolysis, the second step of the process involves, again, ring closure (Scheme 19).[138]

Scheme 19



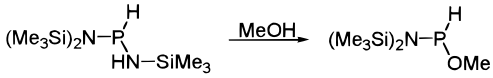
When the molecules contain exocyclic *N*,*N*-bistrimethylsilylamino group[137] or trisubstituted *P*-silyl and *P*-germanyl groups,[141] alcoholysis does not involve the cyclic core of the molecule but starts with rupture of exocyclic N−Si and P−Si(Ge) bonds (Scheme 20).

Scheme 20



The specific character of alcoholysis of acyclic P−N−Si systems deserves attention. When the molecules of these ATPA contain two types of trimethylsilylamide groups, namely, secondary and tertiary groups, the secondary silylamido group is the first to undergo alcoholysis (Scheme 21).[142]

Scheme 21

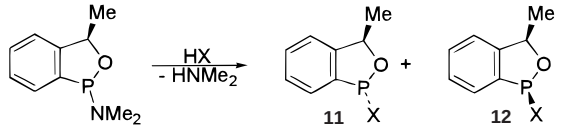


Many researchers paid attention to the stereochemistry of replacement of amido groups at a P(III) atom. This problem seems to be complicated because substitution may be accompanied by the inversion of the phosphorus center (especially for phosphorylation at elevated temperatures) both in the starting ATPA and in the reaction products. This inversion would be facilitated by acidic admixtures[155,156] and some other factors, for example, the presence of excess alcohol. Therefore, the results of early studies, in which the purity of the initial reactants was not stringently checked, should be treated with caution. This refers, most of all, to the publications dealing with the mechanisms of reactions of optically active compounds (see, for example, ref 157) in which conclusions on the chemistry of transformations were based only on measurements of the optical rotations of the reaction mixtures.

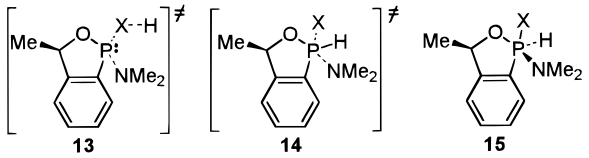
More reliable results have been obtained by NMR analysis of the stereochemical transformations of diastereomers. Thus, J. Nielsen and O. Dahl,[34,158] who

studied the reactions of some phospholane derivatives with phenol by ^{1}H NMR spectroscopy, observed the initial configuration inversion at the phosphorus atom and the subsequent analogous process for the reaction products. The latter resulted in the formation of a thermodynamically stable isomer (<5 min). The data obtained in a ^{1}H and ^{31}P NMR study of the nucleophilic substitution in the diastereomerically pure benzooxaphospholene (Scheme 22; X = OMe, OBu^t, OPh, Nme$_2$, N(CH$_2$)$_5$, NHPh) demonstrated that the reaction with HX (X = OMe, OPh, N(CH$_2$)$_5$) at 25 °C in $CDCl_3$ affords two products, **11** and **12**, and that initially the product with the inverted configuration at the phosphorus atom is formed predominantly. The subsequent transformations evidently yield an equilibrium mixture of diastereomers **11** and **12**. When X = OBu^t and NHPh, the reaction rate is lower than the inversion rate; therefore, in this case, the reaction immediately gives an equilibrium mixture of **11** and **12**. The authors cited believe that the S_N2(P)-type mechanism, proposed previously for the substitution at P(III) (see, for example, ref 16), is unlikely because this would require an unfavorable diequatorial arrangement of the phospholene ring in the transition states of two different types, **13** and **14**; instead, they assume the formation of a phosphorane intermediate of type **15** (Scheme 23).

Scheme 22



Scheme 23

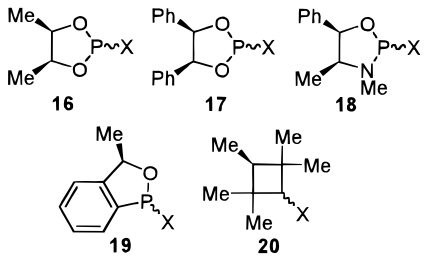


Thus, the stereochemical outcome of the reaction depends on which type of pseudorotation in transition state **15** (needed to bring the NMe_2 group in an axial position, favorable for its removal) would require a lower energy barrier. Analysis of the possible patterns of pseudorotation led the authors to the conclusion that the reaction is preferentially accompanied by inversion if hydrogen proves to be more apicophilic than the NMe_2 group; this is a known fact for this type of phosphorane.[159]

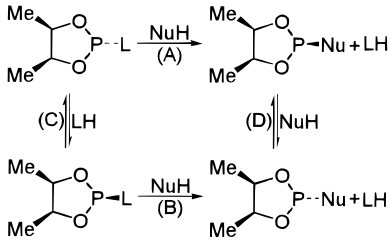
As a continuation of their investigations, J. Nielsen and O. Dahl studied the stereochemistry of nucleophilic substitution in substrates **16**−**20** in their reactions with MeO^-, MeOH + E_3N, Et_3NH, PhOH, HCl, and MeOH (Scheme 24).[34]

The majority of the compounds studied were configurationally stable at 25 °C only in a very pure state, their isomerization being accelerated by nucleophilic or acidic impurities (atmospheric moisture, alcohols, amines, acids, etc). The scheme given below reflects various routes for the isomerization of compounds **16**−**20** (Scheme 25).

Scheme 24



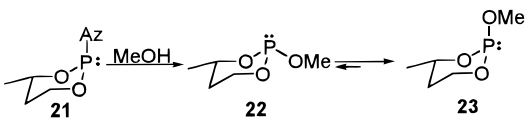
Scheme 25



In the opinion of the researchers cited, pure inversion is possible only when substitution (***A*** and ***B***) occurs much faster than isomerization (***C*** and ***D***) (see also ref 157). It was concluded in the majority of cases that nucleophilic substitution in ATPA is accompanied by complete inversion. This conclusion, however, is somewhat conventional. In fact, many phosphocyclic compounds of trivalent phosphorus with amide groups are normally configurationally unstable, and hence, no stereoselectivity is observed in the reactions of these compounds.

Clearer results have been obtained in a study of the stereodynamics of methanolysis of cycloasymmetric azolides of TPA **21**, which were shown[120−123] to exist in a *trans*-configuration with an axial arrangement of the azolide substituent (Scheme 26).

Scheme 26



It was found by ^{31}P NMR spectroscopy that in this case alcoholysis occurs rapidly even at 20 °C (inversion of the configuration) to give a labile ester, isomer **22**, which is slowly converted into a stable ester, isomer **23**. Stereochemical analysis of cleavage of the endocyclic P−N double bond in the molecules of 1,3,2-phosphorinanes containing chiral centers has been performed.[160,161]

3. Phosphorylation of Alcohols and Phenols. ATPA in Fine Organic Synthesis.

The majority of publications dealing with the chemistry of ATPA deal with the use of these compounds in fine organic synthesis. This is due to the accessibility and high reactivity of ATPA and the possibility of using them under mild conditions. Owing to the latter fact, targeted phosphorylation of complex polyfunctional systems can be carried out without isomerization, dehydration, and other undesirable side processes, which often accompany trans-

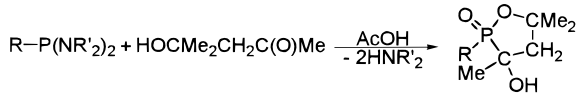
formations of phosphorochloridites and related reagents. Below we consider the main synthetic results, which are classified according to the type of hydroxyl compounds subjected to phosphorylation.

a. Phosphorylation of Alkanols, Phenols, and Their Functional Derivatives

Phosphorylation of alkanols and phenols with ATPA is a general process used to prepare esters (or amido esters) of phosphorous acid and other acids of trivalent phosphorus. Initially, this reaction has been used for the synthesis of simple derivatives of the above-mentioned classes of compounds and has been recognized as being not only convenient but also practically feasible[101] for the preparation, in particular, of sterically hindered phenols.[162,163] Later, the phosphamide method has been widely used to synthesize various functionalized systems, whose molecules contain a trivalent phosphorus atom and other functional groups, e.g., phosphorylated amino[163−168] and amido[169−174] alcohols, choline,[175,176] partially acetalized triols,[177−181] quinine,[182] fagaronin,[183] biotin,[184−186] borneol,[164] structural analogues of porphyrins,[187] and halogenated alcohols.[188−190]

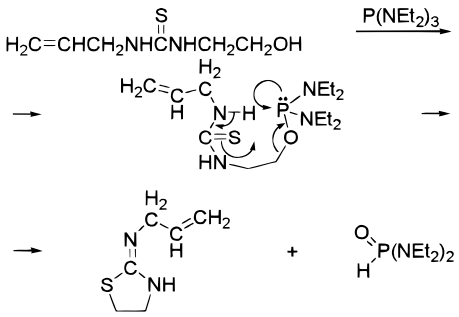
Phosphorylation of functionalized alcohols can be accompanied by additional reactions; this extends the potentialities of classical synthesis and opens up simple routes to interesting heterocycles, for example, Scheme 27.

Scheme 27



In some cases, phosphorylation creates complex systems which subsequently undergo elimination of phosphoryl compounds. This route has been used, in particular, to prepare 2-allyliminothiazolidine (Scheme 28).[191]

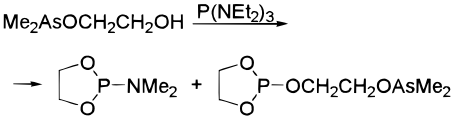
Scheme 28



The transformation pathways presented above have been explained comprehensively by the authors cited. Meanwhile, some other phenomena described in the literature have not been adequately interpreted; this is true, for example, for double phosphorylation of dimethylarsenylated ethylene glycol (Scheme 29).[192]

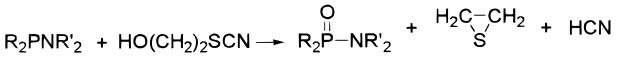
Functionalized alcohols able to generate electrophilic species can react with ATPA according to the phosphorylation pattern. The reaction of phosphorous

Scheme 29



amides with thiocyanato alcohols can be presented as an example (Scheme 30).[175,193]

Scheme 30

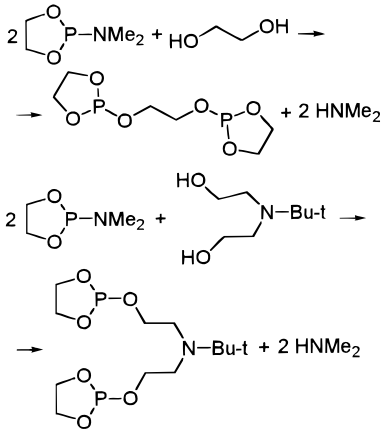


b. Phosphorylation of Diols

Reactions in the ATPA−diol systems have been considered in numerous publications, which is due to the chemical diversity of the performed processes and the importance of the products thus obtained. The following lines in the phosphorylation of diols can be distinguished: (1) bis(phosphorylation) involving both hydroxy groups of the diol and ending in the formation of a diphosphorus system; (2) monophosphorylation resulting in heterofunctional systems—phosphorus-containing alcohols and phenols; (3) cyclophosphorylation. Combination of various phosphorylation and polycondensation routes, resulting in the formation of polymeric esters, is also possible. This variant will be considered separately.

Bis(phosphorylation) of glycols and dihydric phenols has been studied extensively. A series of studies have been published, devoted to reactions of monoamides of trivalent phosphorus acids with glycols taken in a molar ratio of 1:2. This normally yields diesters, for example, see Scheme 31.[194,195] Note that

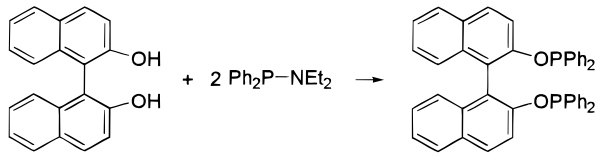
Scheme 31



the alternative (phosphorochloridite) method often leads to poorer results because the hydrogen chloride being evolved reacts with a new reaction center.

Resorcinol,[96] hydroquinone,[96,196] 1,5-dihydroxynaphthalene,[197] and β-dinaphthalene[198] can be phosphorylated in a similar way by alkanediyl phosphoramidites or diphenylphosphinous amides. Some of the bis(esters) obtained by this method are promising ligands for the development of metal complex catalysts. The synthesis of bis(diphenylphosphinite) of β-dinaphthol can serve as an illustration (Scheme 32).

Scheme 32



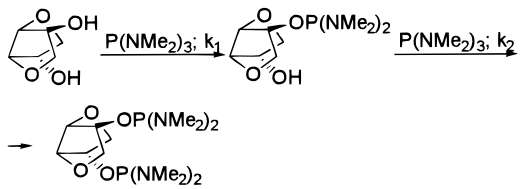
Rhodium complexes, prepared using optically active forms of this diol, are efficient in enantioselective hydroformylation, surpassing in this respect the rhodium complexes of the corresponding diphosphine (BINAP).[199] This comparison is significant because BINAP has been advertised for a long period as the optimum ligand for this type of catalytic system.[200]

Phosphorus triamides[196,201,202] and phosphonous diamides[196,203] can also be used for double phosphorylation of dihydric phenols; however, this can be accompanied by side processes giving rise to more complex systems.[201]

In the case of diols in whose molecules the hydroxy groups are located close to one another in space, cyclization rather than bis(cyclophosphorylation) is the typical reaction pathway. In this case, one-half of the phosphamide does not react. An example is provided by phosphorylation of catechol and its derivatives by hexaalkylphosphorus triamides.[204,205] Meanwhile, phosphorylation of catechol by alkanediyl phosphite derivatives affords bis(alkanediyl phosphites), which are stable compounds and are not converted into benzophospholanes.[206]

The reactions of phosphorus amides with 1,4;3,6-dianhydro-D-mannitol deserve special attention.[207−209] In this case, the alcoholic hydroxyls in the molecule of the initial compound are not located so close to each other as those in catechol; therefore, phosphocyclization is hampered. Meanwhile, the primary phosphorylation event creates an unusual situation: the free hydroxyl in the intermediate proves to be more reactive than the hydroxyl of the initial diol, which is passivated due to the formation of intramolecular hydrogen bonds. The high reactivity of the intermediate accounts for the fact that the reaction between equimolar amounts of dianhydromannitol and hexaethylphosphorus triamide yields mostly the bis(phosphorylated) product ($k_2 > k_1$), some dianhydro-D-mannitol remaining unchanged (Scheme 33).[209]

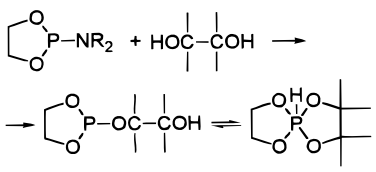
Scheme 33



From the preparative viewpoint, it is most convenient to prepare the bis(phosphorylation) product using a more reactive reagent, namely, the 3,5-dimethylpyrazolide of tetraethylphosphorus diamide, which reacts in acetonitrile to give the required product in a high yield even at 0 °C.

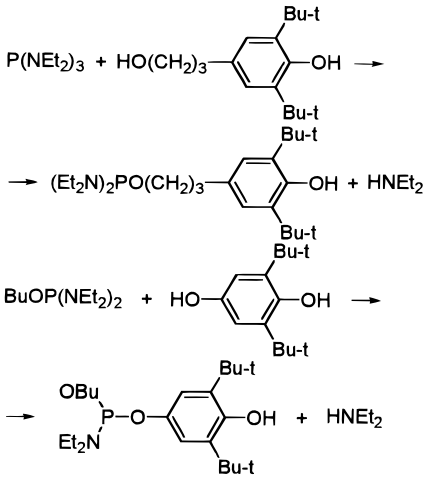
Monophosphorylation of diols with an equimolar amount of a phosph(III)amide seldom gives good results. The group of reactions between cyclic monoamides of trivalent phosphorus acids with 1,2-diols has been studied most comprehensively. In this case, the phosphorylated alcohol formed initially is prone to ring−chain tautomerism (Scheme 34).

Scheme 34



The position of the equilibrium is determined by the structures of the compounds, the solvents, and the temperature. Normally the equilibrium is shifted completely or significantly toward the species with a five-coordinate phosphorus atom, hydrospirophosphoranes. The history of this problem and the depth of the insight into it have been reflected in a series of reviews.[210−213] A different result was obtained in the phosphorylation of diols, whose hydroxy groups have different chemical natures, one of them being spatially open and the other being shielded. 4-(γ-Hydroxypropyl)-2,6-di-*tert*-butylphenol[214] and di-*tert*-butylhydroquinone[215] are examples of such diols. In this case, di- and triamides react regioselectively with an equimolar amount of the diol (Scheme 35).

Scheme 35

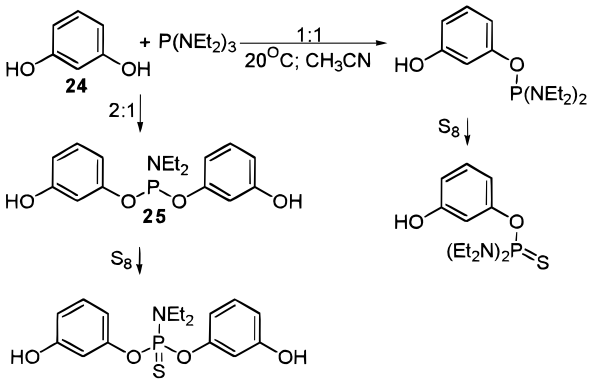


The phenyl phosphites obtained in this way are quite stable compounds; they can be distilled in a high vacuum and enter into phosphorylation of foreign nucleophiles due to their phosphamide fragments.

In recent years, it has been found that ordinary dihydric phenols, for example, resorcinol **24**, react with an equimolar amount of phosphorus triamides at 20 °C to give predominantly *O*-hydroxyphenyl phosphorus diamides. Even more complex derivatives of this type **25** have been obtained with another ratio of the reactants. These phenyl phosphites are labile compounds (their molecules contain both phosphorylating and phosphorylable groups); therefore, they were isolated as sulfides (Scheme 36).[202]

Cyclophosphorylation and cyclooligophosphorylation of diols with amides of TPA have been studied quite comprehensively. It was shown that phosphorus

Scheme 36

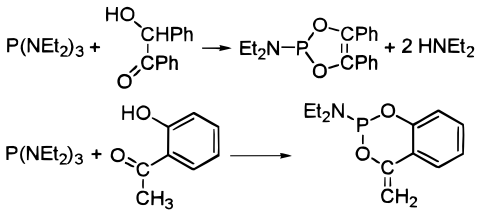


di- and triamides accomplish preparative phosphocyclization of 1,2-,[117,216−218] 1,3-,[117,216,219−221] 1,4-,[222−225] and 1,5-[226]alkanediols to give the corresponding 1,3,2-dioxaphosphorinanes. Phosphorylation of functional derivatives of diols by these phosphamides occurs in a similar way.[227,228]

Normal cyclophosphorylation takes place in the case of catechol,[204,205,229] *o*-naphthodiols,[230] and bis-*β*-hydroxy-α-naphthylmethane.[231] *o*-Diols that belong to the class of aromatic heterocycles, e.g., 2,3-dihydroxypyridine[232] and 2,3-dihydroxyquinoxaline,[233] also react with ATPA giving rise to phosphorus-containing rings. However, note that these cyclizations occur under different conditions. Thus, the latter diol undergoes cyclophosphorylation with great difficulty, apparently due to the high strength of the intermolecular hydrogen bonds.

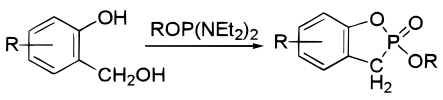
The easy cyclophosphorylation of hydroxy ketones, which react in the corresponding enol form, provided that the hydroxy groups are close in space, also deserves attention (Scheme 37).[100,234,235]

Scheme 37



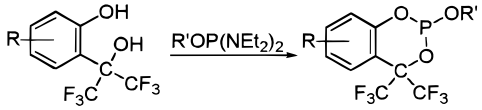
Several researchers have attempted to perform cyclophosphorylation of saligenin or related *o*-hydroxymethylphenols in order to obtain benzophosphorinanes. However, these attempts proved unsuccessful; instead of the expected compounds, benzoxaphospholanes were formed (Scheme 38).[236]

Scheme 38



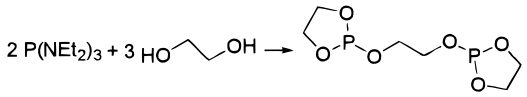
It was suggested that the benzyl cations, readily formed after the primary phosphorylation, play the key role in these reactions. In view of this hypothesis, trifluoromethyl derivatives of saligenin have been subjected to cyclophosphorylation; this resulted in the successful synthesis of previously unknown benzodioxaphosphorinanes (Scheme 39).[237]

Scheme 39



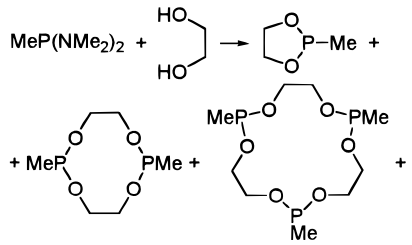
Bis(trifluoromethyl)quinolino-1,3,2-dioxaphosphorinanes were prepared in a similar way.[238] When discussing phosphorylation of diols, we would like to mention some cases of combination of reactions giving finally cyclic bisphosphites. This requires an appropriate ratio of the reactants. This combination is best performed with 1,2-diols, for example, ethylene glycol (Scheme 40).[194]

Scheme 40



Cyclophosphorylation of aliphatic diols results in some cases in the formation of mixtures of 1,3,2-dioxaphosphocyclanes with their dimers and trimers.[208,239,240] These compounds occur in equilibrium with one another, for example, see Scheme 41.[240]

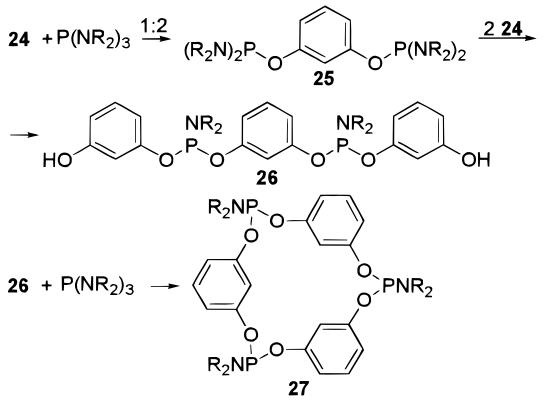
Scheme 41



The individual oligomers, which can be regarded, in essence, as the first representatives of a new class of crown ethers, present great interest for supramolecular chemistry. Unfortunately, the oligocycles shown in Scheme 41 are not, in reality, available compounds. Therefore, the search for the design of new classes of phosphorus-containing macroheterocycles belonging to the crown ether type was initiated. Most recently, a strategy for the synthesis of compounds in whose molecules arylene fragments regularly alternate with phosphorus amide residues was developed.[202] The first stage of the synthesis consists of the formation of oligophosphite blocks **26** based on resorcinol and having two terminal reactive groups. The second stage involves cyclization using phosphamide chemistry techniques. The following synthetic route can be presented as an example (Scheme 42).

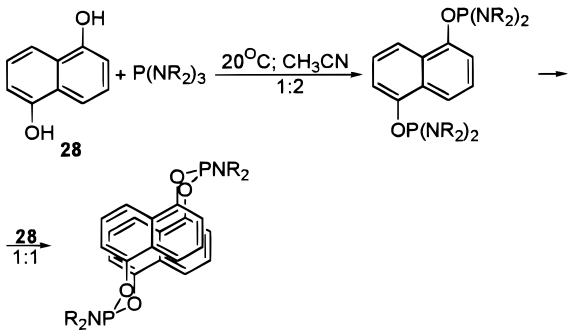
It is very significant that all the synthetic steps occur under mild conditions and give products in high yields.[241] Later analogues of ester **27** containing 4−6 phosphamide residues in the ring have been synthesized.[241,242] All the compounds synthesized were studied regarding their structures and reactivities.

Scheme 42



Macrocycles of yet another class, double-deck systems, have been synthesized based on 1,5-dihydroxynaphthalene **28** and other dihydric phenols with spatially remote hydroxy groups. These compounds are readily phosphorylated by phosphotriamides to give bis(phosphorus diamides). After that, a diol is added to the system and the condensation resulting in a macroheterocycle readily occurs (Scheme 43).[243]

Scheme 43



The resulting compounds are molecular "containers", able to fix molecules of the solvent in which phosphorylation has been carried out in their cavities.

c. Phosphorylation of Tri-, Tetra-, and Higher Oligools

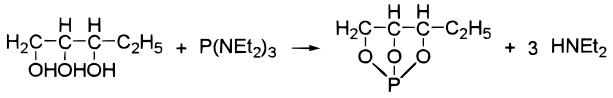
ATPA were included in the set of popular phosphorylating reagents at about the time when investigations of polyphosphorus systems and phosphorus frameworks were shaped as topical problems in organic chemistry. Under these conditions, it has been necessary to evaluate the possibility of performing targeted syntheses of complex three-dimensional structures using the new phosphorylating reagents.

Studies on the subject discussed here proved to be fruitful, but they did not cover all the promising lines of research; therefore, they have not yet resulted in accumulation of a well-structured array of information. Therefore, we classified the published data based on a formal criterion, namely, the number of hydroxy groups in the molecule of the oligool subjected to phosphorylation.

Phosphorylation of Triols. Phosphorylation of glycerol by TPA amides to give open-chain esters and phosphorus-containing rings has been described in the literature. (In addition, considerable attention has been paid to phosphorylation using ATPA of those glycerol derivatives that present interest for the chemistry of phospholipids. These studies will be considered in the section devoted to phospholipids.) Synthesis of triesters was considered only in one publication, which deals with the reaction of glycerol with *N*,*N*-diethylphosphinous amides.[244] It was noted that the reactivity of phosphamides in these reactions is lower than that in the phosphorylation of other alcohols. Apparently, this is due to the presence of strong hydrogen bonds in the substrate.

It should be noted that glycerol is a poor partner for bicyclophosphorylation involving trifunctional derivatives of phosphorous acid. The difficulty of phosphorylation is aggravated by the instability of the target product containing a strained central nucleus.[245] However, terminally substituted glycerols, for example, penta-1,2,3-triol, are smoothly phosphorylated to give stable esters (Scheme 44).[246] In this

Scheme 44

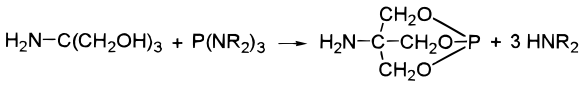


case, bicyclophosphite molecules might experience stereoelectronic interactions involving terminal substituents, which change parameters of valence bonds and, hence, decrease angular strain; in addition, the Thorpe−Ingold effect may also be involved.

Related bicyclophosphites are synthesized even better when phosphorus triamides are made to react with linear triols with more remote hydroxy groups such as butane-1,2,4-triol[247−249] and pentane-1,2,5-triol[250] or related branched systems—1,1,1-tri(hydroxymethyl)alkanes[251] and 1,1,2-tri(hydroxymethyl)-ethane.[252] In all of these cases, the reactions give stable cage bicyclophosphites whose molecules contain fused 1,3,2-dioxaphospholane, 1,3,2-dioxaphosphorinane, and 1,3,2-dioxaphosphepane rings. These cages have found wide use in fine organic synthesis and coordination chemistry. They have attracted the attention of researchers engaged in physicochemical biology due to their ability to control the membrane transport. The synthesis of this type of phosphorus-containing cages is considered further in the section devoted to carbohydrate phosphites.[253]

Phosphorus triamides can also bicyclophosphorylate tris(hydroxymethyl)methylamine (Scheme 45).[254]

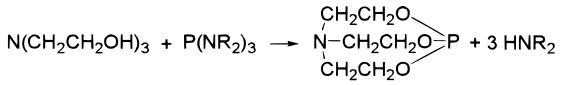
Scheme 45



In this case, a phosphorus cage is formed whose molecules contain two fused six-membered rings and a free amino group. This amino phosphite is a valuable ligand for the preparation of metal complex catalysts soluble in aqueous systems.[254] A formally structurally related and a very labile system, named phosphatrane, has been synthesized by the reaction of triethanolamine with phosphorus triamides (Scheme 46).[255−259]

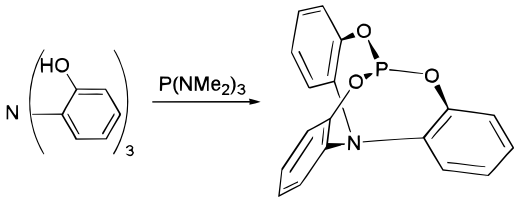
A cage amino phosphite, similar to that described above but having *o*-phenylene groups in place of the

Scheme 46



ethylene groups as the main alkylene units, has been prepared by the phosphorylation of tris(*o*-hydroxyphenyl)amine by hexamethylphosphorus triamide (Scheme 47).[260] This phosphite contains a rigid

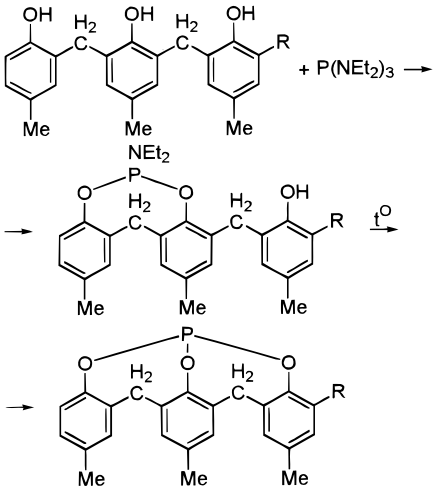
Scheme 47



framework of the cage type in which the phosphorus and nitrogen atoms do not approach one another and do not interact unlike those in phosphatranes.

Methylenephenols, which are components of compositions obtained from formaldehyde and phenols including *p*-cresol, are valuable raw materials for organic synthesis. Some trihydric phenols formed in these compositions have been brought in contact with hexaethylphosphorus triamide. Conditions for preparative cycloamidophosphorylation were chosen (Scheme 48).

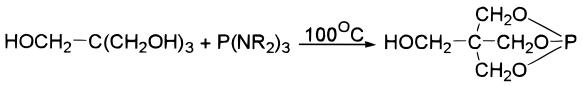
Scheme 48



Heating of these bifunctional compounds results in their transformation into cage bicyclophosphites, the ease of the process being substantially dependent on the radical R.[261]

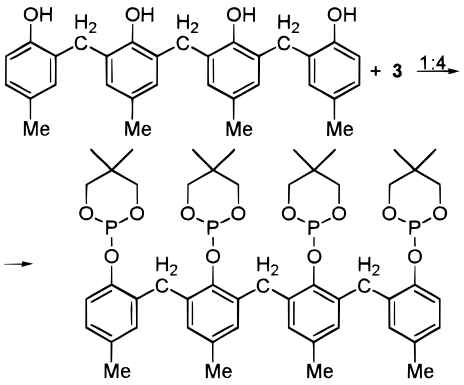
Phosphorylation of Tetraols. The majority of publications along this line have been concerned only with cyclophosphorylation. Pentaerythritol should be mentioned first among the promising substrates for phosphocyclization. This symmetrical tetraol is a readily available compound; it has served as a starting compound in various syntheses. Thus, it has been reported that heating of pentaerythritol with an equimolar amount of hexaethylphosphorus triamide affords a symmetrical cage phosphite, 4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane, in a high yield (Scheme 49).[247]

Scheme 49



This compound presents considerable interest regarding its possible subsequent transformations and as a material stabilizer and a ligand in the synthesis of metal complexes. α,α,*ω*,*ω*-Tetrakis(hydroxymethyl)alkanes introduced in reactions with equimolar amounts of hexamethylphosphorus triamide are converted in a similar way.[252] A linear tetraol in whose molecule *p*-cresol residues alternate with methylene units has been made to react with phosphotriamide **3**. This gave tetrakis(phosphite) in a good yield (Scheme 50).[262]

Scheme 50

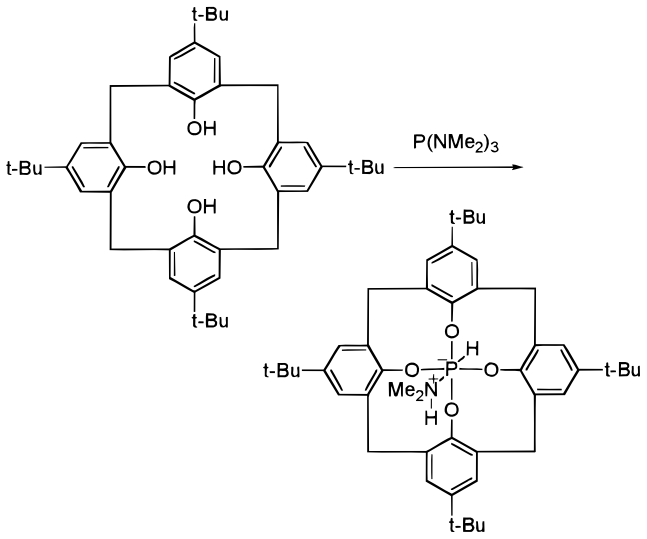


On contacting with *acac*-Rh(CO)$_2$, the tetrakis(phosphite) synthesized was converted into a tetranuclear complex, which proved to be a much more efficient catalyst for alkene hydrogenation than the corresponding complex prepared based on a similar *p*-cresol phosphite.[262] This fact seems significant regarding development of the catalysis by metal complexes with phosphorus(III)-containing ligands.

The study of the reactions of *p*-*tert*-butylcalix[4]-arene with hexamethylphosphorus triamide taken in equimolar amounts appears to be of considerable interest.[263] In this case, the calixarene undergoes triple phosphorylation to give a bicyclophosphite, whose phosphorus atom is located close to the phenolic hydroxyl that remains unreacted. Since these groups are located close in space, they readily react with each other giving rise to a phosphorane structure. This structure captures the dimethylamine molecule evolved in the reaction. Ultimately, the reaction affords a derivative of six-coordinate phosphorus **29** (Scheme 51).

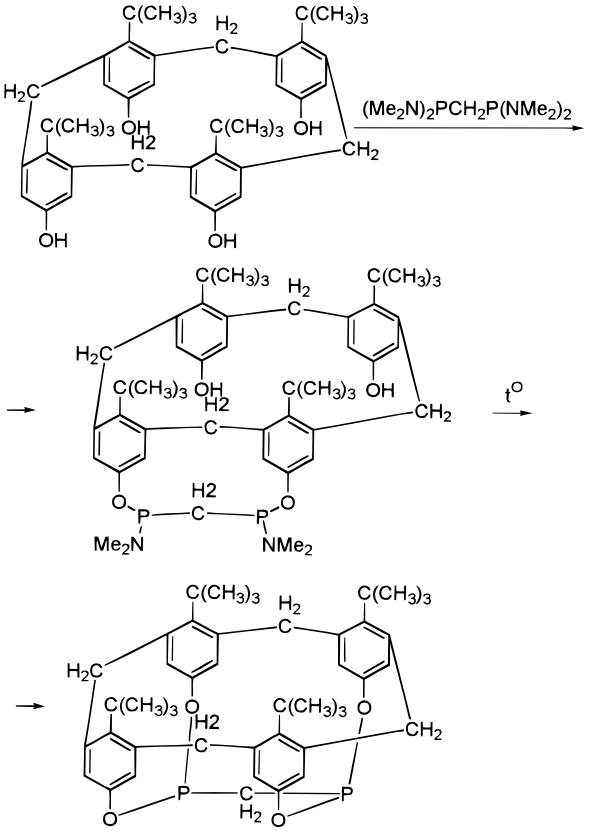
The subsequent study of the compound obtained showed that it can easily be transformed both with retention and change of the coordination number of phosphorus.[264,265] In addition, the above-mentioned calixarene was made to react with an equimolar amount of methylenebis(phosphonous) octamethyltetramide. This gives consecutively di- and tetraphosphorylation products and the compound **29** considered above (Scheme 52).[266]

Scheme 51



29

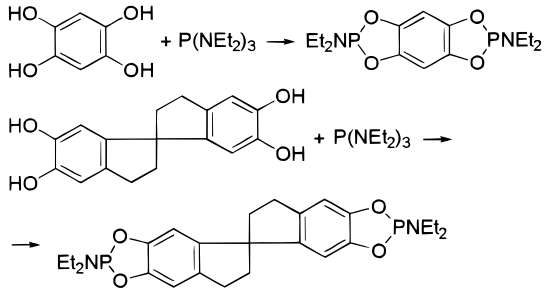
Scheme 52



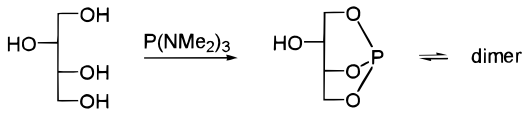
Cyclophosphorylation of other tetrahydric phenols whose molecules contain *o*-diol fragments is also noteworthy (Scheme 53).[267] The resulting bis(phosphamides) are of interest for the design of complex cavity structures.

The phosphorylation of threitol, which is a conformationally flexible tetraol, with phosphorus triamides follows a different pathway. The interaction between equimolar amounts of reactants yields initially a mixture of products, which passes subsequently into 1,2,4-bicyclophosphite, able to undergo reversible dimerization (Scheme 54).[268]

Scheme 53



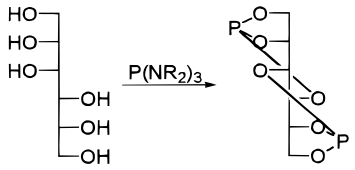
Scheme 54



Phosphorylation of Higher Polyols. Phosphorylation of linear C_4-C_5 polyols with TPA amides affords cyclic esters similar to those described in Scheme 54;[269,270] the structures of these products were reliably established by NMR and X-ray diffraction analysis.

The reaction of mannitol with phosphorus triamides appears to be more promising from the synthetic viewpoint. This made it possible to prepare bis(bicyclophosphite), resulting from complete phosphorylation of the hexaol (Scheme 55).[271] Note that

Scheme 55



a similar reaction with phosphorus trichloride leads to markedly poorer results because some of the hydroxyls are replaced by chlorine atoms.[272]

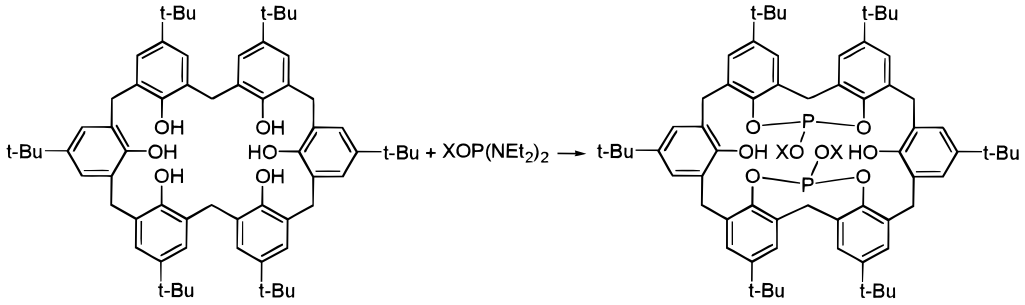
The hexahydric phenol, belonging to the class of calixarenes, has been introduced in the cyclophosphorylation by phosphorus diamides. The major reaction pathway is illustrated, apparently, by Scheme 56.[273]

Among the compounds obtained in this way, the product in which substituent **X** is a sterically hindered piperidine presents particular interest because it is a promising antioxidant for polymers.

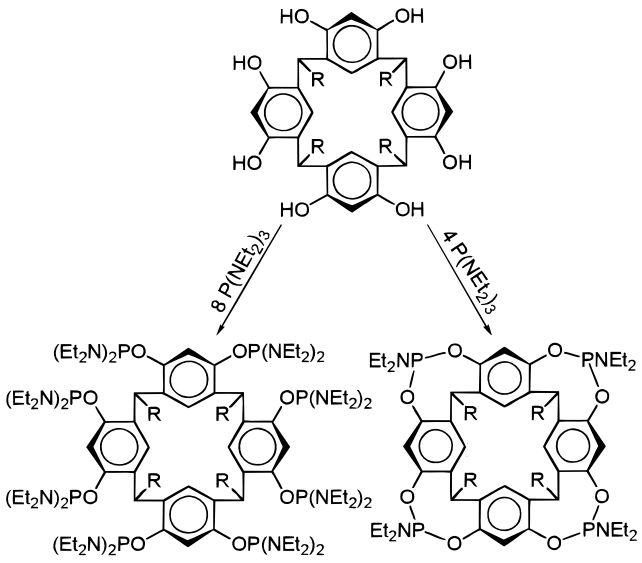
The primary attention in recent studies has been paid to cyclophosphorylation by TPA amides of monohydric phenols corresponding to the resorcinol-calixarenes. On treatment with an 8-fold molar amount of hexaalkylphosphorus triamides, these octaols are converted into oktakis(phosphorus amides), while reactions with a 4-fold excess of the reagent afford tetracyclic derivatives (Scheme 57).[274−277]

It is very significant that the latter reaction is stereospecific. It ends in the formation of symmetrical products containing only equatorial amide groups. This outcome provides the possibility for stereoselective reactions in the molecular bowls obtained.[275,278] The studies have been further advanced by extending the range of the starting calixare-

Scheme 56



Scheme 57



nes.[279,280] In addition, esters of phosphorus diamides have also been introduced in this process. The difference between the use of particular compounds should be mentioned. Methyl and ethyl esters of phosphorus diamides do not ensure stereoselective cyclophosphorylation, whereas the isopropyl ester largely does.[278]

The data on cyclophosphorylation of octaols with phosphorus diamides, whose molecules contain residues of biological molecules (steroids, carbohydrates, and menthol), appear especially promising. In this case, the corresponding conjugates can be formed.[279−281] In addition, coupling of two calixarene residues by a phosphorus diamide to give a complex three-dimensional structure has been reported.[282,283]

4. ATPA in the Chemistry of Natural Products

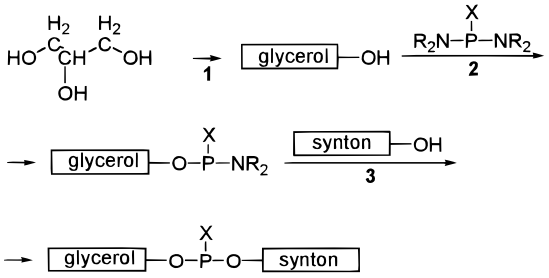
The development of methods of organophosphorus chemistry has contributed to the progress in physicochemical biology. Owing to the active employment of trivalent phosphorus reagents, especially ATPA, fundamental results have been achieved in the last 10−15 years in the effective synthesis of oligonucleotides, phosphorylated saccharides, phospholipids, and other phosphorus-containing natural compounds and their analogues whose molecules contain modified phosphorus-containing functional groups. This has been reflected in the publication of several reviews dealing with the use of phosphamides in the design of particular classes of natural products. These reviews have been very helpful to us in writing this paper because we were able to avoid the very difficult task of exhaustive citing of an ample body of papers, which are alike from the viewpoint of organophosphorus chemistry, and could instead attract the attention of the readers to the principles of phosphamide synthesis and the current trends in its application.

a. Synthesis of Phospholipids

The phospholipids most abundant in nature are glycerophosphates, especially phosphatidic acids and their various derivatives. These compounds perform exceptionally important biological functions; therefore, their synthesis attracts considerable attention.

In view of the foregoing, we start this section with the description of the use of ATPA in the design of glycerophosphatides and their P-analogues. The strategy of these syntheses developed in recent years normally includes the following stages: (1) preparation of monohydric derivatives of glycerol, either 1,2- or 1,3-acetals or 1,2- or 1,3-diacylates; (2) phosphorylation of the glycerol derivatives via the alcoholysis of the phosphamide bond in an appropriate ATPA; (3) oxidation or other transformations needed to prepare phosphatidic acids or other simple phosphoglycerides and the construction of a complex phosphoglyceride by introducing an additional synthon into the glycerophosphite block via alcoholysis of a second phosphamide bond using a specially selected synthetic equivalent of this synthon (Scheme 58).

Scheme 58

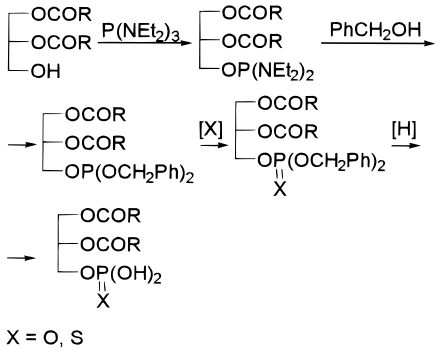


This process ends in oxidation reactions and necessary auxiliary transformations resulting in the formation of the target complex glycerophospholipids.

The above-outlined general strategy has now been embodied in numerous syntheses of phospholipids of various natures; all of these syntheses were accomplished based on a narrow range of starting compounds and using practically feasible synthetic

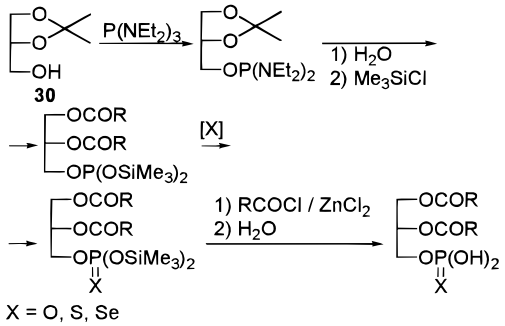
techniques.[284,285] Let us consider the syntheses of phosphatidic acids. They can be prepared from 1,2- or 1,3-acylglycerols, which are made to react with ATPA; this is followed by oxidative reactions and the removal of protective groups, for example, see Scheme 59.[285−287]

Scheme 59



The idea of using diacylglycerols in the ATPA phosphorylation has caused anxiety because the secondary amine being evolved can, in principle, add to the carbonyl group of acylates, resulting in their partial deacylation or isomerization. Therefore, special studies were carried out which demonstrated that these complications can be avoided.[287,288] Simultaneously, an analogous synthetic procedure using glycerol acetals instead of acylates was proposed. Glycerol acetals are easily available compounds convenient to work with. They are readily phosphorylated by ATPA without side processes; the products can be hydrolyzed to give diols, which are then subjected to acylation. Unfortunately, this route is difficult to accomplish in practice and, in addition, requires that reaction conditions be thoroughly selected. Therefore, a more facile and efficient process has been developed, namely, direct acylation of acetals,[289−291] for example, 1,2-isopropylideneglycerol **30**. Later, the general route for the synthesis of phosphatidic acids has been supplemented by other improvements, which are represented by the reaction scheme given in Scheme 60.[284]

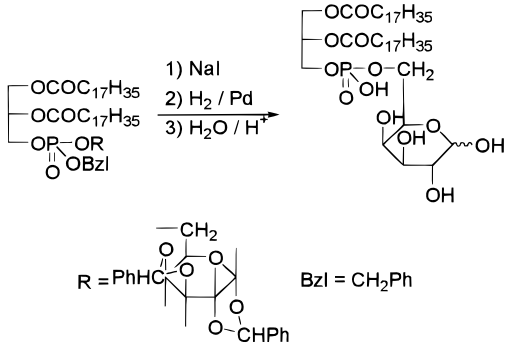
Scheme 60



It should be emphasized that the solution proposed made accessible not only phosphatidic acids, but also their thio and seleno analogues. These analogues have immediately started to be used for solving important scientific problems, for example, in ^{31}P NMR studies of phase transitions in lipid membranes.[292,293]

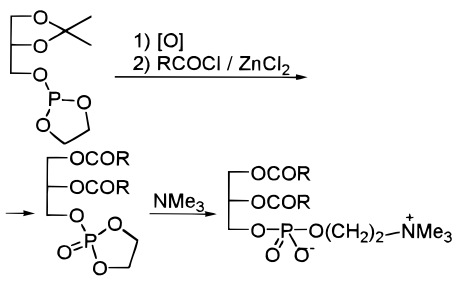
The use of phosphorus amide synthesis to prepare complex natural phosphatides and their analogues is even more promising. For this purpose, glycerol phosphorus amides are made to react with amino alcohols, glycerols, saccharides, nucleosides, amino acids, etc., giving the corresponding esters and amides of phosphatidic acids.[284,285] In some cases, it is expedient to use an alternative approach, according to which a substituted glycerol is phosphorylated by phosphorus amides whose molecules contain residues of carbohydrates, amino acids, etc. As an illustration, we present the route for the synthesis of 6′-(1,2-distearoylglycero-3-phospho)-D-galactose (Scheme 61).[294,295]

Scheme 61



A similar synthetic strategy was used to prepare glycophospholipids containing residues of D-glucose,[296,297] the disaccharide—maltose[298]—and nucleosides.[299] This method has also been employed to synthesize other new structures, for example, the phosphatidic analogues of the thrombocyte activity factor[300] or bioantioxidants derived from sterically hindered phenols.[162,163] The preparations thus obtained can act as membrane-addressed bioantioxidants. Reactions of glycerol phosphorus amides with diols[178,301] and amino alcohols[302] also deserve attention. These reactions, like phosphorylation of substituted glycerols with the corresponding alkanediyl phosphoramidites or phosphorus amides, yield diverse glycerophosphocyclanes. Studies of these glycerophosphocycles have led to the discovery of a promising reaction—alkylation of tertiary amines and other nucleophiles by cyclic alkanediyl phosphates.[284,285,290,303,304] A simple pathway to lecithins based on this reaction is shown in Scheme 62.

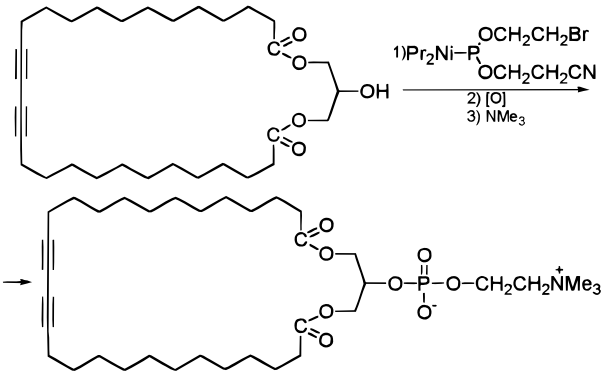
Scheme 62



Compounds whose molecules incorporate residues of naturally widespread acids and those containing residues of unusual acids have been used in the

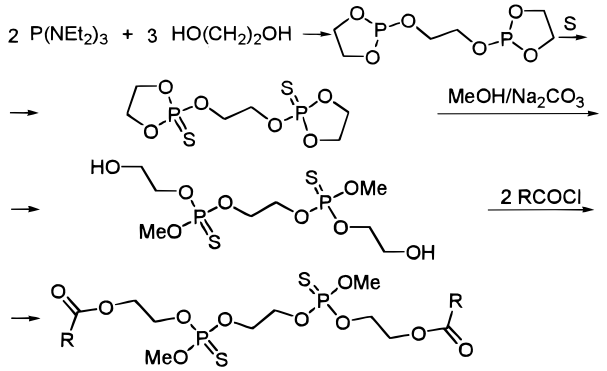
phosphamide syntheses of glycerophosphatides. The latter type of compound is represented by mono- and dibasic alkynoic acids. The synthesis of a macroheterocyclic glycerophosphatide is presented in Scheme 63 as an example.[304]

Scheme 63



The success in the development of glycerophosphorus amide synthesis has triggered investigations dealing with the chemistry of diol phospholipids, a new little-studied class of natural products. A number of useful transformations have been performed, forming the route from simple bis(phosphites) to quite complex substances that are difficult to obtain by other methods, for example, see Scheme 64.[305]

Scheme 64



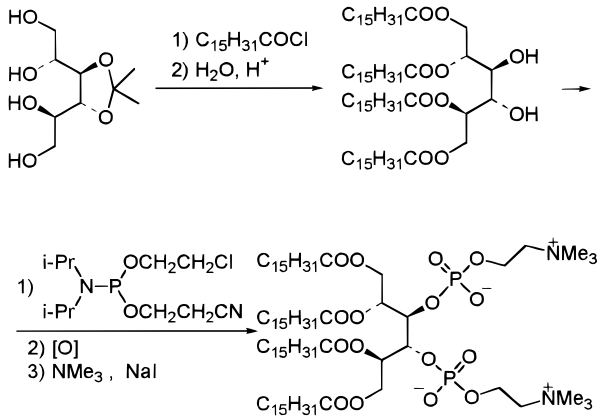
An elegant scheme for the design of tetra- and hexahydric lipids has been proposed. The essence of this scheme is gradual incorporation of needed synthons into readily available monoacetals of selected polyhydric alcohols. β-Chloroethyl-β-cyanoethyl-*N*,*N*-diisopropyl phosphoramidite is an important reagent for this synthesis. The foregoing can be illustrated by the pathway to the bis(phosphomannitol) lipid presented in Scheme 65.[306]

In addition, phospholipids whose molecules are based on pentaerythritol residues or residues of related branched oligools have also been synthesized, for example, see Scheme 66.[307−310]

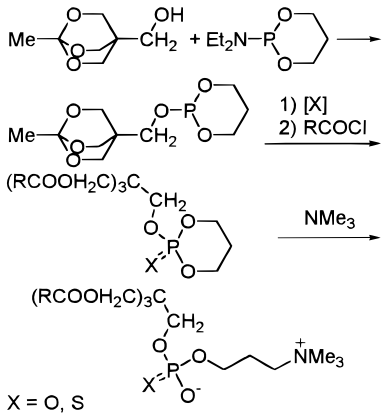
Apparently, these lipids can be used for producing membranes possessing high rigidity and other specific properties.

Design of lipid systems based on ascorbic acid has been a much more complicated problem.[311] To this end, 5,6-isopropylideneascorbic acid was cyclophosphorylated by mild reagents, phosphorus azolides, to

Scheme 65

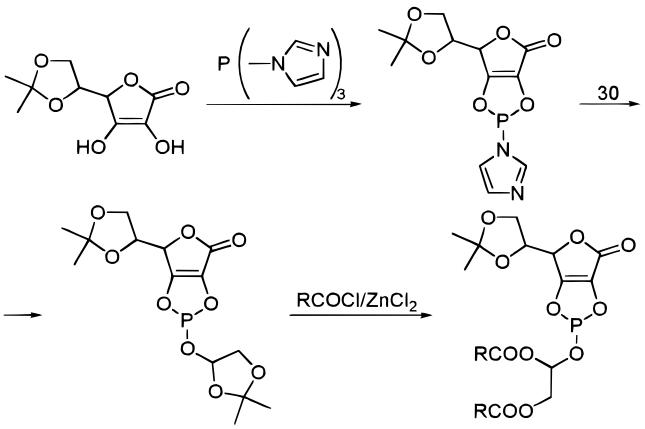


Scheme 66



give ascorbophospholene. The resulting compound was used then as the phosphorylating reagent in the reaction with 1,2-isopropylideneglycerol (**30**) (Scheme 67).

Scheme 67

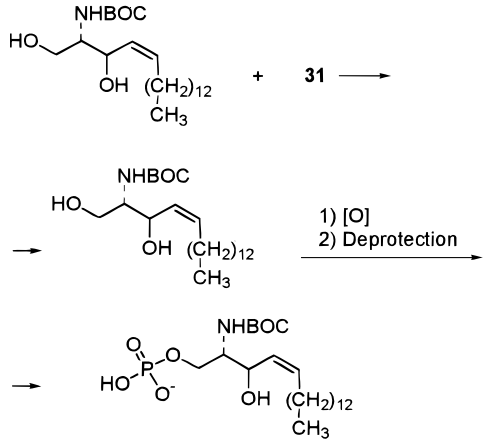


In recent years, systematic studies have been on the use of ATPA in the synthesis of sphingophospholipids,[285] which present great interest biologically.[312] Several research groups have shown that these compounds can be efficiently synthesized by phosphorylation of D-erythro-2-aminoalkane-1,3-diols with protected amino and secondary hydroxy groups by β-cyanoethyl-*N*,*N*-bis(diisopropyl)phosphorus diamide[170,313−316] or bis(β-cyanoethyl) *N*,*N*-diisopropylphosphorus amide (**31**).[315,317,318] Oxidation of the

resulting products and removal of the protecting groups gives rise to terminal phospholipids belonging to the class of primary phosphates. Note that this approach has been used to synthesize tritium-labeled sphingolipids.[319]

A drawback of this scheme is that it is a multistep procedure, due to the necessity to introduce and remove the protective groups. For this reason, interest is aroused by a publication by A. Boumendjel and S. Miller, who discovered the possibility of targeted synthesis of *N*-Boc-sphingosine and -dihydrosphingosine by virtue of phosphorus amide **31** (Scheme 68).[320]

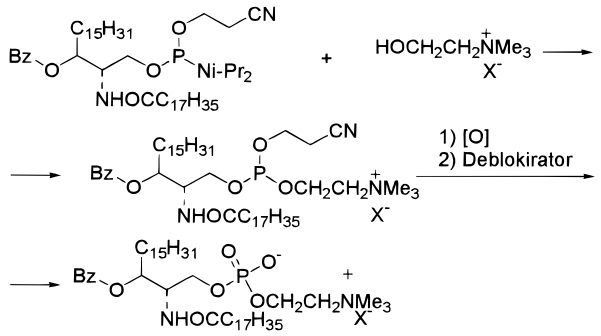
Scheme 68



Having combined the results of TLC and ^{13}C NMR spectroscopy, the researchers cited determined unambiguously the structure of the products obtained and proved that the products are individual compounds and, hence, confirmed the selectivity of phosphorylation. This fact is of fundamental importance.

A separate line of research has been devoted to the synthesis of more complex lipid systems. In this case, the products of primary phosphorylation of sphingosine or ceramide were made to react with sulfur; the required auxiliary transformations gave rise to sphingosine phosphorothioates.[318] The sphingosine phosphorus amides considered above can also been used to phosphorylate various nucleophiles to give (after oxidation and hydrolysis) the corresponding secondary phosphates, for example, see Scheme 69.[170]

Scheme 69



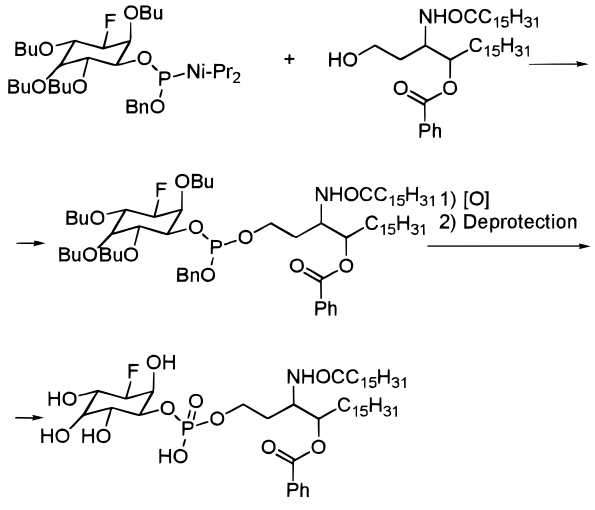
Similar procedures have been proposed to prepare conjugates based on various amino alcohols,[170,314] inositol,[315,318] and nucleosides.[321]

When evaluating the situation in the studies on sphingophosphatides, one can conclude that the use of ATPA is highly important for the design of complex lipids of this class. Apparently, soon, the advances in the synthesis would determine the progress in the investigation of biological functions of these systems, which would harmonize the overall front of development of this field of lipidology.

In this review, we distinguish one more group of phospholipids which has been extensively studied in recent years, namely, phosphorus-containing myoinositols. Filigree experiments on targeted introduction of protective groups into the cyclitol system followed by phosphorylation, giving rise to myoinositols phosphites containing up to five phosphorus atoms, have been described in a number of studies. Phosphorus amide **31**,[322,323] dibenzyl *N*,*N*-dialkylphosphoramidites,[323−325] and *o*-xylylenyl *N*,*N*-dialkylphosphoramidites[326,327] were recommended as phosphorylating reagents for this purpose. The last-mentioned reagents are the most convenient. Oxidation and deprotection (usually catalytic hydrogenolysis) give the desired phosphates in high yields. In addition, methods for the synthesis of inositol phosphites containing deoxy units,[328] tritium,[329] fluorine,[330] and phytoactive groups[331] have also been reported in the literature. Inositol phosphites were made to react with sulfur, which allowed the synthesis of the corresponding phosphorothioates, recommended as inhibitors of some enzymatic reactions.[322]

Phosphorylation of pentakis-protected inositols by equimolar amounts of phosphorus diamides made it possible to synthesize inositol phosphoramidites. Subsequently, these products can be used to phosphorylate other biological molecules, for example, see Scheme 70.[330]

Scheme 70



Yet another route to this type of complex lipid diphosphites consists of the phosphorylation of protected inositol by lipophosphoramidites.[318,328,331−333]

Phosphorylated steroids and higher fused terpenoids can also be placed among the large class of phospholipids. Apparently, the synthesis of these compounds using ATPA was first described in a

study[334] dealing with the reactions of cholesterol and β-sitosterol with alkanediyl phosphamidites or diphenylphosphinous amides. This line of research has been further developed in other publications.[335−337] The transformation of steroid phosphorus amides into metal complexes,[334] compatible with lipid phases and able to control oxidation and other reactions in them, are worth noting as important points. The prospects of using these compounds for the design of conjugates comprising steroid, phosphorus, and nucleoside components are also significant.[336,337] The conjugates incorporating an azothymidine residue seem to be valuable preparations for controlling AIDS.[337]

b. Phosphorylation of Nucleotides. Formation of Internucleotide Bonds

Phosphorylation of nucleotides, formation of internucleotide bonds, and solution of other related problems have long been accomplished using the methods of phosphate chemistry, which have been perfected in many scientific centers. Meanwhile, these methods are unable to satisfy the requirements of modern investigations due to the low phosphorylation rates and side processes. In addition, classical methods give poor results in the preparation of thiophosphorylated nucleotide derivatives and other derivatives with unusual groups in the phosphorus-containing moiety. The way out of this difficult situation could be seen in the use of highly reactive derivatives of trivalent phosphorus, first of all, ATPA.

The theoretical possibility of using phosphorus, phosphonous, and phosphinous amides for the phosphorylation of nucleotides was demonstrated in the late 1960s and early 1970s.[337] Unfortunately, getting accustomed to the new reagents took time, and they became customary reagents in laboratory practice only somewhat later.[70−73] Nowadays, ATPA are widely used in nucleotide syntheses for various purposes in chemistry, molecular biology, and genetic engineering. It should be emphasized that ATPA are used for the synthesis of not only oligonucleotides but also their diverse P-analogues, which extends the scope of investigations in molecular biology and related fields of science.

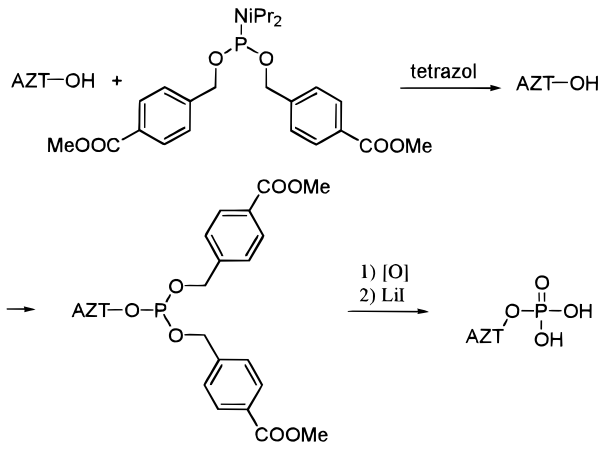
The use of ATPA in the chemistry of nucleic systems is reflected in several comprehensive monographs and reviews;[338] therefore, here we consider only the key points and the most recent publications.

Note that phosphorylation of desoxyribo- and ribonucleotides is often performed by using highly reactive phosphoazolides such as triazolides,[83,339−245] tetrazolides,[77,78,339,346−348] imidazolides,[116−118,339,349] and even indolides.[350] Ordinary ATPA, which are represented most often by diisopropylphosphorus amides, are also widely used; however, phosphorylation with these compounds requires acidic activating additives, most often tetrazole or its derivatives,[77,338,351] diisopropylammonium tetrazolide,[79−86] 4,5-dichloroimidazole,[74,76] benzimidazolium triflate,[352] or some other compounds.

In the majority of cases, phosphorylation is combined with oxidative processes and manipulations with protecting groups. The phosphamide versions of oligonucleotide syntheses normally make use of the β-cyanoethyl protection of the phosphorus atom. However, since phosphorylation is carried out under mild conditions, more complex P-protective groups can also be used, for instance, trimethylsilylethyl,[353] triphenylmethyl-*S*-propyl,[354] *N*-trifluoroacetylalkyl,[355] and acyl-*S*-butyl[356] groups. As a rule, unlike the acid chloride method,[357] phosphorylation of nucleosides in the phosphamide method virtually does not affect the nitrogen-containing rings. However, in some cases this may occur, which is specially noted in the literature.[73,358]

Let us consider the most productive routes of nucleoside phosphorylation using ATPA. In some cases, this reaction has formed the basis of the syntheses of highly important nucleotides, for example, phosphorylated azidothymidine (AZT) and various conjugates based on it (Scheme 71).[356,359−362]

Scheme 71



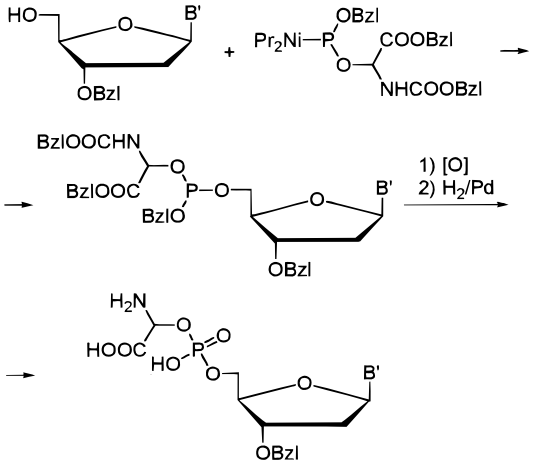
The use of ATPA in the design of complex nucleotidesaccharides including derivatives of sialic acids has been proposed.[363] In addition, compounds have been synthesized whose molecules contain so-called reporter groups, for example, nitroxides, useful in performing fine structural investigations into the functions of nucleotide compositions.[364,365]

Phosphorylation by ATPA containing residues of amino acids or other biomolecules has also attracted the attention of researchers. In this case, the synthesis results in the formation of hinged parts of nucleoproteins or other complicated systems. This can be illustrated by the synthesis of the phosphoserine hinge (Scheme 72).[366]

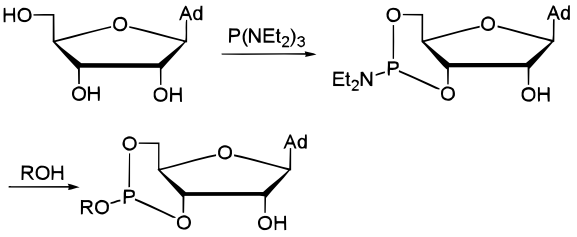
In view of the great importance of adenoside-(thymidine) monocyclophosphates, studies on the synthesis of their phosphite and phosphonite analogues have been carried out[362,366−372] (Scheme 73). The compounds obtained in this way were involved in additional phosphorylation, Arbuzov alkylation, oxidation, and other reactions.

The publications devoted to the use of phosphamides for the formation of an internucleotide bond, especially for the preparation of oligonucleotides, appear to be the most plentiful. The most commonly used route for the synthesis of oligodesoxyribonucleotides is presented in Scheme 74. Note that oligonucleotide condensations are normally carried out on solid supports using automated synthesizers, which

Scheme 72



Scheme 73



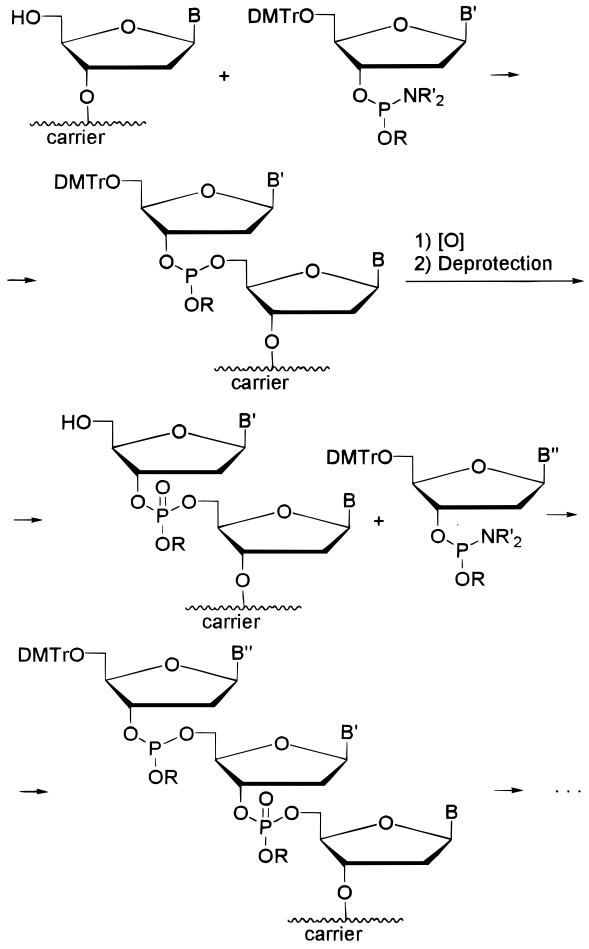
ensure high process efficiency. Suffice it to say that a typical phosphorylation step requires in such a setup several minutes at 20 °C. Fixing of phosphorus amide reagents on a solid support can be attained via both O- and N[373−375]-phosphorylation. It is significant that nucleoside phosphorus amides, which are the main reagents in these condensations, have now become available as commercial preparations.[376−378]

The synthesis of oligoribonucleotides and their derivatives occurs in a similar way but according to a more complex route.[78,347,377−387] It is very important that, apart from oligonucleotides, the phosphorus amide scheme allows the preparation of their phosphonate,[388,391] phosphoramidate,[79,358,392−395] phosphorimidate,[396] thio,[344,358,392,397−399,400−403] dithio,[88,345,404−414] and fluorinated[42,67,415] analogues by invoking for this purpose the great potential of the chemistry of trivalent phosphorus. In this connection, mention should be made of the use of phosphorus amide systems for phosphorylation of nucleosides,[416,417] whose 1,3,2-oxazaphospholane or 1,3,2-phosphorinane rings are opened during the reaction with the nucleophile (Scheme 75).

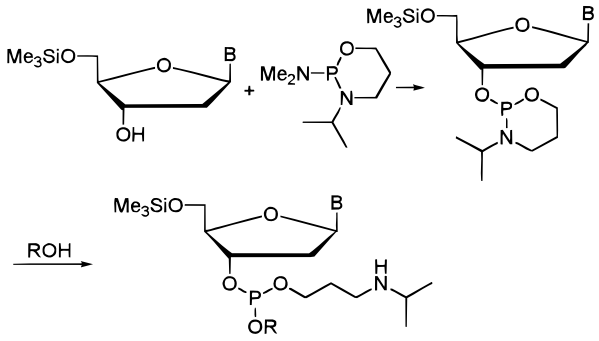
The synthetic schemes that permit the assembly of complex structures combining oligonucleotide and other chains based on nucleoside phosphorus amides and diol oligomers present great interest for molecular biology.

Finally, phosphorylation of nucleosides by ATPA supplemented by hydrolysis, sulfohydrolysis, or acidolysis provides a pathway to prototropic systems of the hydrogenphosphonate (hydrophosphoryl) type. This method was used to prepare primary[343,417−424] and secondary[349,394] nucleoside phosphites, phosphoramidites,[425] and phosphorothioites,[400,403,426] which

Scheme 74



Scheme 75



are now widely used in various hydrophosphoryl and thiophosphoryl syntheses.

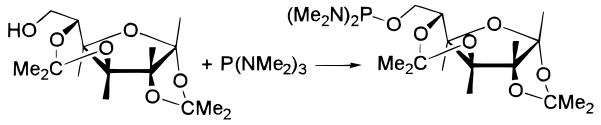
In recent years, methods of phosphorus amide chemistry have found wide application in solving many other particular problems of oligonucleotide chemistry, for example, for the formation of 2′,5′-phosphodiester bonds;[427−429] design of halo-,[382,430,431] pyren-,[432] and fluorescein-labeled[433] oligonucleotides and longmers;[407] lipophilic modification of oligonucleotides;[434] and the preparation of prebiotic RNA precursors,[435] the Park nucleotide,[436] and some 1-,[437,438] 2-,[383−386] and 4-[439] modified oligonucleotides. The foregoing demonstrates that phosphorylation of nucleosides by ATPA and its synthetic applications can be evaluated not only as an important but also a very promising stage in the development of nucleotide chemistry.

c. Phosphorylation of Monosaccharides

Esters formed by trivalent phosphorus acids and monosaccharides have been considered as self-maintained investigation objects only since the 1970−80s, i.e., since the time when active use of ATPA in fine organic synthesis began. The use of these reagents in working with carbohydrates, which often exhibit high chemical lability, is due to a set of their merits. These include, for example, combination of high phosphorylating capacity with the possibility of conducting preparative reactions under mild conditions. The fact that phosphorylation by ATPA allows introduction into carbohydrate molecules of phosphorus-containing groups having various substituents at the phosphorus atom, which influence the reactivity of phosphorus in various transformations, is also significant.[440]

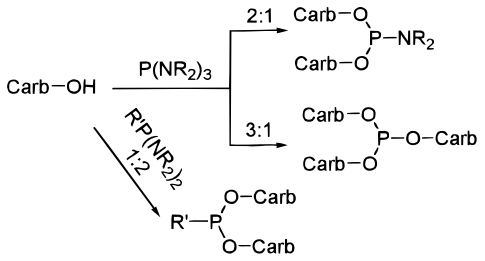
Phosphorus triamides phosphorylate efficiently monosaccharides, whose molecules contain one free alcoholic hydroxyl,[441−444] for example, 1,2:3,5-diisopropylidene-D-glucofuranose (Scheme 76).[441]

Scheme 76



Phosphorylation by dialkyl[322] or alkanediyl phosphoramidites,[445] phosphonamidites,[446] and phosphinamidites[447] follows a similar pathway. In the case where two or three moles of a monosaccharide per mole of the phosphorylating reagent are introduced into the reaction, di- and triglycophosphites or -phosphonites can be formed (Scheme 77).[440]

Scheme 77

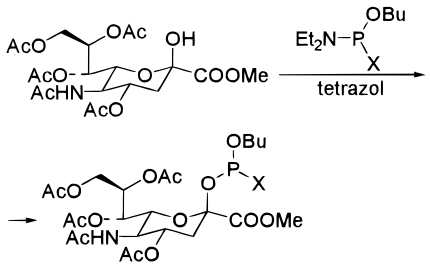


The studies cited above were concerned with phosphorylation of cyclic forms of monosaccharides. Meanwhile, this reaction can also provide good results with the corresponding linear derivatives.[448]

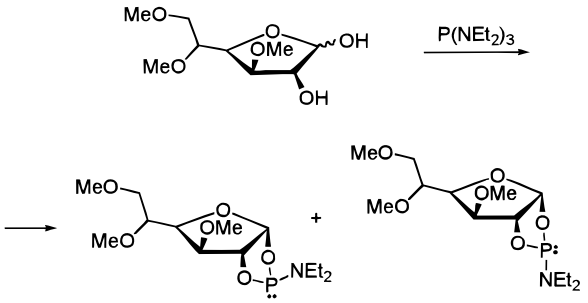
Monosaccharide derivatives are efficiently phosphorylated at the glycoside hydroxy group,[448−450] the stereochemistry of the phosphorylating center remaining unchanged during the reaction.[451] In recent years, this type of phosphorylation has been extended to fairly complex objects. For example, β-sialyl phosphites and phosphoramidites were prepared with the aid of ATPA (Scheme 78).[450]

Treatment of monosaccharide derivatives whose molecules contain two closely located hydroxy groups with phosphamides results in cyclophosphorylation (Scheme 79).[443,452,453]

Scheme 78

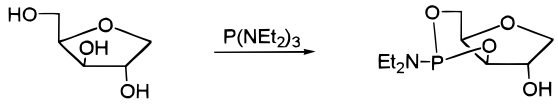


Scheme 79



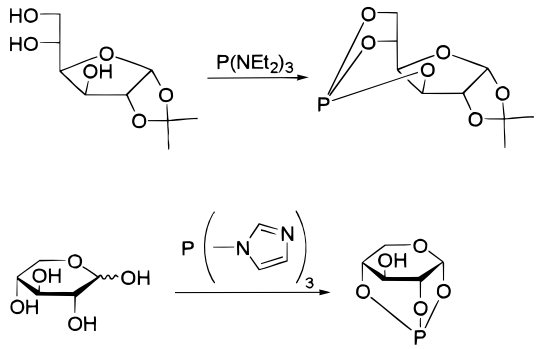
Phosphorylation of triol systems can follow different routes. Spatially separated hydroxy groups, in, e.g., xylitan, are phosphorylated yielding bis(phosphites) (Scheme 80).[454]

Scheme 80



Monosaccharides (triols and tetraols) with closely arranged hydroxy groups are phosphorylated especially readily, being thus converted into bicyclophosphites, for example, see Scheme 81.[455,456]

Scheme 81



As can be seen from Scheme 81, the latter reaction occurs as selective bicyclophosphorylation, whose pathway is governed by the steric features of the monosaccharide molecule. Development of the phosphamide method of bicyclophosphorylation of partially substituted and unsubstituted monosaccharides resulted in the synthesis of a large number of cage systems,[457] including those based on phosphonatomonosaccharides.[458]

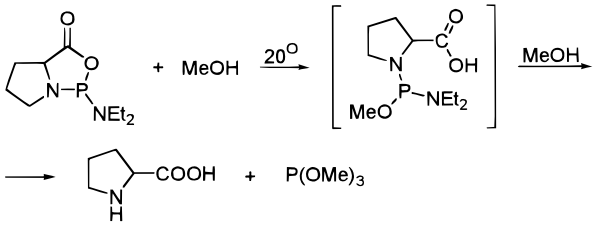
Phosphorus amides and phosphites, whose preparation is described above, have found application in the synthesis of important natural products. In

addition, they are used in the design of new types of phosphorus-containing carbohydrate derivatives, which present interest regarding the investigation and control of the vital activity of organisms and for the solution of other scientific problems. A wide range of transformations have been proposed for this purpose, which are based on the phosphorylation of nucleophiles, alkylation, oxidation, other related processes,[440] and coordination to transition metals.[443,459−461] The latter process gives rise to chiral metal complexes, deserving application in enantioselective metal complex catalysis.

d. Phosphorylation of Other Natural Products

Nowadays, amino acids and peptides whose molecules contain pentavalent phosphorus residues are studied in various scientific centers. These studies include the search for the synthesis of compounds employing new techniques of organophosphorus chemistry.[462−464] In this connection, the investigation of phosphorylation of aminohydroxycarboxylic acids by various ATPA, for example, di(4-chlorobenzyl)-*N*,*N*-diisopropyl phosphorus amide[465] and bis(*N*,*N*-diisopropyl)-benzyl phosphorus diamide,[366,466] has been started. The resulting amino acid phosphites have been introduced into oxidative reactions or used as phosphorylating means. The latter case is highly interesting from the chemical viewpoint. Thus, proline phosphorus cycloamide, whose molecules contain two P−N bonds, readily undergoes dephosphorylation by an equimolar amount of methanol. Apparently, the first step of the process gives the carboxyl, which intramolecularly activates the subsequent alcoholysis of the two phosphamide bonds (Scheme 82).[467]

Scheme 82



It is significant that the reaction mixture contains only two phosphorus-containing products, namely, trimethyl phosphite and the initial proline phosphorus cycloamide.

ATPA have become conventional reagents for the phosphorylation of monosaccharides and other oligools in relation to the synthesis of the corresponding primary phosphites. At present, the latter are successfully used in the syntheses of teichoic acid fragments[468,469] and capsular polysaccharides.[470−472]

5. ATPA in the Synthesis of Phosphorus-Containing Polymers

ATPA have also been used for the purposes of macromolecular chemistry. The studies carried out along this line can be divided into two groups. One group is devoted to the introduction of phosphorus into hydroxyl-containing polymers, and the other one is devoted to the polycondensation processes involving di- and other oligools.

The former line of research has been developed in the greatest detail in relation to natural polymers. Thus, it has been shown that anhydrous cellulose is phosphorylated in a heterogeneous system on heating to 80−120 °C by hexaethylphosphorus triamide, various phosphoramidites, and *N*,*N*-diethyl diethylphosphinous amide.[473,474] In the reaction with the last-mentioned reagent, the extent of substitution was monitored and the phosphorylation degree $\gamma =$ 180 per cellulose macromolecular unit was attained.

Phosphorus and diphenylphosphinous azolides proved to of be the best phosphorylation. These reagents modify cellulose at 20−50 °C to attain high phosphorylation degrees.[118] On treatment with solutions of palladium chloride or bis(π-allylpalladium chloride), the products thus obtained are converted into heterogeneous subcatalysts of hydrogenation, which have exhibited high catalytic activity in styrene hydrogenation under mild conditions.[118] It is very significant that the efficiency of the above-mentioned polymeric complexes exceeds that of the complexes obtained using chlorides of the corresponding trivalent phosphorus acids, instead of the amides.[118]

Quite recently, phosphorylation of organo-soluble chitosan derivatives has been accomplished.[475] The publication cited is the first communication dealing with the phosphorylation of chitosan.

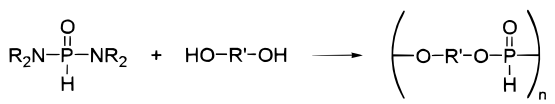
Examples of phosphorylation of synthetic hydroxyl-containing oligomeric and polymeric resins[476] and polyallyl alcohol[477] by ATP amides have been reported.

The second line of using ATPA in macromolecular chemistry includes studies on the phosphorylation of glycols[478] and dihydric phenols[479] by equimolar amounts of phosphonous and alkylphosphonous amides. Unfortunately, this seemingly simple case of polycondensation is accompanied by the competing formation of monophosphorus rings[478] and, perhaps, the corresponding macrocyclic systems;[479,480] consequently, the molecular weights of the reaction products are relatively low. It might be expected that the use of the latest-generation phosphamides, for example, phosphorus azolides, would permit conducting efficient condensation at low temperatures and thus avoid the transformation of linear systems into cyclic ones.

Hexitols have also been used in the polycondensation with ATPA.[481] The reactions carried out at the reagent ratios chosen and under the conditions selected resulted in the synthesis of phosphorus-containing oligomers and polymers, which present practical interest.

In addition to phosphorus triamides, diamides have also been used in the reactions with equimolar amounts of glycols (see Scheme 83). The advantages

Scheme 83

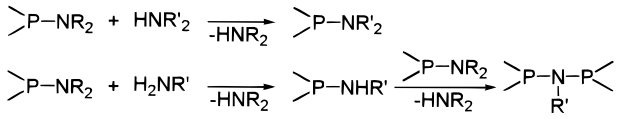


and prospects of this synthetic procedure have been considered in a study.[482]

III. Phosphorylation of Amines

Alcoholysis, phenolysis, and aminolysis of ATPA are, in principle, related reactions; they are comparable regarding their outcome and experimental conditions. In addition, they were discovered almost simultaneously with the first studies on transamidation (see refs 112 and 483). However, tentative analysis of these transformations also points to certain differences between them. First, aminolysis, unlike alcoholysis and phenolysis, can involve not only single but also double phosphorylation steps. Triple phosphorylation steps are, in principle, also possible when ammonia is used as the substrate; however, these reactions are little studied (Scheme 84).[483]

Scheme 84



Second, the above-listed reactions differ substantially regarding the structure of intermediates. In the case of alcoholysis and phenolysis, the leaving and entering groups have different central atoms (nitrogen and oxygen), whereas in the case of aminolysis, these atoms are identical. This situation raises complications in elucidating the route of hydrogen migration in the intermediate.

1. The Chemistry of Aminolysis of ATPA

Early studies along this line were concerned only with the simplest cases of transamidation and did not involve solution of complex theoretical problems. In the experiments, the volatile amine (most often, diethylamine) formed as a reaction product was usually distilled off.[384,485] Reactions involving phosphinous, phosphonous, and phosphorus amides gave roughly the same results.[486] Di- and triamides of these acids have been used for complete and partial transamidation.

All of these studies demonstrated high reactivity of the phosphamide function. In this connection, note that even the reaction of difluoro(dimethylamino)-phosphine with higher secondary amines involves the P−N rather than the P−F bond (Scheme 85).[487]

$$F_2P{-}NMe_2 + HNR_2 \rightarrow F_2P{-}NR_2 + HNMe_2$$

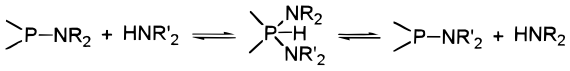
Scheme 85

In recent years, studies of the reactions of primary and secondary amides with phosphenous imines have been started. Different versions of σ and π P−N bond cleavage were attained. These include replacement of a secondary amino group[488] and the addition of the amine to the double bond.[489]

Besides conventional amides, other PN systems, for instance, phosphorus azides[132] and hydrazides,[490] have also been used in transamidation. Apart from ammonia and amines, imines[491] and hydrazines[492] are applicable for the reactions with phosphamide substrates.

Many researchers have expressed opinions on the mechanism of ATPA transamidation and on the dependence of the ease of the reaction on the substrate and reagent structures, which were based either on their observations or on general considerations. A scheme has been proposed that included mutual addition of the phosphamide and amine to give a phosphorane and decomposition of the latter to give the reaction products (Scheme 86).[12,34,158,493,494]

Scheme 86

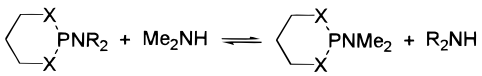


Mechanisms including a four-membered transition state[15] and those based on direct nucleophilic substitution at the phosphorus atom have also been discussed. The latter version is encountered most frequently in standard reactions. In recent years, it has been discussed in relation to the experimentally observed acid catalysis, i.e., acceleration of phosphorylaton by the addition of AHC[25,30,151,484,485] or acids.[31]

Convincing evidence in favor of the nucleophilic substitution mechanism was first presented in a study[22] whose authors estimated the influence of the basicities of the entering and leaving amine on the reaction rate. This was done for the reaction between ethanediyl *N*,*N*-dimethylphosphoramidite with amines having different basicities. The phosphorylation rate was found to decrease with an increase in the basicity of the entering amine. Thus, on passing from morpholine (pK_a 8.70, H_2O) to pyrrolidine (pK_a 11.27), the rate increases, while in the case of methylaniline (pK_a 4.85) and pyrrole (pK_a −0.27), no displacement of dimethylamine (pK_a 10.77) occurs.

It is also noteworthy that the above-mentioned amide is more reactive than *N*,*N*-dimethyl diphenylphosphinous amide, which is consistent with the general principles known for nucleophilic substitution at a trivalent phosphorus atom.[495] Unfortunately, the transamidation in the former amide was carried out under nonequilibrium conditions and that in the latter amide was performed under equilibrium conditions; therefore, strictly speaking, their comparison is not legitimate. Note that the problem of equilibration in transamidation reactions has not been properly taken into account in some other studies (e.g., see ref 484). Therefore, the paper by J. A. Mosbo,[31] who rigorously considered the transamidation of 1,3,2-dioxa- and 1,3,2-diazaphosphorinane amides (Scheme 87), was so important.

Scheme 87



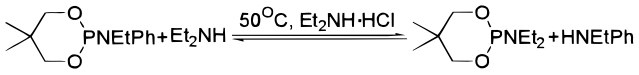
X = O, NMe; R = Et, R_2 = $(CH_2)_4$

In this series of reactions, it was shown that equilibrium can be attained when conducting the aminolysis in both the forward and back directions;

the conclusion about the importance of the amine basicity for the occurrence of substitution (the position of the equilibrium under the equilibrium conditions) was confirmed.[30,38,496] The results of this study do not support the earlier statement that the initial amide is necessarily converted during the reaction into the corresponding chloride, which then phosphorylates the amine substrate.[29,30]

The acid chloride concept has also been rejected in another study,[165] dealing with the kinetics of acid-catalyzed aminolysis (Scheme 88). This work clearly

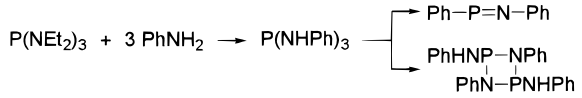
Scheme 88



demonstrated the fact of catalysis and confirmed that the ease of the reaction depends on the amine basicity. The influence of the solvent on the phosphorylation rate was also demonstrated. In addition, it was found that an excess of the substrate inhibits phosphorylation. Thus, study of ATPA transamidation at the kinetic level made it possible to reveal some specific features of this process, which distinguish it from the corresponding alcoholysis reactions.

The comparison of the phosphorylation rates in transamidation of ATPA resulted in some recommendations concerning the synthetic applications of this process. For example, it became clear that anilides (*N*-alkylamides) are the best phosphorylation reagents among the available phosphamides.[104,165,486] Note that dialkylamides do react with aniline but only on heating and when the dialkylamine evolved is being distilled off,[36,38] which shifts the equilibrium in the required direction. This reaction is very complex from the experimental viewpoint and requires that the constant phosphorylation conditions be thoroughly maintained. Otherwise, the resulting phosphamides would undergo elimination and self-phosphorylation (Scheme 89).[36,38,497−500]

Scheme 89



Phosphorylation of dialkylamines with phosphazolides merits special attention.[120−123] The efficiency of phosphazolides increases in the order phosphinous azolide−phosphorus diamide azolide−diester of phosphorus azolide. The reverse reactions, i.e., the reactions between phosphodialkylamides with azoles, do not always occur. For example, ATP diethylamides do not react with imidazole.[120] Apparently, this phosphorylation, which is an autocatalytic reaction, is precluded by the fact that the abstraction of a proton together with the imidazole residue is an obviously preferred pathway for the transformation of the intermediate. However, it should be noted that the problem of the chemical behavior of phosphazolides, which are peculiar substances, has not yet received adequate attention.

The rates of the phosphazolide reactions in question depend in some way on the type of substituents at the phosphorus atom. Alkoxy groups ensure the maximum reaction rates, while alkyl groups lead to the minimum rates,[120−123] which is also consistent with the views on nucleophilic P-substitution. Meanwhile, no detailed description of the mechanism of acid-catalyzed ATPA transamidation can be found in the literature. It can be assumed that this description would, in principle, be similar to that of the ATPA alcoholysis but would differ in the details of proton migration between the linked nitrogen centers.

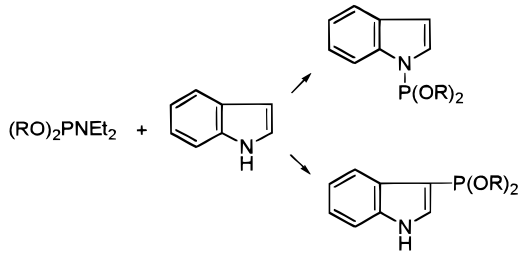
2. Applications of the ATPA Transamidation for the Purposes of Fine Organic Synthesis

a. Phosphorylation of Higher and Functionally Substituted Primary and Secondary Amines

Aminolysis of simple phosphamides is often an expedient route for the synthesis of higher and other complex phosphamides. Thus, hexamethyl(or ethyl)-phosphorus triamides, which are available commercial products, function as key substances in the preparation of various more complex triamides.[501,502] Alkyl phosphoramidites[486,503] and phohphonous[36] and phosphinous amides[504] are also used efficiently for this purpose.

Transamidation can also be used to synthesize complex asymmetrical systems including phosphorylated ethyleneimines[25,485,505] and glucosylamines.[506,507] In some cases, transamidation can be supplemented by C-phosphorylation, as in the experiments with indole presented in Scheme 90.[508]

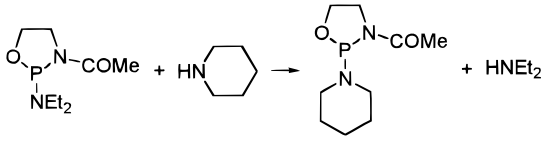
Scheme 90



3-Mercaptoindole[509] and 3-hydroxymethylindole[510] are phosphorylated either at nitrogen or at sulfur (oxygen), depending on the reaction conditions.

Considerable attention has been paid to the transamidation of phosphorus diamides in which one nitrogen atom carries an acyl group. These phosphamides were shown to exhibit low reactivity; the exchange involves the nonfunctionalized amide group, for example, see Scheme 91.[511]

Scheme 91



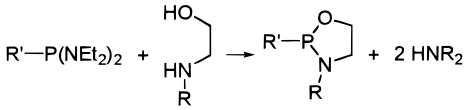
Data on the reactions of phosphamides whose molecules contain a residue of a polymeric amide bound to a phosphitenucleoside oligomer via an N−P bond should also be included in this review. In some cases, the oligonucleotide block can easily be removed

from the substrate by treatment with an excess of amine, for example, tetrazole.[466,467]

b. Phosphorylation of Amino Alcohols and o-Amino Phenols

Secondary and primary amino alcohols are widely used in reactions with ATPA. Attention is focused on the design of phosphorus-containing heterocycles. It was shown that phosphorus-containing reagents whose molecules contain two or three amido groups readily phosphorylate equimolar amounts of 1,2- and-1,3-amino alcohols including derivatives of 1,2-ethanolamine,[148,150,179,205,512−514] 1,3-propanolamine,[151,515−517] and prolinol[518,519] to afford 1,3,2-oxazaphospholanes (Scheme 92) and -phosphorinanes. 1-Desoxy-1-aminosaccharides[520] and 1-*N*-hydroxyethyl-3-iminopyrazoline[521] are phosphorylated in a similar way.

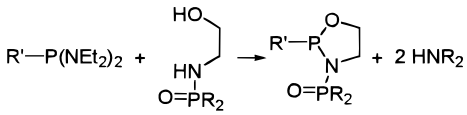
Scheme 92



These reactions of amino alcohols with ATPA are highly important for synthetic purposes and are widely used to solve many synthetic problems. We mention the synthesis of phosphocyclic ligands for metal complex catalysis,[522,523] phospholipid systems,[303] and phosphacyclane saccharide derivatives.[457]

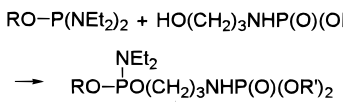
N-Phosphorylated amino alcohols react with ATPA in a similar way (Scheme 93).[173] Note that this

Scheme 93



scheme describes reactions for the case where R = Alk or $NAlk_2$. When phosphorus diamides, i.e., compounds possessing lower phosphorylation capacity, are introduced in the reaction, mono-*O*-phosphorylation proves to be more likely (Scheme 94).[173]

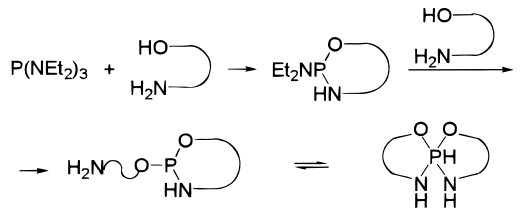
Scheme 94



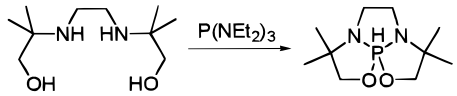
The reactions of many primary and some secondary 1,2- and 1,3-amino alcohols with phosphorus triamides taken in a 2:1 molar ratio follow a more complex pathway; the first stage of the synthesis yields 2-amino-1,3,2-oxazaphospholanes (-phosphorinanes), which then phosphorylate amino alcohols, being thus converted into amino phosphites. The latter can pass either completely or partially into hydrospirophosphoranes (ring−chain tautomerism) (Scheme 95).[217,218,501,512,524−526.]

Similar hydrospirophosphorane, which are tricyclic in this case, are formed in the phosphorylation of bisaminoethanols (Scheme 96).[527,528]

Scheme 95

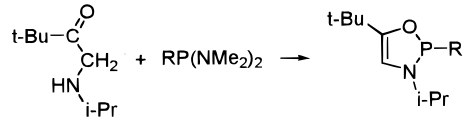


Scheme 96



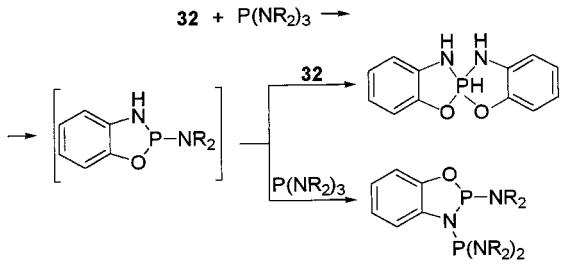
Some secondary amino acids and phosphonous amides can be involved in heterocyclic condensations, for example, see Scheme 97.[529]

Scheme 97



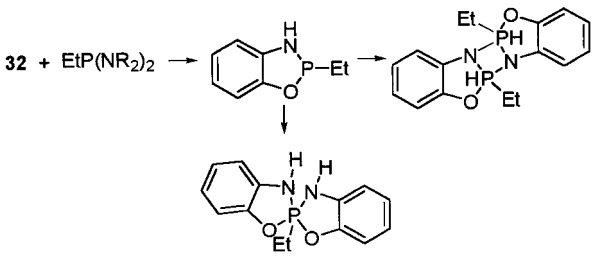
ATPA with two or three amido groups readily phosphorylate *o*-(*N*-alkylamino)phenols to give 4,5-benzo-1,3,2-oxazaphospholanes.[530,531] *N*-Acylaminophenols undergo a similar type of cyclophosphorylation.[532] The simplest *o*-aminophenol **32** reacts with phosphorus triamides according to a more complex pattern. In this case, the structure of the final product is determined by the molar ratio of the reactants (Scheme 98).[533]

Scheme 98



Ethylphosphonous diamides exhibit a peculiar chemical behavior in the reaction with *o*-aminophenol **32**; this reaction follows two original pathways (Scheme 99).[533,534]

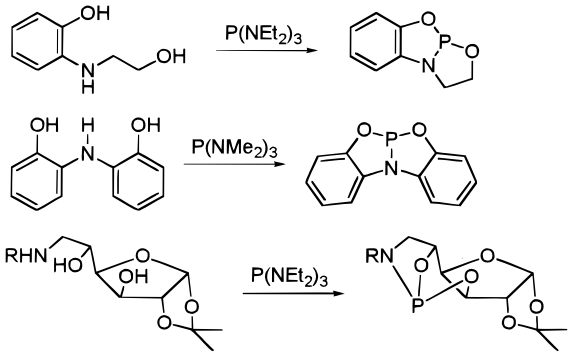
Scheme 99



The occurrence of redox disproportionation should cause suspicion of researchers who turn to new types of heterocyclic condensations involving ATPA and aromatic amines.

Phosphorylation of aminophenols—*N*-*β*-hydroxyethyl-*o*-aminophenol[535] and di(*o*-hydroxyphenylene)amine[536,537]—and 1,2-isopropylidene-6-desoxy-6-amino-(3-desoxy-3-amino)glucofuranose[538] by phosphorus triamides follows an interesting pathway. These reactions give rigid fused systems (Scheme 100).

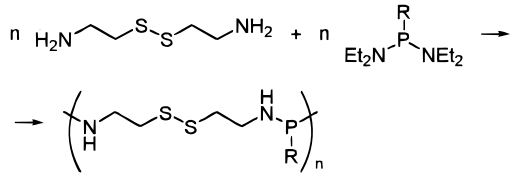
Scheme 100



c. Phosphorylation of Di-, Tri-, and Tetramines

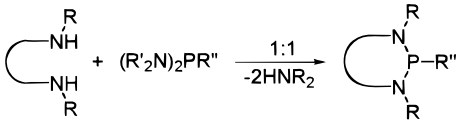
Two groups of phosphorylation reactions between diamines and ATPA have been studied. The first includes reactions of equimolar amounts of di- or triamides with primary diamines in whose molecules the functional groups are located far from each other (hexamethylenediamine, *p*-phenylenediamine). In this case, polycondensation occurs to give polyphosphamides.[539] The reaction with cystamine occurs in a similar way (Scheme 101).[540]

Scheme 101



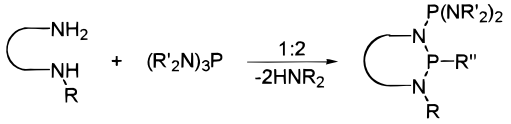
The second line of research includes heterocyclizations. It has been shown for numerous examples that 1,2-,[541,542] 1,3-,[543−545] and 1,4-[546−550] di-primary, primary-and-secondary, and di-secondary diamines are efficiently phosphorylated by phosphorus and phosphonous di- and triamides (Scheme 102).

Scheme 102



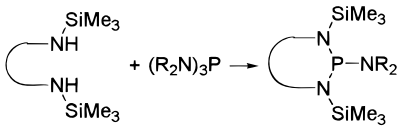
When a diamide is made to react with a 2- or 3-fold molar amount of a phosphamide, di-[542] and triphosphorus[551]-containing heterocycles are produced, for example, see Scheme 103.

Scheme 103



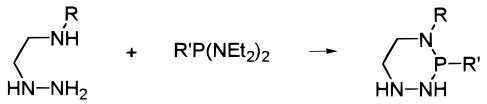
1,3-Disilylamines enter into similar reactions (Scheme 104).[543]

Scheme 104



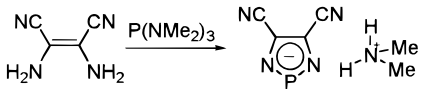
It is of interest that *β*-aminoethylhydrazine can undergo a similar phosphocyclization (Scheme 105).[27]

Scheme 105



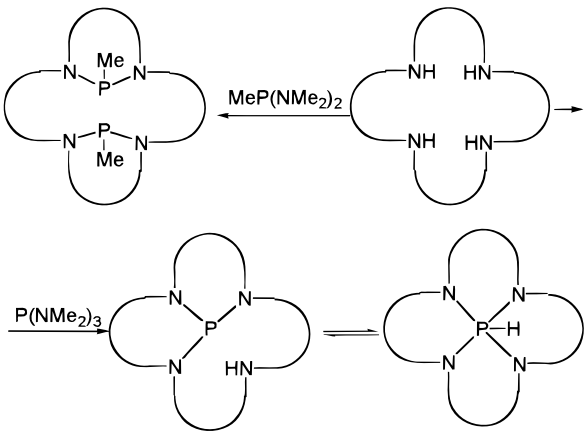
Phosphocyclization of dicyanodiaminoethylene with phosphorus triamide may give rise to a stable anion, isoelectronic to 1,3,2-diazaphospholanes (Scheme 106).[552]

Scheme 106



Studies of phosphorylation of linear and alicyclic tri- and tetramines, which have received considerable attention in recent years, should also be mentioned. It was found that 2,5,8-triazanonane reacts with an equimolar amount of hexamethylphosphorus triamide giving rise to a fused bicyclic compound.[553] Phosphorylation of trialkylenetriamines occurs in a similar way.[554−556] Phosphorylation of alkylenetetramines by phosphorus triamides has been studied even more extensively (Scheme 107).[557−559]

Scheme 107

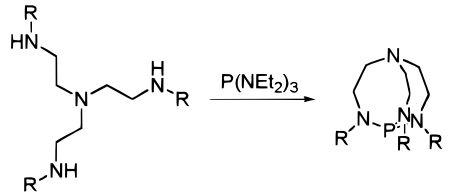


In the studies along this line, an interesting example of prototropy, resulting in the formation of a symmetrical hydrospirophosphorane, has been observed. Recently it was shown that tetraethylenetetramine reacts with methylenebis(phosphonous) tetramide with rupture of the C−P bond.[560]

Symmetrical nitrogen-containing systems, which can be represented as triethylamine whose methyl groups contain additional phosphorylable amino

groups, are also phosphorylated by hexamethylphosphorus triamide. This gives rise to original cage structures.[561,562] They possess properties of superbases, either nonionic or ionic after solvent deprotonation (when one of the R is H) (Scheme 108).[563]

Scheme 108



In recent years, it has been proved convincingly that these superbases can be used to initiate various reactions, for example, trimerization of isocyanates,[564] acylation of isocyanoacylates,[565] silylation of tertiary alcohols and sterically hindered phenols by low-reactivity chlorosilanes,[566] and acylation of sterically hindered alcohols and those prone to undergo elimination.[567]

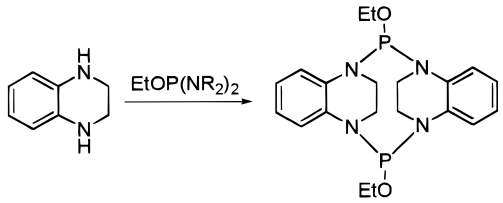
Cyclophosphorylation of aliphatic−aromatic diamines by ATPA has been studied even more extensively. Thus, *N*,*N*-dialkyl(aryl)-2-aminobenzylamines readily react with phosphorus di- and triamides to give 1,3-disubstituted 4,5-benzo-1,3,2-dioxaphosphorinanes in good yields.[568] Two types of nitrogen-monosubstituted 2-aminobenzylamines exist. Both types have been involved successfully into phosphocyclization to give 4,5-benzo-1,3,2-diazaphosphorinanes.[568] Unsubstituted 2-aminobenzylamine also reacts with ATPA. Alkyl phosphorus diamides are converted in these reactions into 2-alkoxy-4,5-benzo-1,3,2-diazaphosphorinanes, and phosphorus triamides give rise to 2-dialkylamido-4,5-benzo-1,3,2-diazaphosphorinanes; these products immediately undergo cyclotetracondensation.[569] Attention is attracted by the high efficiency (yields about 90%) and regiospecificity of this reaction, which yields a product containing only aminobenzyl nitrogen atoms in the tetraazaphosphacyane ring. X-ray diffraction data show that the molecules of the compound obtained are shaped like a symmetrical crown in which the nitrogen atoms lie in a plane parallel to the plane through the phosphorus atoms. It can be seen that this system and other related systems present considerable interest regarding the design of new coordination compounds.

It should be noted that all of the phosphocyclizations considered above are more efficient than the corresponding reactions involving phosphorous acid chlorides.

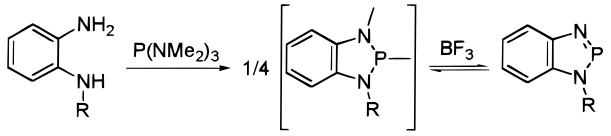
Now we shall consider phosphorylation of aromatic diamines. Secondary *o*-diaminobenzenes easily react with ATPA to give 4,5-benzo-1,3,2-diazaphospholanes.[570] Cyclophosphorylation of *o*-phenylenediamine, in whose molecule the nitrogen atoms are linked via a 1,2-ethylene bridge, follows a more complex route giving rise to a diphosphorus-containing species (Scheme 109).[571]

Primary and secondary *o*-phenylenediamines react with hexamethylphosphorus triamide to afford tetramers (Scheme 110).[532,572,573]

Scheme 109

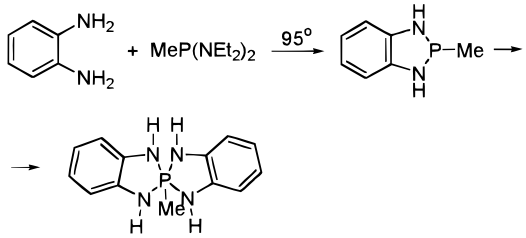


Scheme 110



Depending on the reaction conditions and the ratio of the reactants, unsubstituted *o*-phenylenediamine is converted upon phosphorylation by phosphorus di- and triamides into either ordinary phosphorus-containing rings or the products of their additional phosphorylation at nitrogen.[551,574,575] It can be seen that *N*,*N*-tetraethyl phenylphosphonous diamide can react according to a standard scheme[576] or according to an abnormal route, which includes disproportionation (Scheme 111).[577]

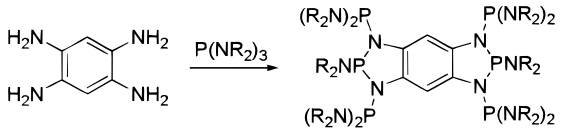
Scheme 111



Note that systems related to the resulting phosphorane regarding the coordination of phosphorus are being thoroughly studied now.[568]

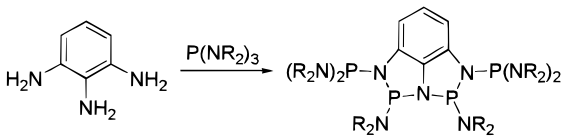
Complex phosphorus-containing rings are also formed upon phosphorylation of 1,2,4,5-tetraaminobenzene by phosphotriamides (Scheme 112).[578]

Scheme 112



It is noteworthy that 1,2,3-triaminobenzene is converted under similar conditions into a phosphocyclic system of a different chemical nature (Scheme 113).[578,579]

Scheme 113



A more complex aromatic amine, *o*,*o*′-diaminobiphenyl, reacts with phosphorus di- and triamides giving rise to 4,5,6,7-dibenzo-1,3,2-diazaphopsphorinanes.[580]

In the case where X = NEt_2, the primary product can undergo elimination of the amine to give a derivative of two-coordinate phosphorus, which partially dimerizes as a result of regular 1,2-cycloaddition.

d. Phosphorylation of Natural Products

This line of research is little developed as of now. Data on cyclophosphorylation of ephedrine by phosphorus amides[581,582] and phosphonous diamides[583,584] have been reported. Unfortunately, modification of more complex alkaloids by phosphamides has not yet been studied. Meanwhile, studies dealing with the use of phosphamides to form a link connecting nucleoside and amino acid residues via a phosphamide bond have been initiated.[585] In addition, a series of studies on the synthesis of conjugates whose structure contains a polymeric amine conjugated with phosphitonucleoside oligomers has been carried out. It was shown that an oligonucleotide block can be easily removed from the polymeric substrate by aminolysis.[586]

IV. Phosphorylation of Amides and Other Nitrogen-Containing Derivatives of Acids

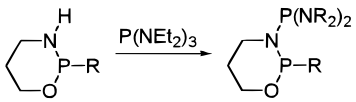
Much attention has been paid in several scientific centers to the introduction of ATPA into the reactions with amides and other related nitrogen-containing derivatives of acids. The data obtained are ample and diversified regarding their chemical content.

1. Phosphorylation of Amides of Phosphorus and Sulfur Acids

a. Phosphorylation of Amides of Trivalent Phosphorus Acids

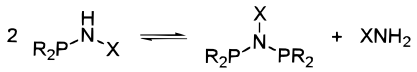
In the previous section, we considered the interaction of simple ATPA with aniline and similar amines and noted that primary phosphorylation affording >P−NHR systems can be followed by some spontaneous processes. Actually, from the viewpoint of synthetic chemistry, all the observed reactions should be classified into phosphorylation of amines. Meanwhile, phosphorylation of primary amides of trivalent phosphorus acids can be performed as self-contained reactions. An example is provided by phosphorylation of oxazaphosphorinanes (Scheme 114).[587]

Scheme 114



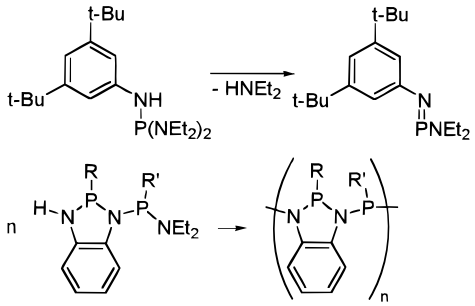
This type of phosphorylation occurs as well when two identical molecules of primary phosphamides react with each other, one of them being the phosphorylating reagent and the other being the phosphorylated component (Scheme 115).[588,589] Note that

Scheme 115



some other related self-phosphorylation reactions occurring as intramolecular[590] or intermolecular[591] processes have been reported (Scheme 116).

Scheme 116

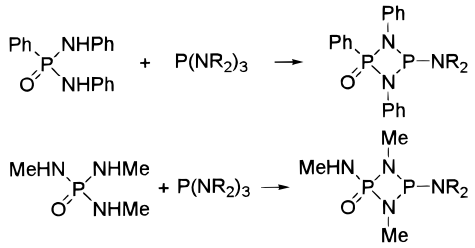


b. Phosphorylation of Amides and Imides of Pentavalent Phosphorus Acids

Dialkyl(aryl) phosphoric monoamides[592] and the corresponding cyclic phosphoryl and thioxophosphoryl compounds[593,594] have been successfully introduced into phosphorylation by simple ATPA. These reactions result in the formation of molecules containing both tri- and pentavalent phosphorus groups linked through a nitrogen atom.

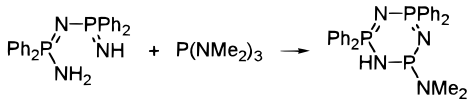
Secondary phosphonic diamides[592,594] and the corresponding phosphoric triamides[595] react with ATPA to give four-membered phosphorus-and-nitrogen containing rings (Scheme 117).

Scheme 117



A diphenylphosphinic amidoimide with a complex structure has also been studied in phosphocyclizations with ATPA[596] (Scheme 118). Diamides of sul-

Scheme 118



furic acid also enter into phosphocyclization with ATPA.[592,597] This gives PSN_2 four-membered rings.

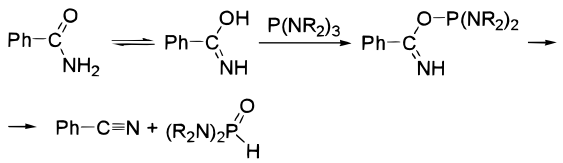
2. Phosphorylation of Carboxamides

Studies of the reactions of ATPA with compounds whose molecules contain complex functional groups such as C(X)NH have shown that the route and the course of phosphorylation are largely determined by the structural features of the carboxamide reagents.

On heating with ATPA, primary amides of carboxylic acids are converted into nitriles and hydrophosphoryl compounds. It is assumed that in the first step of the process, the initial compounds, being prototropic systems, are phosphorylated at the hy-

droxy group and then they are converted into enol phosphates. The latter decompose to give the final products, for example, as shown in Scheme 119.[598]

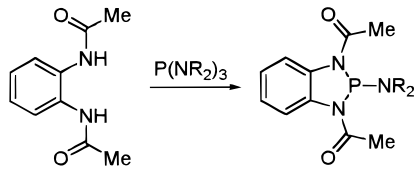
Scheme 119



Data indicating that the reaction with thioamides follows a similar pathway have been reported.[598] Some functionalized primary amides react in a similar way. Thus, salicylamide reacts with phosphorus triamides (molar ratio of the reactants 1:2) to give a nitrile containing a diaminophosphinoxy group in the *ortho*-position.[599] Conversely, phthalimide is phosphorylated at the nitrogen atom.[600]

ATPA have also been studied in reactions with secondary amines. Compounds with two functional groups located closely in space and, hence, prone to form phosphorus-containing rings have been chosen for this purpose (Scheme 120).[601,602]

Scheme 120

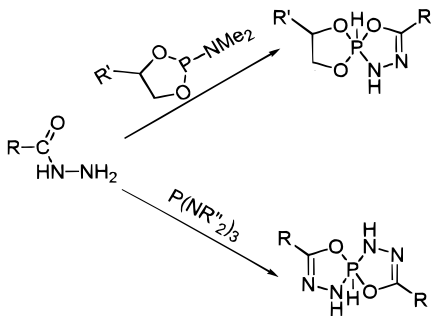


Functionalized secondary carboxamides have also been vigorously studied in the reactions with ATPA. Thus, α-[603] and *β*-[604]amino amides as well as hydroxy[511,602,605,606] and mercapto[607] amides have been converted into the corresponding 1,3,2-diheterophosphocyclanes.

3. Phosphorylation of Hydrazides and Amidines of Carboxylic Acids

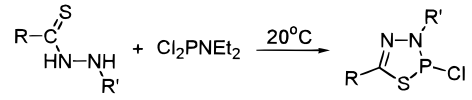
The simplest hydrazides of carboxylic acids have been studied in reactions with phosphorus mono-[608] and tri-[609]amides. Primary phosphorylation is followed by the formation of hydrospirophosphorane systems. Terminally substituted hydrazides yield only monocyclic compounds (Scheme 121).[609]

Scheme 121



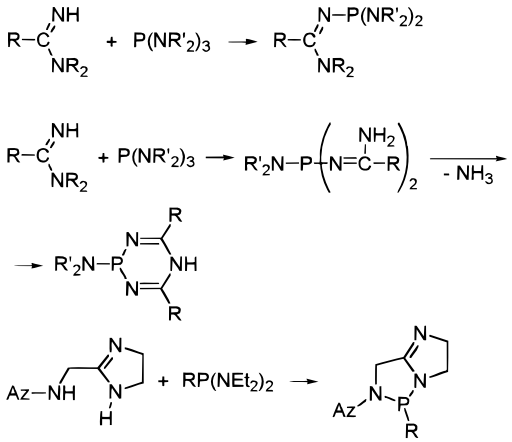
The reactions of all of the above-mentioned hydrazides with phosphonous diamides afford monocyclic structures.[609] Related monocyclic heterocycles are formed when phosphorus triamides react with terminally substituted hydrazides of thiocarboxylic acids.[610] It was noted that the condensation of thiohydrazides with dichloro(diethylamino)phosphine is accompanied by rupture of the P−N bond, the P−Cl bond being retained (Scheme 122).

Scheme 122



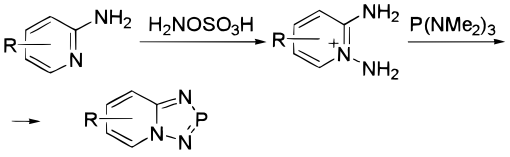
Amidines of various types have been studied in reactions with ATPA more extensively than hydrazides. The simplest amidines are readily phosphorylated at their imido[611] and amido[612] groups. This may be accompanied by secondary processes, resulting in the formation of interesting heterocyclic systems. Functionalized representatives of this class of compounds, for example, arylaminomethylimidazolines, are phosphorylated giving rise to diazaphospholane rings (Scheme 123).[613]

Scheme 123



Hydrazine analogues of amidines react with mono-, di-, and triphosphamides according to the obvious route to give triazaphospholenes.[614−616] Synthesis of 1,2,4,3-triazaphospholo[1,5-α]pyridines is more interesting (Scheme 124).[617]

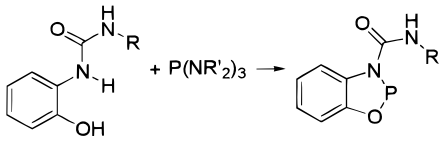
Scheme 124



4. Phosphorylation of Urea and Guanidine Derivatives

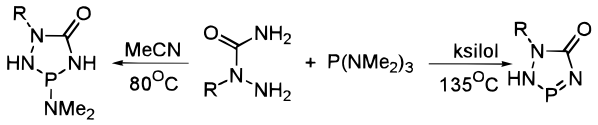
N,*N*′-Disubstituted ureas can be singly[597] or doubly[597,611,618] phosphorylated by phosphorus triamides. The latter process affords four-membered heterocycles, whose structures have been studied in detail.[619] Arylureas containing a hydroxy group in the *o*-position of the aromatic ring react with the above-mentioned phosphamides, being thus converted into oxazaphospholane rings (Scheme 125, for example.)[532]

Scheme 125



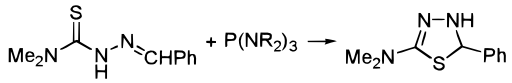
Semicarbazides have also been involved in reactions with phosphorus triamides. In this case, phosphocyclic compounds are also formed, their structures being determined by the type of solvent used (Scheme 126).[620]

Scheme 126



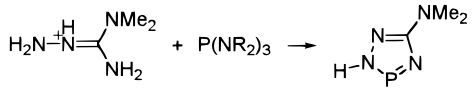
Thiosemicarbazides undergo a similar transformation. Conditions for aromatization of the resulting compounds have been selected, and some other aspects of their chemistry have been brought to light.[620] It is noteworthy that some semicarbazones react with ATPA in such a way that the role of the phosphorylating reagent is merely to induce condensation to give five-membered aromatic heterocycles, for example, see Scheme 127.[621]

Scheme 127



Data on phosphocyclization of guanidinium salts can also be found in the literature (Scheme 128).[622]

Scheme 128



The resulting compounds were introduced in a series of transformations, which permitted the design of even more complex heterocyclic systems.

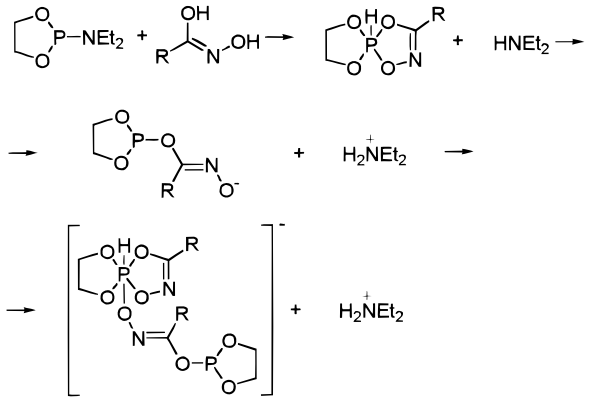
5. Phosphorylation of Hydroxamic Acids and Their Derivatives

Alkanediyl phosphoramidites react with hydroxamic acids according to a fairly complex pathway, for example, see Scheme 129.[623]

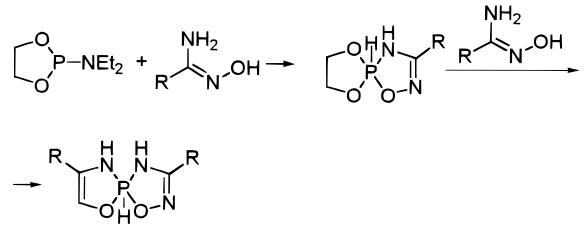
When phosphorylation is carried out in the presence of trifluoroacetic acid, the diethylamine formed is trapped and hydrospirophosphorane is formed as the major reaction product. Experiments on the interaction of ATPA with *O*-alkylated hydroxamic acids are discussed in the literature. These reactions are accompanied by the replacement of the amido group at the phosphorus atom by an alkoxy group and by some other reactions, whose essence is little known.[624]

The reactions of ATPA with hydroxomatoamides have received much attention. It was found that the process starts with phosphorylation, which is followed by cyclization giving rise to hydrospirophosphoranes. These products can react with excess hydroxomatoamides to yield symmetrical hydrospirophosphoranes, for example, see Scheme 130.[625,626] In some cases, secondary transformations can afford derivatives of six-coordinate phosphorus.[626]

Scheme 129



Scheme 130



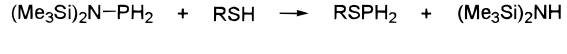
To conclude the consideration of the reactions of ATPA with various nitrogen-containing derivatives of carboxylic acids, one can note that the data accumulated on this topic (mainly by the French school of organophosphorus chemistry) have markedly extended the views on ring−chain prototropic transformations of phosphorus derivatives.

V. Phosphorylation of Mercaptans

1. General Principles

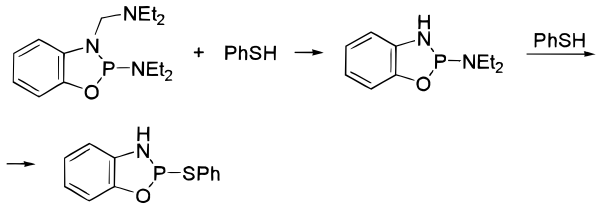
The possibility of phosphorylating mercaptans by ATPA was first demonstrated by G. Stuebe and H. Lankelma[627] in the late 1950s in relation to the reactions of phosphorus triamides with phenylmethanethiol. Later this reaction was extended to various phosphamides including nucleoside phosphamides[402] and to peculiar structures, primary silylated phosphorus amides[628] (Scheme 131).

Scheme 131



Some competitive relationships have been elucidated; for example, it was shown that on treatment with benzenethiol, *N*-aminomethylated phosphamides are first deaminomethylated and only after completion of this process phosphorylation occurs (Scheme 132).[629] Note that the above-mentioned aminomethylated phosphamide reacts with alcohols only with cleavage of the phosphamide bond.[9]

Scheme 132



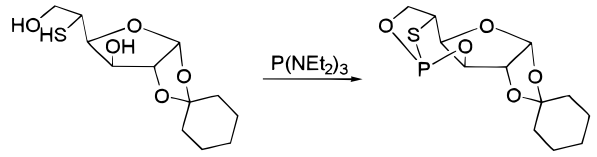
Mercaptans are also phosphorylated by phosphimides; when equimolar amounts of reactants are taken, only the π-bond of the phosphimine function is cleaved.[630]

The reactions of ATPA with aromatic thiols usually lead to good results.[629,631] The use of aliphatic thiols is not always fruitful because their desulfuruzation occurs in parallel.[631] This trouble can be eliminated by using acid catalysis, which, in addition, permits phosphorylation to be carried out under milder conditions.[632]

2. Phosphorylation of Mercaptans in Fine Organic Synthesis

In synthetic practice, researchers normally make use of mercaptans with complex structures. The reaction of 1,2-ethanedithiol with phosphorus triamides, resulting in the formation of triethylenebis(trithiophosphite), has been reported.[633] Phosphorylation of 1,2-cyclohexylidene-5-mercapto-5-desoxyglucofuranose affords the corresponding 3,5,6-bicyclo phosporothioite (Scheme 133).[634] The 6-desoxy-6-

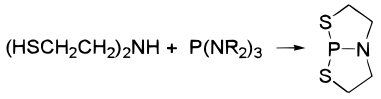
Scheme 133



mercapto derivative is phosphorylated in a similar way.

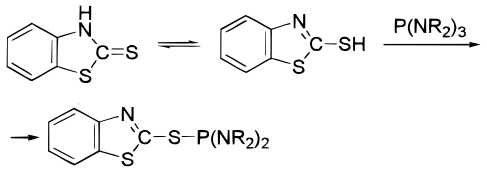
Bis(β-mecraptoethylamine) reacts with equimolar amounts of phosphorus triamides to give an interesting bicyclic product (Scheme 134).[635]

Scheme 134



o-Mercaptoaniline[636,637] and its *N*-derivatives[638] are readily cyclophosphorylated by various ATPA to give benzo-1,3,2-azathiaphospholanes. Cyclizations of this type have also been reported for geminal mercaptocarbonyl compounds—mercapto amides,[639] mercapto esters,[631] and mercapto ketones.[640] The reaction of β-cyanoethanethiol with alkyl phosphorus diamides occurs as standard replacement of one amido group.[403] The known commercial product Captax is phosphorylated by ATPA yielding thio esters, for example, see Scheme 135.[641]

Scheme 135



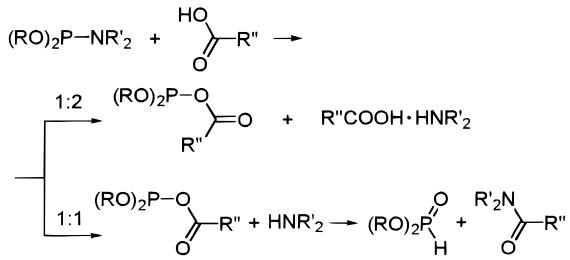
VI. Phosphorylation of Acids

This section consists of three parts, which are devoted to the use of ATPA in phosphorylation of carboxylic acids, heteroorganic acids, and simple inorganic compounds exhibiting acidic properties.

1. Phosphorylation of Carboxylic Acids

It has already been noted that ATPA and carboxylic acids form complexes which can efficiently phosphorylate alcohols.[68] Meanwhile, other processes can also occur in ATPA−carboxylic acid systems. For instance, it has been shown that *N*,*N*-dialkylphosphorus amides react with carboxylic acids at a molar ratio of 1:2 to give dialkyl acyl phosphites (Scheme 136).[642]

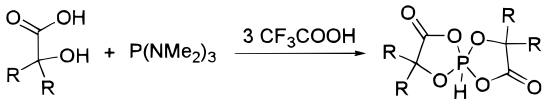
Scheme 136



Subsequently, this reaction has been further developed regarding its use for synthetic purposes.[28,514,535,643,644] It became clear that excess acid is needed to neutralize the secondary amine being evolved, because the amine can attack the carbonyl group in acyl phosphite as a hard nucleophile. In fact, the use of equimolar amounts of the reactants gives a totally different result (Scheme 136).[642,645]

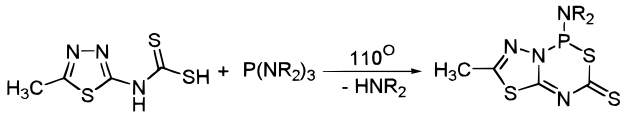
The latter reaction has proved to be highly fruitful and found application in the solution of various chemical problems. It can be carried out for phosphorus mono-,[216,646,647] di-,[648,649] triamides[497,643,648] and phosphonous amides.[514,644] According to the desire of the researcher, di- and triamides can be dealkylated either partially[648,649] or completely.[497] Note that the greater part of works were devoted to acidolysis of cyclic ATPA. In this case, stereoselective versions for the syntheses of important compounds were developed,[216,646] intramolecular deacylation to give bifunctional products was performed, and unusual behavior of phosphorothious amides was observed.[650] Acidolysis of ATPA by functionalized carboxylic acids can display peculiar features. Thus, hexamethylphosphorus triamide reacts with α-hydroxycarboxylic acids to give hydrospirophosphoranes. Addition of trifluoroacetic acid to the reaction mixture was proposed in order to stabilize the reaction products (Scheme 137).[651]

Scheme 137



Spirophosphoranes have also been synthesized in a similar way from α-aminocarboxylic acids.[652] An even more complex example of heterocyclization is provided by the synthesis of a new bicyclic system using an unusual derivative of dithiocarbaminic acid (Scheme 138).[653] Note that in this case the secondary

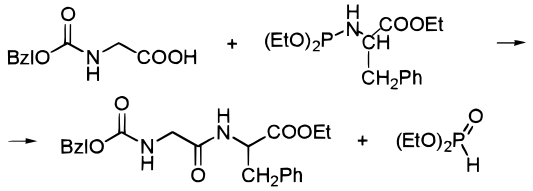
Scheme 138



amine evolved does not affect the primary phosphorylation product.

The data on the reactions in the ATPA−carboxylic acid systems considered above present interest not merely for the solution of problems of organophosphorus chemistry; they are also significant for the development of fine organic synthesis and polymer chemistry. Thus, specialists engaged in nucleotide synthesis have been attracted by the possibility of binding two amino acids, the amino group in one of which is activated by a functional group based on trivalent phosphorus (Scheme 139).[654] In this case,

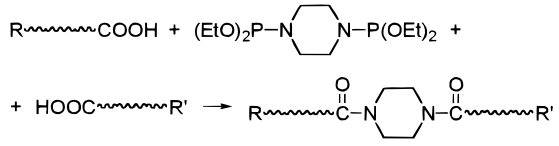
Scheme 139



the phosphorus-containing compound is a side product.

Bisphosphorylated piperidines proved to be useful reagents for increasing the molecular weights of polymers whose molecules contain carboxyl groups (Scheme 140).[655]

Scheme 140

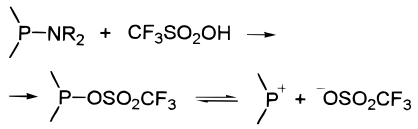


A similar approach has been proposed for the modification of polyacrylamide. This amide was phosphorylated, and the polymeric phosphorus amide thus obtained was treated with carboxylic acids.[656] It has been proposed to convert oligomeric[657] and polymeric[658] acids directly into dialkylamides by treatment with ATPA.

2. Phosphorylation of Heteroorganic Acids

O. Dahl reported[52] transformations of some phosphorus triamides and alkyl phosphoramidites in the reaction with trifluoromethanesulfonic acid. From his point of view, the reaction starts with the protonation of the substrate; after that, the resulting triflatophosphites occur in equilibrium with the products of their ionization (Scheme 141). However, hexaeth-

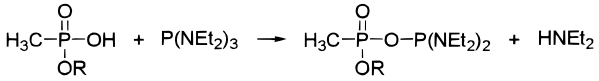
Scheme 141



ylphosphorus triamide reacts with *p*-chlorobenzenesulfonic acid to give only phosphonium salt, which is a stable compound.[55]

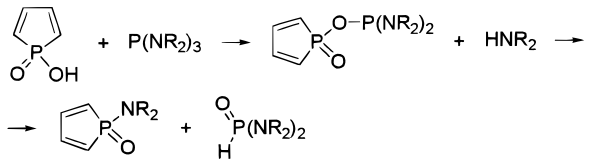
Much attention has been paid to the reactions of ATPA with organic phosphorus acids. Monoalkyl methylphosphonates have been made to react with hexaethylphosphorus triamide. It was found that when the reactants are taken in equimolar amounts, mixed anhydrides and diethylamine are formed initially. When diethylamine is distilled off during the reaction, anhydrides are formed in high yields (Scheme 142).[659]

Scheme 142



If the amine is not distilled off, the mixed anhydride is cleaved. The reaction of ATPA with phosphinic acids belonging to the class of 3-phospholenes has also been studied. The researchers cited[55] paid attention to the reaction between the mixed anhydride formed initially and the amine and concluded that the amine attacks the pentavalent phosphorus atom, which results in phosphinic amides being formed as the final products, for example, as shown in Scheme 143.

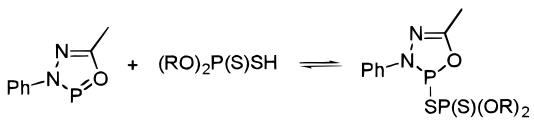
Scheme 143



Generally, mono-[660] and di-[661−663]thio acids of pentavalent phosphorus behave in a similar way in the reaction with ATPA. Normally excess acids are used in these reactions in order to bind the amine being evolved; this allows mixed anhydrides to be synthesized in high yields.

An interesting result was obtained when dialkyl phosphorothioates were made to react with 5-methyl-2-phenyl-1,2,3-diazaphospholanes. In these cases, the acid adds the −P═N− bond with heat evolution. The resulting adducts are unstable and decompose on heating to give the initial compounds (Scheme 144).[664]

Scheme 144



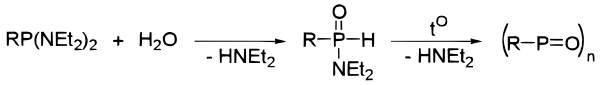
3. Phosphorylation of Simple Inorganic Acids

a. Phosphorylation of Water

Phosphorylation of water by ATPA, i.e., hydrolysis of ATPA, is widely employed in synthetic studies for various purposes. The reaction of ATPA with water is appreciably accelerated in the presence of amine hydrohalides[33,665] or azoles.[423] In this respect, the chemical essence of the reaction in question corresponds to that of the above-discussed processes. It should be noted that this reaction is much more sensitive (for the catalytic coefficient k_c, see eq 2) than alcoholysis.[665]

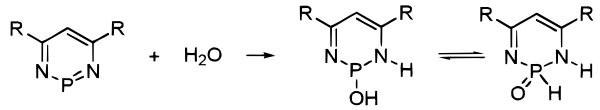
By now, hydrolysis of phosphorus,[423,665−667] phosphonous,[33] and phosphinous[668,669] amides has been studied in detail. The results of decomposition of oligomeric and monomeric derivatives were specially compared. It was shown that the first phosphamide bond splits more readily than the other ones.[33,55,666,670] It is significant that oligoamides can undergo deamidation, after the first hydrolysis event, to give anhydrides (Scheme 145).[670]

Scheme 145



The nature of the phosphamide group has a substantial influence on the ease of its hydrolysis. Azolides are hydrolyzed especially easily.[120,671] Amide groups carrying small alkyl radicals are replaced faster than those with bulky or branched radicals.[630,669] The tendency of an amide group to be replaced in the presence of water can also determine on its position in the substrate molecule. Thus, in cyclic systems, an exocyclic amido group is normally replaced more readily.[666] It is also worth noting that phosphamide and phosphimide bonds differ in their basicity in hydrolytic processes, the latter being more reactive, for example, see Scheme 146.[630]

Scheme 146



b. Phosphorylation of Hydrogen Sulfide

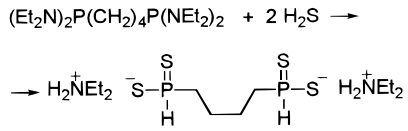
Hydrogen sulfide is often used in experimental studies to destroy phosphamide functions and construct instead thiohydrophosphoryl groups. It is clear that sulfhydrolysis does not require catalysts. This process is highly significant from the synthetic viewpoint; it has been carried out for phosphorus,[672−675] phosphonous,[675−677] and phosphinous[678] amides. Di- and triamides can cleave selectively only one P−N bond[674,676] or all of these bonds present in the molecule. In the latter case, the reaction products are isolated as ammonium salts (Scheme 147).[103]

In recent years, sulfhydrolysis has been actively used in bioorganic chemistry, especially to prepare analogues of nucleotides and nucleic acids.[400]

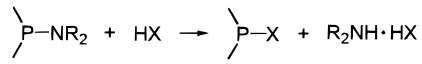
c. Phosphorylation of Hydrogen Halides

The reactions of hydrogen halides with ATPA can follow different pathways. The most frequently encountered reaction route is the phosphorylation of these acids (Scheme 148).

Scheme 147



Scheme 148

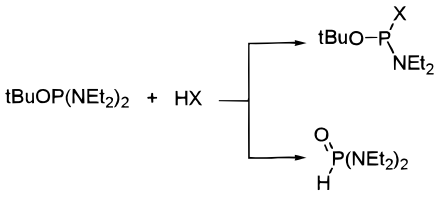


This process has not been studied in detail. Apparently, in the majority of cases, the reaction starts with the formation of some complexes, whose subsequent transformations involve cleavage of the P−N bond. This reaction route has been noted for HCl,[679−682] HBr,[682−684] and HI.[684,685] In the case of HF, the reaction can either follow this route or involve as well other processes leading to the expansion of the coordination sphere of phosphorus.[686]

The advantages of the reaction in question are obvious. It occurs under mild conditions and is highly efficient. Depending on the quantity of the reagent used, either one[687] or several phosphamide bonds can be cleaved.[683,688] In the case of amidocyanides, only the P−N bond is cleaved whereas the C−N bond remains intact.[689] Note also that splitting of P−N bonds in chiral systems is stereoselective;[157] no disproportionation occurs.[690] These features made it possible to perform hydrohalogenolysis for ATPA whose molecules contain other labile fragments, for example, vinyl phosphite[691] or phosphocyclopropenyl[692] fragments or phosphonocyclic fragments, prone to undergo isomerization.[693]

The reactions of amido esters of trivalent phosphorus acids with hydrogen halides, unlike those of full amides, can involve rupture of either the phosphamide or the ester bond (see Scheme 149).[47,694] The reaction pathway is determined by the type of acid and by the solvent.

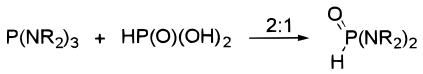
Scheme 149



d. Phosphorylation of Other Acids

It has been shown for several examples that ATPA can react with hydrogen cyanide, being thus converted into nitriles. The substitution occurs at 20 °C at a high rate.[695] Hexaalkylphosphorus triamides react efficiently with phosphorous acid; this results in exchange of the substituents at the central atoms of the reactants (Scheme 150). This reaction is a convenient method for the synthesis of hydrophosphoryl amide derivatives.[696,696] Phosphonous acids

Scheme 150



react with equimolar amounts of their diamides in a similar way.[697]

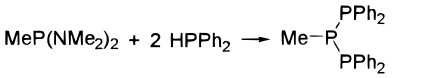
VII. Phosphorylation of Phosphorus, Carbon, and Boron Hydride Derivatives

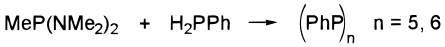
Above we have considered phosphorylation of numerous and diversified polar proton-donating nucleophiles on treatment with ATPA. In this section, we demonstrate the chemical virulence of these compounds, which manifests itself as the ability to phosphorylate low-polarity systems also, such as hydrides of elements of the central groups of the periodic table. Among these compounds, hydrides of tricoordinated phosphorus resemble to the greatest degree the nucleophiles considered above. In fact, phosphinous monoamides react with primary phosphines with the formation of a phosphorus−phosphorus bond (Scheme 151).[157,698]

Scheme 151

The productivity of this reaction is high, although the synthesis conditions have not apparently been optimized. Phosphorylation of primary and secondary phosphines by phosphonous amides also proceeds smoothly (see Scheme 152[699,700] for example).

Scheme 152

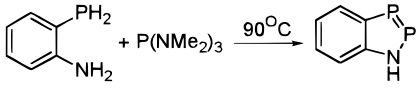




Bicyclic fused P−P systems arise upon reaction of equimolar amounts of phosphorus triamides and bis-*β*-mercaptoethyl(diethyl)phosphine.[635]

The reactions of *o*-aminophenylphosphine with phosphorus triamides, giving rise to an original heterocyclic structure, are especially interesting (Scheme 153).[701]

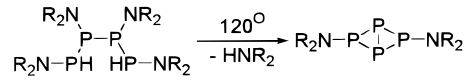
Scheme 153



Even more complicated systems have been reported by E. Niecke, who studied the synthesis and transformations of a series of oligophosphines containing both hydrogen atoms and amino groups, i.e., both phosphorylable and phosphorylating sites, at phosphorus atoms. Among his experiments, the design of bicyclotetraphosphine diamides may be signed out (Scheme 154).[702]

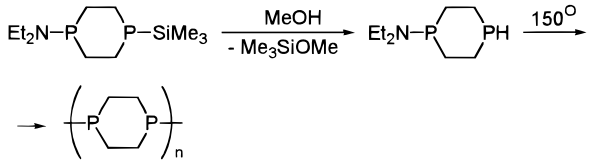
Polymeric P−P derivatives have been synthesized based on phosphorus analogues of piperazine containing nitrogenous and silyl substituents at the phosphorus atoms. It was found that trityl functions

Scheme 154



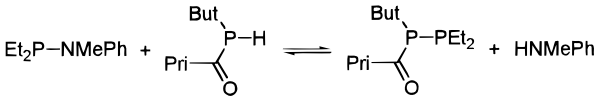
can be removed selectively by methanolysis. On heating, the resulting asymmetrical phosphopiperazines are converted into polymers (Scheme 155).[703]

Scheme 155



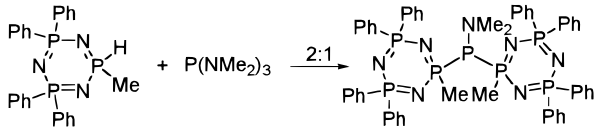
In some cases, the above reactions are reversible. This is favored by the presence of an acyl group in the molecule of the phosphine component (Scheme 156).[704]

Scheme 156



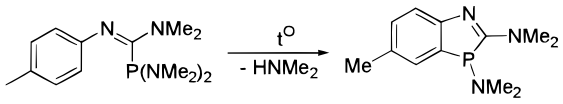
Iminophosphoryl compounds can also enter into P−P condensations with ATPA. This possibility was studied in the greatest detail in relation to the corresponding phosphazene rings (Scheme 157).[705]

Scheme 157



Let us turn to C-phosphorylation of organic compounds by ATPA. This possibility has already been noted in relation to phosphorylation of hydrogen cyanide[695] and indole.[508] Azaphosphole condensation is a more interesting example of this reaction (Scheme 158).[706]

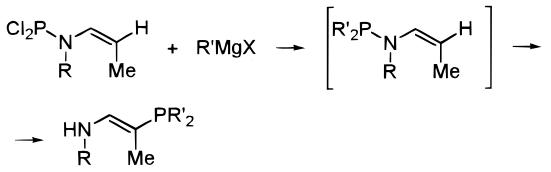
Scheme 158



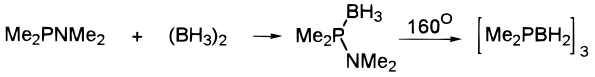
Isomerization of phosphorylated vinylamines consisting in the replacement of the amido group by a hydrocarbon radical with migration of a hydrogen atom from carbon to nitrogen also deserves attention. It should be emphasized that this process involves necessarily reorganization of the phosphorus center. If this is a phosphorus chloride center, it becomes fixed at the nitrogen atom. If the chlorine atom has been replaced by a hydrocarbon radical, the localization of the phosphorus atom changes (Scheme 159).[707]

Quite recently, other variants of N → C migration of phosphorus have been found.[708] The reactions of ATPA with boron hydrides are even less studied. Very few data on this topic are available (Scheme 160).[709]

Scheme 159



Scheme 160



Meanwhile, the interest in the design of complex systems containing trivalent phosphorus, boron, and nitrogen is enhancing (see, for example, ref 710). Therefore, further development of these studies using ATPA should be expected.

VIII. Phosphorylation of Hydride Metal Complexes

Nowadays, the coordination chemistry of transition-metal hydride complexes is being vigorously developed. Among other aspects, phosphorylation of these compounds using ATPA has also been investigated. Thus, it has been shown that iron, molybdenum, and tungsten complexes can react with ATPA in different ways. For example, dicarbonyl(pentamethylcyclopentadienyl)iron hydride is readily phosphorylated with dimethylphosphinous amides with evolution of dimethylamine. However, the corresponding molybdenum and tungsten complexes react in a different way with pinacolone phosphorus amides. The reaction starts with ligand coordination upon displacement of one carbonyl group; after that, intramolecular phosphorylation occurs, resulting in the formation of a phosphorus−metal double bond.[711,712]

IX. Conclusion

Amides of trivalent phosphorus acids, which are actively used now, constitute a large class of efficient and practically convenient phosphorylating reagents. The scope of their application is constantly expanding. Nevertheless, the great chemical potential inherent in ATPA is realized only partly. In fact, the use of these reagents as selective phosphorylating means still receives little attention. Therefore, it should be emphasized that phosphamides, unlike chlorides and other popular phosphorylation reagents, can differ appreciably in the spatial organization of the leaving (amide) group. This difference may prove to be significant regarding the choice of reagents for selective phosphorylation of nucleophiles containing several reactive sites. An example of these nucleophiles is provided by primary and secondary glycols. ATPA whose molecules contain small amide groups react with these glycols nonselectively. However, in the case of phosphamides with bulky amide groups, the attack at the secondary hydroxyl group faces steric restrictions; therefore, these reagents possess potential for selective phosphorylation of the primary hydroxyl.

Yet another new promising line of research is concerned with enantioselective phosphorylation of racemic nucleophiles by phosphamides containing chiral amide groups. Other reaction routes involving molecular recognition in the nuclepophile−phosphamide system, attained by virtue of selection of an appropriate amide group, are also possible.

Thus, the line of scientific research associated with study of ATPA, which is now becoming nearly classical, has a chance to alter its status by entering the stage of searching for new horizons.

X. Acknowlegments

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XI. References

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