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Methods of Preparation and Properties of Compounds with Unsaturated Groups at the Phosphorus Atom

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The review deals with problems connected with the synthesis, chemical properties, and applications of organophosphorus compounds with unsaturated groups at the heteroatom. A systematic account is given of the methods of preparation of these substances and the characteristic features and limits of applicability of the synthetic methods, in accordance with the wide variety of structures of the products considered, are noted. The section dealing with the properties of the compounds describes the addition reactions of nucleophilic agents, reactions with substances with a tendency towards homolysis, certain rearrangements, condensations, and other processes. The practical value of compounds with unsaturated groups at the phosphorus atom is noted. The bibliography comprises 344 references.

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I. INTRODUCTION

The chemistry of organophosphorus compounds has developed considerably in recent years. A large number of substances of practical value have been synthesised and compounds with unsaturated groups at the phosphorus atom are of definite interest in view of the wide variety of their chemical properties. Non-combustible and self-extinguishing polymers, effective preparations with a wide variety of physiological activity, etc. have already been obtained on their basis.

At the present time there are no publications dealing with the main features of such investigations and the present review is an attempt to fill this gap. It deals with two topics, the methods of preparation of alkenylphosphorus compounds and their reactivity, the literature data published up to the middle of 1966 being discussed.

II. PREPARATION OF COMPOUNDS WITH UNSATURATED GROUPS AT THE PHOSPHORUS ATOM

Compounds of this type were synthesised about 50 years ago in the study of the reaction of phosphorus pentachloride with olefins, but the principal methods of their preparation have been developed only in the last 20 years.

1. Interaction of Halogeno-derivatives of Phosphorus with Metal Alkyls

This method of synthesis was quite recently developed and is used mainly for the preparation of phosphorus(III) compounds. In 1959 Kaesz and Stone [1] carried out the vinylation of phosphorus trichloride with divinylmercury [1]:

$$(CH_2{=}CH)_2Hg + PCl_3 \rightarrow CH_2{=}CHPCl_2 + CH_2{=}CHHgCl.$$

The yield of vinyldichlorophosphine was 50%; the compound proved to be very sensitive to air and moisture. Sterlin et al. [2] carried out a similar reaction with perfluorovinyl derivatives:

$$CF_2{=}CFMgX + PCl_3 \rightarrow (CF_2{=}CF)_3P.$$

Related methods have been proposed in Foster's [3,4] and Feder's [5] patents. In 1960 Leavitt and coworkers synthesised cyclic phosphorus compounds from dilithium derivatives and phenyldichlorophosphine [6,7]. Next one may refer to the work of Rabinowitz [8], Maier [9], and Zeiss [10] on further improvement of the method and the investigation of the properties of these compounds.

Kabachnik and Chang Jung-Yü [11,12] and Razumov [13] extended these reactions to dialkyl- and dialkoxy-chlorophosphines.

Double decomposition reactions of alkyl(aryl)magnesium halides with unsaturated phosphines are also possible [14]:

$$C_6H_5CH{=}CHPCl_2 + 2\ RMgHal \rightarrow C_6H_5CH{=}CHPR_2\ .$$

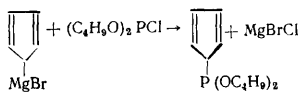
Similar reactions can be performed with metallic derivatives of acetylenes. For example, Chodkiewicz and coworkers studied the following reactions of alkynylmagnesium halides [15,16]:

$$RC{\equiv}CMgX^+ \left| \begin{array}{l} PCl_3 \rightarrow (RC{\equiv}C)_3P, \\ POCl_3 \rightarrow (RC{\equiv}C)_3P{=}O, \\ (C_6H_5)_2PCl \rightarrow (C_6H_5)_2PC{\equiv}CR\ . \end{array} \right.$$

Kabachnik and coworkers carried out similar reactions with dialkyl phosphorochloridites [17] and Maretina and Petrov with dialkylchlorophosphines [18]. The yield of alkyl derivatives was 50–70% [19–23]. Hartmann and coworkers [24,25] and Maler [26] carried out the interesting synthesis of acetylenic diphosphines:

$$2\ (C_6H_5)_2PCl + BrMgC{\equiv}CMgBr \xrightarrow{ether} (C_6H_5)_2PC{\equiv}CP(C_6H_5)_2 + MgCl_2 + MgBr_2\ .$$

Kabachnik and Tsvetkov established that the method can be used for the synthesis of phosphorus compounds with cyclic unsaturated groups, for example, derivatives of cyclopentadiene, indene, and fluorene [27–29]:



Instead of phosphorochloridites, in some cases the alkoxyderivatives can react with organomagnesium compounds [30]:

$$RR'POR'' + CH_2{=}CHMgX \rightarrow RR'PCH{=}CH_2 + MgX(OR)\ .$$

2. Interaction of Metal Derivatives of Phosphorus with Alkyl Halides

The second method of preparation of unsaturated phosphorus compounds is based on the reaction

$$MP^{III(V)} + R{-}Hal \rightarrow MHal + R{-}P^{III(V)}\ ,$$

where M is an alkali metal and Hal a halogen atom. The reactions of metal derivatives of phosphines with halogenoalkenes take place in an inert medium over a wide range of temperatures [31–33]:

$$C_6H_5PHNa + Br(CR')_nC{=}CH_2 \rightarrow C_6H_5PH(CR')_nCR{=}CH_2 + NaBr$$

An interesting process is dealkylation with a secondary phosphide ion, which leads to alkenylphosphines [34]:

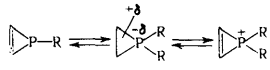
$$(C_6H_5)_2PH + C_4H_9Li \rightarrow (C_6H_5)_2P{-}Li + C_4H_{10}\ ,$$

$$C_6H_5OCH_2CH{=}CH_2 \xrightarrow{(C_6H_5)_2PLi} C_6H_5OLi + (C_6H_5)_2PCH_2CH{=}CH_2\ .$$

Lithium phosphides react with acetylenes [35,36] to form addition products:

$$R_2PLi + CH{\equiv}C{-}CH{=}CH_2 \rightarrow \left\{ \begin{array}{l} CH{\equiv}C{-}CH_2{-}CH_2{-}PR_2, \\ CH_2{=}C{=}CH{-}CH_2{-}PR_2, \\ CH_2{=}CH{-}CH{=}CH{-}PR_2\ . \end{array} \right.$$

Some investigators have discussed the possibility of the existence of three-membered structures with phosphorus as a heteroatom [37,38]:



and also other intermediate alkenyl derivatives of phosphorus [39]. The Michaelis–Bekker reaction is a variant of the above method preparation of organophosphorus compounds with unsaturated groups at the phosphorus atom. Alkenylphosphonates are formed in the reaction of alkenyl halides with alkali metal salts of dialkyl phosphorous aicds [40,41]:

$$R'CH{=}CHCH_2Cl + NaOP(OR)_2 \rightarrow R'CH{=}CHCH_2\overset{\overset{O}{\|}}{P}(OR)_2 + NaCl\ .$$

The Michaelis–Bekker method permits the synthesis of the same substances as the Arbuzov rearrangement, although it is not quite so universal because of the occurrence in many cases of side reactions, for example, the allyl rearrangement [42,43]. The yield of alkenylphosphonate esters in the Michaelis–Bekker reaction is usually lower than in the Arbuzov reaction. Nevertheless a wide variety of alkenylphosphonates have been obtained by this method: allyl- [44], butenyl- [45], butoxypentenyl- [43], cycloalkenyl- [46–48], and others [49–53]. The sodium salt of diethylphosphorothious acid can be used in this reaction instead of sodium diethyl phosphite [43,44]:

$$CH_2{=}CHCH_2Br + (RO_2)P{-}SNa \rightarrow CH_2{=}CHCH_2\overset{\overset{S}{\|}}{P}(OR)_2\ .$$

Diphosphono-derivatives, which are products of the subsequent condensation of dialkyl phosphites with the alkenylphosphonates formed, are almost absent in this case [54,55].

3. The Arbuzov Rearrangement

This most general method of synthesising organophosphorus compounds can be used also for the preparation of compounds with unsaturated groups at the phosphorus atom. The starting materials are either alkenyl halides or polyhalogenoalkanes; in the latter case the products of the rearrangement are dehydrohalogenated [56–59]:

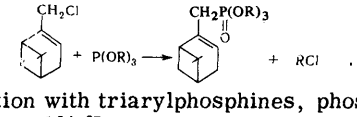
$$CH_2{=}CHCH_2Hal + P(OR)_3 \rightarrow CH_2{=}CHCH_2\overset{\overset{O}{\|}}{P}(OR)_2 + RHal\ ,$$

$$CH_3\underset{Br}{\underset{|}{C}}H{-}CH_2\underset{Br}{\underset{|}{}} + P(OR)_3 \xrightarrow[-RBr]{} CH_3\underset{Br}{\underset{|}{C}}H{-}CH_2{-}\overset{\overset{O}{\|}}{P}(OR)_2 \xrightarrow[-HBr]{} CH_3CH{=}\overset{\overset{O}{\|}}{C}HP(OR)_2\ . \quad (Hal{=}Cl, Br)$$

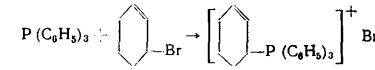
The rate of the process depends on a number of factors—temperature, proportions of the reactants, nature of the alkyl halide, and also the structure of the initial phosphorus(III) compound. Liorber and Razumov found that allylphosphonite esters undergo the Arbuzov rearrangement much more readily than alkyl- and vinyl-phosphonites. Thus, depending on the nature of the group joined to the phosphorus atom, phosphorus(III) compounds can be arranged in the following series [60]:

$$CH_2{=}CHCH_2P(OR)_2 > AlkP(OR)_2 > CH_2{=}CHP(OR)_2\ .$$

Certain more complex alkyl halides readily undergo the Arbuzov reaction [61–63]:

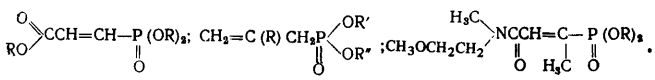


In the reaction with triarylphosphines, phosphonium halides are formed [64–67]:

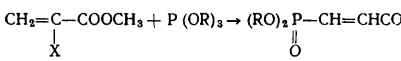


When α-halogeno-ketones are used as the initial alkyl halides, the rearrangement can be more profound [67–69].

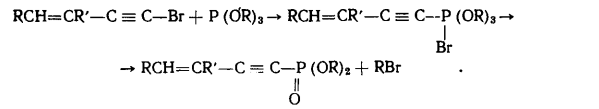
At the present time the Arbuzov rearrangement constitutes a widely used method for the synthesis of alkenylphosphonates, whereby it is possible to obtain very complex compounds, for example[70-74]:



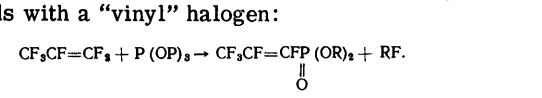
The reaction of trialkyl phosphites with α-halogenoacrylates is very interesting[75]:



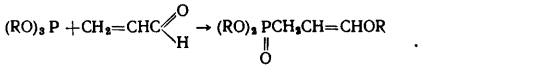
Ionin and Petrov found that halogenoacetylenes can also undergo the Arbuzov rearrangement[76,77]:



Such rearrangements take place particularly readily when the triple bond is conjugated with another multiple bond or a benzene ring[78,79]. Knuyants and coworkers showed that perfluoro-olefins can react with trialkyl phosphites[80-84], this being the first example of the Arbuzov rearrangement of compounds with a "vinyl" halogen:

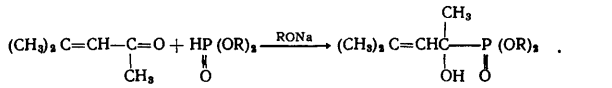


Trialkyl phosphites react by an Arbuzov rearrangement mechanism with $\alpha\beta$-unsaturated carbonyl compounds[85-88], the reaction being extremely specific:

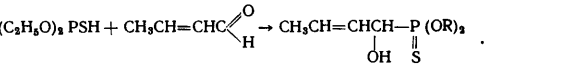


4. Addition Reactions of Dialkyl Phosphites

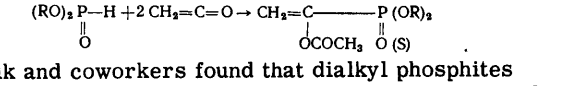
The methods of synthesis of alkenylphosphonates via various reactions of dialkyl phosphites are very unusual and as a rule comparatively simple. Thus Abramov, Pudovik et. al. found that dialkyl phosphites readily react with unsaturated carbonyl compounds forming derivatives of α-hydroxyallylphosphonic acid[89-93]:



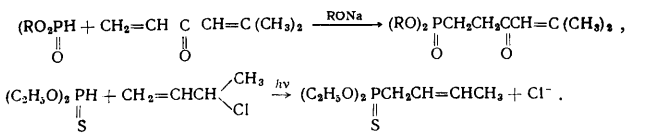
Dialkyl phosphorothi-ites react similarly[94]:



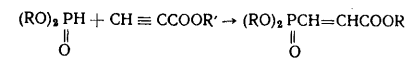
Reactions with ketones yield esters of α-acetoxyvinylphosphonic acid[95-97]:



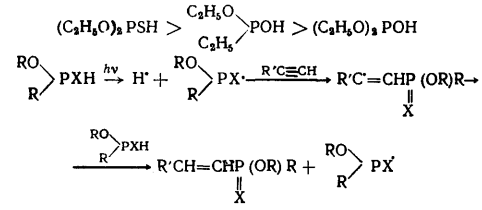
Pudovik and coworkers found that dialkyl phosphites readily add to certain $\alpha\beta$-unsaturated carbonyl compounds, yielding alkenylphosphonates[98-105]:



The yield of products is 50–70%. The reaction with propiolic acid derivatives gives β-alkoxycarbonylvinylphosphonates[106]:

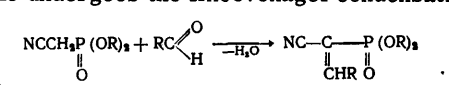


Pudovik and coworkers showed that the reaction of dialkyl phosphoric acids with certain acetylenes can involve a radical mechanism. The addition takes place contrary to the Markovnikov rule; the rate of the process decreases in the series[105]:

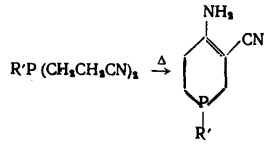


5. Certain Special Methods for the Preparation of Alkenylphosphonates

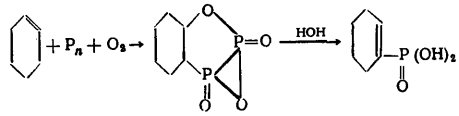
According to the data of Kirillov and Petrov, phosphonoacetonitrile undergoes the Knoevenagel condensation[107]:



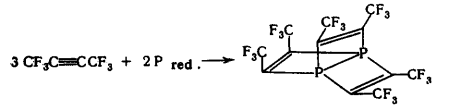
Alkylbis-(β-cyanoethyl)phosphines isomerise to phosphorins in boiling toluene[108-111]:



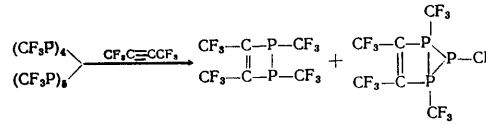
Certain cyclic alkenylphosphines can be obtained from elemental phosphorus[112-114]:



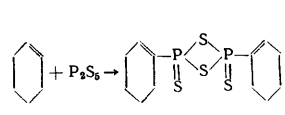
or[115,116]:



Similar polyphosphine heterocycles are formed in high yield when tetra and penta-trifluoromethylphosphines are heated with *sym*-hexafluorobutyne[117]:



Unusual alkenyl structures are produced in the reaction between phosphorus pentasulphide and olefins[118,119]:



6. Reactions Using Phosphorus Trichloride

Much work has been done on the study of the possibility of using phosphorus trichloride to synthesise compounds with a C–P bond, including alkenylphosphonates. Usually the second component is an olefin [120]:

$$PCl_3 + RCH{=}CH_2 \xrightarrow[H_2O]{(CH_3CO)_2O} RCH{=}CHP(O)(OH)_2 \quad .$$

Sometimes ketones are used in the reaction [121–125]:

$$C_6H_5CCH_3 + PCl_3 + CH_3COOH \xrightarrow{HOH;\ HCl} CH_2{=}C(C_6H_5){-}P(O)(OH)_2 \quad .$$

Kinnear, Perren, and other investigators have successfully employed in these processes the complex-forming capacity of aluminium chloride [126,127]:

$$RCl + PCl_3 + AlCl_3 \rightarrow RPCl_4 \cdot AlCl_3 \xrightarrow{HOH} RP(O)Cl_2 + HCl + Al(OH)_3 \quad ,$$

where R = alkenyl.

An extensive series of investigations by Soborovskii, Zinov'ev, and coworkers dealt with the oxidative chlorophosphination of hydrocarbons, including unsaturated hydrocarbons, which makes certain alkenylphosphonates extremely easy to obtain [128–134]:

$$CH_2{=}CHCl + PCl_3 + O_2 \rightarrow CH_2ClCHClP(O)Cl_2 \xrightarrow{ROH}$$

$$\rightarrow CH_2ClCHClP(O)(OR)_2 \xrightarrow{Zn} CH_2{=}CHP(O)(OR)_2 ,$$

$$RC{\equiv}CH + 2\,PCl_3 + O_2 \rightarrow RCCl{=}CHP(O)Cl_2 + POCl_3 \quad .$$

Recently a method has been found, and has been developed successfully, for the synthesis of alkenylphosphonates by the thermal (so called "pseudo-Claisen") rearrangement of various phosphite esters, primarily allyl and propargyl esters [135–140]:

$$(RO)_2P{-}OCH_2CH{=}CHCH_3 \xrightarrow{180^\circ} (RO)_2P(O){-}CHCH{=}CH_2 ,$$

$$(RO)_2P{-}OCH_2C{\equiv}CH \xrightarrow{180^\circ} (RO)_2PCH{=}C{=}CH_2 \rightarrow (RO)_2PC{\equiv}C{-}CH_3 \quad .$$

A possible mechanism of the isomerisation has been put forward [139,140].

7. Reactions of Phosphorus Pentachloride and Its Derivatives with Unsaturated Compounds

The most familiar and most thoroughly developed method for the synthesis of various compounds with alkenyl groups at the phosphorus atom is based on the interaction of phosphorus pentachloride with olefins. As early as 1894, Marsh and Gardner [141,142] stated that camphene reacts with phosphorus pentachloride to form a product which yields camphenylphosphonic acid after hydrolysis. Later, reactions of phosphorus pentachloride with styrene, isobutene, and other unsaturated hydrocarbons were described and it was found that the process takes place best with asymmetric polar systems; the PCl_4 group becomes attached to the most hydrogenated carbon atom and chlorine to the least hydrogenated carbon atom [143,144]. Bergmann and Bondi noted that at least a twofold excess of phosphorus pentachloride is necessary for satisfactory yields [145–147]:

$$RCH{=}CH_2 + 2\,PCl_5 \rightarrow RCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{HOH} RCH{=}CHP(O)(OH)_2 \quad .$$

It was found that the intermediate complexes can be treated with agents other than water under different conditions [148–150], namely phosphorus pentasulphide [151–152], sulphur [152–155], hydrogen sulphide [156–159], hydrogen selenide [160], and elemental phosphorus [151,158], or they can be heat-treated [151,159]. The yield of the acid chlorides of alkenylphosphonic acids and their analogous thio-derivatives is in the range 60–80%. The method was successfully extended to various styrene derivatives [148,161–163], diene hydrocarbons [164–166], and acetylenes [148,167–172].

It has been established that, depending on the structure of the initial diene and the reaction conditions, phosphorus pentachloride can add both in 1,2- [153,173] and 1,4-positions [174]. Anisimov, Nesmeyanov, Kolobova, and others employed extensively the reaction of phosphorus pentachloride with alkyl vinyl ethers [175–178] and alkyl vinyl sulphides [179,180]:

$$ROCH{=}CH_2 + 2\,PCl_5 \rightarrow ROCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{SO_2} ROCH{=}CHP(O)Cl_2 ,$$

$$RSCH{=}CH_2 + 2\,PCl_5 \rightarrow RSCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{SO_2} RSCH{=}CHP(O)Cl_2 \quad .$$

As can be seen from the above equations, it was found that the addition takes place in accordance with the Markovnikov rule [178–182]; cycloalkenyl ethers react similarly [183,184].

The treatment of the intermediate complexes with elemental phosphorus is now attracting increasing attention as a convenient method for the preparation of $\alpha\beta$-unsaturated phosphines [185,186]:

$$ROCH{=}CH_2 + 2\,PCl_5 \rightarrow ROCHClCH_2PCl_4 \cdot PCl_5 \xrightarrow{P} ROCH{=}CHPCl_2 \quad .$$

Lutsenko, Kirillov et al. found that the reaction of phosphorus pentachloride with enol esters leads to a wide variety of products. Various substituted alkenylphosphonates can be isolated [187–192]:

$$CH_3C(OCOCH_3){=}CH_2 + PCl_5 \rightarrow CH_3CCl(OCOCH_3)CH_2PCl_4 \xrightarrow{PCl_5,\ CH_3COCl,\ SO_2} CH_3CCl(COCH_3){=}C(O){-}PCl_2 \quad .$$

Apart from phosphorus pentachloride, other phosphorus(V) derivatives, primarily alkyl-and aryl-tetrachlorophosphoranes, can add to olefins [193–196]:

$$C_6H_5PCl_4 + CH_2{=}CHOC_2H_5 \rightarrow C_6H_5PCl_3CH_2CH(Cl)(OC_2H_5) \xrightarrow{SO_2} C_6H_5P(O)(Cl)(CH{=}CHOC_2H_5) \quad .$$

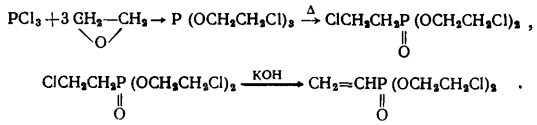
Recently it has been found that certain phosphorus(III) derivatives, mainly phosphorus trichloride [197,198] and tribromide [199–201], alkyl- and aryl-halogenophosphines [202,203], and alkyl and aryl phosphorochloridites [204–212], add readily to dienes, for example:

$$CH_2{=}CH{-}CH{=}CH_2 + ClP(O{-}CH_2{-}CH_2{-}O) \rightarrow \text{bicyclic product } O{=}P{-}OCH_2CH_2Cl \quad .$$

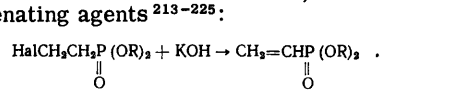
8. Elimination of Water and Acids from Saturated Organophosphorus Compounds

To conclude this review of synthetic methods for compounds with unsaturated groups at the phosphorus atom, we shall consider various methods for the elimination of the elements of water and acids from saturated organophosphorus compounds. Much attention has been devoted to this problem in the literature because various kinds of β-halogenophosphonates are at the present time some of the most widely available organophosphorus compounds and are obtained as a rule by the reaction of phosphorus halides

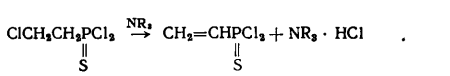
or their derivatives with epoxyalkanes followed by thermal isomerisation[213-218]:



A wide variety of basic substances, especially aqueous or aqueous-alcoholic solutions of alkalis, can be used as dehydrohalogenating agents[213-225]:

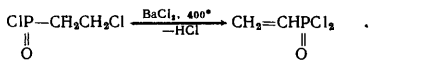


Tertiary amines and in particular triethylamine are dehydrohalogenating agents which come next in order of importance as regards frequency of application. In this case acid halides can also be introduced into the reaction[218,225]:



Alkali metal acetates[226-230], sodium carbonate[231], potassium t-butoxide[227], alkali metal hydrides[221], and activated charcoal[232-234] can be used as dehalogenating agents.

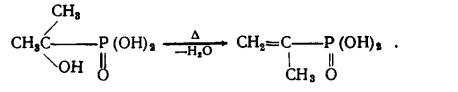
Thermal elimination of hydrogen halides, in the first place hydrogen chloride, is applicable to a comparatively narrow range of substances, but is technologically very promising and is now being effectively developed[235-241]:



The elimination of the elements of acids other than hydrogen halides takes place less completely and is frequently accompanied by side processes[97,242]:



Thermal degradation has been developed to an even lesser extent, although there are certain promising results showing that such a process is in principle possible[243,244]:



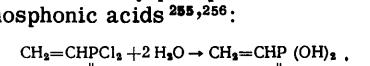
On the whole, the synthesis of organophosphorus structures with unsaturated groups at the heteroatom by the elimination of the elements of acids is at the present time most widely used both in the laboratory and in industrial practice[242,245-254].

III. PROPERTIES OF COMPOUNDS WITH UNSATURATED GROUPS AT THE PHOSPHORUS ATOM

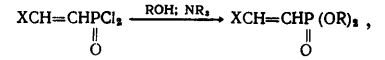
1. Reactions Not Involving the Multiple Bond

a. Synthesis of esters, thioesters, and amides. It is noteworthy that, whereas the methods of preparation of the compounds under consideration have been developed comparatively fully, their chemical properties have been investigated to a much lesser extent. Only the double-decomposition reactions of alkenylphosphonic halides, certain nucleophilic addition reactions, and the tendency towards polymerisation have been investigated. Oxidation and reduction processes and certain specific rearrangements and condensation have been studied to a very limited degree.

The hydrolysis of alkenylphosphonic halides yields unsaturated phosphonic acids[255,256]:

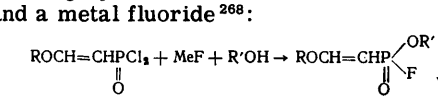


Esters of these acids are usually obtained from their chlorides and alcohols in an inert solvent; various tertiary amines are used as acceptors for hydrogen chloride[257-267]:

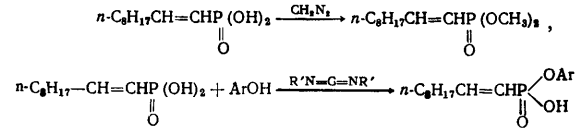


where X = H, alkyl, halogen, Sr, etc.

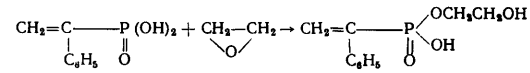
The yields of esters prepared in this way amount to 40-60%. Certain monoester acid fluorides can be obtained by acting upon the dichloride simultaneously with an alcohol and a metal fluoride[268]:



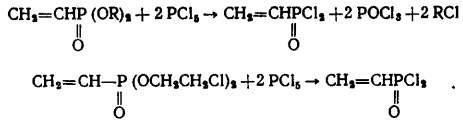
Higher unsaturated phosphonic acids can be esterified with diazomethane and also alcohols and phenols in the presence of carbodi-imide[269]:



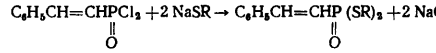
Ivin and coworkers showed that certain higher alkenylphosphonic acids react with epoxides to form mono-β-hydroxyalkyl esters[270]:



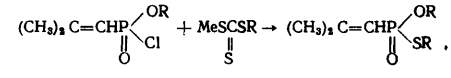
The reverse reaction – the interaction of alkenylphosphonates with phosphorus pentachloride–is possible[256,268]:



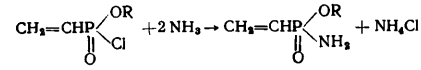
Thioesters of alkenylphosphonic acids [phosphonodithiolates (Translator)] are obtained in good yields when mercaptides react with the acid dichlorides[271-274]:



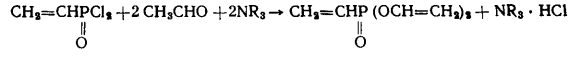
The reaction with salts of alkyltrithiocarbonic acid is similar[274]:



When the acid dichlorides react with ammonia and amines, the amides of alkenylphosphonic acids are formed[275-279]:



Gefter, Kabachnik, and coworkers extended the general method to alkenylphosphonates for the synthesis of vinyl esters[280,281]:

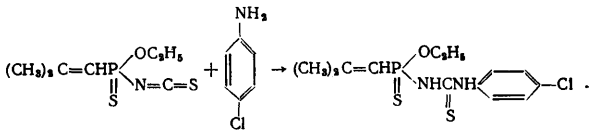


In the presence of halogen atoms in the saturated group, there is a possibility of their exchange for amino-groups, NR_2 groups, etc.[282]:

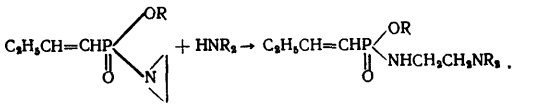
$$CH_2{=}CHP(O)(OCH_2CH_2Cl)_2 + 2\,H_2NCH_2CH_2OH \rightarrow CH_2{=}CHP(O)(OCH_2CH_2NHCH_2CH_2OH)_2 \cdot 2HCl,$$

$$CH_2{=}CHP(O)(OCH_2CH_2Cl)_2 + 2\,NH_3 \rightarrow CH_2{=}CHP(O)(OCH_2CH_2NH_2)_2 \cdot 2\,HCl\ .$$

Alkenylphosphonyl thiocyanates enter into all the reactions characteristic of thiocyanates[283]:



Ethyleneimides are fairly readily cleaved by compounds containing a mobile hydrogen atom[284]:



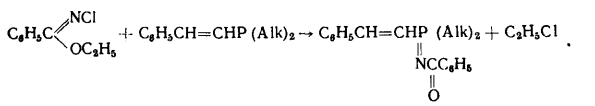
b. Oxidation and reduction reactions. Oxidation and reduction reactions of compounds with unsaturated groups at the phosphorus atom have been very little studied. Whereas the oxidation of various phosphorus(III) structures with oxygen, sulphur, selenium, and tellurium is known if only in principle, there have been almost no studies on reduction. The oxidation of phosphorus(III) compounds with oxygen has been most thoroughly investigated[8-13]. This process, which takes place very readily as a rule, begins sometimes when the substance simply comes into contact with atmospheric oxygen:

$$CH_2{=}CHCH_2P(OR)_2 + O_2 \rightarrow CH_2{=}CH{-}CH_2{-}P(O)(OR)_2\ .$$

Sulphur, selenium, and tellurium add under much more severe conditions[12-16, 19-22, 285]:

$$RP(OR')_2 + Se\ (Te) \rightarrow RP(Se\ (Te))(OR')_2\ .$$

The reaction of tertiary unsaturated phosphines with chloroiminoethers must be classified as an oxidation reaction[286]:

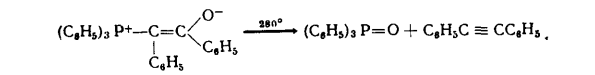


The oxidation of the compounds considered with ozone occupies a special place. As with ordinary olefins, this reaction causes a profound degradation of the molecule, which leads to carbonyl compounds or acids depending on the conditions[96,173].

Lithium aluminium hydride can be used as the reducing agent, since the multiple bond is then unaffected in the reduction process[287,288]:

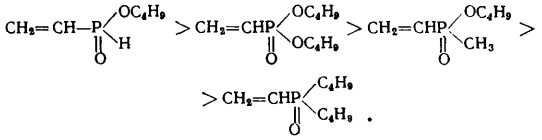
$$C_6H_5CH{=}CHP(O)Cl_2 \xrightarrow{LiAlH_4} C_6H_5CH{=}CHPH_2\ .$$

Pyrolysis of certain alkenylphosphonates results in the degradation of the molecule at the C – P bond[289]:



2. Reactions at the Multiple Bond

a. Nucleophilic addition. The specific features of alkenylphosphonates are shown in the study of various reactions involving the multiple bonds. The reviews of Kabachnik[290], Gefter[291], and Pudovik[54] have dealt with certain aspects of these interactions and their systematic description. The general properties of organophosphorus compounds with vinyl groups are described in Kabachnik's review and the problem of the conjugation of the multiple bond with trivalent and pentavalent phosphorus atoms is discussed. The author concludes that, although physicochemical methods such as infrared and ultraviolet spectroscopy and calculations of molar refractions fail to confirm the occurrence of conjugation, ESR data do indicate its existence. This is also shown by a whole series of chemical properties. For example addition reactions of various nucleophilic agents involving the double bond of organophosphorus compounds take place very readily, the proton always adding at the α-position with respect to the P=O group. Unsaturated organophosphorus compounds can be arranged in the following sequence in terms of decreasing capacity for such addition[292-294]:



The addition to the first member of the series takes place vigorously with evolution of much heat, while the addition to the last member requires prolonged heating. This is due to the increasing positive inductive effect of the substituents at the phosphorus atom. Therefore the addition of electrophilic agents should follow the opposite sequence—dibutylvinylphosphine oxide should be the most reactive.

The addition of a nucleophilic group to phosphorus(III) compounds of the type $CH_2{=}CHPR_2$ also takes place at the β-position (although the inductive effect should lead to α-addition. Here evidently the participation of phosphorus d-orbitals in conjugation has an effect, as happens in vinylsilanes[295-297]:



In agreement with the above findings, dialkylamides of vinylphosphonic acid have lost almost completely the capacity to combine with nucleophilic agents, but readily combine with electrophilic agents (chlorine and bromine). If only the inductive effect operated in this case, vinylphosphonic dialkylamides would combine with compounds of the type X–H as readily as tertiary phosphine oxides.

Since vinyl compounds of four-coordinated phosphorus combine with nucleophilic agents and polymerise with greater difficulty than the corresponding carbonyl compounds, the conjugation of the heteroatom with the double bond is weaker in this case. Dipole moment measurements have shown that the conjugation of the phosphorus atom with a triple bond is more pronounced than with a double bond[298].

Of the general properties of compounds with unsaturated groups at the phosphorus atom, their inability to undergo disproportionation reactions, in contrast to the analogous antimony and bismuth compounds, should also be mentioned[299]:

$$(CH_2{=}CH)_3Sb + SbCl_3 \rightarrow (CH_2{=}CH)SbCl_2 \text{ et al.}$$

$$(CH_2{=}CH)_3Bi + BiCl_3 \rightarrow (CH_2{=}CH)BiCl_2 \text{ et al.}$$

$$(CH_2{=}CH)_3P + PCl_3 \rightarrow \text{no disproportionation}\ .$$

Isomerisation processes of alkenylphosphonic esters in the presence of alkali metal alkoxides on heating merit attention. The phosphonates are then converted into species with maximum conjugation of the multiple bond [300-302]:

$$CH_2{=}CH{-}CH_2{-}P(OC_2H_5)_2 \xrightarrow{C_2H_5ONa} CH_3CH{=}CHP(OC_2H_5)_2,$$

$$CH_3CH{=}CHCH_2P(OR)_2 \xrightarrow{RONa} C_2H_5CH{=}CHP(OR)_2,$$

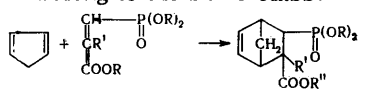
$$H_2C{=}C{=}CH{-}P(OR)_2 \xrightarrow{RONa} CH_3C{\equiv}C{-}P(OR)_2.$$

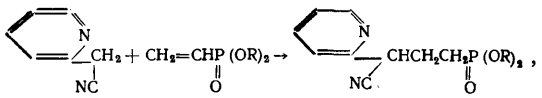
We shall now consider in detail various examples of nucleophilic addition to alkenylphosphonates. Reactions of this type have been investigated most fully for vinylphosphonic acid and have already been treated systematically to some extent [54]. The principal investigations in this field have been carried out by Pudovik, Kabachnik, and their coworkers. Since these reactions have the same mechanism, Pudovik called them "phosphonoethylation" [54], which reflects very correctly the essential features of this type of condensation addition. The reaction takes place readily with alcohol [303-305], hydrogen sulphide, mercaptans and selenium derivatives [17,297,306-311], ammonia and amines [312,313], various phosphorus(III) acids [314-317], thioacetic acid [318], and also thioacetic and malonic esters [309,310,315,319,320]. All the reactions with reagents of the type X – H have the same mechanism and take place as a rule in the presence of alkali metal alkoxides:

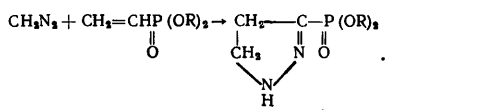
$$X{-}H + CH_2{=}CHP(OR)_2 \xrightarrow{RONa} XCH_2CH_2P(OR)_2,$$

where X = OR, SR, SeAr, NR_2, $P(O)(OR)_2$, $C(NO_2)_3$, etc.

Diene synthesis with vinylphosphonates and also reactions with the nitrile and esters of 2-pyridylacetic acid [321] and diazomethane [322] belong to the same class:







Dienylphosphonates also enter into nucleophilic addition reactions, with preferential 1,4-addition [127,308,323]:

$$CH_2{=}CH{-}C{=}CH{-}P(OR)_2 + X{-}H \xrightarrow{RONa} XCH_2CH{=}CCH_2P(OR)_2,$$

where X = SR, NR_2, or $P(S)(OR)_2$. Diene synthesis with these substances is possible but, in contrast to vinylphosphonates, here they constitute the diene component [324].

Recently the nucleophilic addition reactions have been extended to derivatives of acetoxyvinylphosphonic acid [325], triphenylvinylphosphonium bromide [326,327], alkynylphosphonates [328], vinylphosphonites [11], and perfluoroalkenylphosphonates [78,79,283,329,330].

b. Addition of reagents of the type —Hal. Addition to alkenylphosphonates of compounds with an active X–Hal bond has only just begun to be studied, if one disregards certain earlier investigations of the chlorination and bromination of these compounds [290]. In 1963 Schicke and Schrader took out a patent for the application of the products of the addition of alkanesulphenyl chlorides to vinylphosphonates [331]. At the same time and independently of these investigators similar studies were carried out by Ivin and coworkers [332]. It was found that the addition takes place in accordance with the polarisation of the sulphenyl chloride molecule, which corresponds to the formula RS^+Cl^-:

$$C_2H_5SCl + CH_2{=}CHP(OR)_2 \rightarrow ClCH_2CH(SC_2H_5){-}P(OR)_2,$$

$$C_2H_5SCl + CH_2{=}CHCH_2P(OR)_2 \rightarrow C_2H_5SCH_2CHClCH_2P(OR)_2.$$

The reaction was extended to a wide range of alkenylphosphonates and sulphenyl chlorides. Further development of the reaction showed that sulphur derivatives such as arenesulphenyl chlorides, alkyl dithiochlorides [333] [Ref. 333 refers to reaction of 2-chloroethyldithiochloride with derivatives of vinyl(alkyl)phosphic acid (Ed. of Translation)], sulphur dichloride [334], and acetyl dithiochloride [335] [Ref. 335 refers to acylsulphenyl chlorides (Ed. of Translation)] can enter into it:

$$CH_2{=}CHP(OR)_2 + \begin{cases} ClSCl \rightarrow ClCH_2CH(SCl){-}P(OR)_2 \\ ArSCl \rightarrow ClCH_2CH(SAr){-}P(OR)_2 \\ 2\,CH_3CSCl \xrightarrow{-CH_3COCl} ClCH_2CH(SSCOR){-}P(OR)_2 \end{cases}.$$

Similar reactions have been carried out with allylphosphonates. Later it was shown that vinyl- and allyl-phosphonates react with nitryl chloride and hypochlorites [336,337]:

$$CH_2{=}CH(CH_2)_nP(OR)_2 + NO_2Cl \rightarrow O_2NCH_2CH(Cl)(CH_2)_nP(OP)_2,$$

$$CH_2{=}CH(CH_2)_nP(OR)_2 + (CH_3)_3C{-}O{-}Cl \rightarrow (CH_3)_3C{-}O{-}CH_2CH(Cl)(CH_2)_nP(OR)_2,$$

where n = 0 or 1.

The structure of the addition products was proved by their dehydrochlorination and by the ozonolysis of the unsaturated compounds produced.

Addition reactions in the presence of initiators of radical processes are possible with certain alkynylphosphines [19,20]:

$$C_2H_5SH + h\nu \rightarrow C_2H_5S^{\cdot} + H^{\cdot},$$

$$R_2PC{\equiv}CH + C_2H_5S^{\cdot} \rightarrow R_2PC^{\cdot}{=}CHSC_2H_5,$$

$$R_2PC^{\cdot}{=}CHSC_2H_5 + C_2H_5SH \rightarrow R_2PCH{=}CHSC_2H_5 + C_2H_5S^{\cdot}.$$

c. Oxidation and reduction reactions. It has been shown that in the presence of the usual hydrogenation catalysts such as platinum, palladium, and Raney nickel, hydrogen readily adds to double bonds without involving the P=O group [338-340]:

$$\begin{matrix} p\text{-}ClC_6H_4 \\ CH_3OC_6H_4 \end{matrix}\!\!> C{=}CH{-}P(OH)_2 \xrightarrow{H_2;\ Pd} \begin{matrix} p\text{-}ClC_6H_4 \\ CH_3OC_6H_4 \end{matrix}\!\!> CHCH_2P(OH)_2.$$

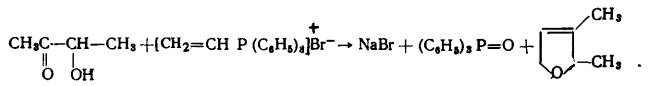
Rosental and Geyer made a successful attempt to oxidise allylphosphonates by the Bayer–Williger method [341]:

$$CH_2{=}CHCH_2P(OR)_2 + HCOOH + H_2O_2 \rightarrow CH_2(OH){-}CH(OH){-}CH_2{-}P(OR)_2.$$

Pudovik and Gareev found that, in contrast to vinylphosphonates, allylphosphonates react with diazoacetic ester [342]:

$$CH_2{=}CHCH_2P(OR)_2 + N_2CH{-}COOC_2H_5 \rightarrow CH_2{-}CH(CHCOOC_2H_5){-}CH_2{-}P(OR)_2 + N_2.$$

Finally, we may note the capacity of triphenylphosphonium bromide to form cyclic compounds with α-hydroxycarbonyl compounds with simultaneous elimination of triphenylphosphine oxide[343,344]:



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Copolymerisation of Cyclic Compounds

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The number of studies dealing with the synthesis of copolymers and the investigation of the copolymerisation of cyclic monomers of a single class is large. The present review is concerned with the polymerisation of cyclic compounds, in which the ring is opened, with monomers of other classes, i.e. of a different chemical type. These processes include the copolymerisation of a number of cyclic compounds with olefins and also the copolymerisation of two cyclic compounds of different classes. The conditions of synthesis, the mechanism of formation, and certain properties of such copolymers are considered. The bibliography comprises 88 references.

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