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Reactions of halophosphines with conjugated heterodienes

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Abstract. Data on reactions of halophosphines $PHal_3$, $-PHal_2$, and $>PHal$ with hetero-1,3-dienes resulting mostly in the formation of phosphorus-containing heterocycles are generalised and systematised. The influence of the nature, the number and positions of heteroatoms (O, N) in the heterodiene system, and of the nature of the substituents at the phosphorus atom on the reaction pathways and mechanisms is analysed. The bibliography includes 155 references.

I. Introduction

Reactions of tricoordinate phosphorus derivatives with diene systems is an important route to cyclic phosphorus-containing compounds, first of all following the [4 + 1]-cycloaddition mechanism. In this regard, reactions of halophosphines (HP) $PHal_3$, $-PHal_2$, and $>PHal$ are most numerous. Their reactions with 1,3-dienes containing no heteroatoms are well studied. The reaction of [4 + 1]-cycloaddition of HP to 1,3-dienes was discovered by McCormack in 1953 [1,2] and most intensively studied in the 1960's and early 1970's simultaneously by several groups of investigators. Reactions of HP with conjugated dienes have been adequately covered in reviews [3,4] and monographs.[5–7] Despite a wide variety of compounds obtained, they all belong to phosphol-2(3)-enes ([4 + 1]-cycloaddition reaction), to polymers or oligomers containing a phosphorus atom in the chain (1,4-addition reaction), or to the products of cyclisation occurring with retention of the system of conjugated bonds. The studies in this field [8,9] reported after publication of a book by Quin [6] in 1981 contain no radically new data, except for a series of studies dedicated to investigation of reactions of 1,3-dienes with HP of the X_2CHPX_2 (X = Cl, Br, I) type in the presence of triethylamine.[10–16] Under the action of excess triethylamine, this type of HP undergo dehydrohalogenation to form unstable phosphaethenes $XP=CX_2$. The latter enter *in situ* into the Diels – Alder reaction with dienes following the [4 + 2]-cycloaddition mechanism to give aromatic compounds, *viz*., 2-halophosphorinines containing a dicoordinate phosphorus atom, *via* intermediate six-membered 1,2,2-trihalo-1,2,3,6-tetrahydrophosphorinines.

The study of reactions of HP addition to hetero-1,3-dienes was begun by Conant [17] in 1917 taking unsaturated carbonyl compounds as an example and is being developed successfully at present. These reactions are very diverse and result in the formation of not only five-, but also six-membered rinds, and open-chain structures as well. Recently, the range of heterodienes under study has been considerably extended, which has led, in particular, to obtaining of novel classes of phosphorus-containing heterocycles, which are not only of theoretical, but also of considerable practical interest.

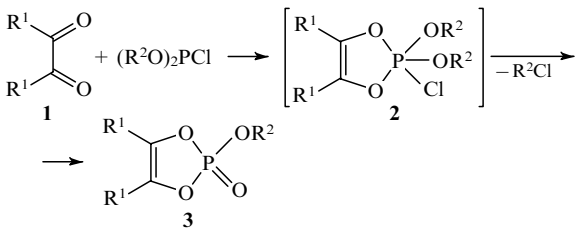
The aim of the present review is to systematise the available information on the reactions of HP with heterodienes and to reveal peculiarities of the influence of heteroatoms in the diene system on the direction and mechanisms of these reactions. We do not discuss here the reactions of compounds that formally contain a heterodiene system, if one or both double bonds of a diene are fragments of arene or hetarene systems.

II. Reactions with oxadienes

1. Reactions with α-dicarbonyl compounds

Investigation of the reactions of P(III) derivatives with α-dicarbonyl compounds was carried out almost simultaneously with the study of analogous reactions of dienic hydrocarbons. However, it should be noted that in most cases it was phosphites that have been used as dienophiles, whereas reactions with HP have been the subject of an insignificant number of publications; moreover, all of them involved α-diketones only.

Like dienic hydrocarbons, α-diketones **1** react with dialkylphosphorochloridites by the [4 + 1]-cycloaddition mechanism to form adducts **2** containing a pentacoordinate phosphorus atom. Further elimination of alkyl chloride from the adducts **2** according to the mechanism of the second stage of the Arbuzov reaction (see Refs 18, 19) gives 2-alkoxy-2-oxo-1,3,2-dioxaphospholes **3**.[20,21]



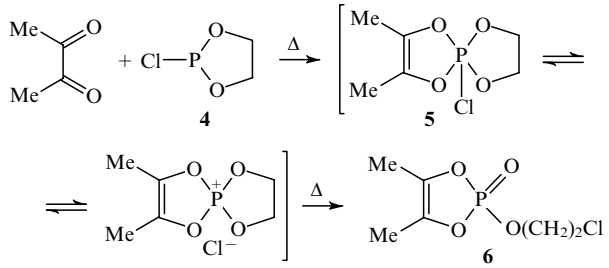
R^1 = Me, Ph; R^2 = Et, Pr^n, Bu^i, Bu^n.

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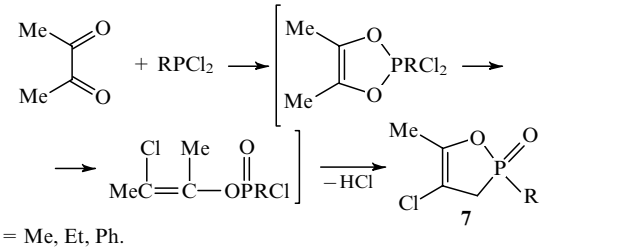
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Uspekhi Khimii **68** (2) 167 – 183 (1999); translated by A M Raevsky

Dialkyl phosphorochloridites are less reactive than trialkyl phosphites and phosphoramidites.[20–22] It is believed [22] that the closure of the dioxaphosphole ring occurs as a result of a concerted or almost concerted passage of the lone electron pair of the phosphorus atom to the conjugated π-system of the α-diketone and transfer of the π-electrons of this system to orbitals of the phosphorus atom.

The reaction of 2-chloro-1,3,2-dioxaphospholane (**4**) with biacetyl occurs to give initially spirophosphorane **5** containing a P(V)–Cl bond and is followed by its conversion into 4,5-dimethyl-2-oxo-2-(2-chloroethoxy)-1,3,2-dioxaphosphole (**6**) by the mechanism of the second stage of the Arbuzov reaction.[23]

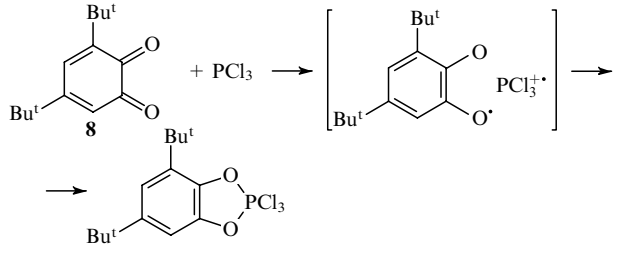


Biacetyl reacts with dichlorophosphines in a different way, *viz*., with the formation of 4-chloro-3*H*-5-methyl-2-oxo-1,2-oxaphosphole **7**, following a mechanism involving recyclisation.[24, 25]



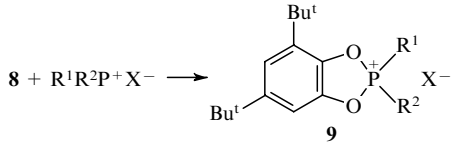
R = Me, Et, Ph.

A phosphorane-type product of [4 + 1]-cycloaddition is obtained in the reaction of phosphorus trichloride with 3,5-di-*tert*-butyl-*o*-quinone (**8**).[26] Based on detection of signals in the EPR spectra recorded during this reaction, it was argued [26] that its mechanism involves a stage of one-electron transfer.



Similar signals in the EPR spectra were also observed in the reactions of PCl_3 with *o*-chloranil, *o*-naphthoquinone, and 9,10-phenanthrenequinone; however, the final products have not been isolated.[26] It should be noted that the appearance of paramagnetic intermediates, detected by the EPR technique, in the reaction mixture is not the unambiguous evidence for the formation of the final phosphorane as a result of one-electron transfer.

Phosphenium salts, which are closest analogues of HP, react with *o*-quinone **8** similarly to HP, following the [4 + 1]-cycloaddition mechanism to form 1,3,2-dioxaphospholenium salts **9**.[27]



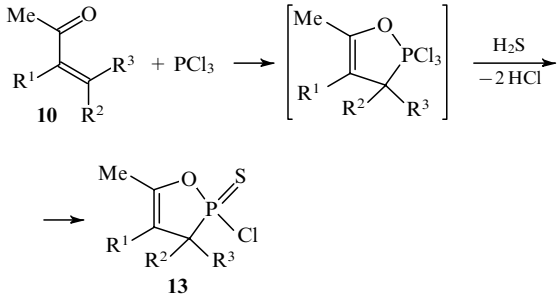
$R^1 = Pr^i_2N$: R^2 = Cl, N = PPh_3; R^1, R^2 = Alk;
$R^1 - R^2$ = MeN $(CH_2)_2$NMe; X = $AlCl_4$, CF_3SO_3.

In the reactions with phosphenium salts the *o*-quinone **8** behaves analogously to 1,3-dienes.[28–30] At the same time, $(Pr^i_2N)_2PCl$ in which the phosphorus atom is less electrophilic than in the phosphenium cation, does not enter into this reaction.[27]

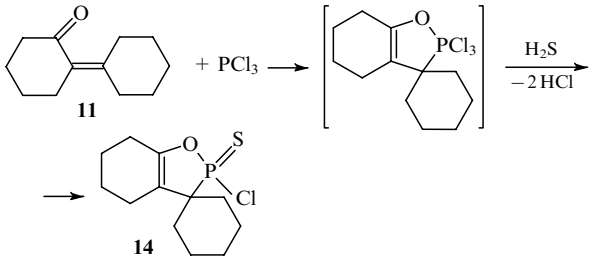
Thus, as in the case of dienic hydrocarbons, symmetric heterodiene systems of diketones and *o*-quinone add a phosphorus-containing dienophile at positions 1 and 4 with the formation of a cycloadduct containing a pentacoordinate phosphorus atom in the first stage. The final reaction products are derivatives of 1,3,2-dioxaoxaphospholes or 3*H*-1,2-oxaphospholes. No indications of the existence of intermediate bipolar ions were found. The intermediate **2** was detected by ^{31}P NMR spectroscopy.[22]

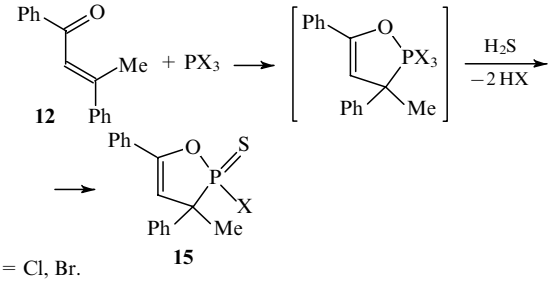
2. Reactions with α,β-unsaturated carbonyl compounds

Mesityl oxide and benzylideneacetophenone were the first 1,3-heterodienes used to study the reactions with HP taking PCl_3 and PBr_3 as an example.[18] The assumption that the reactions with phosphorus trihalides follow the [4 + 1]-cycloaddition mechanism with the formation of five-membered cycles, *viz*., 3*H*-1,2-oxaphospholes,[17] was confirmed in further studies. A brief summary of the results obtained in these earlier studies has been reviewed,[3] so we do not discuss them here. After the review [3] was published, it was established that passage of hydrogen sulfide through a mixture of phosphorus trihalide and α,β-unsaturated ketones **10**–**12** afforded 3*H*-1,2-oxaphosphole sulfides **13**–**15** in good yields.[31, 32] This is evidence in favour of [4 + 1]-cycloaddition.



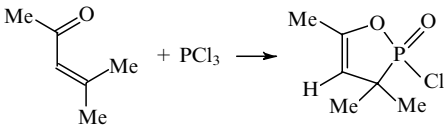
R^1, R^2, R^3 = H, Me.



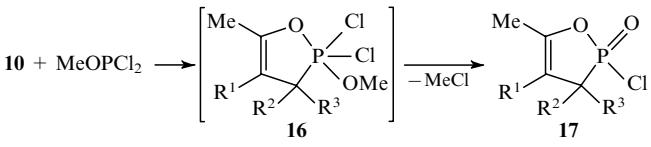


X = Cl, Br.

It was also shown later that heating phosphorus trichloride and mesityl oxide in a sealed tube in the absence of a solvent gave 2-chloro-3,3,5-trimethyl-2-oxo-3*H*-1,2-oxaphosphole.[33] We believe that the formation of this compound can be explained by the replacement of two chlorine atoms in the intermediate [4 + 1]-cycloaddition product by the carbonyl oxygen atom of the second mesityl oxide molecule.

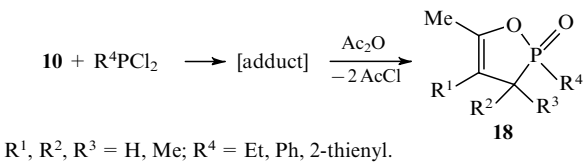


The reactions of methyl phosphorodichloridite with ketones **10** also follow the Diels–Alder reaction mechanism, subsequent elimination of methyl chloride from the adduct **16** results in 2-chloro-2-oxo-3*H*-1,2-oxaphospholes **17**.[34]



R^1, R^2, R^3 = H, Me.

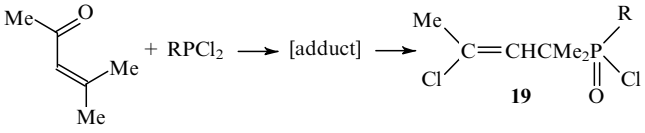
Reactions of dichlorophosphines with α,β-unsaturated ketones **10** in acetic anhydride give first the adducts of the type **16** and then 3*H*-1,2-oxaphospholes **18**.[35–37]



R^1, R^2, R^3 = H, Me; R^4 = Et, Ph, 2-thienyl.

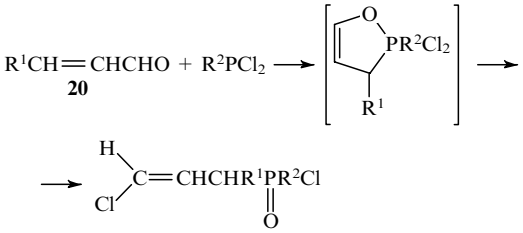
Benzylideneacetone and phenyl(dichloro)phosphine do not enter into this reaction in acetic anhydride.[35]

However, the reactions of dichlorophosphines and phenyl phosphorodichloridites with mesityl oxide (heating in sealed tubes in the absence of a solvent) afford acyclic β,γ-unsaturated phosphorus acid chlorides **19** in which the coordination number of P atom is 4. The latter result from a ring–chain isomerisation of the adducts of the type **16** initially formed in the Diels–Alder reaction.[33]



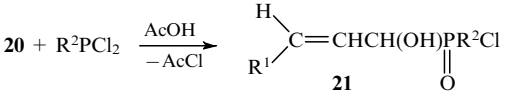
R = Me, Et, Ph, PhO.

Analogous products are obtained in the reaction of dichlorophosphines with α,β-unsaturated aldehydes **20**. In this case the reaction occurs under milder conditions (in solution).[38]



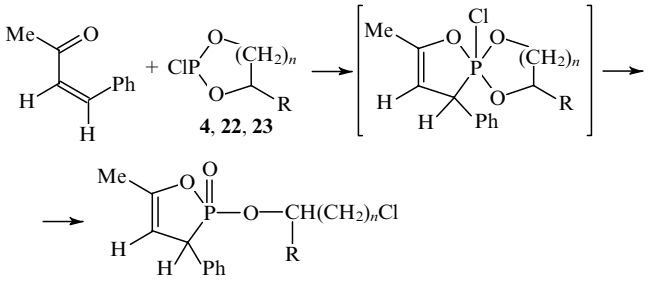
R^1 = Me, H; R^2 = Et, Ph.

Aldehydes **20** react with phenyl(dichloro)phosphine or PCl_3 in acetic acid to give α-hydroxy-β,γ-unsaturated phosphorus acid dichlorides **21** in which the coordination number of the P atom is 4.[38]



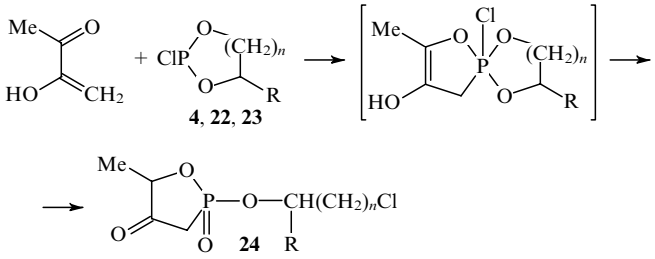
R^1 = Et, Ph; R^2 = Ph, Cl.

Compounds **4**, **22** and **23** react with α,β-unsaturated ketones **10** (heterodienes) by mechanisms involving cycloaddition followed by dealkylation, which is analogous to the second stage of the Arbuzov rearrangement. This results in the formation of 3*H*-1,2-oxaphosphole derivatives,[39,40] as is shown below taking the reaction with benzylideneacetone as an example.

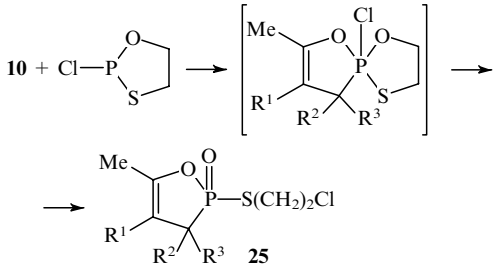


4: R = H, *n* = 1; **22**: R = Me, *n* = 1; **23**: R = H, Me; *n* = 2.

As was mentioned in Section II.1, biacetyl reacts with phospholane **4** following a conventional mechanism of cycloaddition to the O=C–C=O bond system. However, it was reported[41] that the reactions of biacetyl with compounds **4**, **22** and **23** under virtually the same conditions resulted in the formation of quite different products, *viz.*, 1,2-oxaphospholan-4-ones **24**. This was rationalised by a [4+1]-cycloaddition of compounds **4**, **22** and **23** to the enol form of biacetyl as the heterodiene.



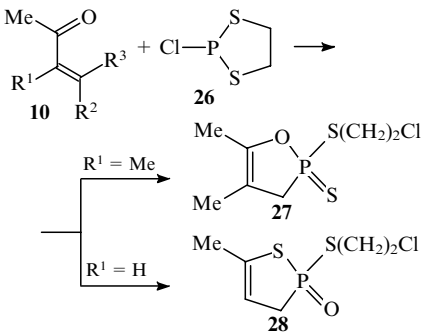
Condensation of ketones **10** with 2-chloro-1,3,2-oxathiaphospholane occurs analogously to the reaction with compound **4**. The second stage of the Arbuzov rearrangement of the intermediate adduct occurs with the cleavage of the C–O bond (not the C–S bond, as in the reaction with butadiene) to give derivatives of 2-oxo-3*H*-1,2-oxaphospholes **25** containing the P–S bond.[42]



R^1, R^2, R^3 = H, Me.

The structure of the final product of reaction between 2-chloro-1,3,2-dithiaphospholane (**26**) and ketones **10** (R^1 = H, Me; R^2 = R^3 = H) is determined by the nature of the substituent R^1. 2-Thioxo-3*H*-1,2-oxaphosphole **27** and 2-oxo-3*H*-1,2-thiaphosphole **28** are respectively formed at R^1 = Me and H.[43]

The reaction of compound **26** with ketone **10** (R^1 = H) occurs either with the rearrangement of an intermediate adduct or with the initial formation of thioxo derivative of the type **27**, which after the Pishchimuka rearrangement[44] is converted into the phosphoryl compound **28**.

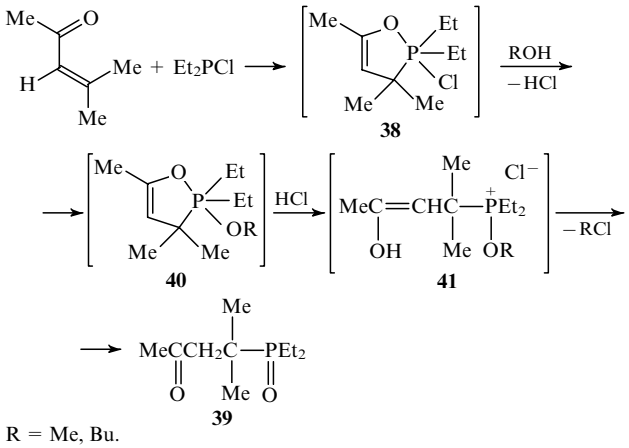


R^1 = H, Me; R^2 = R^3 = H.

Alkylphosphonochloridothioites **30** react with ketones **10** in a similar way; however, in this case, alkyl halide is eliminated from the intermediate [4 + 1]-cycloaddition product **29** to give 2-ethyl(-phenyl)-2-thioxo-3*H*-1,2-oxaphospholes **31** (Scheme 1, route *a*).[45] In the presence of proton-donor reagents (acetic acid or water) this reaction results in the formation of *S*-alkyl phosphinothioates **32**[46] (Scheme 1, route *b*). The formation of products **32** is explained as follows.[46] The ambident ion **33** formed in the first reaction stage as a result of nucleophilic C-addition of alkylphosphonochloridothioite **30** to the unsaturated ketone **10** reacts with acetic acid[46] to give an intermediate acyclic adduct **34**. The latter undergoes the Arbuzov rearrangement with the elimination of acyl chloride and the formation of the final product **32**. If the reaction is performed in the presence of water, alkylphosphonochloridothioite **30** is initially hydrolysed into the corresponding acid **35**, which then is added to the ketone **10** to give the ester **32** (Scheme 1, route *c*).

We believe that it is possible to combine the routes *a*, *b* and *c* into a unified scheme assuming that betaine **33** can be a common intermediate to routes *a* and *b* and that in the presence of water the process can follow not only route *c*, but also route *b* (the latter can be considered as a route common to any proton-donor reagents). Under the action of proton-donor reagents, the halogen atom in the phosphorane **29** can be replaced by an OX group to form a product **36**. The latter adds hydrogen halide to give an ion **34**, which is in equilibrium with an ion **37**, and then the final product **32**.

Heating of diethylchlorophosphine and mesityl oxide in a sealed tube in the absence of a solvent resulted in a crystalline adduct **38**, which was converted into phosphine oxide **39** upon treatment with alcohols following the scheme shown below:[47]

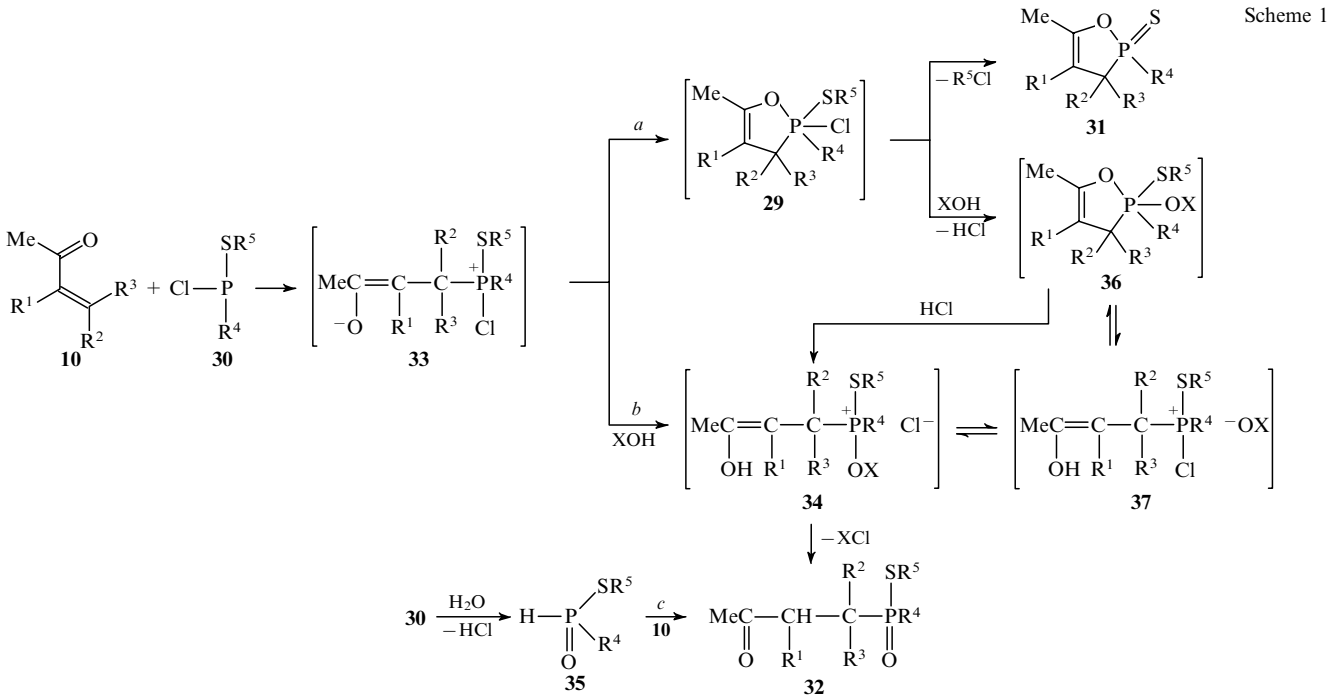


R = Me, Bu.

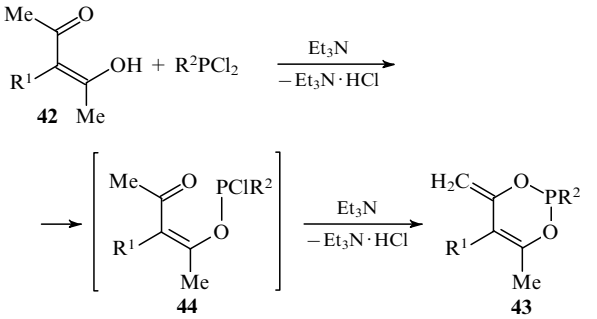
Apparently, the intermediates **3**, **40** and **41** are the analogues of intermediates **29**, **36** and **34**, respectively, while the product **39** is an analogue of the products **32**. It is quite possible that both products **39** and **32** are formed *via* intermediates **33**. Thus, a conclusion can be drawn that the reactions of P(III) acid monochlorides with unsaturated ketones in the presence of proton-donor reagents follow a common mechanism irrespective of the reaction conditions.

A peculiar type of reaction is that of HP with β-diketones in the presence of organic base. It is believed that β-diketones **42** enter into reaction in the enol form, *i.e.*, that they can be considered as a particular case of α,β-unsaturated ketones **10** (R^2 = Me, R^3 = OH). Reactions of P(III) dichlorides with β-diketones give 4-methylene-4*H*-1,3,2-dioxaphosphorinines **43** with a semicyclic homodiene system of bonds.[48–51]

Scheme 1



R^1, R^2, R^3 = H, Me; R^1 = R^2 = H, R^3 = Ph; R^4 = Et, Ph; R^5 = Et, Pr^n, Pr^i, Bu^n, Bu^i; X = H, Ac.

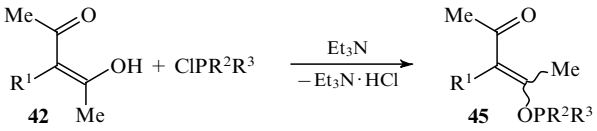


R^1 = H, Et, Cl, Ac; R^2 = Et, Ph, MeO, EtO, Pr^nO, Pr^iO, Me_2N, Et_2N, EtS.

The reaction proceeds *via* intermediate heterodienes, *viz*., α,β-unsaturated ketones **44**, which are formed upon O-phosphorylation of the hydroxyl group of the ketones **42**, which leaves the diene system intact. Subsequent intramolecular O-phosphorylation leads to the closure of the six-membered ring and the formation of dioxaphosphorinines **43** containing an exocyclic methylene group.[49–51]

If P(III) monochlorides are used instead of P(III) dichlorides in the reaction with ketones **42**, in most cases the process is completed by the formation of acyclic products **45**, *viz*., O-phosphorylated derivatives of the ketones **42**, which are analogous to the ketones **44**.[51–55]

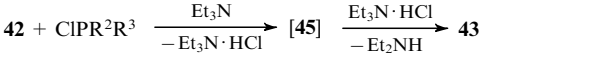
Thus, unlike all reactions considered above, this reaction occurs without involvement of the system of conjugated bonds of the heterodiene at all.



R^1 = H, Ac, Cl; R^2 = EtO, Pr^nO, Me_2N, Et_2N; R^3 = Me, MeO, EtO, Pr^iO, Bu^iO, Ph, Et_2N; R^2–R^3 = $O(CH_2)_2O$, $OCH_2CH(Me)O$, *o*-$O_2C_6H_4$.

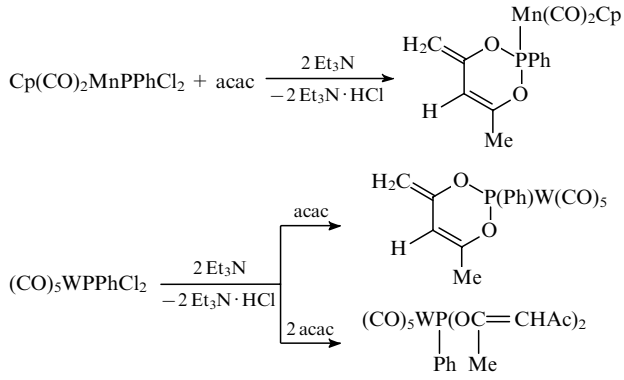
In the case of acetylacetone, it was established that the reaction product **45** is a mixture of *Z*- and *E*-isomers with a considerable predominance of the *E*-isomer.[51, 54]

If P(III) monochlorides containing a dialkylamino group are introduced into the reaction with acetylacetone (**42**, R^1 = H), the linear heterodienes **45** formed initially undergo cyclisation into dioxaphosphorinines **43** with the elimination of dialkylamine. Dioxaphosphorinines **43** are isolated as final products after distillation. The reaction occurs successfully in the presence of acidic admixtures, which behave as catalysts and favour the conversion of the dialkylamino group into a good leaving group. Cyclisation occurs with particular ease if the intermediate linear heterodienes **45** contain two dialkylamino groups at the phosphorus atom. An interesting peculiarity was observed in those cases where it was possible to isolate the intermediates **45** or to obtain them by independent synthesis, *viz*., the yields of the cyclisation products **43** were higher than the portion of *Z*-isomer in the intermediates **45**. This indicates that *Z*,*E*-isomerisation of heterodienes **45** occurs under the cyclisation conditions.[51, 54]

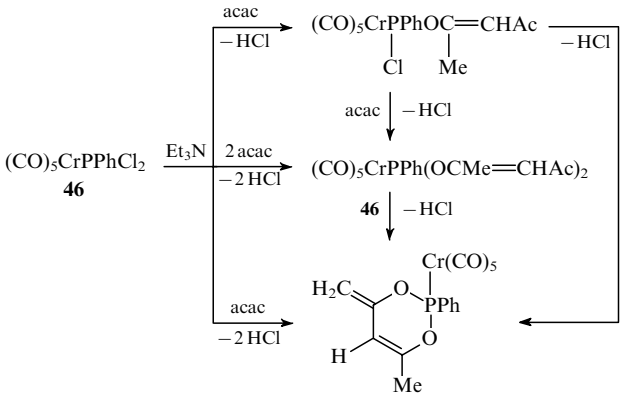


R^1 = H; R^2 = EtO, Pr^nO, Pr^iO, Et_2N; R^3 = Me_2N, Et_2N.

Metal complexes of phenyl(dichloro)phosphine react with acetylacetone in the presence of triethylamine analogously to uncoordinated dichlorophosphines, leaving the metal-containing groups intact.[56, 57]

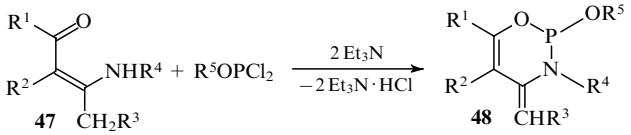


This type of reactions was studied in more detail taking the reaction of pentacarbonylchromium complex **46** with acetylacetone as an example.[57]



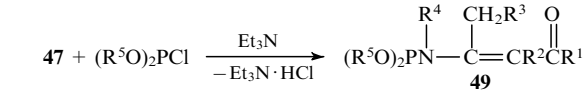
Finally, it should be noted that ethyl(dichloro)phosphine reacts in acetic acid with acetylacetone in its diketone form rather than in its enol form.[58]

Reactions of enamino ketones **47** (nitrogen analogues of the diketones **42**) with alkyl phosphorodichloridites yield azaanalogues of dioxaphosphorinines **43**, *viz*., 4-alkylidene-4*H*-1,3,2-oxazaphosphorinines **48**.[51, 59]



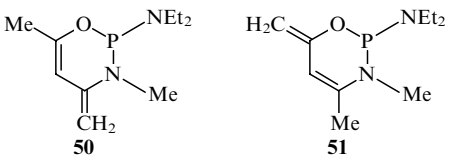
R^1 = H, Me; R^2 = R^3 = H; R^4 = Me, Ph; R^1–R^2 = $(CH_2)_3$; R^2–R^3 = $(CH_2)_2$; R^5 = Me, Et, Pr, Bu.

The reaction of enamino ketones **47** with dialkyl phosphorochloridites halts in the stage of N-phosphorylation of the amino group and the formation of acyclic dialkyl phosphoramidites **49**.[51, 60]



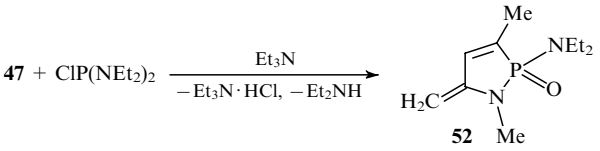
R^1 = H, Me; R^2 = R^3 = H; R^4 = Me; R^5 = Et, Pr.

However, as in the case of diketones **42**, the reaction of enamino ketone **47** (R^1 = R^4 = Me; R^2 = R^3 = H) with bis(diethyl)phosphorodiamidochloridite occurs in a more complex way. Observation of weak signals along with other signals in the ^{31}P NMR spectrum indicates that the reaction mixture contains 4-methylene-4*H*-1,3,2-oxazaphosphorinene **50** and/or isomeric 6-methylenephosphorinene **51**.



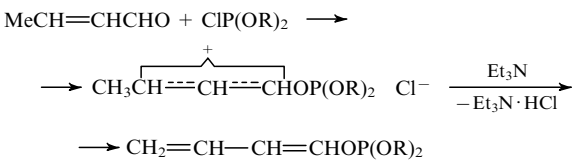
50 **51**

However, only 5-methylene-2-oxo-5*H*-1,2-azaphosphole **52** was isolated after distillation [51, 59] due to the vinyl phosphite–vinylphosphonate rearrangement.[50, 51, 53]



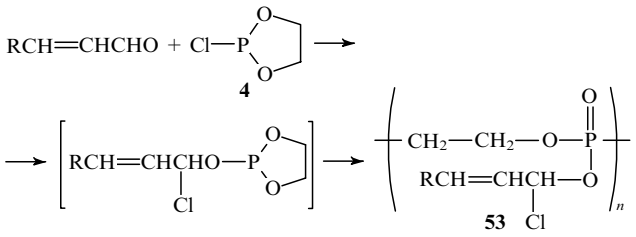
52

Reactions of phosphorochloridites and crotonaldehyde in the presence of triethylamine occur with proton abstraction from the methyl group at the double bond and the formation of butadienyl phosphites.[61] We believe that the initial attack of phosphorochloridite on the oxygen atom of the carbonyl group is followed by proton abstraction from the methyl group.



R = Et, Ph; $(OR)_2 = O(CH_2)_2O$.

2-Chloro-1,3,2-dioxaphospholane (**4**) reacts with α,β-unsaturated aldehydes only on the carbonyl group to form phosphorus-containing oligomers **53** with retention of the C=C bond.[39]



4 **53**

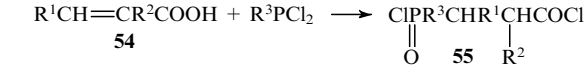
R = H, Me.

The distinction between the reactions of functionalised ketones **42** and **47** with HP and those of aldehydes **20** with phosphoromonochloridites from the reactions of other heterodienes with HP is that these α,β-unsaturated carbonyl compounds react analogously to saturated carbonyl compounds,[62] *i.e.*, they enter into O-phosphorylation reactions rather than into the [4+1]-cycloaddition reactions. In turn, HP act simply as the corresponding acid chlorides rather than as P(III) derivatives, the coordination number of the phosphorus atom in which is increased immediately in the reaction with (hetero)dienes (as in the case of [4+1]-cycloaddition reaction). It should be noted that in the formation of oligomers **53** the coordination number of the phosphorus atom increases to four only upon subsequent dioxaphospholane ring opening.

The system of the C=C–C=O bonds can be a fragment of a more extended conjugated cyclic system, *e.g.*, *p*-benzoquinone and its anthraquinone type analogues. A few reactions of these compounds with HP have been documented; however, since they occur with involvement of the entire quinone system, we do not discuss them here and restrict ourselves to referring to the corresponding reviews.[63, 64]

Numerous studies have been dedicated to reactions of HP with α,β-unsaturated acids and their derivatives. Several early studies have been reviewed.[3]

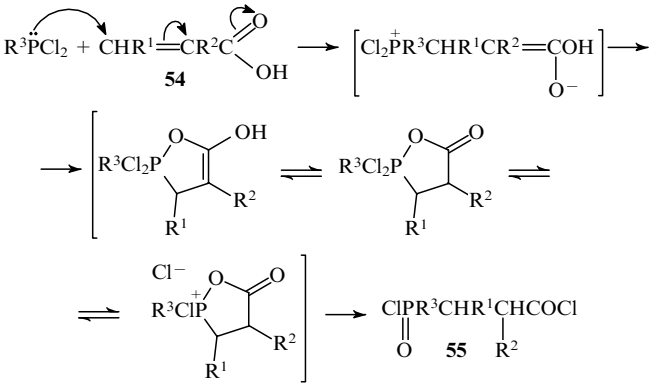
Reactions of HP with acids **54** can follow several pathways. Dihalides most often add to the acids **54** to form β-phosphinicocarboxylic acid dichlorides **55**.[65–77]



R^1, R^2 = H, Me; R^3 = Me, Et, Ph, *p*-MeC_6H_4, 2-thienyl, EtO, $Me_2(CCl_3)CO$, CH_2Cl.

Two different mechanisms of this reaction have been proposed. According to the first of them, HP react with unsaturated acids **54** following the [4+1]-cycloaddition pathway, which most often is considered as stepwise, to give linear phosphoranes, which undergo the intramolecular Arbuzov rearrangement resulting in the final products **55** (Scheme 2).[65, 66, 68, 71, 73, 76]

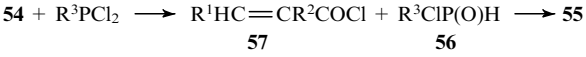
Scheme 2



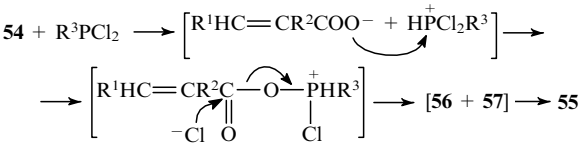
Here the P(III) atom acts as a nucleophile, since the higher the nucleophilicity of the R^3 substituent the more readily the reaction proceeds.[76] However, this is also consistent with an alternative scheme involving no [4+1]-cycloaddition.

According to the alternative scheme,[73, 75–79] (Scheme 3) the chlorine atom in the HP molecule and the hydroxyl group in the molecule of acid **54** exchange in the initial step. Then the hydrophosphoryl compound **56** that formed is added to the unsaturated acid chloride **57** according to the Pudovik reaction.[80, 81]

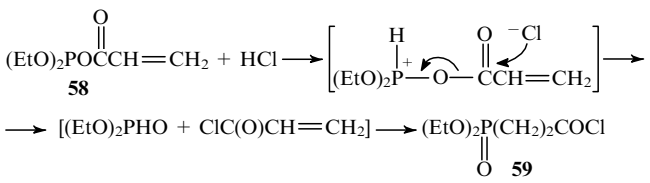
Scheme 3



It is believed [82] that this scheme involves a preliminary stage of P-protonation of HP by the unsaturated acid **54**.

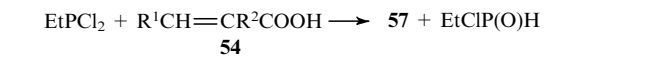


The presence of the hydrophosphoryl compound **56** and unsaturated acid chloride **57** in the reaction mixture is detected by NMR spectroscopy; sometimes it is possible to isolate these compounds. Moreover, compounds **56** and **57** do add to each other to give the final product **55**, which has been proved in a model reaction.[77, 82] Scheme 3 is also consistent with increase in the reaction rate with the increase in the electron-donor ability of the substituents at the phosphorus atom. Finally, which is also proved by kinetic studies,[78] hydrogen chloride, which is always present in the reaction mixture, plays an important role in these reactions. In this connection it is noteworthy that diethyl acryloyl phosphite (**58**) protonated under the action of HCl rearranges into β-diethoxyphosphorylpropionyl chloride (**59**) in good yield. It is most likely that in this case the reaction follows the same sequence of stages as that discussed for the preceding scheme.[82]



Thus, it can be considered as proved that P(III) acid dichlorides react with unsaturated acids **54** according to Scheme 3. However, this does not imply that the [4 + 1]-cycloaddition scheme is wrong and makes no contribution to the reaction under consideration.

The rate of the reaction of the α,β-unsaturated acids **54** with HP decreases if acids **54** contain α- and/or β-substituents.[71, 76, 79] Moreover, only acid chlorides **57** can be isolated as the reaction products of ethyl(dichloro)phosphine with several β-substituted α,β-unsaturated acids.[76, 83, 84]

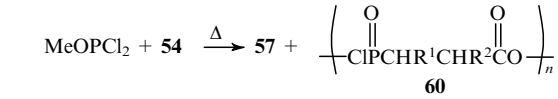


R^1 = Ph, HOOC, *trans*-Cl, 2-furyl; R^2 = H.

This fact is consistent with both reaction schemes proposed. According to Scheme 2, the phosphorus atom attack on the β-carbon atom of the acid **54** is the key reaction step. β-Substituents in the acid molecule produce steric hindrances, which only results in the formation of acid chlorides **57** from the carboxylic acid **54**. In the framework of Scheme 3, the attack on the carboxylic group in all cases is the initial and necessary stage. Obviously, if acid chlorides **57** contain substituents indicated in the scheme, the addition of ethyl(dichloro)phosphine to compounds **57** occurs very slowly due to both spatial shielding of the β-carbon atom and delocalisation of the electron density on the β-substituent and only these compounds can be isolated from the reaction mixtures.[82]

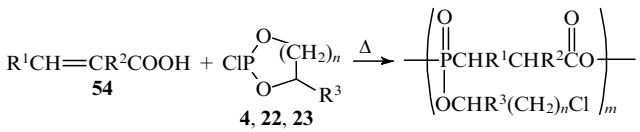
The reaction of dibutyl phosphorochloridite with acrylic acid at a reduced pressure gave only acryoyl chloride.[77]

The acids **54** react with methyl phosphorodichloridite to give unsaturated carboxylic acid chlorides **57** and oligomers **60**.[34]



R^1, R^2 = H, Me.

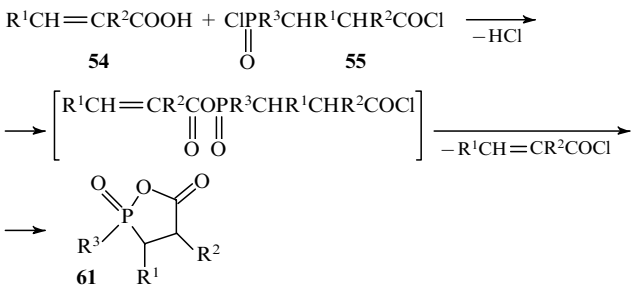
Only oligomeric products were isolated in the reactions of acids **54** with compounds **4**, **22** and **23**.[39, 85]



R^1, R^2, R^3 = H, Me; n = 1, 2.

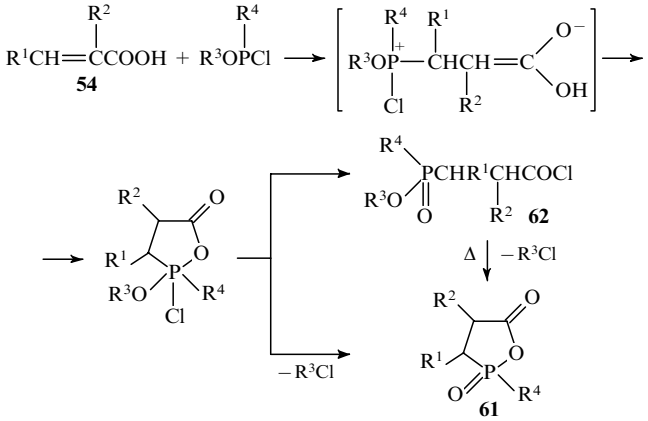
It was assumed [34, 39, 85] that the reactions of the acids **54** and other (hetero)dienes with HP occur according to the [4 + 1]-cycloaddition mechanism and are followed by the Arbuzov rearrangement of the adduct containing a pentacoordinate phosphorus atom with the formation of oligomers. However, it was shown later that no adduct containing a P(V) atom is formed in the reaction of ethyl phosphorodichloridite with acrylic acid without heating the reaction mixture at very high temperatures. Therefore, the formation of oligomeric products in the reactions of HP with α,β-unsaturated acids was explained by thermal conversions of acid dichlorides **55** that were formed.[77] It should be noted that the formation of oligomers together with distillable addition products [65, 68, 79] was also considered as a result of thermolysis of primary reaction products upon distillation.

2,5-Dioxo-1,2-oxaphospholanes **61** are occasionally isolated along with the products **55** in the reactions of P(III) acid dichlorides with acids **54**.[86–89] These originate from mixed anhydrides formed as byproducts from acid dichlorides **55** and acids **54** and are produced on heating during distillation.[71, 86]

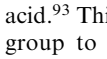


R^1, R^2 = H, Me; R^3 = $ClCH_2$, 2-thienyl, 5-chlorothienyl-2, Et, *p*-MeC_6H_4.

Oxaphospholanes **61** were also obtained in the reactions of phosphorochloridites and phosphonochloridites with the acids **54**. Their formation (as a result of elimination of alkyl chloride from intermediate addition products) competes with the formation of acyclic compounds **62** analogous to acid dichlorides **55**.[75, 79, 82, 90–92] Either or both linear acid chlorides **62** and oxaphospholanes **61** were isolated under different conditions. Since cyclisation of acid chlorides **62** in the course of distillation can also result in the formation of the phospholanes **61**, it is unclear whether the latter are formed as a result of either or both direct reaction of HP with the acids **54** and thermolysis of the products **62**.

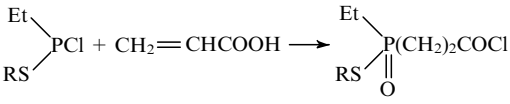


R^1 = H; R^2 = H, Me; R^3 = Et, $Me_2(CCl_3)C$, $(ClCH_2)_2CH$, $ClCH_2CH_2$,



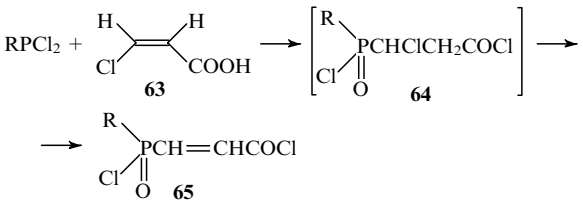
; R^4 = Et, Ph, MeO, PhO, $Me_2(CCl_3)CO$, $MeEt(CCl_3)CO$.

Only linear products analogous to compounds **62** are formed in the reactions of alkyl phosphorochloridothioites with acrylic acid.[93] This is associated with the lesser tendency of the AlkS–P group to undergo dealkylation as compared to the AlkO–P group (see monograph [94]).



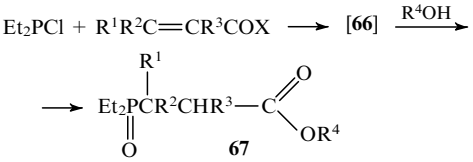
R = Et, Pr^n, Pr^i, Bu^n, Bu^i.

Reaction of dichlorophosphines with *cis*-β-chloroacrylic acid (**63**) occurs with elimination of HCl from intermediate compounds **64** to give unsaturated acid dichlorides **65**.[76]



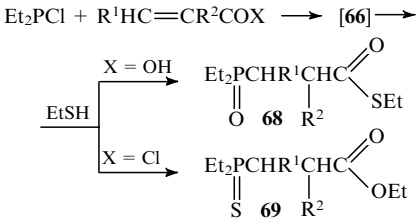
R = Me, Et, Ph.

The products of reactions of dialkyl(chloro)phosphines with α,β-unsaturated acids and their derivatives were not isolated and characterised after treatment with alcohols. For instance, diethyl(chloro)phosphine reacts with α,β-unsaturated acids or their chlorides to form crystalline adducts **66**, the structure of which is not established. Treatment of these adducts with alcohols gave phosphine oxides **67**.[47, 73, 76, 95–97]



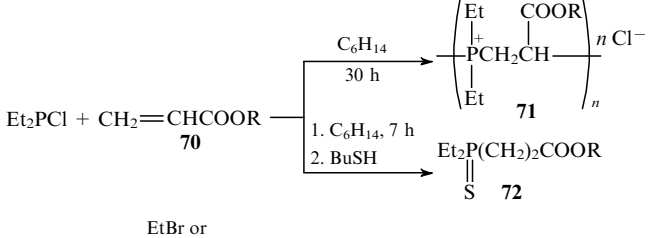
R^1, R^2, R^3 = H, Me; R^4 = Me, Et, Pr, Bu, C_5H_{11}; X = OH, Cl.

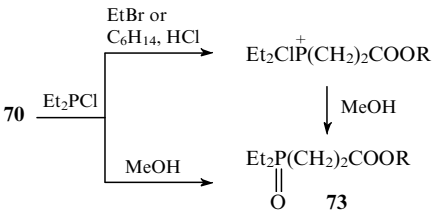
Treatment of the adducts **66** formed from acids (X = OH) and acid chlorides (X = Cl) with ethanethiol instead of alcohols gives phosphine oxides **68** containing a thioester group and phosphine sulfides **69**, respectively.[96]



R^1, R^2 = H, Me; X = OH, Cl.

Reactions of alkyl acrylates **70** with diethyl(chloro)phosphine result in different products depending on the reaction conditions. For instance, polymers or oligomers **71** containing a quaternary phosphonium unit in the main chain are formed quantitatively in a hexane solution after 30 h. However, monomeric phosphine sulfides **72** can be isolated in high yields from the reaction mixtures after 7 h following treatment with butanethiol. The adducts formed in the reaction conducted in ethyl bromide (or in hexane, in the presence of HCl) and then treated with methanol decompose to give phosphine oxides **73**.[98] These contradictory results require additional proof.

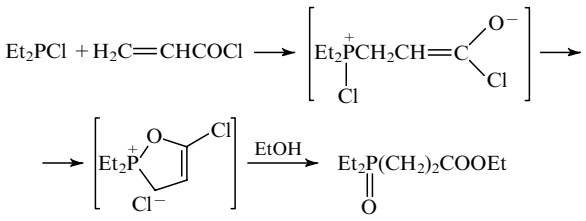




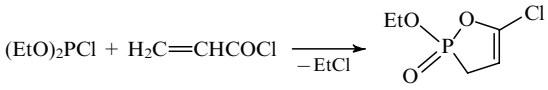
R = Me, Et, Bu.

It is believed that the mechanisms of reactions of unsaturated acids and their derivatives with diethyl(chloro)phosphine are the same or similar to those of their reactions with P(III) acid dichlorides.[47, 73, 76, 95–97] However, it is likely that higher nucleophilicity of the phosphorus atom in diethyl(chloro)phosphine than in P(III) acid dichlorides favours [1 + 4]-cycloaddition. This assumption is confirmed by the fact that methyl acrylate readily reacts with diethyl(chloro)phosphine[98] where the formation of an intermediate hydrophosphoryl compound is impossible.

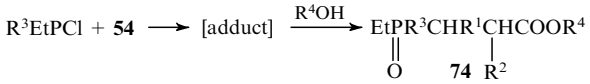
A similar mechanism was proposed[97] for the reaction of diethyl(chloro)phosphine with acryloyl chloride.



It is confirmed by preparative isolation of 5-chloro-2-ethoxy-2-oxo-3*H*-1,2-oxaphosphole from the reaction of diethylphosphorochloridite with acryloyl chloride.[97]

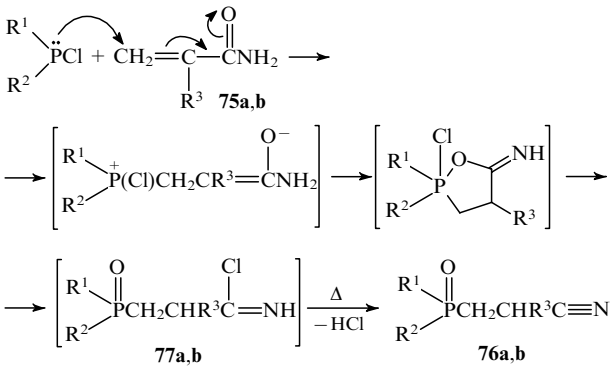


Other monochlorophosphines react with the acids **54** analogously to diethyl(chloro)phosphine. Treatment of initially formed adducts of unknown structure with alcohols results in their decomposition and the formation of phosphine oxides **74**.[99, 100]



R^1 = H, Ph; R^2 = H, Me; R^3 = $(CH_2)_2CN$, $CH_2CH(Me)CN$, $CH_2CH=CH_2$, 2-thienyl; R^4 = Me, Et.

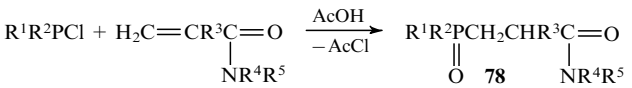
Acrylamide and methacrylamide (compounds **75a** and **75b**, respectively) react with various HP analogously to the corresponding acids. Nitriles **76a**,**b** resulting from dehydrochlorination of imidoyl chlorides **77a**,**b** are the major reaction products.[76, 99, 101–110]



R^1, R^2 = Me, Et, Ph, Bu^i, $(CH_2)_2CN$, $CH_2CH(Me)CN$, $CH_2CH=CH_2$, $OC(CCl_3)Me_2$, OBu, $OCH(CH_2Cl)_2$, *p*-MeC_6H_4, CH_2Cl, Cl, ;

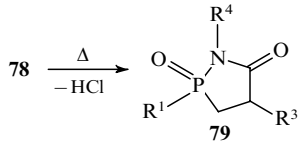
R^3 = H (**a**), Me (**b**).

In the presence of acetic acid, HP react with primary and tertiary acrylamides to form compounds **78** with the amide group remaining intact.[99, 100, 111, 112]



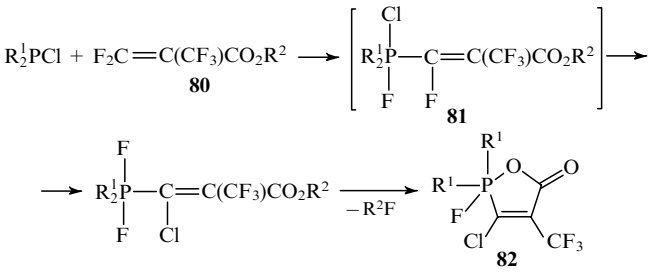
$R^1 = Me, Et, Ph, p\text{-}MeC_6H_4$; $R^2 = Cl, Et, 2\text{-thienyl}, EtOOC(CH_2)_2, Me_2(CCl_3)CO$; $R^3 = H, Me$; $R^4, R^5 = H, Et, Pr^i$.

In some instances, distillation of products **78** is accompanied by elimination of hydrogen chloride (probably, due to thermolysis) and the formation of 2,5-dioxo-1,2-azaphospholanes **79**.[112]



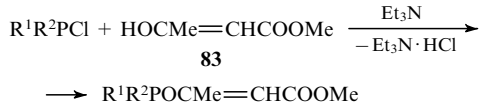
$R^1 = Et, Ph$; $R^2 = Cl$; $R^3 = H, Me$; $R^4 = H, Bu, CH_2=CHCH_2$; $R^5 = H$.

Halophosphines react with several other functional derivatives of acids in a somewhat different pathway. Reactions of dialkyl(chloro)phosphines with alkyl perfluoromethacrylates **80** occur with a characteristic replacement of a fluorine atom at the C=C bond to form an intermediate **81**. Then, the chlorine atom and a fluorine atom in compound **81** are exchanged. The reaction results in the formation of phosphines, which usually undergo cyclisation into 5-oxo-5*H*-1,2-oxaphospholes **82** in the isolation.[113]

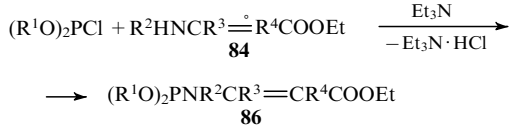


$R^1 = Et$, $R^2 = Me$; $R^1 = Pr^i$, $R^2 = Et$.

β-Hydroxy derivatives **83**[52] and β-amino derivatives[51,60,114] of esters of α,β-unsaturated carboxylic acids **84** (enol tautomers of acetoacetic esters and β-aminocrotonates, respectively) react with P(III) monochlorides in the presence of triethylamine to undergo O- or N-phosphorylation without affecting the double bonds. The reaction occurs due to the presence of an acidic proton of the hydroxyl or amino group in the heterodiene and results in unsaturated phosphites **85** and **86**, respectively.

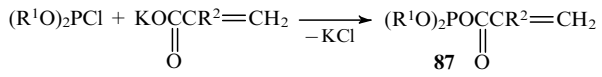


$R^1, R^2 = EtO, Et_2N$.



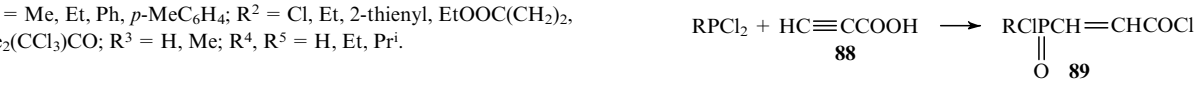
$R^1 = Et, Pr$; $R^2, R^3 = H, Me$; $R^4 = H, CN$.

Acrylates and methacrylates react with dialkyl phosphorochloridites in a similar way, *i.e.*, without affecting the heterodiene system. The reactions result in mixed anhydrides **87**, which are the products of O-phosphorylation.[115]



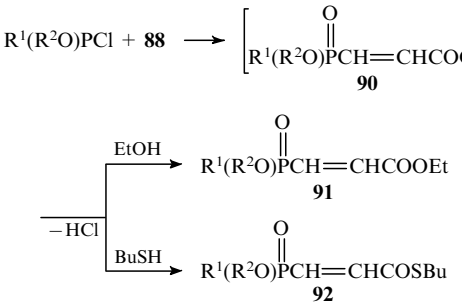
$R^1 = Et, Pr, Bu$; $R^2 = H, Me$.

α,β-Acetylenic acids also react with HP analogously to α,β-unsaturated acids. For instance, propiolic acid (**88**)[70,76,116–118] reacts with dichlorophosphines to form unsaturated acid dichlorides **89** similar to the acid dichlorides **55**.

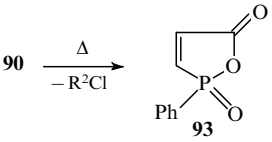


$R = Et, ClCH_2, Ph$.

When alkylphosphonochloridites were used in this reaction instead of dichlorophosphines, the products **90** were not isolated but rather were directly converted into diesters **91** by treatment with ethanol or into thioesters **92** by treatment with butanethiol. An attempt at distilling compound **90** [$R^1 = Ph$, $R^2 = Me_2(CCl_3)C$] resulted in isolation of a product of its cyclisation, *viz.*, 2,5-dioxo-5*H*-1,2-oxaphosphole **93**, which is an unsaturated analogue of phospholane **61**.[119]

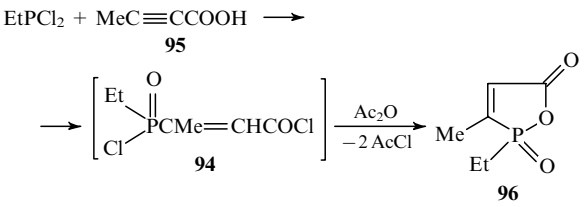


$R^1 = Et, Ph, p\text{-}MeC_6H_4$; $R^2 = Me_2(CCl_3)C$, .



$R^1 = Ph$, $R^2 = Me_2(CCl_3)C$.

Treatment of an intermediate product **94**, obtained in the reaction of tetrolic acid (**95**) with ethyl(dichloro)phosphine, with acetic anhydride resulted in the 5*H*-1,2-oxaphosphole **96**.[120]



III. Reactions with azadienes

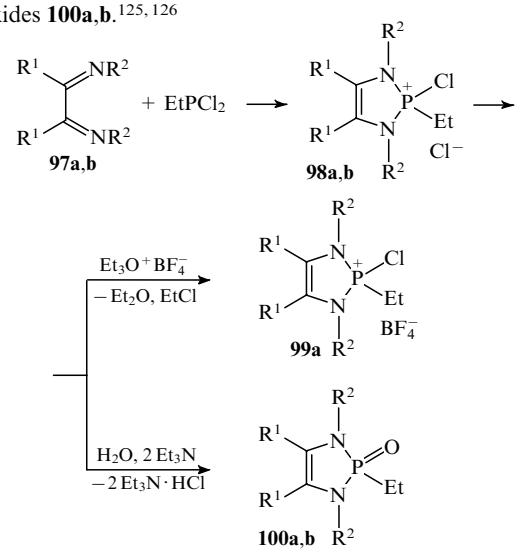
Investigation of reactions of HP with dienes containing one or several nitrogen atoms in the conjugation chain was begun recently. Most studies in this field were carried out in the late 1980's and the early 1990's. Currently, it is azadienes (among different types of heterodienes that react with HP) that attract the greatest attention of researchers. However, whereas the reactions of azadienes with dienophiles containing no phosphorus atom have long been studied and are well known (see, *e.g.*, a review [121]), almost no overview information concerning their reactions with phosphorus-containing dienophiles is available.

1. Reactions with α-diimines

Characteristic of α-diimines capable of adopting *s-cis*-conformation [122] are [4 + 1]-cycloaddition reactions.[121,123]

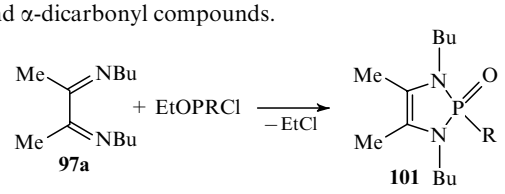
Diimines **97a**,**b** react with ethyl(dichloro)phosphine to form cyclic diaminophosphonium salts **98a**,**b**. It is convenient to isolate

them as the corresponding tetrafluoroborates **99a**[124] or phosphine oxides **100a**,**b**.[125, 126]



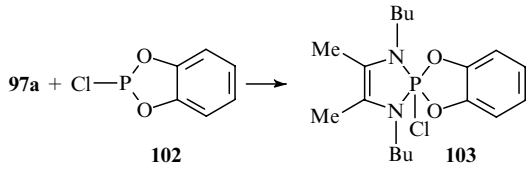
R^1 = Me, R^2 = Bu (**a**); $R^1 - R^1 = (CH_2)_4$ (**b**).

Reactions of HP with *N*,*N*′-dibutylbiacetyldiimine **97a** occur to give 1,3-dihydro-1,3,2-diazaphospholes **101**.[127] The reaction occurs with dealkylation, as in the case of dienic hydrocarbons and α-dicarbonyl compounds.

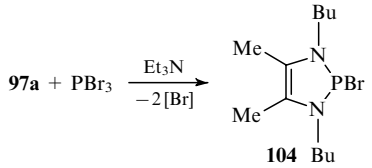


R = Cl, EtO, Et_2N.

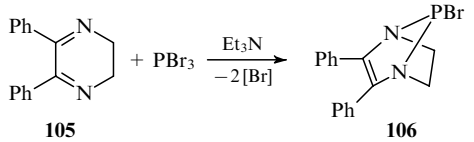
Reaction of 2-chlorobenzo-1,3,2-dioxaphosphole **102** with the diimine **97a** resulted in the phosphorane **103**.[128] An analogous product was obtained in the reactions of compound **102** with 1,3-dienes.



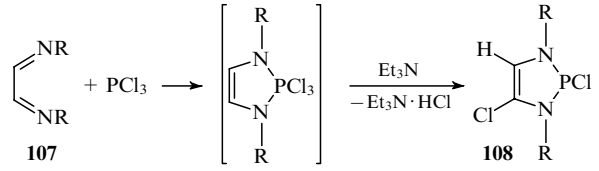
The reaction of the diimine **97a** with phosphorus trichloride results in resinification only.[128] However, its reaction with phosphorus tribromide in the presence of an organic base follows the [4 + 1]-cycloaddition pathway, and the reaction product is a tricoordinate phosphorus derivative, *viz*., 2-bromo-1,3-dihydro-1,3,2-diazaphosphole **104**.[128]



2,3-Diphenyl-5,6-dihydropyrazine (**105**) reacts with PBr_3 in an analogous manner to give a bridged product **106**.[129]



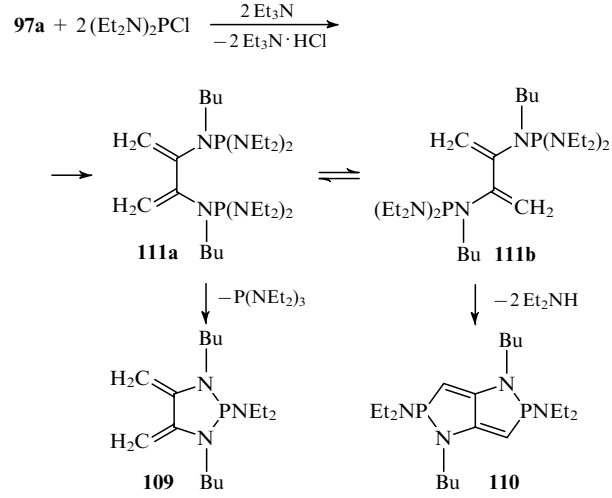
Reactions of glyoxal diimines **107** with PCl_3 in the presence of a base also follow the [4 + 1]-cycloaddition pathway to form tricoordinate phosphorus derivatives, *viz*., 2,4-dichloro-1,3-dihydro-1,3,2-diazaphospholes **108** as the reactions products. Their formation can be rationalised by elimination of HCl from an intermediate cyclic adduct.[128, 130, 131]



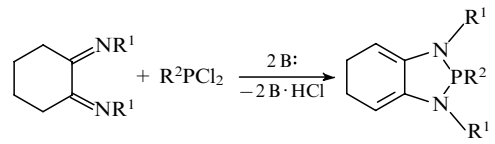
R = cyclo-C_6H_{11}, Bu^t.

Diimine **97a** reacts with tetraethylphosphorodiamidochloridite in the presence of triethylamine [132] to give a mixture of two 1,3-dienes, *viz*., 1,3,2-diazaphospholane **109** with an exocyclic system of conjugated double bonds and bicyclic compound **110**.

It was assumed[132] that N-phosphorylation of both imino groups followed by dehydrochlorination results in an intermediate diene **111** as a mixture of *s-cis*- (**111a**) and *s-trans*-conformers (**111b**) (analogously to the formation of phosphorylated enamines from imines of saturated aldehydes [128, 133]). Then, the reactions of *cis*- and *trans*-forms of compound **111** follow different pathways. Elimination of tris(diethylamino)phosphine from the *s-cis*-form **111a** results in monocyclic diazaphospholane **109**. *s-trans*-Isomer **111b** is converted into diazadiphosphabicyclooctadiene **110** as a result of elimination of two molecules of diethylamine. The bicyclic compound **110** was isolated in an individual form, while the formation of phospholane **109** was proved by spectroscopic methods.[132]

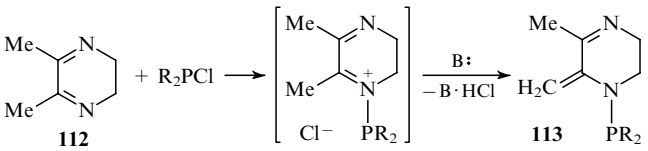


Reactions of PCl_3 and phosphorodichloridites with diimines containing an exocyclic system of double bonds in the presence of a base result in bicyclic 1,3,2-diazaphospholane derivatives containing a cyclohexadiene fragment. These reaction products are bicyclic analogues of the phospholanes **109**.[126]



R^2 = Cl, AlkO, Alk_2N.

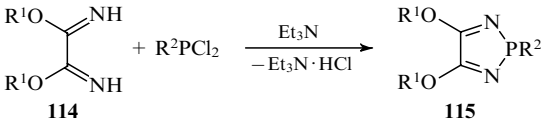
Reaction of 2,3-dimethyl-5,6-dihydropyrazine (**112**, a cyclic analogue of diimine **97**) with dialkyl(chloro)phosphines (alkyls were not specified) in the presence of a base occurs with the formation of monophosphorylated tetrahydropyrazine **113** containing one exocyclic methylene group,[129] which means that the reaction proceeded only on one C = N bond.



112 **113**

R = Alk.

Reactions of dialkyloxalimidates **114** with dichlorophosphines and phosphorodichloridites occur with elimination of two mobile protons to form derivatives of 1,3,2-diazaphospholes **115**,[134] *i.e.*, compounds **114** undergo cyclisation without participation of the heterodiene system as such.

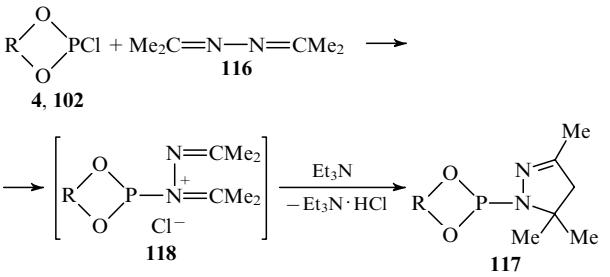


114 **115**

R^1 = Me, Et; R^2 = Bu, Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, PhO, *p*-MeC_6H_4O, *p*-ClC_6H_4O.

2. Reactions with azines

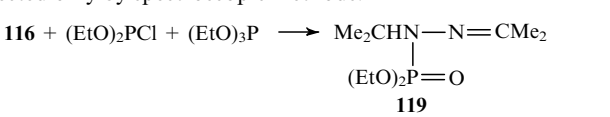
It was argued [39,135] that the reactions of cyclic phosphorochloridites with azines and with other conjugated systems proceed as [4 + 1]-cycloadditions; the 1,3,2-dioxaphospholane that forms undergoes ring opening according to the second stage of the Arbuzov reaction to give 3,5-dihydro-1,2,4-diazaphospholes. However, it was established later that dioxaphospholanes **4** and benzodioxaphospholes **102** react with acetonazine (**116**) in the presence of triethylamine to form 3,5,5-trimethyl-4,5-dihydropyrazolophosphites **117**. Initially, electrophilic attack of the phosphorus atom on the nitrogen atom of ketazine **116** occurs, as in reactions of HP with imines.[128,133] The immonium salt **118** that forms undergoes the pyrazoline condensation to give the final product **117**.[136]



4, **102** **116** **118** **117**

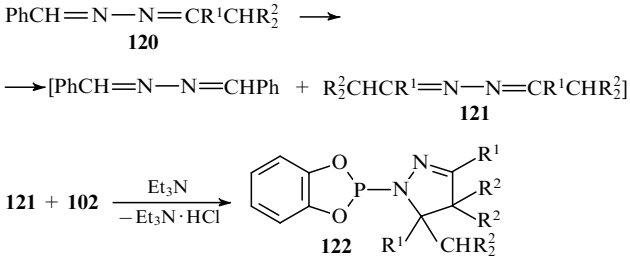
R = $(CH_2)_2$ (**4**), *o*-C_6H_4 (**102**).

Reaction of diethyl phosphorochloridiite with acetonazine **116** in the presence of triethyl phosphite only resulted in compound **119**, the product of addition of diethyl phosphite to one of the C = N bonds. The formation of pyrazolinophosphite **117** was detected only by spectroscopic methods.[137]



119

Reactions of asymmetrical azines **120** with the phosphite **102** occur with symmetrisation of the azine in the initial step.[138] This process is accelerated by diethyl phosphorochloridite (a Lewis acid) present in the reaction mixture. The symmetrical azine **121** that forms then reacts with phosphite **102** analogously to acetonazine **116** to form pyrazolinophosphites **122**.[137]



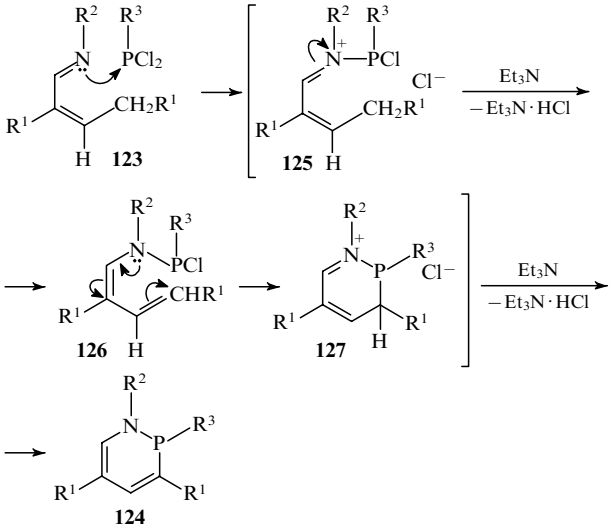
120 **121** **122**

R^1, R^2 = H, Me.

3. Reactions with α-enimines

It was postulated [135] that α-enimines, as well as other 1,3-dienes and heterodienes, react with 1,3,2-dioxaphospholanes according to the [4 + 1]-cycloaddition pathway. However, the absence of any specific information on the products of these reactions makes one treat such an argument with precaution.

Reactions of enimines **123** with phosphorus trichloride or ethyl(dichloro)phosphine in the presence of an organic base [139–141] result in 1,2-dihydro-1,2-azaphosphorinines **124**.



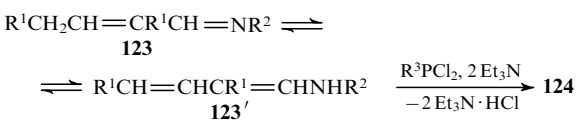
123 **125** **126** **127** **124**

R^1 = Et, R^2 = Bu^n, R^3 = Cl, Et; R^1 = H, R^2 = Bu^t, R^3 = Cl.

The reaction begins with electrophilic attack of the phosphorus trichloride or ethyl(dichloro)phosphine on the lone electron pair of the nitrogen atom of enimine **123**, which results in an immonium salt **125** containing a P – N bond and a positive charge delocalised over the system of conjugated bonds. Then the first triethylamine molecule eliminates an acidic proton from the δ-carbon atom of the salt **125** to give an intermediate adduct **126**. This reaction is analogous to that leading to phosphorylated enamines from imines of saturated aldehydes and is similar to reactions resulting in the formation of heterodienes **111** and **118**.[128,133] Then, the closure of the six-membered ring containing the P – C bond occurs to form the intermediate **127** as a result of the intramolecular interaction of the phosphorus atom with the δ-carbon atom on which partial negative charge is localised due to conjugation with the lone electron pair of the nitrogen atom. The second molecule of the base eliminates hydrogen chloride from the intermediate **127**, which results in 1,2-dihydro-1,2-azaphosphorinine **124** as the final product.

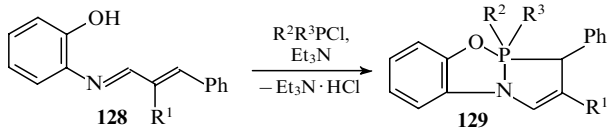
It was assumed [141] that in this case the [4 + 1]-cycloaddition reaction cannot compete with the attack on the nitrogen atom due to kinetic control because of asymmetry of the enimine molecule. In addition, the nitrogen atom in α-enimines is more nucleophilic than that in α-diimines, since two electronegative azomethine groups in the latter interact with each other to weaken the nucleophilicity of the nitrogen atom in each of them.

Butadienylamine **123′**, the possible existence of which has been discussed,[121] is the minor tautomer of the enimine **123** and can also contribute to the formation of azaphosphorinine **124**.



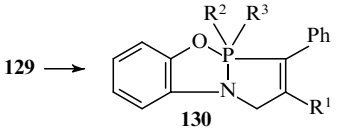
The similarity of behaviour of the enimines **123** and their oxygen analogue, crotonaldehyde, in reactions with HP in the presence of an organic base is obvious. These asymmetrical heterodienes can be represented by a general formula $RCH_2CH=CRCH=Y$ (Y = O, NAlk). In contrast to their symmetrical analogues, α-diimines and α-diketones, the above-mentioned heterodienes undergo phosphorylation at the nucleophilic centre Y rather than enter into [4 + 1]-cycloaddition reactions leading to the increase in the coordination number of the phosphorus atom.

However, reactions of functionalised enimines, *e.g.*, cinnamaldehyde *o*-hydroxyanils **128**, with P(III) chlorides proceed by [4 + 1]-cycloaddition, which precedes O-phosphorylation of the hydroxyl group or follows it. This reaction results in fused five-membered heterocyclic compounds **129** containing the pentacoordinate phosphorus atom.[142]



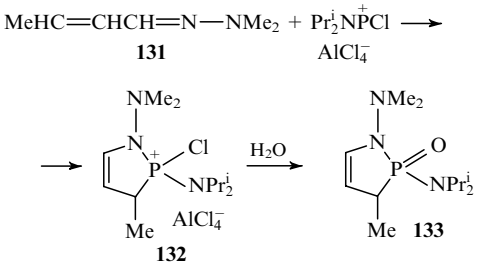
R^1 = Me: R^2-R^3 = $MeN(CH_2)_2NMe$; R^1 = H, Me; R^2 = R^3 = Me, Ph, OMe; R^2-R^3 = $O(CH_2)_2O$, *o*-$C_6H_4O_2$.

As in the case of reactions of dienes with HP,[4–7] tricyclophosphoranes **129** can have structural isomers as a result of the double bond migration in azaphosphole (prototropism), and geometric isomers due to pseudorotation.[143] For instance, if amino groups are bonded to the phosphorus atom, the primary reaction product **129** undergoes partial [for R^2-R^3 = $MeN(CH_2)_2NMe$] or complete (for R^2 = R^3 = NMe_2) rearrangement into a thermodynamically more stable isomer **130**. The latter is isolated as the final reaction product of compounds **128** with bis(dimethylamino)-chlorophosphine.

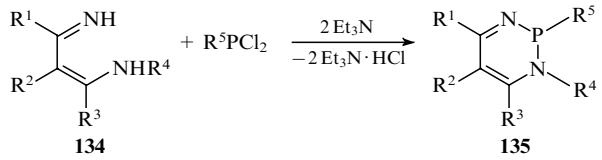


R^1 = Me: R^2-R^3 = $MeN(CH_2)_2NMe$, R^2 = R^3 = NMe_2.

Reaction of diisopropylamino(chloro)phosphenium tetrachloroaluminate with crotonaldehyde dimethylhydrazone (**131**)[144] proceeds as a classical [4 + 1]-cycloaddition and is analogous to reactions with 1,3-dienes[28–30] and α-dicarbonyl compounds;[27] this results in cyclic phosphonium salt **132**, which is hydrolysed to give 2-oxo-1,2-dihydro-3*H*-1,2-azaphosphole **133**.



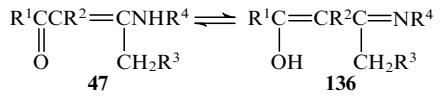
Aminoenimines **134** react with P(III) chlorides in the presence of triethylamine. Their cyclisation occurring with elimination of two HCl molecules results in 1,2-dihydro-1,3,2-diazaphosphorinines **135**,[145] like the reaction of dialkyloxalimidates with dichlorophosphines leading to derivatives of 1,3,2-diazaphospholes (see Section III.3).



R^1 = H, Me; R^2, R^4 = Ph, *p*-MeC_6H_4, cyclo-C_6H_{11}; R^3 = H, Ph; R^5 = Ph, Cl.

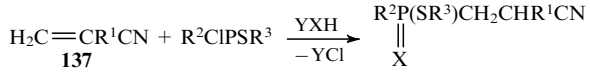
This is an example of synthetic procedures used for the preparation of nitrogen heterocycles based on azadienes, which has been discussed in detail.[146–148]

Reactions of HP with enamino ketones **47**, which are nitrogen analogues of β-diketones, were considered in Section II.2.a; however, these can also be discussed in this Section. Indeed, compounds **47** can also exist in the imine form **136**.[149]



Tautomers **47** and **136** can react with HP concurrently to give the same final products.

Finally, reactions of HP with heteroenyne C=C–C≡N systems are formally similar to the reactions of HP with enimine C=C–C=N systems considered in this Section. Acrylo- and methacrylonitriles **137** react with alkylphosphonochloridothioites in the presence of proton donors according to the scheme:[46]

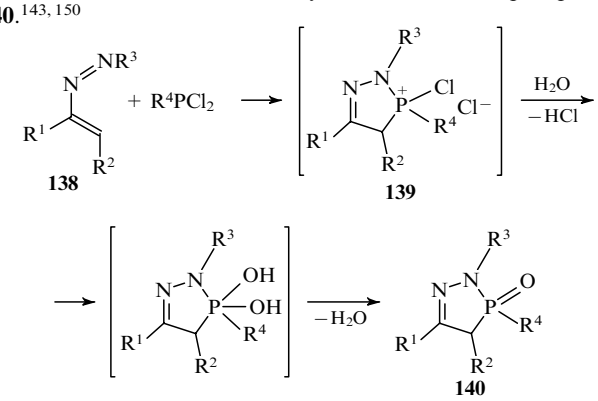


R^1 = H, Me; R^2 = Et, Ph; R^3 = Et, Pr, Bu; X = O, S; Y = H, Ac.

These reactions are analogous to those of compounds **30** with α,β-unsaturated ketones in the presence of proton donors and follow the same mechanism (see Section II.2.a).

4. Reactions with azoalkenes

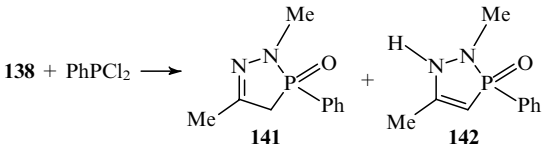
Dichlorophosphines react with azoalkenes **138** to give [1 + 4]-cycloaddition products, *viz.*, cyclic phosphonium salts **139**. Hydrolysis of compounds **139** results in a mixture of stereoisomers, *viz.*, 3-oxo-2,3-dihydro-4*H*-1,2,3-diazaphospholes **140**.[143,150]



R^1 = Me, Ph, Bn; R^2 = H, Me, Ph; R^3 = Me, Ph; R^4 = Me, Ph, Bu^t, Bn, *o*-ClC_6H_4, *p*-MeC_6H_4, *p*-$MeOC_6H_4$.

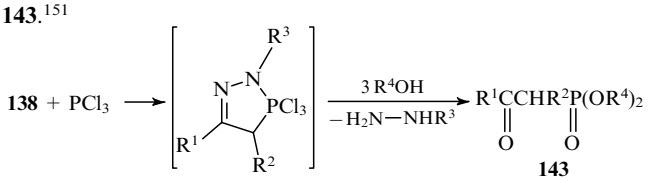
Reaction of the azoalkene **138** (R^1 = R^3 = Me, R^2 = H) with $PhPCl_2$ results in a mixture of products with different position of

the double bond, *viz*., 2,3-dihydro-4*H*- and 1*H*-1,2,3-diazaphospholes (**141** and **142**), as is observed for isomerisation of phosphoranes **129** into phosphoranes **130**.



An analogous double bond migration in the ring is also often observed for phospholes formed in reactions of HP with dienic hydrocarbons.[5,6]

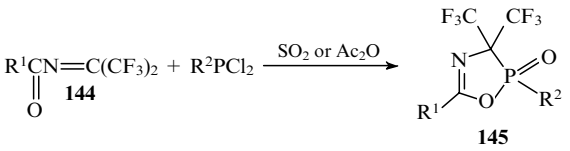
The azoalkenes **138** react with PCl_3 to give diazaphosphole intermediates; treatment of the latter with alcohols causes elimination of a hydrazine fragment to form β-oxo phosphonates **143**.[151]



$R^1 = R^2 = R^3$ = Me, Ph; R^4 = Me, Et, Ph; $R^1 - R^2 = (CH_2)_4$; $R^3 = R^4$ = Me.

IV. Reactions with oxazadienes

Reactions of HP with 1,3-oxaza-1,3-dienes (*N*-acylketimines) **144** follow the [4 + 1]-cycloaddition pathway to give 5-oxo-4,5-dihydro-1,3,5-oxazaphospholes **145**.[152]

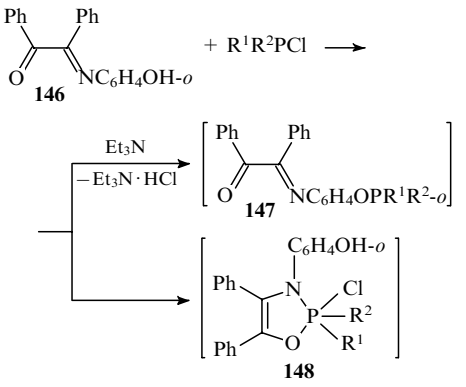


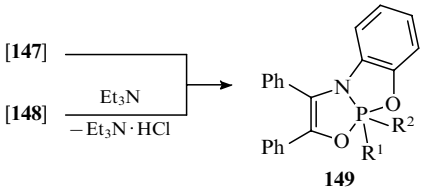
$R^1 = CF_3$, OEt; R^2 = Me, OEt.

The reaction proceeds only in the presence of acetic anhydride or sulfur dioxide. Trialkyl phosphites[153] react according to the same scheme without these additives.

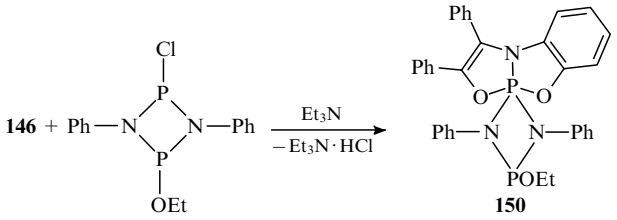
Halophosphines can be added to 1,4-oxaza-1,3-dienes (monoimines of α-diketones) as has been exemplified in benzyl *o*-hydroxyanil (**146**).[154,155] The latter reacts with different HP with the formation of intermediate compounds **147** and **148**, which are then transformed into polycyclic phosphoranes **149** or diphosphethanes **150** and **151**.

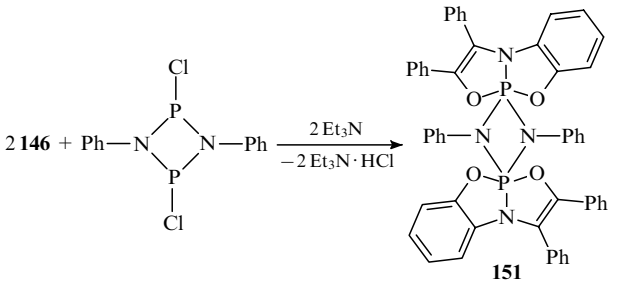
The key stage of this reaction is [4 + 1]-cycloaddition, which precedes phosphorylation of the hydroxyl group and/or follows it.



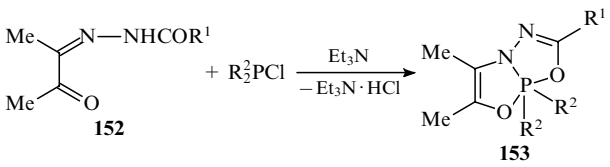


R^1, R^2 = Me, Ph, OMe, OPh, OCH_2Ph, NMe_2; $R^1 - R^2 = O(CH_2)_2O$, $O(CH_2)_3O$, $S(CH_2)_3S$, *o*-$C_6H_4O_2$, $MeN(CH_2)_2NMe$.





Biacetyl acylmonohydrazones **152** react analogously. As in the case of oxazadiene **146**, the final bicyclic dioxadiazaphosphoranes **153** result from [4 + 1]-cycloaddition and O-phosphorylation.[154]



R^1 = Me, Ph, Bn; R^2 = Me, Ph.

V. Conclusion

Though certain judgements on the mechanisms of the reactions considered in this review cannot be called indisputable, summing up the above information makes is possible to state that, despite the variety of types of HP, heterodienes, and the products that formed, the initial steps of these reactions belong to three types:

(1) 1,4-addition reaction, in particular, [4 + 1]-cycloaddition reaction (concerted or stepwise);

(2) reaction involving one of the multiple bonds of a heterodiene; and

(3) reaction without particiption of multiple bonds.

Differences in the structure of the final products formed in each of these three types of reactions are determined by further transformations of the primary reaction products.

Most often the reactions under consideration follow the [4 + 1]-cycloaddition pathway to give usually cycloadducts containing the pentacoordinate phosphorus atom. In some instances, it is possible to isolate them or to detect them by spectroscopic methods. However, [4 + 1]-cycloaddition reactions of HP with α-diketones, their diimines and mono-*o*-hydroxyanils, α,β-unsaturated ketones, azoalkenes and 1,2-oxazadienes result in various five-membered phosphole-type heterocycles containing P(III), P(IV) or P(V) atoms as the final products. α,β-Unsaturated carboxylic acids and their derivatives also react with HP according

to this scheme (not always) to give acyclic compounds. In some instances, linear products are also formed from unsaturated carbonyl compounds.

If only one of two double bonds of the heterodiene system is involved in the reaction with HP in the initial stage, the second double bond can be either involved in further transformations or left intact. This occurs in the reactions of HP with different types of heterodienes in the presence of organic bases, *e.g.*, in the reactions with crotonaldehyde and enimines, which are nitrogen analogues of α,β-unsaturated aldehydes. Unlike their symmetrical analogues (α-diketones, α-diimines), enimines do not enter into [4 + 1]-cycloaddition reactions, which result in an increase in the coordination number of the phosphorus atom, since HP react with their nucleophilic centre (the oxygen or nitrogen atom) thus phosphorylating it. Reactions of several cyclic α-diimines (dihydropyrazines) and azines proceed analogously involving one C=N bond. The same occurs in the reaction of tetraethylphosphorodiamidochloridite with acyclic α-diimine: each of the C=N bonds reacts independently. Usually, the alkyl group adjacent to the double bond is inert and left intact in the first reaction stage; the involvement of such a group in the reaction is one of the peculiarities of the reactions of HP wuth heterodienes in the presence of an organic base. Under the action of a base, proton abstraction from these groups occurs, which results in the formation of a new double bond and/or in the closure of phosphorus-containing rings. Reactions involving one of the double bonds can also occur in the absence of a base and, correspondingly, without dehydrohalogenation. For instance, unsaturated aldehydes react with 2-chloro-1,3,2-dioxaphospholane at the C=O bond, which results in the formation of phosphorus-containing oligomers. Perfluoromethacrylates react with dichlorophosphines only at the C=C bond leaving the ester group intact. It is possible to consider the reactions of α,β-unsaturated acids with HP as those occurring at the C=C bond if they proceed *via* exchange of the chlorine atom by the hydroxyl of the carboxy group followed by reaction between hydrophosphoryl compound and unsaturated acid chloride that formed according to the Pudovik reaction. Alkylphosphonochloridothioites react analogously with α,β-unsaturated ketones in the presence of proton donors.

Finally, reactions of several heterodienes (capable of eliminating one or two protons in the presence of an organic base) and salts of α,β-unsaturated carboxylic acids with HP proceed without participation of conjugated bonds at all. These reactions result in the formation of phosphorylation products. In these cases, HP behave as ordinary acid halides. If the phosphorus atom carries appropriate substituents, the phosphorylated heterodiene that formed can enter into further intramolecular reactions. These involve the diene system and result in its cyclisation. Acyclic P(III) derivatives initially obtained from HP and enol tautomers of β-diketones or their nitrogen analogues react in such a manner.

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