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Reactions of the Chlorides of Phosphorus Acids with Unsaturated Compounds

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The review deals with the reactions of the chlorides of acids derived from trivalent and tetravalent phosphorus with unsaturated compounds. Apart from their theoretical importance, these reactions are of great practical interest, since with their aid it is possible to obtain a wide variety of new and interesting types of organophosphorus compounds. In the first part of the review the addition reactions of various halides of trivalent phosphorus acids to ethylene and diene hydrocarbons, $\alpha\beta$-unsaturated aldehydes, ketones, and acids are considered, as well as the oxidative chlorophosphination of unsaturated compounds. The second part of the review is devoted to the reactions of the chlorides of pentavalent phosphorus acids with ethylenic, acetylenic, and diene hydrocarbons and with vinyl ethers and esters and also the addition reactions of dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides.

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I. INTRODUCTION

Apart from the widely known substitution reactions of the halides of trivalent and pentavalent phosphorus in which halogen atoms are exchanged for a hydroxy-group, a carbonyl oxygen, or any organic residue, the reactions involving their addition to unsaturated compounds are assuming increasing importance. In addition to their theoretical value these reactions are also of great practical interest, since with their aid it is possible to prepare a wide variety of new and interesting types of organophosphorus compounds. Until recently the range of addition

reactions investigated was fairly narrow and included mainly ethylenic and acetylenic hydrocarbons and unsaturated ketones. These and other addition reactions of phosphorus halides (reactions with epoxides and carbonyl compounds) were reviewed in 1947 by M. I. Kabachnik. During the past two decades the addition reactions of phosphorus halides to unsaturated compounds have been studied very vigorously; apart from the development of earlier studies, a number of new very interesting reactions have been found, such as the addition of phosphorus(III) halides to compounds containing a conjugated system of double bonds and to unsaturated acids, oxidative chlorophosphination, reactions of phosphorus(V) halides with diene hydrocarbons and enol ethers and esters, and the addition reactions of dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides to unsaturated compounds. The majority of these reactions were discovered and developed by Soviet chemists.

Intensive study of reactions of this type is being continued at the present time and they include both new types of phosphorus halides and of unsaturated compounds. Definite advances have also been made in the study of the mechanism of certain reactions.

We believe it is interesting and timely to compile these extensive and interesting data on the addition reactions of trivalent and pentavalent phosphorus to unsaturated compounds which have accumulated during twenty years. In the review we did not consider the earlier studies which have been summarised by Kabachnik with the exception of those few cases where this was necessary either for the explanation of the systematic development of studies on definite problems or for the examination of the mechanism of certain reactions.

II. REACTIONS OF THE CHLORIDES OF TRIVALENT AND PENTAVALENT PHOSPHORUS ACIDS WITH UNSATURATED COMPOUNDS

1. Addition of phosphorus trichloride and tribromide to alkenes

Under the usual conditions phosphorus trihalides do not add to alkenes. In 1945 Kharasch and coworkers[1,2] described for the first time a process of this kind in the presence of free radicals in the reaction medium. The radicals were generated by the thermal decomposition of acetyl peroxide introduced into the reaction:

$$(CH_3COO)_2 \rightarrow \dot{C}H_3 + CO_2 + CH_3C\dot{O}O,$$
$$\dot{C}H_3 + PCl_3 \rightarrow CH_3Cl + \dot{P}Cl_2,$$
$$RCH{=}CH_2 + \dot{P}Cl_2 \rightarrow R\dot{C}H{-}CH_2PCl_2,$$
$$R\dot{C}H{-}CH_2PCl_2 + PCl_3 \rightarrow RCHCl{-}CH_2PCl_2 + \dot{P}Cl_2 \text{ etc.}$$

The chain reaction results in the formation of chloroalkyldichlorophosphines. The main addition reaction is accompanied by a telomerisation reaction which leads to high-boiling products:

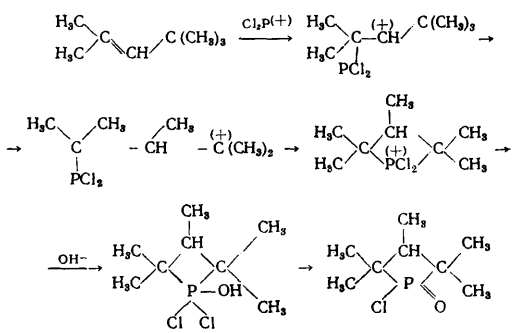
$$R\dot{C}H{-}CH_2PCl_2 + RCH{=}CH_2 \rightarrow R\dot{C}H{-}CH_2{-}CHR{-}CH_2PCl_2,$$
$$R\dot{C}H{-}CH_2{-}CHR{-}CH_2PCl_2 + PCl_3 \rightarrow RCHCl{-}CH_2{-}CHR{-}CH_2PCl_2 + Cl_2\dot{P}.$$

Reactions involving the addition of phosphorus trihalides to a double carbon–carbon bond can be initiated by ultraviolet radiation[3]. When phosphorus tribromide reacts with ethylene under the usual conditions, β-bromoethyldibromophosphine forms in 14% yield; when the reaction temperature is raised to 150°C, the yield increases to 40%. A mixture of isomers is formed with asymmetric olefins, this being confirmed by NMR spectra and gas chromatography. The authors of these investigations suggest that Br• and Br_2P• radicals participate in the reaction:

$$PBr_3 \xrightarrow{h\nu} Br^{\bullet} + Br_2P^{\bullet},$$
$$Br^{\bullet} + CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}\dot{C}H{-}CH_2Br,$$
$$CH_3{-}\dot{C}H{-}CH_2Br + PBr_3 \rightleftarrows CH_3{-}CH(\dot{P}Br_3){-}CH_2Br,$$
$$CH_3{-}CH(\dot{P}Br_3){-}CH_2Br + CH_3CH{=}CH_2 \rightarrow CH_3{-}CH(PBr_2)CH_2Br + CH_3{-}\dot{C}H{-}CH_2Br,$$
$$Br_2\dot{P} + CH_3{-}CH{=}CH_2 \rightarrow CH_3\dot{C}H{-}CH_2PBr_2,$$
$$CH_3\dot{C}H{-}CH_2PBr_2 + PBr_3 \rightarrow CH_3{-}CHBr{-}CH_2PBr_2 + Br_2P^{\bullet}.$$

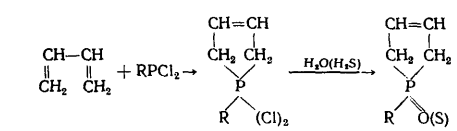
The first type of reaction takes place preferentially. A similar mechanism has been proposed by Little and coworkers[4,5] for reactions involving the addition of phosphorus trichloride to asymmetric olefins under the action of ultraviolet radiation. Trivedi's data[6] concerning the presence of a number of special absorption bands in the spectrum of phosphorus trichloride exposed to ultraviolet radiation confirm this mechanism (involving the participation of Cl• and Cl_2P• radicals).

Phosphorus trichloride adds to olefins in the presence of aluminium trichloride[7–10]. The intermediate complexes are decomposed by methanol and water. According to NMR spectroscopic data the phosphorus-containing acids formed have a cyclic structure. It is suggested (but it has not been confirmed experimentally so far) that reactions of this type involve an ionic mechanism with formation in the first stage of the $Cl_2P^{(+)}$ cation, for example in the case of 2,2,4-trimethylpent-2-ene we have



2. Addition of the Chlorides of Phosphorus(III) Acids to Hydrocarbons with Conjugated Double Bonds

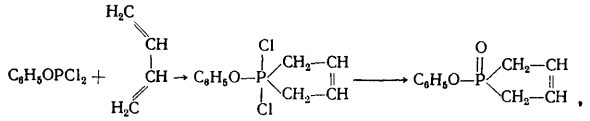
In 1953 McCormack[11,12] found that alkyl-(or aryl-)dichloro-(or dibromo-)phosphines add to diene hydrocarbons with formation of phosphorus-containing cyclic compounds—derivatives of *PP*-dihalogeno-1-phosphacyclopent-3-ene. On their decomposition with water or hydrogen sulphide, 1-oxo- or 1-thiono-phosphacyclopentenes were obtained:



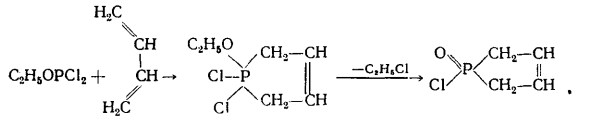
These interesting studies underwent considerable development in subsequent years.

Arbuzov and Shapshińskaya[13,14,15] investigated the addition of aryldichlorophosphines to various diene hydrocarbons. They suggested a reaction mechanism and obtained compounds of the 1-oxo-1-phosphacyclopentene series hitherto not described in the literature. They discovered

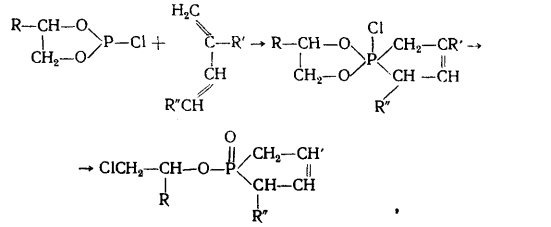
for the first time the reaction of phenyl and ethyl phosphorodichloridites with diene hydrocarbons. Phenyl phosphorodichloridite reacts without the Arbuzov arrangement



while the reaction of ethyl phosphorodichloridite does involve the rearrangement with elimination of alkyl halide:



At the same time Petrov and Razumova[16] studied the reaction of the glycol esters of phosphorochloridous acid with diene hydrocarbons (the final structure of the adducts is not quoted) and obtained the esters of the oxaphospholene oxide series[17]:

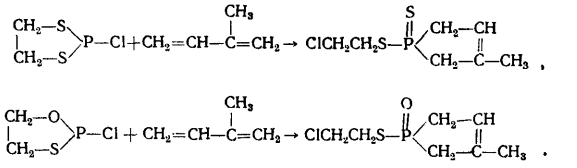


where (1) R = R′ = R″ = H, (2) R = R″ = H and R″ = CH_3, (3) R = CH_3 and R′ = R″ = H, (4) R = R′ = CH_3 and R″ = H, (5) R = R″ = CH_3 and R′ = H, and (6) R = CH_3, R′ = Cl, and R″ = H. They demonstrated the structure of their products by nuclear and proton magnetic resonance and infrared spectroscopy and chemically. A mechanism was suggested for this reaction, involving the Arbuzov rearrangement without the elimination of alkyl halide. When the catechol ester of phosphorochloridous acid is condensed with dienes, the Arbuzov rearrangement does not take place and the reaction terminates at the addition stage, evidently because of the stable bond between the oxygen and the carbon of the aromatic ring[18].

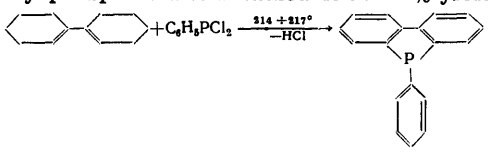
Arbuzov et al.[19,20] showed that cyclic phosphorochloridites add to various dienes with a conjugated system of double bonds by a 1,4-addition mechanism. Since in these reactions the cyclic phosphorochloridites behave as electron-donor components, the ease of the addition is determined by the electron-donor properties of the dienes. The latter become less pronounced in the series cyclopentadiene > anthracene > dicyclohexenyl > diisopropenyl > cyclohexadiene > divinyl > tetracyclone > hexachlorocyclopentadiene. Phosphorochloridites react at the highest rates with dienes at the end of the series and do not react with those pronounced electron-donor properties.

Subsequently Petrov and Razumova[21] showed that cyclic six-membered glycol esters of phosphorochloridous acid react with divinyl, isoprene, and diisopropenyl similarly as the corresponding esters with a five-membered ring. The products are 3-(γ-chloroalkoxy)phospholen 1-oxides. It has been established that in the Arbuzov rearrangement the ester ring is ruptured at the primary carbon atom.

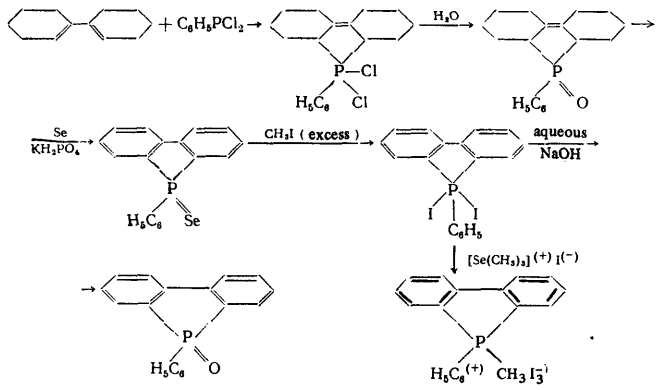
The reactions of the cyclic esters of phosphorochloridothious and phosphorochloridodithious acids with diene hydrocarbons take place similarly as those of their oxygen analogues[22]:



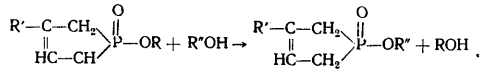
The adducts of dienes with halogen-containing derivatives of trivalent phosphorus can undergo a wide variety of very interesting reactions: for example when the adduct of dicyclohexenyl and phenyldichlorophosphine was heated, the tertiary phosphine was obtained in 50–60% yield[23,24]:



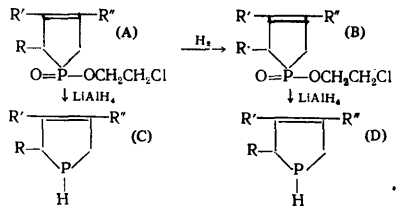
In the presence of selenium and the monopotassium salt of phosphoric acid, cyclic phosphine oxides are dehydrogenated, the oxygen bound to phosphorus being replaced by selenium:



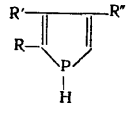
Alkoxyoxophosphacyclopentenes readily undergo transesterification with alcohols in the presence of potassium hydroxide[25]:



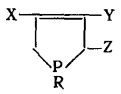
In the catalytic hydrogenation of phosphacyclopentene derivatives (A), compounds with the phospholan ring (B) were obtained[26]. When the esters (A and B) are reduced with lithium aluminium hydride, the phospholenes (C) and (D) are formed:



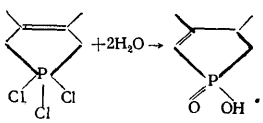
Phospholes can be obtained from these products by halogenation and dehydrohalogenation[27]:



The above syntheses of ring compounds containing phosphorus are simpler and more convenient than those already described in the literature[28]. When the adducts of methyl- or phenyl-dichlorophosphines with various dienes are reduced with magnesium in tetrahydrofuran solution, phospholens are obtained[29]:

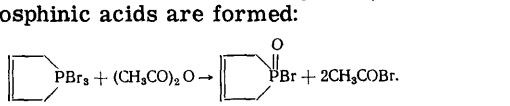


The results of studies on the hydrolysis and alcoholysis of the adducts of phosphorus trihalides with dienes are interesting. In the reaction of phosphorus trichloride and tribromide with divinyl, isoprene, diisopropenyl, dicyclohexene, and 1-phenylbuta-1,3-diene, Hasserodt et al.[30] and Weikamp and Korte[31] obtained the corresponding derivatives of 1,1,1-trihalogenophosphapentene. The authors showed by NMR and infrared spectroscopy that the hydrolysis and alcoholysis of 1,1,1-trichlorophosphapentene takes place with the migration of the double bond in the ring from position 3, 4 to position 2, 3:

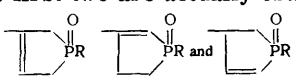


In the study of the reactions of 1,1,1-trichlorophosphapentene[30,31], a wide variety of derivatives of 1-hydroxy-1-oxo-1-phosphapent-2-enes were obtained.

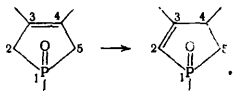
Arbuzov and Vizel'[32,33] isolated 1,1,1-trihalogenocyclopentenes in a pure form. Phosphorus tribromide reacts with diene hydrocarbons more vigorously than phosphorus trichloride. When the adducts of dienes with phosphorus tribromide are treated with acetic anhydride, the bromides of cyclic phosphinic acids are formed:



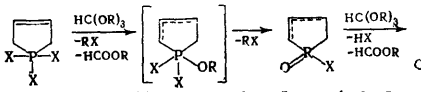
Their hydrolysis yields the acids and their reaction with alcohols the corresponding esters. In these reactions migration of the ring double bond was not observed. In subsequent studies of these investigators[34,35] it was shown that the lability of the double bond, its tendency to prototropic isomerisation, is a specific property of 1,1,1-trichlorophosphacyclopentene only. The migration of the double bond in this compound on hydrolysis, alcoholysis, or treatment with acetic anhydride occurs under very mild conditions. When 1,1,1-trichlorophosphacyclopentene is treated with sulphur dioxide, a mixture of isomeric 1-chloro-1-oxo-1-phosphacyclopentenes is formed. On the other hand, 1,1,1-tribromophosphacyclopentes do not show a tendency towards the migration of the double bond under similar conditions. This makes it possible to synthesise phosphacyclopentene derivatives with a specified position of the double bond in the ring. It has been shown by proton magnetic resonance spectroscopy and double nuclear magnetic resonance[35] that, of the three possible structures of phosphacyclopentene derivatives based on isoprene, only the first two are actually obtained:



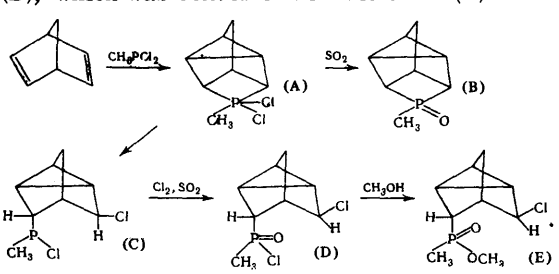
The position of the double bond depends not only on the nature of the halogen and the synthetic pathway but also on the nature of the diene and the symmetry of the distribution of the substituents in the ring. The position of the double bond can be demonstrated by NMR spectra. The application of NMR spectroscopy established that the migration of the double bond from position 3, 4 to position 2, 3 is accompanied by the displacement of one methyl group from the plane of the ring[33]:



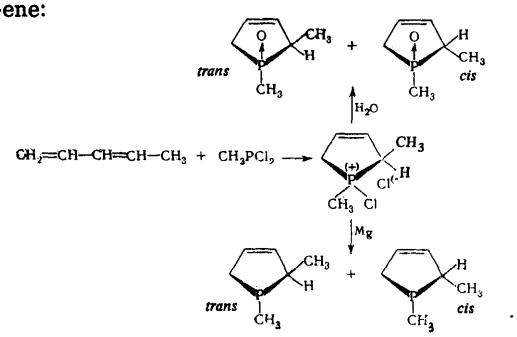
As a result, the phosphorus atom and C_4 become asymmetric. This behaviour is also observed in the reactions of 1,1,1-trihalogenophosphacyclopent-3-ene with orthoesters[36,37]:



When the reactant ratio is equimolar, 1-halogeno-1-oxophosphacyclopentenes are formed. When X = Br, the reaction takes place without migration of the double bond, the final product being 1-alkoxy-1-oxophosphacyclopent-3-ene. With chloro-derivatives, these reactions are accompanied by the migration of the double bond in the ring. Green[38] studied the addition of methyldichlorophosphine to bicyclo[2,2,1]heptadiene, a compound with isolated double bonds. The resulting crystalline adduct (A) yields the phosphine oxide (B) as a result of hydrolysis or under the action of sulphur dioxide. The structure of adduct (A), a substituted nortricyclene, was established by means of chemical conversions and by physical methods. Pyrolysis of the adduct gave the liquid isomer (C); its oxidation with chlorine and sulphur dioxide gave the acid chloride (D), which was converted into the ester (E):



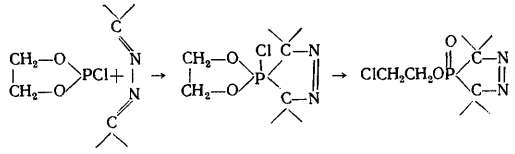
The stereochemistry of phosphacyclopentenes has been inadequately investigated so far. In the reaction of a mixture of the *cis*- and *trans*-forms of piperylene with methyldichlorophosphine followed by hydrolysis of the addition products, Quin and coworkers[39] obtained a mixture of the geometrical isomers of 1,2-dimethyl-1-oxophosphacyclopent-3-ene:



One isomer was isolated in a pure form by means of gas chromatography. The lack of migration of the double bond in the ring during hydrolysis in the suggested reaction mechanism is striking. Probably these reactions

require additional investigation. Reduction of the addition products with magnesium led to two stereoisomeric phosphines. When these are oxidised with hydrogen peroxide, the geometry of the molecules remains unaffected.

Not only hydrocarbons but also compounds with conjugated carbon–nitrogen double bonds can react with phosphorus(III) halides[40,41]. For example the reaction of cyclic phosphorochloridites with acetaldazine takes place by the following mechanism:



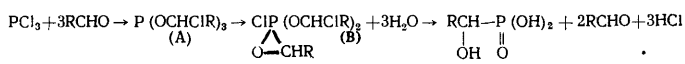
The structure of the products was confirmed by infrared and NMR spectroscopy.

The reactions of phosphorus(III) halides with diene systems open up wide possibilities for the preparation of a great variety of phosphocyclopentene derivatives and other organophosphorus compounds. Compounds of this type are of both theoretical and practical importance. Some of the phosphorus cyclopentene derivatives are recommended as catalysts for the preparation of carbodiimides and carbopolyimides[42,43].

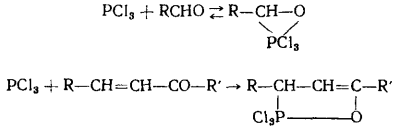
3. Addition of the Chlorides of Phosphorus(III) Acids to αβ-Unsaturated Aldehydes and Ketones

The study of this process was preceded by investigations of analogous reactions with saturated aldehydes and ketones. The results were subsequently used to account for the mechanism of reactions with both saturated and αβ-unsaturated carbonyl compounds; therefore it is useful to consider them briefly in the present review.

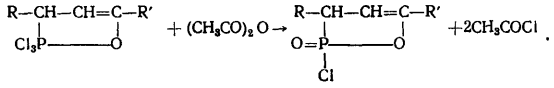
The first information about the reactions of aldehydes and ketones with phosphorus trichlorides is to be found in the work of Fossek[44–46] and Michaelis[47–51]. By hydrolysing the addition products, Fossek obtained a series of α-hydroxy-phosphonic acids. In the study of these reactions, Page[52] attempted to isolate the addition of products in a pure form by vacuum distillation, but his attempts failed because of the thermal instability of the products. After hydrolysis of the reaction products, he also isolated α-hydroxy-phosphonic acids. He suggested that the product of the addition of phosphorus trichloride to aldehydes formed initially is an ester of phosphorous acid (A), which subsequently rearranges to compound (B):



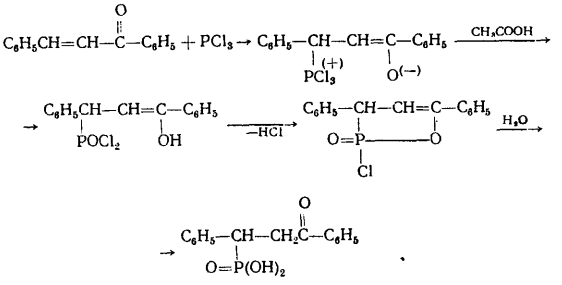
Thorough investigations of the addition of phosphorus trichlorides and certain other phosphorus(III) halides to saturated and unsaturated carbonyl compounds were begun in 1917 by Conant and coworkers[53–64]. In agreement with Michaelis' suggestions, Conant put forward the hypothesis of 1,2-addition of saturated aldehydes and ketones and 1,4-addition of αβ-unsaturated carbonyl compounds with formation of addition products containing three- and five-membered rings respectively:



The products were not isolated in a pure form; their hydrolysis yielded α-hydroxy-phosphonic or γ-oxo-phosphonic acid. Reaction with acetic anhydride gives rise to chlorides of cyclic acids with pentavalent phosphorus:

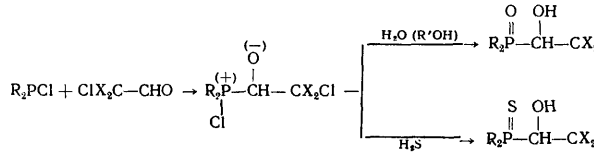


Subsequently, having carried out the reaction in glacial acetic acid, Conant and Wallingford[63] concluded that in the first stage a betaine-like addition product is formed, which is converted into a hydroxy- or oxo-phosphonic acid under the action of acetic acid and in subsequent hydrolysis. For example, for benzylideneacetophenene, these reactions can be described by the following mechanism:



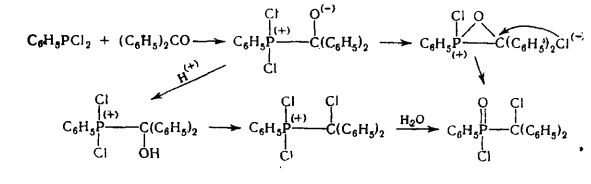
Evidently in this mechanism too the formation of a cyclic product is postulated, but only as a secondary reaction product. Conant's hypothesis concerning the formation in the reactions considered here of betaine-like, dipolar, and cyclic intermediates was widely used in subsequent investigations.

Tsivunin et al.[65], who studied the reactions of dialkyl- and diaryl-chlorophosphines with α-halogeno-aldehydes, suggest that in these reactions there is initial nucleophilic attack on the carbonyl carbon by the phosphorus atom with formation of an adduct in which the phosphorus is sp^3-hybridised. The subsequent decomposition of the complexes with water or alcohols leads to the formation of oxides of dialkyl- or diaryl-α-hydroxyethylphosphines. When the complexes are decomposed with hydrogen sulphide, the corresponding thiones are produced:

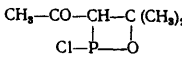


where R = C_2H_5 or C_6H_5 and X = H or Cl.

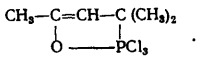
Freeman and Gallagher[66] studied the reaction of phenyldichlorophosphine with benzophenone in the presence of partially hydrated aluminium trichloride. This reaction gave a 65% yield of the chloride of (diphenylchloromethyl)-phenyl phosphinic acid. When the reaction is carried out in the presence of anhydrous aluminium trichloride, the yield of the acid chloride falls. The authors propose the following reaction mechanism:



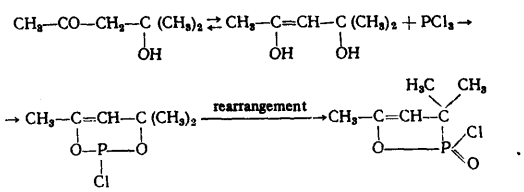
In 1884 Michaelis suggested that a cyclic intermediate, "diacetonephosphorus chloride", forms in the reaction between phosphorus trichloride and acetone in the presence of aluminium trichloride:



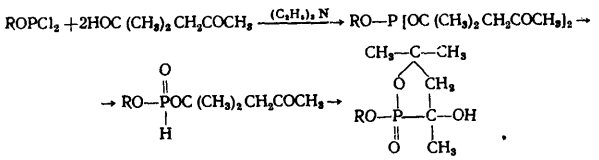
In their study of the reaction of phosphorus trichloride with mesityl oxide in the presence of acetic anhydride, Drake and Marvel[67] showed that 4-methylpentan-2-one-4-phosphonic acid forms as a result of the hydrolysis of the reaction product. On this basis, the following formula with a five-membered ring and pentavalent phosphorus was proposed for the "Michaelis chloride" (by analogy with Conant's views):



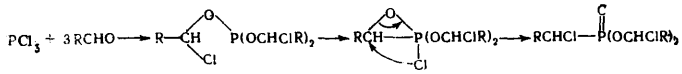
Anschutz et al.[68] and Michaelis[48] believed that diacetone alcohol formed initially and subsequently reacted with phosphorus trichloride to form the "Michaelis chloride":



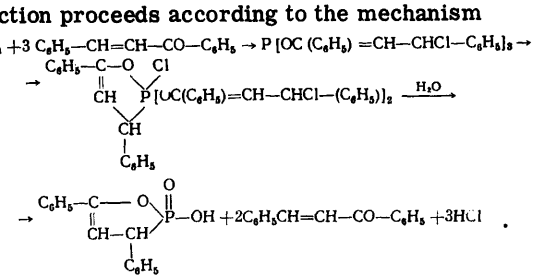
To confirm this mechanism, Anschutz carried out the reaction between phosphorus trichloride and diacetone alcohol. According to his data, the same "Michaelis chloride" is then formed. However, this hypothesis is probably incorrect, since Rizpolozhenskii[69] showed that esters of phosphorous acid are formed in the reaction between diacetone alcohol and monochlorides of phosphorus acids in the presence of a base. The reaction proceeds acccording to the following mechanism:



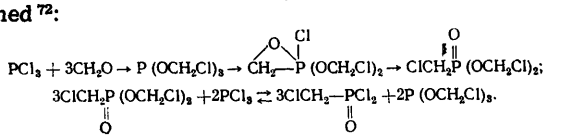
Kabachnik[70,71] believes that the mechanism proposed by Conant for the reaction between phosphorus halides and carbonyl compounds is unlikely because of the difficulty of the first stage, namely alkylation. He thinks that the more probable mechanism, very similar to the mechanism proposed by Page, is one consisting in the formation in the first reaction stage of a tri(α-halogeno-ester) of phosphorous acid, which subsequently undergoes the Arbuzov rearrangement to the ester of α-chloroalkylphosphonic acid:



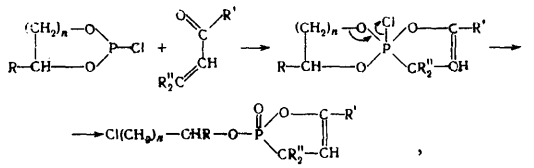
Hydrolysis of the α-chloroalkylphosphonic acid ester of the cyclic intermediate leads to the formation of the α-hydroxyalkylphosphonic acid. With unsaturated ketones, the reaction proceeds according to the mechanism



The validity of these mechanisms was confirmed for a number of examples. Thus in the reaction of phosphorus trichloride with paraformaldehyde in sealed tubes at 250°C, the dichloride of chloromethylphosphonic acid was obtained[72]:

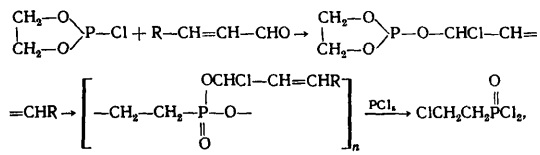


With benzaldehyde, the product was the dichloride of α-chlorobenzylphosphonic acid[73]. Kabachnik and Shepeleva[74] showed that these reactions are common to a wide range of aldehydes. Petrov and coworkers[39,40,75] demonstrated that the reaction of various glycol phosphorochloridites with methyl vinyl ketones or mesityl oxide involve 1,4-addition with subsequent Arbuzov rearrangement of the cyclic intermediate[75]:

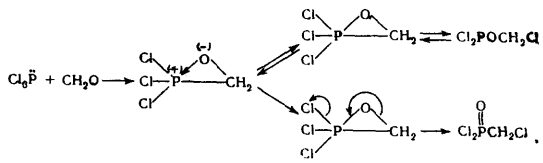


where n = 1 or 2, R = H or CH_3, R′ = CH_3, and R″ = H or CH_3.

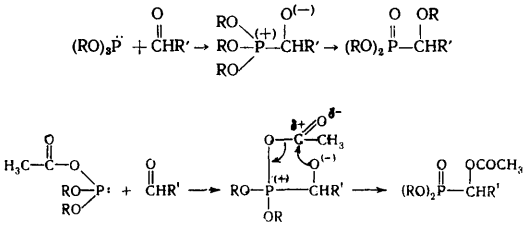
The structure of the final reaction products, isoxaphospholens, was demonstrated by infrared and nuclear and proton magnetic resonance spectroscopy. The reaction of glycol phosphorochloridite with acrolein and crotonic aldehydes leads to oligomeric products[40]. When these oligomers are treated with phosphorus pentachloride, the dichloride of β-chloroethylphosphonic acid is formed:



where R = H or CH_3. Probably the first stage of reactions of this type involves the attack by the nucleophilic phosphorus atom on the electrophilic carbon of the carbonyl group in the saturated aldehyde or the β-carbon atom in the unsaturated ketone. The dipolar ion produced cyclises with simultaneous migration of the P–C and O–C bonds, resulting in ring opening. Depending on the conditions, the rearrangement of the intermediate can lead to the formation of compounds with an ester of phosphorus–carbon bond:



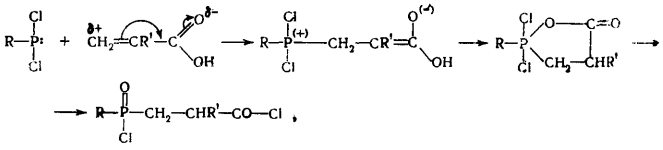
The validity of the suggested first reaction stage, the nucleophilic attack by the three-coordinated phosphorus atom, is confirmed by analogy with numerous reactions between carbonyl compounds and phosphites, which have been investigated in recent years [76]:



In the second reaction R′ can be an alkyl or a chloroalkyl group [77].

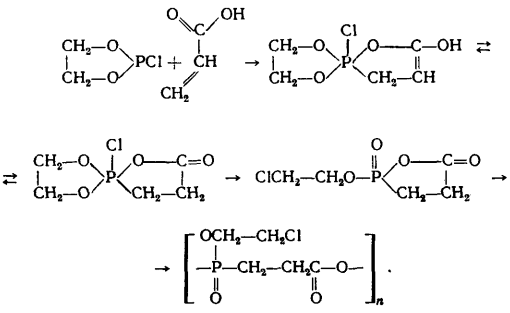
4. Addition of the Chlorides of Phosphorus(III) Acids to αβ-Unsaturated Carboxylic Acids

In 1964 one of the authors of the present review [78] found that, in the reaction between alkyl- or aryl-dichlorophosphines and αβ-unsaturated acids, the chlorides of alkyl- or aryl-(β-chloroformylalkyl)phosphinic acid are formed in good yields:



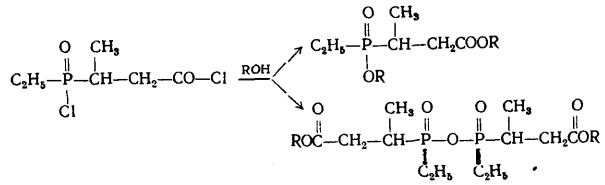
where R = CH_3, C_2H_5, C_6H_5, or C_7H_7 and R′ = H or CH_3.

According to the suggested reaction mechanism, the unshared pair of electrons of the three-coordinated phosphorus atom attacks the most electrophilic β-carbon atom of the αβ-unsaturated acid. The dipolar ion formed is converted into an adduct with a five-coordinated phosphorus atom, which undergoes the Arbuzov rearrangement to form the chloride of alkyl- or aryl-(β-chloroformylalkyl)phosphinic acid [79,80]. In the same year Petrov and coworkers [39] pointed out the possibility of the reaction of glycol phosphorochloridites with acrylic and methacrylic acids. In the reaction between ethylene phosphorochloridite and acrylic acid [40], they obtained an oligomer:

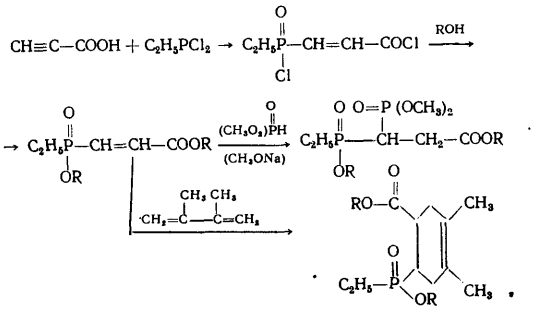


The structure of the oligomer was confirmed by infrared spectroscopy; when it was treated with phosphorus pentachloride, the chloride of dichlorophosphonopropionic acid was obtained.

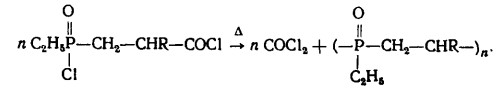
Continuing their investigation of this interesting reaction, the authors of the present review showed that the reaction of ethyldichlorophosphine with crotonic acid leads to the formation of the chloride of ethyl(β-chloroformyl-α-methylethyl)phosphinic acid in 78% yield [81]. When this acid chloride reacts with alcohols, anhydrides of ethyl(β-alkoxycarbonylisopropyl)phosphinic acid are formed together with the esters:



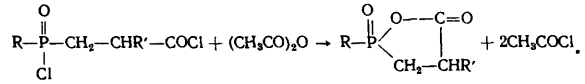
The chloride of ethyl(β-chloroformyl-α-methoxycarbonylethyl)phosphinic acid was obtained by the reaction of ethyldichlorophosphine with the monomethyl ester of maleic acid [82]. On the other hand, under the usual conditions maleic acid itself forms only maleic anhydride; when the reaction mixture is heated in sealed tubes, hydrogen chloride adds to the double bond of maleic anhydride. The reaction of ethyldichlorophosphine with pyromucic and cinnamic acids leads to the formation of considerable amounts of the chlorides of these acids. Evidently in these reactions the β-carbon atom of the acrylic system is blocked by substituents which reduce its positive charge. As a result, the reaction takes place mainly at the carbonyl group. Propiolic acid [83] reacts with ethyldichlorophosphine according to a mechanism similar to that for acrylic acid. The presence of the double bond in the resulting chloride of ethyl(β-chloroformylvinyl)phosphinic acid was confirmed by infrared spectroscopy, by its esterification with subsequent addition to the double bond of dimethyl phosphite esters, and by diene synthesis with 2,3-dimethylbutadiene:



In all cases the yields of the acid chlorides are fairly high when the reaction products are subjected to film distillation in a high vacuum (in the usual vacuum distillation the chlorides are extensively or completely decomposed with the evolution of phosgene and the formation of a polymer):



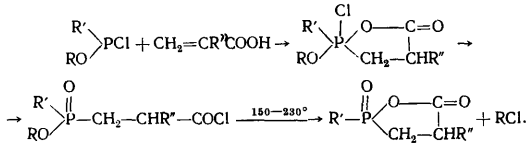
When acetic acid or acetic anhydride react with the chlorides of alkyl- or aryl-(β-chloroformylalkyl)phosphinic acids, cyclic anhydrides are formed:



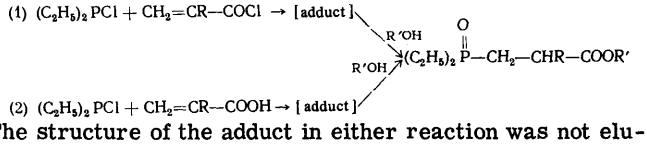
The P–O–C bond in these anhydrides is readily broken under the action of alcohols or amines.

In the reaction with acrylic acid, alkyl phosphorochloridites yield the chlorides of phosphono-carboxylic acids

[RO–P(O)–CH_2CH_2COCl] only when R is a chloro-substituted tertiary alkyl group. Phosphorochloridites with two tertiary chloro-substituted alkyl groups form with acrylic acid the chlorides of dialkylphosphinopropionic acid. Alkyl- or aryl-alkoxychlorophosphines react with $\alpha\beta$-unsaturated acids to form β-phosphono-carboxylic acids, which, on heating to 150–230°C, are converted into cyclic anhydrides with elimination of alkyl chloride:



Tsivunin et al.[85] showed that diethylchlorophosphine reacts with acrylic or methacrylic acid chlorides to form crystalline complexes, which, on treatment with an excess of alcohol, are converted into a dialkylphosphinylcarboxylic acid. The same esters were obtained by treating with alcohol complexes of diethylchlorophosphine with acrylic or methacrylic acids:



The structure of the adduct in either reaction was not elucidated but it is probably (in the second case) the oxide of diethyl(β-chloroformylalkyl)phosphine.

5. Oxidative Chlorophosphination of Unsaturated Compounds

One of the new very interesting and promising methods for the preparation of the dichlorides of alkyl- and chloroalkyl-phosphonic acids is oxidative chlorophosphination of saturated and unsaturated hydrocarbons and their various derivatives. This reaction was described almost simultaneously by Clayton and Jensen[86] in 1948 and by Soborovskii et al.[87] in 1949. (However, in his paper on the oxidative chlorophosphination of hydrocarbons, published in 1952, Graf[88] disputes the priority in the discovery, referring to the patent which he took out in 1942). The oxidative chlorophosphination of unsaturated hydrocarbons was first investigated by Soborovskii and coworkers[87].

The first step in the oxidative chlorophosphination of alkanes and alkenes is the addition of oxygen to phosphorus trichloride with formation of an adduct[88], which may be regarded as the biradical $Cl_3\dot{P}O\dot{O}$ [89,90] or the dipolar ion $Cl_3\overset{(+)}{P}O\overset{(-)}{O}$. In the absence of the hydrocarbon the adduct reacts with a second molecule of phosphorus trichloride, forming phosphorus oxychloride: $Cl_3\dot{P}O\dot{O} + PCl_3 \rightarrow 2POCl_3$. On the other hand, in the presence of the hydrocarbon the dichloride of alkyl- or chloroalkyl-phosphonic acid is formed as the final product:

$$Cl_3\dot{P}O\dot{O} + RH + PCl_3 \rightarrow RP(O)Cl_2 + POCl_3 + HCl,$$

$$Cl_3\dot{P}O\dot{O} + RCH{=}CH_2 + PCl_3 \rightarrow RC_2H_3Cl{-}P(O)Cl_2 + POCl_3.$$

The oxidative chlorophosphination of ethylene, propene, butene, and isobutene has been investigated[87]. When ethylene is used [with the molar ratio $PCl_3 : C_2H_4 = 1 : (3-15)$, at atmospheric pressure, and at a temperature between −140° and −110°C [91-94]], the dichloride of β-chloroethylphosphonic acid forms in yields of up to 80%. In this reaction the solvent may be methyl and ethyl chlorides, methylene chloride, carbon tetrachloride, chloroform, etc. When propene and butene are used in the reactions, a mixture of isomeric dichlorides of chloro-substituted alkylphosphonic acids, differing in the position of the chlorine atom and the $POCl_2$ group, is obtained[95]. There are two reasons for the formation of isomers in these reactions. There is a possibility of different sequences of addition of the chlorine atom and the $POCl_2$ group to the double bond of the olefin, or initially one of the hydrogen atoms of the methylene group is substituted by the $POCl_2$ group with subsequent addition of the resulting hydrogen chloride to the C=C bond. But-2-ene, which does not contain a methylene group, is an exception. Its oxidative chlorophosphination takes place only by the first pathway with formation of the dichloride of 2-chloro-1-methylpropylphosphonic acid. Despite the results of Isbell and Wadworth[96], Zinov'ev and Soborovskii[95] succeeded in isolating in the oxidative chlorophosphination of cyclohexene a mixture of isomeric dichlorides of chlorocyclohexylphosphonic acid. Apart from this mixture, the dichloride of cyclohexenylphosphonic acid formed, as a result of the elimination during distillation of hydrogen chloride from the dichlorides. The oxidative chlorophosphination of cyclohexane and cyclohexane was also studied by American workers[97]. The reactivity of cyclohexane proved to be higher by a factor of 2.3 than the reactivity of cyclohexane. The oxidative chlorophosphination of vinyl chloride, allyl chloride[98,99], 1,2-difluoroethylene, vinyl bromide, vinyl fluoride, 1,2-difluoroethylene, and vinylsulphonyl fluoride[100,101] takes place in most cases with formation of the dichlorides of dihalogeno-substituted alkylphosphonic acids. Their separation presents considerable difficulties but in some cases proved to be possible. Trichloroethylene and tetrachloroethylene do not enter into the oxidative chlorophosphination reaction. In the reaction with vinyl cyanide[102,103] a mixture of isomeric dichlorides of chlorocyanoethylphosphonic acids forms. In view of the impossibility of separating them by fractionation, they were converted into dimethyl esters. One of the esters proved to be liquid and the other crystalline. When oxygen was passed into a mixture of phosphorus trichloride and methyl acrylate[102], the dichloride of β-chloro-α-methoxycarbonylethylphosphonic acid was formed in high yield. In the dehydrochlorination of its esters with the aid of triethylamine, esters of α-alkoxycarbonylvinylphosphonic acid were obtained[104]. The dichloride of (triethylsilyl)chloroethylphosphinic acid was prepared in low yields by the oxidative chlorophosphination of triethylvinylsilane[105]. Acetylenic hydrocarbons react with phosphorus trichloride and oxygen without liberation of free hydrogen chloride[106]. The dichlorides of chloroalkenylphosphonic acids are then formed. The first member of the series (acetylene) reacts with the dichloride β-chlorovinylphosphonic acid to form the tetrachloride of dichloroethylenediphosphonic acid:

$$CH \equiv CH + 2PCl_3 + O_2 \rightarrow CHCl{=}CH{-}P(O)Cl_2 + POCl_3,$$

$$CHCl{=}CH{-}P(O)Cl_2 + 2PCl_3 + O_2 \rightarrow Cl_2\overset{O}{\overset{\|}{P}}{-}CHCl{-}CHCl{-}\overset{O}{\overset{\|}{P}}Cl_2.$$

The yields of the dichlorides, which are low for acetylene, increase for its homologues, hex-1-yne and phenylacetylene, reaching 24%. With vinylacetylene, the reaction takes place only at the triple bond:

$$CH_2{=}CH{-}C \equiv CH + 2PCl_3 + O_2 \rightarrow CH_2{=}CH{-}CCl{=}CH{-}P(O)Cl_2 + POCl_3.$$

Subsequent studies showed that methyl- and ethyl-dichlorophosphines[107,108], phenyldichlorophosphine[109], methyl phosphorodichloridite[110], and diethylaminodichlorophosphine[110] can enter into olefin oxidative chlorophosphination

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reactions. The reaction products in this case are mixed monochlorides of various acids based on pentavalent phosphorus.

III. REACTIONS OF THE CHLORIDES OF PHOSPHORUS(V) ACIDS WITH UNSATURATED COMPOUNDS

1. Reactions of the Chlorides of Phosphorus(V) Acids with Alkenes

A reaction of phosphorus pentachloride with unsaturated compounds was first described by Marsh and Gardner [111,112] in 1891–1894. They showed that camphene forms a complex compound with phosphorus pentachloride; its hydrolysis leads to camphenylphosphonic acid. In subsequent studies by Harnist [113], Bergman and Bondi [114-117], and other investigators [118-121] this reaction was extended to a large range of ethylenic and acetylenic hydrocarbons; the effect of their structure on the reactivity was established. These investigations were reviewed by Kabachnik [70] in 1947. In subsequent years new data accumulated, the range of application of this reaction was extended, and its mechanism was studied. Woodstock [122,123] and Kosolapoff [184] investigated the mode of addition of phosphorus pentachloride to asymmetric ethylenic hydrocarbons with a terminal double bond. Woodstock treated the complexes formed with phosphorus pentoxide or pentasulphide and obtained the dichlorides of chloroalkylphosphonic or chloroalkylphosphonothionic acids; he assumed that they had the structures $R-CH(POCl_2)CH_2Cl$ and $R-CH(PSCl_2)CH_2Cl$, and accordingly he postulated that the addition of phosphorus pentachloride to asymmetric ethylenes takes place contrary to the Markovnikov rule. Kosolapoff [121,124] showed that Woodstock's conclusions were erroneous. From the complex of phosphorus pentachloride with but-1-ene, he obtained the dichloride which he esterified and converted the product by dehydrochlorination into the ester of an unsaturated phosphonic acid. When this ester was ozonolysed, propionaldehyde was formed. Kosolapoff thus showed that the addition of phosphorus pentachloride to asymmetric olefins takes place in accordance with the Markovnikov rule:

$$RCH{=}CH_2 + 2PCl_5 \rightarrow RCHCl{-}CH_2PCl_4{\cdot}PCl_5$$

$$\xrightarrow[\text{or } SO_2]{P_2O_5 \text{ or } P_2S_5} \begin{cases} RCH{=}CH{-}PCl_2 \\ \| \\ O \end{cases} \qquad \begin{cases} RCH{=}CH{-}PCl_2 \\ \| \\ S \end{cases}$$

Dibromo- and tribromo-isosafrole [125] and also vinyl and allyl chlorides [126] (at 20°C in benzene) react with phosphorus pentachloride to yield only chlorination products, chlorine adding to the double bond. At 100–110°C under pressure vinyl and allyl chlorides give, together with their double-bond chlorination products, also halogenohydrocarbons with twice as many carbon atoms as the initial olefin.

Kirsanov and coworkers [127,128] made interesting studies on the structure of the complexes formed. Before their investigation, it was assumed (without experimental justification) that the complexes formed from phosphorus pentachloride and olefins are β-chloroalkyltetrachlorophosphoranes $RCHCl-CH_2PCl_4$ or their double salts with phosphorus pentachloride [129-133]. The complexes were not isolated in a pure form. Fedorova and Kirsanov [127,128] were the first to suggest that the reaction of phosphorus pentachloride, which consists in the crystalline state of the tetrahedral cation $P^{(+)}Cl_4$ and the octahedral anion $P^{(-)}Cl_6$, with unsaturated compounds takes place by an ionic mechanism:

$$RCH{=}CH_2 + \overset{(+)}{P}Cl_4 \rightarrow (RCH{-}CH_2PCl_4)^{(+)} \rightarrow HCl + (R{-}CH{=}CH{-}PCl_3)^{(+)} \xrightarrow{\overset{(-)}{PCl_6}} RCH{=}CH{-}\overset{(+)}{P}Cl_3 \cdot \overset{(-)}{P}Cl_6.$$

With styrene as an example, it was shown that the complex formed is $C_6H_5CH{=}CH{-}P^{(+)}Cl_3P^{(-)}Cl_6$. At 70°C its yield was about 70%. The structure of this complex is confirmed by reactions with sulphur dioxide, styrene, and red phosphorus:

$$C_6H_5CH{=}\overset{(+)}{C}HPCl_3 \cdot \overset{(-)}{P}Cl_6{-} \begin{cases} \xrightarrow{2SO_2} POCl_3 + 2SOCl_2 + C_6H_5{-}CH{=}CH{-}P(O)Cl_2 \\ \xrightarrow{C_6H_5CH=CH_2} HCl + 2C_6H_5CH{=}CH{-}PCl_4 \xrightarrow[SO_2]{P} \\ \xrightarrow{1\frac{1}{3}\,P} 2\tfrac{1}{3}\,PCl_3 + C_6H_5CH{=}CH{-}PCl_2 \end{cases}$$

Similar complexes were obtained in yields up to 70% when phosphorus pentachloride was allowed to react with the dichlorides of arylphosphonic acids:

$$ArPOCl_2 + 2PCl_5 \rightarrow POCl_3 + \overset{(+)}{ArP}Cl_3 \cdot \overset{(-)}{P}Cl_6.$$

On reduction with red phosphorus, they are converted into aryldichlorophosphines. It was shown, using the reaction of phenyltetrachlorophosphorane with styrene as an example [134], that hydrogen chloride formed in the reaction dissolves in phenylstyryltrichlorophosphorane and can be removed when the latter is reprecipitated from phosphorus oxychloride with petroleum ether or by vacuum distillation:

$$C_6H_5CH{=}CH_2 + C_6H_5\overset{(+)}{P}Cl_3 \rightarrow C_6H_5\overset{(+)}{C}HCH_2(C_6H_5)PCl_3 \xrightarrow{Cl^{(-)}}$$

$$\rightarrow HCl + C_6H_5CH{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}H{-}PCl_3.$$

Phenylacetylene reacts with phenyltetrachlorophosphorane by a similar mechanism, but the α-carbon atom in the initially formed cation $C_6H_5C^{(+)}{=}CH{-}P(C_6H_5)Cl_3$ is more firmly bound to the hydrogen, as a result of which the chloride ion adds to the most electropositive β-carbon atom:

$$C_6H_5\overset{(+)}{C}{=}CHP(C_6H_5)Cl_3 \xrightarrow{Cl^{(-)}} C_6H_5CCl{=}CH{-}P(C_6H_5)Cl_3.$$

In the reaction of styryltetrachlorophosphorane with styrene and of β-chlorostyryltetrachlorophosphorane with phenylacetylene [135], distyryltrichlorophosphorane and di-(β-chlorostyryl)trichlorophosphorane were obtained respectively:

$$C_6H_5CH{=}CH{-}PCl_4 + C_6H_5CH{=}CH_2 \rightarrow (C_6H_5CH{=}CH)_2PCl_3 + HCl,$$

$$C_6H_5CCl{=}CHPCl_4 + C_6H_5C{\equiv}CH \rightarrow (C_6H_5CCl{=}CH)_2PCl_3.$$

The structure of the complexes of phosphorus pentachloride with ethylenic hydrocarbons is consistent with the studies on their reduction. Walsh et al. [136] obtained alkenyldichlorophosphines by reducing complexes of olefins and phosphorus pentachloride with phosphorus in the presence of iodine:

$$3RCH{=}CHPCl_4 + 2P \xrightarrow{I_2} 3RCH{=}CHPCl_2 + 2PCl_3.$$

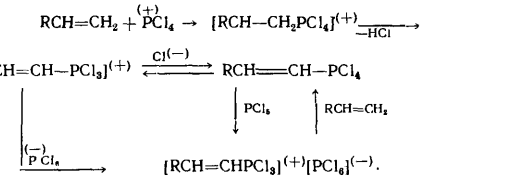
Kamai et al. [137] also obtained these compounds using antimony:

$$3(CH_3)_2C{=}CH_2 + 6PCl_5 \xrightarrow[-HCl]{} [(CH_3)_2C{=}\overset{(+)}{C}HPCl_3][PCl_6^{(-)}] \xrightarrow{4Sb}$$

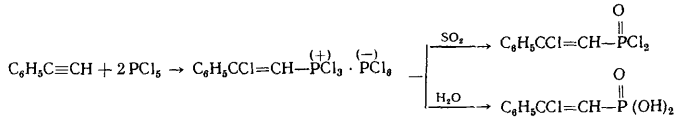
$$\rightarrow 4SbCl_3 + 3PCl_3 + 3(CH_3)_2C{=}CHPCl_2.$$

Grechkin and Kalabina regard the reaction between phosphorus pentachloride and olefins as electrophilic substitution of hydrogen, adopting a mechanism [138] very similar to

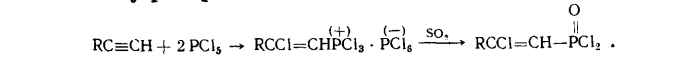
that proposed by Fedorova and Kirsanov. The authors[138] suggest that a π-complex of the olefin and the cation $P^{(+)}Cl_4$ forms initially and is then converted into a stable complex with elimination of hydrogen chloride: $[RCH{=}CH{-}PCl_3]^+$. The latter reacts with a chloride ion and is converted into an alkenyltetrachlorophosphorane or reacts with the ion $P^{(-)}Cl_6$ to form a saltlike product. It can also form in the reaction between the alkenyltetrachlorophosphorane and phosphorus pentachloride:



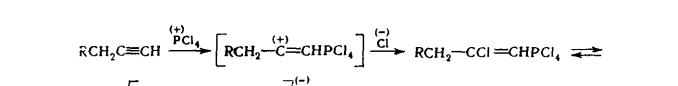
The reaction between phosphorus pentachloride and acetylenic hydrocarbons has been less investigated. The reaction of phenylacetylene[117,129] with phosphorus pentachloride yields a complex, which, after treatment with sulphur dioxide, gives rise to the dichloride of β-chloro-β-phenylvinylphosphonic acid, while on hydrolysis it is converted into β-chloro-β-phenylvinylphosphonic acid itself:



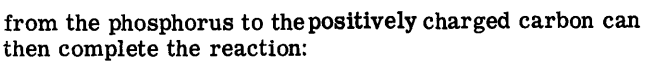
p-Nitrophenylacetylene, diphenylacetylene, and phenylethylacetylene do not react with phosphorus pentachloride[117]. However, Bergman and Bondi[117] succeeded in obtaining 2-chloro-3-phenylpropenylphosphonic acid from 1-phenylpropyne and phosphorus pentachloride. They explained this synthesis by postulating that initially 1-phenylpropyne isomerises to 3-phenylpropyne. By analogy with phenylacetylene, it was assumed that the ionic complexes and products obtained from alkynes[105,117] (5-ethoxy- and 5-phenoxy-pent-1-ynes[139]) and phosphorus pentachloride are vinylphosphine derivatives:



The position of the double bond was not determined. Meisters and Swan[140] observed in the NMR spectrum of the complex of oct-1-yne with phosphorus pentachloride an intense two-proton doublet (δ = 3.8 p.p.m., J = 17 Hz), indicating the presence of a CH_2 group bound to the phosphorus atom. They concluded that the ionic complexes and the substances obtained from them are allylphosphines and not vinylphosphine derivatives as was believed earlier. Not even traces of vinylphosphine derivatives were observed in any of the products even before their purification. The reaction with hexa-1,5-diyne involves only one acetylenic group. The authors assume that a rearrangement takes place after the electrophilic addition of $\overset{(+)}{P}Cl_4$ and then $\overset{(-)}{Cl}$ to the triple bond:



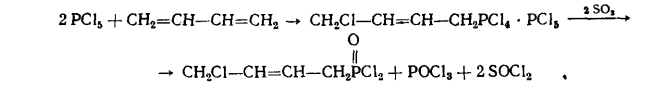
Alternatively they assume that a rearrangement may occur in the carbonium ion with formation of an intermediate allene derivative. The migration of the chlorine atom from the phosphorus to the positively charged carbon can then complete the reaction:



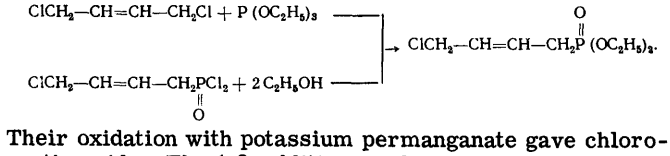
The new hypothesis which has been developed concerning the mechanism of the reactions of phosphorus pentachloride with unsaturated compounds permit certain conclusions about the reactivity of unsaturated hydrocarbons in these reactions. With increase of acidity in a series of unsaturated hydrocarbons, their phosphorylation with phosphorus pentachloride should be facilitated, and this is indeed observed.

2. Reactions of Phosphorus Pentachloride with Hydrocarbons Containing a Conjugated System of Double and Triple Bonds

The first information about the reaction of phosphorus pentachloride with the simplest hydrocarbon containing a conjugated system of double bonds (divinyl) was published by Kosolapoff[141] in 1946. The complex formed in the reaction was treated with alcohol and the resulting chlorobutenylphosphonic esters were dehydrochlorinated to butadienylphosphonic esters. According to Kosolapoff's data, a mixture of diethylbuta-dien-1-yl- and diethylbutadien-2-yl-phosphonates was obtained. On this basis, it was suggested that the initial addition of phosphorus pentachloride took place in positions 1, 2 and 1, 4. In the subsequent studies by Short[142,143] and also by Anisimov and Kolobova[144-146] it was asserted that the addition of phosphorus pentachloride to divinyl takes place in position 1, 2. It has been shown[147] that these data are erroneous. It has been demonstrated by infrared spectroscopy and by syntheses that the decomposition of the complex of phosphorus pentachloride and divinyl with sulphur dioxide yields the dichloride of 4-chlorobut-2-enylphosphonic acid:



The dialkyl esters of 4-chlorobut-2-enylphosphonic acid proved to be identical to those obtained in the reaction of 1,4-dichlorobut-2-ene with trialkyl phosphites:



Their oxidation with potassium permanganate gave chloroacetic acid. The 1,2-addition products could be present in the reaction mixture only as an impurity. The decomposition of the complex with hydrogen sulphide leads to the chloride of 4-chlorobut-2-enyl phosphonothionic acid. Butadienylphosphonic esters are very reactive compounds, which readily combine with nucleophilic reagents, enter into the diene synthesis reaction, and are capable of polymerisation and copolymerisation[148]. Isoprene[146,147] and 4-methylpenta-1,3-diene[148,149] react with phosphorus pentachloride to form 1,2-addition products. In the reaction of phosphorus pentachloride with phenylbutadiene in proportions of 1 : 3 and of phenyl- and styryl-tetrachlorophosphoranes with phenylbutadiene in proportions of 1 : 1, diphenylbutadienyltrichlorophosphorane, phenylbutadienyltrichlorophosphorane, and styrylbutadienyltrichlorophosphorane

are formed[150]. Vinylacetylene[151] and other hydrocarbons of this series, vinylethylacetylene[152], isopropenylacetylene[151,153], and ethynylcyclohexene[154], react with phosphorus pentachloride under mild conditions. The intermediate complexes were not isolated. They were immediately decomposed with sulphur dioxide. The dichloride of β-vinyl-β-chlorovinylphosphonic acid was obtained from vinylacetylene, the dichloride of β-cyclohexenyl-β-chlorovinylphosphonic acid was obtained from ethynylcyclohexene, and the dichloride of β-vinyl-β-chloro-α-ethylvinylphosphonic acid was obtained from vinylethylacetylene. It follows from these results that phosphorus pentachloride reacts with hydrocarbons of the vinylacetylene series to form products resulting from addition to the triple bond. Interesting results were obtained with isopropenylacetylene[153]. The final reaction product was the dichloride of 2-chloro-3-chloromethylbutadienylphosphonic acid together with 1,2,3,4-tetrachloro-3-methylbut-1-ene.

3. Reactions of the Chlorides of Phosphorus(V) Acids with Vinyl Ethers

This reaction, first described by Anisimov and Nesmeyanov[155], has attracted the attention of a large number of investigators in recent years. In a series of investigations Anisimov and Nesmeyanov showed that the reaction of phosphorus pentachloride with vinyl ethers yields complex compounds. The decomposition of these complexes with sulphur dioxide or with acetic acid results in the formation of the dichlorides of β-alkoxyvinylphosphonic acids[155-158].

$$RO{-}CH{=}CH_2 + 2\,PCl_5 \rightarrow RO{-}CHCl{-}CH_2PCl_4 \cdot PCl_5$$

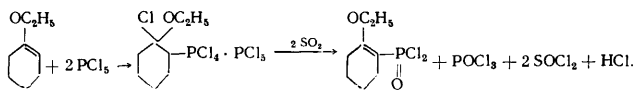
$$\xrightarrow{2\,CH_3COOH} ROCH{=}CHPCl_2 + POCl_3 + 2\,CH_3CCl + 3\,HCl$$

$$\xrightarrow{2\,SO_2} ROCH{=}CHPCl_2 + HCl + POCl_3 + 2\,SOCl_2.$$

A wide variety of alkyl vinyl ethers[144,155,156,158], monoalkyl vinyl ethers of ethylene glycol[157], and aryl vinyl ethers[144,159] were used in these reactions. β-Chloroethyl vinyl[160] and alkyl β-bromovinyl[161], ethers and vinyl sulphides[162] react similarly with phosphorus pentachloride. When the complexes are decomposed with hydrogen sulphide, the dichlorides of β-alkoxyvinylphosphonothionic acids are formed:

$$ROCHCl{-}CH_2PCl_4 \cdot PCl_5 + 2\,H_2S \rightarrow RO{-}CH{=}CH{-}\overset{S}{\overset{\|}{P}}Cl_2 + PSCl_3 + 5\,HCl.$$

Alkoxyvinylphosphonic and alkoxyvinylphosphonothionic esters, compounds which are very difficult to obtain by other methods, can be prepared in good yields by the esterification with alcohols of the dichlorides of β-alkoxyvinylphosphonic and β-alkoxyvinylphosphonothionic acids. When the ratio of the alkyl vinyl ethers to phosphorus pentachloride is 4 : 1, the chlorides of bis(β-alkoxyvinyl)phosphinic acid are obtained ultimately[163]. Arbuzov and coworkers carried out the reaction with phosphorus pentachloride of α-substituted vinyl ethers[164] and cyclic vinyl ethers with a double bond in the ring[165,166]. In these cases too the reactions take place in accordance with the general mechanism:



Apart from the decomposition of the complexes by various reagents, their reduction[167,168] and thermal decomposition[160] were investigated. When the complexes were treated with white phosphorus in the presence of iodine, β-alkoxyvinyldichlorophosphines were obtained, and the products of thermal decomposition were alkoxy-αβ-dichloroethyl vinyl ethers.

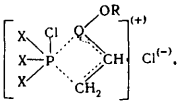
A number of studies have been made on phenyl- and alkyl-tetrachlorophosphoranes. Anisimov and Kolobova[169] studied the reaction of phenyltetrachlorophosphorane with ethyl vinyl ether. When the complex was treated with sulphur dioxide, the chloride of β-ethoxyvinylphenylphosphinic acid was formed, while treatment with white phosphorus in the presence of iodine gave β-ethoxyvinylphenylchlorophosphine. Similar results were obtained by Tsivunin et al.[170]. Thermal decomposition of the complex of phenyltetrachlorophosphine with n-butyl vinyl ether gives the chloride of β-chlorovinylphenylphosphinic acid[171]. In the thermal decomposition of the complex of ethyltetrachlorophosphorane with vinyl ethers[170,172], the same substance, the chloride of β-chlorovinylethylphosphinic acid, is formed regardless of the structure of the alkoxy-group:

$$CH_2{=}CH{-}OR + C_2H_5PCl_4 \xrightarrow{\Delta} C_2H_5\overset{O}{\overset{\|}{P}}(Cl){-}CH{=}CHCl + RCl + HCl.$$

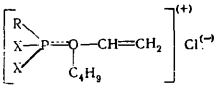
The reactions with diethyl and diphenyl-trichlorophosphoranes take place in an interesting way. Diethyltrichlorophosphorane forms with n-butyl vinyl ether a complex which has the structure of diethyl-α-chloroethoxydichlorophosphorane[173]:

$$(C_2H_5)_2PCl_3 + CH_2{=}CH{-}OC_4H_9 \rightarrow (C_2H_5)_2\overset{Cl}{\overset{|}{P}}(Cl){-}O{-}\overset{Cl}{\overset{|}{C}}H{-}CH_3 + (C_4H_8)_n.$$

Thermal decomposition of this complex leads to the chloride of diethylphosphinic acid. In the reactions of diphenyltrichlorophosphorane and triphenyldichlorophosphorane with n-butyl vinyl ether, diphenyl-α-chloroethoxydichlorophosphorane and triphenyl-α-chloroethoxychlorophosphorane were obtained respectively. It is suggested[173] that in these reactions the vinyl ether molecule forms with the phosphorus chloride a many-centre system due to the presence of the free *d*-orbitals of phosphorus and the conjugated system of $p\pi$-electrons (π-complex):



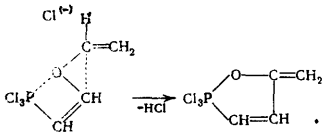
Compared with phosphorus pentachloride, the population of the $d\pi$-orbitals of phosphorus and chlorides of the type $RPCl_4$, R_2PCl_3, and R_3PCl_2 gradually decreases. This leads to an increase in the stability of the π-complexes:



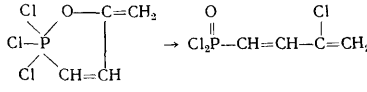
where X may be R or Cl. Their thermal decomposition leads to the formation of a large amount of the chlorides of alkylphosphonic or dialkylphosphinic acids.

The σ-stabilisation of the complexes is due to the formation of β-alkoxyvinylalkylchlorophosphoranes. These postulates were also used to account for the mechanism of the reaction of phosphorus pentachloride with divinyl ether[174,175]. The decomposition of the complex with hydrogen sulphide

leads to a crystalline product, the formation of which can be represented by the mechanism



When the product is heated, the dichloride of γ-chlorobutadienylphosphonic acid is formed:

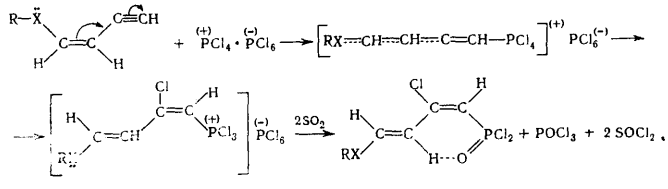


The structure of the cyclic product is consistent with PMR and NMR spectra.

Shostakovskii and coworkers[176-178], who investigated the reactions of phosphorus pentachloride with alkyl ethynylvinyl ethers and alkyl ethynylvinyl sulphides, initially suggested that they take place at the double bond with formation (after decomposition of the complexes with sulphur dioxide) of products with the structure

$$ROCH{=}C(POCl_2){-}CCl{=}CH_2 \text{ and } RSCH{=}C(POCl_2){-}CCl{=}CH_2.$$

Subsequently they showed that their initial hypotheses were erroneous[179]; the reaction takes place at the triple bond in accordance with the mechanism:



where X = O or S. The products are the dichlorides of 4-alkoxy(alkylthio)-2-chlorobuta-1,3-dienylphosphonic acids.

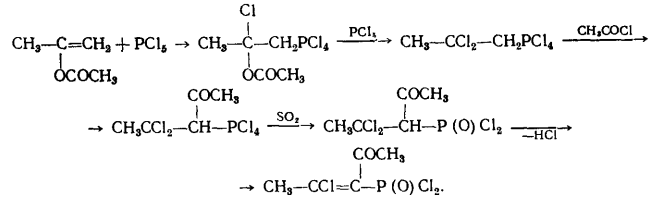
A very convenient method for the synthesis of the dichlorides of alkoxyvinylphosphonic acids or β-alkoxy-α-alkylvinylphosphonic acids has been recently developed by Petrov et al.[180] It is suggested that phosphorus pentachloride be allowed to react with ethers, which, after chlorination, are dehydrochlorinated and converted into vinyl ethers:

$$ROCH_2{-}CH_2R' + PCl_5 \xrightarrow{-HCl} ROCHCl{-}CH_2R' \xrightarrow{-HCl} RO{-}CH{=}CHR'.$$

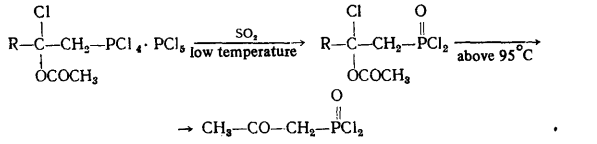
Subsequently the reaction takes place by the usual mechanism. When the complex is treated with hydrogen sulphide, the dichlorides of β-alkoxy-α-alkylvinylphosphonothionic acids are formed in yields up to 80%. This simple reaction makes it possible to obtain a number of interesting organophosphorus compounds.

4. Reactions of Phosphorus Pentachloride with Enol Esters

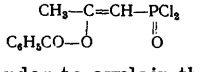
Lutsenko and Kirilov, who were the first to investigate reactions of this type, suggested that in the first stage the usual mechanism obtains; the addition product formed is then chlorinated by phosphorus pentachloride this being followed by reaction with acetyl chloride[181]: Treatment of the complexes with sulphur dioxide should yield the dichlorides of α-acetyl-ββ-dichloroalkylphosphonic acids:



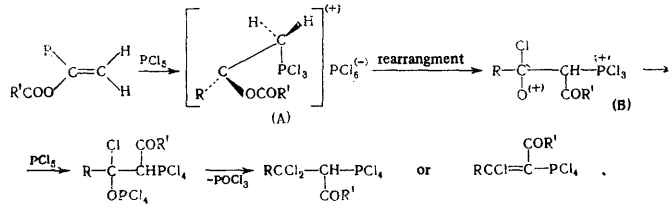
The authors isolated the initial complex at a low temperature. Its treatment with sulphur dioxide yields the dichlorides of β-acetoxy-β-chloroalkylphosphonic acids[182-184]. On heating, acetyl chloride is given off and the complex is converted into the dichloride of acetonylphosphonic acid:



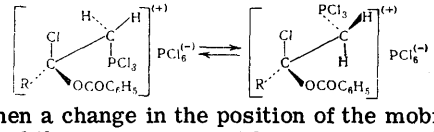
With the benzoate ester, evolution of hydrogen chloride from the complex and the ultimate formation of an unsaturated acid chloride were observed[185]:



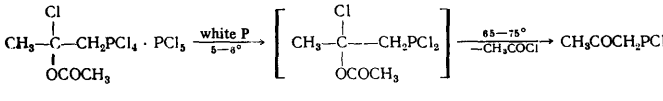
Subsequently, in order to explain the mechanism of the reaction of phosphorus pentachloride with enol esters, the authors suggested a new mechanism involving the intramolecular rearrangement of the complex formed initially[185-187]:



A proton is removed from the α-carbon atom in (A) by the anion $PCl_6^{(-)}$. The resulting dipolar ion (B) reacts with phosphorus pentachloride and is converted into the intermediate (C), which then breaks down the formation of the final products. When account is taken of the conformation of the intermediate complex (A), this mechanism can explain, for example , the unusual behaviour of isopropenyl benzoate in the reaction with phosphorus pentachloride. Because of the large size of the benzoyloxy- and PCl_3 groups, their *cis*-disposition in the complex is difficult; the conformation involving the *trans*-disposition of the groups is more favourable:



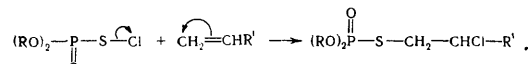
There is then a change in the position of the mobile hydrogen atom and the rearrangement becomes more difficult—the *trans*-elimination of hydrogen chloride becomes more probable. When the complexes (A) are reduced with white phosphorus at a low temperature (5–6°C), i.e. under conditions excluding the possibility of rearrangement, β-oxoalkyldichlorophosphine is formed[167]:



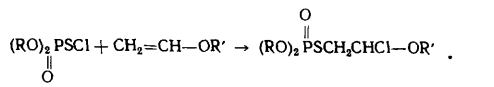
At a higher temperature (10–12°C), the reaction takes place in two ways–reduction and rearrangement. The products are then acetonyldichlorophosphine and the dichloride of α-acetyl-β-chloropropenylphosphonic acid.

5. Addition of Dialkoxyphosphinothiolic and Dialkoxyphosphinoselenolic Chlorides to Unsaturated Compounds

Dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides contain a very mobile halogen atom which ensures the ready addition of these compounds to a multiple carbon–carbon bond. Dialkoxyphosphinothiolic chlorides have been obtained by the action of chlorine or sulphuryl chloride on dialkyl phosphorothioates, trialkyl phosphorothionates, and bis(dialkoxyphosphinyl) disulphides. Diethoxyphosphinoselenolic chloride was obtained by the action of sulphuryl chloride on triethyl phosphoroselenoate[188]. Michalski and coworkers, who were the first to obtain compounds of this type, achieved their addition to a number of symmetrical and asymmetric hydrocarbons of the ethylene series: ethylene[189–192], propene[193], isobutene[194], tetramethylethylene[189], cyclohexene[188], styrene, and stilbene[195]. The reactions take place very readily when the gaseous hydrocarbons are passed through and liquid hydrocarbons are slowly added to the dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides at room or a lower temperature, usually in benzene solution. With asymmetric olefins, the mode of addition of the reagents is determined by their polarisation:



The yields of the addition products amount to 60–95%. Dialkoxyphosphinothiolic and dialkoxyphosphinoselenolic chlorides also add very readily to vinyl ethers[188,196,197] and vinyl sulphides[198]. In these reactions too the mode of addition is determined by the nucleophilic properties of the double bond with electron-donor alkoxy- or alkylthio-substituents:



Of the compounds with a conjugated system of double bonds, only divinyl has been used in the reaction with diethoxyphosphinothiolic chloride[199]. The 1,2-addition product is formed:



REFERENCES

1. M.S.Kharasch, E.V.Jensen, and W.H.Urry, J.Amer. Chem.Soc., **67**, 1864 (1945).
2. M.S.Kharasch, U.S.P. 2 489 091 (22.11.1949); Chem.Abs., **44**, 2009 (1950).
3. B.Fontal and H.Goldwhite, Chem.Comm., **6**, 111 (1965).
4. E.C.Ladd and J.R.Little, U.S.P. 2 510 699 (6.5.1950); Chem.Abs., **44**, 7348 (1950).
5. J.R.Little and P.E.Hartman, J.Amer.Chem.Soc., **88**, 96 (1966).
6. H.Trivedi, Bull.Acad.Sci.United Provinces Agra and Oudh Allahabad, India, **3**, 23 (1933); Chem.Abs., **28**, 1272 (1934).
7. E.Jungermann and J.J.McBride, J.Org.Chem., 26, 4182 (1961).
8. E.Jungermann, J.J.McBride, R.Clutter, and A.Mais, J.Org.Chem., **27**, 606 (1962).
9. J.J.McBride, E.Jungermann, J.V.Killheffer, and R.J.Clutter, J.Org.Chem., **27**, 1833 (1962).
10. E.Jungermann, J.J.McBride Jnr., R.Clutter, and A.Mais, Angew.Chem., **74**, 392 (1962).
11. W.B.McCormack, U.S.P. 2 663 737 (1953); Chem.Abs., **49**, 7601 (1955).
12. W.B.McCormack, U.S.P. 2 663 738 (1953); Chem.Abs., **49**, 7602 (1955).
13. B.A.Arbuzov and L.A.Shapshinskaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 65 (1962).
14. B.A.Arbuzov and L.A.Shapshinskaya, Symposium, "Khimiya i Primenenie Phosphoroorganicheskikh Soedinenii. Trudy II Konferentsii" (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the Second Conference), Izd.Akad.Nauk SSSR, Moscow, 1962, p.153.
15. B.A.Arbuzov and L.A.Shapshinskaya, Izv.Akad.Nauk SSSR, Ser.Khim., 581 (1964).
16. N.A.Razumova and A.A.Petrov, Zhur.Obshch.Khim., **31**, 3144 (1961).
17. N.A.Razumova and A.A.Petrov, Zhur.Obshch.Khim., **33**, 783 (1963).
18. N.A.Razumova and A.A.Petrov, Zhur.Obshch.Khim., **33**, 3858 (1963).
19. B.A.Arbuzov, L.A.Shapshinskaya, and V.M.Erokhina, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 2074 (1962).
20. B.A.Arbuzov, L.A.Shapshinskaya, and V.M.Erokhina, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 1820 (1965).
21. N.A.Razumova and A.A.Petrov, Zhur.Obshch.Khim., **34**, 1886 (1964).
22. N.A.Razumova and A.A.Petrov, Zhur.Obshch.Khim., **34**, 356 (1964).
23. I.G.M.Campbell, R.C.Cookson, and M.B.Hoching, Chem. and Ind., 359 (1962).
24. I.G.M.Campbell, R.C.Cookson, M.B.Hoching, and N.N.Hyghes, J.Chem.Soc., 2184 (1965).
25. N.A.Razumova and I.M.Treskunova, Zhur.Obshch.Khim., **34**, 2949 (1964).
26. G.M.Bogolyubov, N.A.Razumova, and A.A.Petrov, Zhur. Obshch.Khim., **33**, 3419 (1963).
27. G.Markl, Angew.Chem., **77**, 1109 (1965).
28. E.Howard, Jnr. and M.Braid, Diss.Abs., **23**, 434 (1962); Angew.Chem., **77**, 1109 (1965).
29. L.D.Quin and D.A.Mathewes, J.Org.Chem., **29**, 836 (1964).
30. U.Hasserodt, K.Hunger, and F.Korte, Tetrahedron, **19**, 1563 (1963).
31. H.Weikamp and F.Korte, Z.analyt.Chem., **204**, (4), 245 (1964).
32. B.A.Arbuzov and A.O.Vizel', USSR P. Application 820 601/23-4 (from 18th Feb., 1963); Referat.Zhur.Khim., 2N118P (1966).
33. B.A.Arbuzov and A.O.Vizel', Dokl.Akad.Nauk SSSR, **158**, 1105 (1964).
34. B.A.Arbuzov, A.O.Vizel', Yu.Yu.Samitov, and T.V.Zykova, Dokl.Akad.Nauk SSSR, **159**, 582 (1964).
35. B.A.Arbuzov, Yu.Yu.Samitov, A.O.Vizel', and T.V.Zykova, Dokl.Akad.Nauk SSSR, **159**, 1062 (1964).
36. K.Hunger, U.Hasserodt, and F.Korte, Tetrahedron, **20**, 1594 (1964).
37. K.Hunger and F.Korte, Tetrahedron Letters, 2855 (1964).
38. M.Green, J.Chem.Soc., 541 (1965).
39. L.D.Quin, I.P.Gratz, and R.E.Montgomery, Tetrahedron Letters, 2187 (1965).
40. A.A.Petrov, N.A.Razumova, and A.Kh.Voznesenskaya, Zhur.Obshch.Khim., **34**, 3512 (1964).
41. N.A.Razumova, A.A.Petrov, A.Kh.Voznesenskaya, and K.I.Novitskii, Zhur.Obshch.Khim., **36**, 244 (1966).
42. T.W.Campbell and J.J.Monagle, J.Amer.Chem.Soc., **84**, 1493 (1962).

43. T.W.Campbell, J.J.Monagle, and V.S.Foldi, J.Amer. Chem.Soc., **84**, 3673 (1963).
44. W.Fossek, Monatsh, **5**, 121 (1884); Chem.Zentr., 454 (1884).
45. W.Fossek, Monatsh, **5**, 627 (1884); Chem.Zentr., 88 (1885).
46. W.Fossek, Monatsh, **7**, 20 (1886); Chem.Zentr., 321 (1886).
47. A.Michaelis, Chem.Ber., **17**, 1273 (1884).
48. A.Michaelis, Chem.Ber., **18**, 898 (1885).
49. A.Michaelis, Chem.Ber., **19**, 1009 (1886).
50. A.Michaelis, Annalen, **293**, 193 (1896).
51. A.Michaelis and A.Flemming, Chem.Ber., **34**, 1291 (1901).
52. H.J.Page, J.Chem.Soc., **101**, 423 (1912).
53. J.B.Conant and A.D.MacDonald, J.Amer.Chem.Soc., **42**, 2337 (1920).
54. J.B.Conant, J.Amer.Chem.Soc., **43**, 1705 (1921).
55. J.B.Conant and B.B.Coyne, J.Amer.Chem.Soc., **44**, 2530 (1922).
56. J.B.Conant, J.B.S.Braverman, and R.E.Hyssey, J.Amer. Chem.Soc., **45**, 165 (1923).
57. J.B.Conant, A.D.MacDonald, and A.M.Kinney, J.Amer. Chem.Soc., **43**, 1928 (1921).
58. J.B.Conant, V.H.Wallingford, and S.S.Gandheker, J.Amer. Chem.Soc., **45**, 762 (1923).
59. J.B.Conant, J.Amer.Chem.Soc., **39**, 2679 (1917).
60. J.B.Conant and A.A.Cook, J.Amer.Chem.Soc., **42**, 830 (1920).
61. J.B.Conant and S.M.Pollack, J.Amer.Chem.Soc., **43**, 1665 (1921).
62. J.B.Conant, A.H.Bump, and H.S.Holt, J.Amer.Chem. Soc., **43**, 1677 (1921).
63. J.B.Conant and V.H.Wallingford, J.Amer.Chem.Soc., **46**, 192 (1924).
64. J.B.Conant and E.L.Jackson, J.Amer.Chem.Soc., **46**, 1003 (1924).
65. V.S.Tsivunin, G.Kamai, R.R.Shagidullin, and R.Sh.Khisamutdinova, Zhur.Obshch.Khim., **35**, 1998 (1965).
66. K.L.Freeman and M.J.Gallagher, Tetrahedron Letters, 121 (1966).
67. L.R.Drake and C.S.Marvel, J.Org.Chem., **2**, 387 (1937).
68. L.Anschutz, E.Klein, and G.Germark, Chem.Ber., **77**, 726 (1944).
69. N.I.Rizpolozhenskii, Symposium, "Nekotorye Voprosy Organicheskoi Khimii" (Some Problems of Organic Chemistry); Izd.Kazan.Gos.Univ., Kazan, 1964, p.122.
70. M.I.Kabachnik, Uspekhi Khim., **16**, 403 (1947).
71. M.I.Kabachnik and T.I.Medved', Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 540 (1952).
72. M.I.Kabachnik and E.S.Shepeleva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 185 (1951).
73. M.I.Kabachnik and E.S.Shepeleva, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 39 (1950).
74. M.I.Kabachnik and E.S.Shepeleva, Dokl.Akad.Nauk SSSR, **75**, 219 (1950).
75. N.A.Razumova and A.A.Petrov, Dokl.Akad.Nauk SSSR, **158**, 907 (1964).
76. V.S.Abramov, Dokl.Akad.Nauk SSSR, **95**, 991 (1954).
77. A.N.Pudovik, T.Kh.Gazizov, Yu.Yu.Samitov, and T.V.Zykova, Dokl.Akad.Nauk SSSR, **166**, 615 (1966).
78. V.K.Khairullin, USSR P. based on Application 913 555/23-4 (from 23rd July, 1964); Byull.Izobret., 16 (6th August, 1965).
79. V.K.Khairullin, Dokl.Akad.Nauk SSSR,162, 827 (1965).
80. V.K.Khairullin and R.R.Shagidullin, Zhur.Obshch.Khim., **36**, 289 (1966).
81. V.K.Khairullin and A.V.Pudovik, Zhur.Obshch.Khim., **36**, 494 (1966).
82. A.N.Pudovik, V.K.Khairullin, and T.I.Sobchuk, Izv.Akad. Nauk SSSR, Ser.Khim., 932 (1966).
83. V.K.Khairullin, T.I.Sobchuk, and A.N.Pudovik, Zhur. Obshch.Khim., **36**, 296 (1966).
84. V.N.Eliseenkov, A.N.Pudovik, and V.K.Khairullin, Izv. Akad.Nauk SSSR, Ser.Khim., 1582 (1966).
85. V.S.Tsivunin, G.Kamai, and S.Kh.Nurtdinov, Zhur.Obshch. Khim., **36**, 1223 (1966).
86. I.O.Clayton and W.L.Jensen, J.Amer.Chem.Soc., **70**, 3880 (1948).
87. L.Z.Soborovskii, Yu.M.Zinov'ev, and M.A.Englin, Dokl. Akad.Nauk SSSR, **67**, 293 (1949).
88. R.Graf, Chem.Ber., **85**, 9 (1952).
89. L.S.Soborovskii, Yu.M.Zinov'ev, and M.A.Englin, Dokl. Akad.Nauk SSSR, **73**, 333 (1950).
90. M.K.Baranov, Yu.M.Zinov'ev, T.K.Skripach, and L.Z.Soborovskii, Zhur.Obshch.Khim., **28**, 1628 (1958).
91. H.Vilcsek and F.Rochlitz, German P. 1 103 922 (1961).
92. F.Rochlitz and H.Vilcsek, German P. 1 108 687 (1962).
93. F.Rochlitz,and H.Vilcsek, Angew.Chem., **74**, 970 (1962).
94. C.Hauck, F.Rochlitz, H.Vilcsek, German P. 1 123 667 (1962).
95. Yu.M.Zinov'ev and L.Z.Soborovskii, Zhur.Obshch.Khim., **29**, 615 (1959).
96. A.F.Isbell and E.T.Wadworth, J.Amer.Chem.Soc., **78**, 6042 (1956).
97. F.R.Mayo, L.J.Durham, and K.S.Griggs, J.Amer.Chem. Soc., **85**, 3156 (1963).
98. L.Z.Soborovskii, Yu.M.Zinov'ev, and L.I.Muler, Dokl. Akad.Nauk SSSR, **109**, 98 (1956).
99. L.Z.Soborovskii, Yu.M.Zinov'ev, and L.I.Muler, Zhur. Obshch.Khim., **29**, 3947 (1959).
100. L.Z.Soborovskii, Yu.M.Zinov'ev, and T.G.Spiridonova, Zhur.Obshch,Khim., **29**, 1139 (1959).
101. Yu.M.Zinov'ev, T.G.Spiridonova, and L.Z.Soborovskii, Zhur.Obshch.Khim., **29**, 3594 (1959).
102. A.Ya.Yakubovich, L.Z.Soborovskii, L.I.Muler, and V.S.Faermark, Zhur.Obshch.Khim., **28**, 317 (1958).
103. R.I.Bystrova, Yu.M.Zinov'ev, and L.Z.Soborovskii, Zhur. Obshch.Khim., **24**, 380 (1954).
104. A.N.Pudovik and R.G.Kuzovleva, Zhur.Obshch.Khim., **35**, 354 (1965).
105. E.A.Chernyshev, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 96 (1958).
106. Yu.M.Zinov'ev, L.I.Muler, and L.Z.Soborovskii, Zhur. Obshch.Khim., **24**, 380 (1954).
107. Yu.M.Zinov'ev and L.Z.Soborovskii, Zhur.Obshch.Khim., **30**, 1571 (1960).
108. L.Z.Soborovskii and Yu.M.Zinov'ev, Zhur.Obshch.Khim., **24**, 516 (1954).
109. Yu.M.Zinov'ev and L.Z.Soborovskii, Zhur.Obshch.Khim., **26**, 3030 (1956).
110. Yu.M.Zinov'ev, V.N.Kulakova, and L.Z.Soborovskii, Zhur.Obshch.Khim., **28**, 1551 (1958).
111. J.E.Marsh, M.A.Balliol, and J.A.Gardner, J.Chem.Soc., **59**, 648 (1891).
112. J.E.Marsh and J.A.Gardner, J.Chem.Soc., **65**, 37 (1894).
113. C.Harnist, Chem.Ber., **63**, 2307 (1930).
114. E.Bergman and A.Bondi, Chem.Ber., **63**, 1158 (1930).
115. E.Bergman and A.Bondi, Chem.Ber., **64**, 1455 (1931).
116. E.Bergman and A.Bondi, Chem.Ber., **66**, 286 (1933).
117. E.Bergman and A.Bondi, Chem.Ber., **66**, 278 (1933).
118. W.Schlenk and E.Bergman, Annalen, **463**, 1 (1928).
119. C.M.Moureu and C.Difraisse, Bull.Soc.chim.France, [4], **43**, 1381 (1928).
120. L.Anschutz, F.Koenig, F.Otto, and H.Walbrecht, Annalen, **525**, 297 (1936).
121. G.M.Kosolapoff and W.F.Huber, J.Amer.Chem.Soc., **68**, 2540 (1946).

122. W.H. Woodstock, U.S.P. 2 471 472 (1949); Chem. Abs., **43**, 7499 (1949).
123. W.H. Woodstock, U.S.P. 2 495 799 (1950); Chem. Abs., **44**, 3517 (1950).
124. G.M. Kosolapoff and J.F. McCullough, J. Amer. Chem. Soc., **73**, 855 (1951).
125. P. Hoering and F. Baum, Chem. Ber., **41**, 1914 (1908).
126. Yu.M. Zinov'ev, V.N. Kulakova, and L.Z. Soborovskii, Zhur. Obshch. Khim., **27**, 151 (1957).
127. G.K. Fedorova and A.V. Kirsanov, Zhur. Obshch. Khim., **30**, 4044 (1960).
128. G.K. Fedorova and A.V. Kirsanov, Dopovidi Akad. Nauk Ukrain. RSR, **8**, 1086 (1960).
129. K.N. Anisimov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 803 (1954).
130. K.N. Anisimov and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 16 (1956).
131. E.N. Walsh, U.S.P. 2 685 603 (3.8.1954); Chem. Abs., **49**, 10 358 (1955).
132. W.H. Woodstock and E.N. Walsh, U.S.P. 2 685 602 (3.8.1954); Chem. Abs., **49**, 10 358 (1955).
133. H. Yoshioka and S. Horie, Jap. P. 11 823 (1962); Ref. Zhur. Khim., 2 N367 (1964).
134. G.K. Fedorova, Ya.P. Shaturskii, and A.V. Kirsanov, Zhur. Obshch. Khim., Problemy Organicheskogo Sinteza, 258 (1965).
135. G.K. Fedorova, Ya.P. Shaturskii, and A.V. Kirsanov, Zhur. Obshch. Khim., Problemy Organicheskogo Sinteza, 263 (1965).
136. E.N. Walsh, T.M. Beck, and W.H. Woodstock, J. Amer. Chem. Soc., **77**, 929 (1945).
137. G. Kamai, V.S. Tsivunin, and S.Kh. Nurtdinov, Zhur. Obshch. Khim., **35**, 1817 (1965).
138. E.F. Grechkin and L.V. Kalabina, Dopovidi Akad. Nauk Ukrain. RSR, **10**, 1354 (1963).
139. K.N. Anisimov and B.V. Kopylova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 277 (1961).
140. A. Meisters and J.M. Swan, Austral. J. Chem., **18**, 155 (1965).
141. G.M. Kosolapoff, U.S.P. 2 871 263 (1945); Chem. Abs., **40**, 1536 (1946).
142. J.N. Short, U.S.P. 2 818 406 (1957); Chem. Abs., **52**, 6407 (1958).
143. J.N. Short, U.S.P. 2 871 263 (1959); Chem. Abs., **53**, 11 225g (1959).
144. K.N. Anisimov and N.E. Kolobova, Symposium, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii. Trudy I Konferentsii" (The Chemistry and Applications of Organophosphorus Compounds. Proceedings of the First Conference), Izd. Akad. Nauk SSSR, Moscow, 1957, p. 232.
145. K.N. Anisimov and N.E. Kolobova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 923 (1956).
146. K.N. Anisimov and N.E. Kolobova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 927 (1956).
147. A.N. Pudovik and I.V. Konovalova, Zhur. Obshch. Khim., **31**, 1693 (1961).
148. A.N. Pudovik, I.V. Konovalova, and E.I. Ishmaeva, Zhur. Obshch. Khim., **33**, 2509 (1963).
149. G.B. Bachman and R.E. Hatton, J. Amer. Chem. Soc., **66**, 1513 (1944).
150. G.K. Fedorova and Ya.P. Shaturskii, Zhur. Obshch. Khim., **36**, 1262 (1966).
151. B.A. Vovsi, Yu.A. Sharanin, A.A. Petrov, L.K. Maslii, and T.V. Yakovleva, Nauch Dokl. Vys. Shkoly, Khim. i Khim. Tekhnol., No. 2, 335 (1958).
152. A.A. Petrov, Yu.I. Porfir'eva, and V.I. Savchenko, Zhur. Obshch. Khim., **29**, 4096 (1959).
153. K.N. Anisimov, G.M. Kunitskaya, and N.A. Slovokhotova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 64 (1961).
154. K.N. Anisimov and G.M. Kunitskaya, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 274 (1961).
155. K.N. Anisimov and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 610 (1954).
156. K.N. Anisimov, N.E. Kolobova, and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 796 (1954).
157. K.N. Anisimov, N.E. Kolobova, and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 799 (1954).
158. K.N. Anisimov and B.V. Raisbaum, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1208 (1958).
159. A.V. Kalabina and N.A. Dubovik, Izv. Fiz.-Khim. Inst. Irkutsk. Univ., **6**, 131 (1961).
160. V.S. Tsivunin, G. Kamai, and S.V. Fridland, Zhur. Obshch. Khim., **33**, 2146 (1963).
161. M.F. Shostakovskii, L.I. Shmonina, and I.M. Tikhomirova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2193 (1963).
162. K.N. Anisimov, N.E. Kolobova, and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 23 (1956).
163. G.K. Fedorova and A.V. Kirsanov, Zhur. Obshch. Khim., **35**, 1483 (1965).
164. B.A. Arbuzov, V.S. Vinogradova, N.A. Polezhaeva, and A.K. Shamsutdinova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 675 (1963).
165. B.A. Arbuzov, V.S. Vinogradova, and N.A. Polezhaeva, Dokl. Akad. Nauk SSSR, **137**, 855 (1961).
166. B.A. Arbuzov, V.S. Vinogradova, and N.A. Polezhaeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk., 71 (1962).
167. K.N. Anisimov and N.E. Kolobova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 442 (1962).
168. L.V. Foss, E.V. Kudinova, G.V. Postnikova, and I.S. Lutsenko, Dokl. Akad. Nauk SSSR, **146**, 1106 (1962).
169. K.N. Anisimov and N.E. Kolobova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 444 (1962).
170. V.S. Tsivunin, G.Kh. Kamai, and D.B. Sultanova, Zhur. Obshch. Khim., **33**, 2149 (1963).
171. V.S. Tsivunin, G.Kh. Kamai, R.Sh. Khisamutdinova, and A.M. Smirnov, Zhur. Obshch. Khim., **35**, 1231 (1965).
172. V.S. Tsivunin, G.Kh. Kamai, and G.K. Makeeva, Dokl. Akad. Nauk SSSR, **135**, 1157 (1960).
173. V.S. Tsivunin, G.Kh. Kamai, and R.Sh. Khisamutdinova, Dokl. Akad. Nauk SSSR, **164**, 594 (1965).
174. V.S. Tsivunin, G.Kh. Kamai, and S.V. Fridland. Zhur. Obshch. Khim., **36**, 436 (1966).
175. V.S. Tsivunin, S.V. Fridland, T.V. Zykova, and G.Kh. Kamai, Zhur. Obshch. Khim., **36**, 1424 (1966).
176. M.F. Shostakovskii, I.I. Guseinov, L.I. Shmonina, G.S. Vasil'ev, and B.V. Lopatin, Zhur. Obshch. Khim., **30**, 2836 (1960).
177. M.F. Shostakovskii, I.I. Guseinov, and G.S. Vasil'ev, Zhur. Obshch. Khim., **30**, 2832 (1960).
178. M.I. Batuev, L.I. Shmonina, A.D. Matveeva, and M.F. Shostakovskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 513 (1961).
179. G.S. Vasil'ev, E.N. Prilezhaeva, V.F. Bystrov, and M.F. Shostakovskii, Zhur. Obshch. Khim., **35**, 1350 (1965).
180. K.A. Petrov, M.A. Raksha, and V.L. Vinogradov, Zhur. Obshch. Khim., **36**, 715 (1966).
181. I.F. Lutsenko and M. Kirilov, Dokl. Akad. Nauk SSSR, **128**, 89 (1959).
182. I.F. Lutsenko, M. Kirilov, and G.B. Postnikova, Zhur. Obshch. Khim., **31**, 2034 (1961).
183. I.F. Lutsenko and M. Kirilov, Dokl. Akad. Nauk SSSR, **132**, 842 (1960).
184. I.F. Lutsenko and M. Kirilov, Godishnik Sofiisk. Univ., Fiz.-Mat. Fak., Book 3, 135 (1962); Referat. Zhur. Khim., 1Zh243 (1964).
185. I.F. Lutsenko and M. Kirilov, see Ref. 14, p. 237.

186. I. F. Lutsenko and M. Kirilov, Zhur. Obshch. Khim., 31, 3594 (1961).
187. I. F. Lutsenko and M. Kirilov, Godishnik Sofisk. Univ., Fiz.-Mat. Fak., Book 3, 165 (1962); Referat. Zhur. Khim., 3Zh290 (1964).
188. J. Michalski and A. Markowska, Dokl. Akad. Nauk SSSR, 136, 108 (1961).
189. J. Michalski and B. Lenard, Roczniki Chem., 30, 655 (1956).
190. B. Borecka, J. Michalski, and S. Musierowicz, Roczniki Chem., 32, 1301 (1958).
191. K. A. Petrov and A. A. Neimysheva, Zhur. Obshch. Khim., 29, 3030 (1959).
192. J. Michalski, B. Pliszka-Krawiecka, and A. Skoweronska, Roczniki Chem., 37, 1479 (1963).
193. B. Borecka, T. Kapecka, and J. Michalski, Roczniki Chem., 36, 87 (1962).
194. J. Michalski and J. Modro, Roczniki Chem., 35, 1537 (1961).
195. A. Markowska and J. Michalski, Roczniki Chem., 38, 1141 (1964).
196. J. Michalski and S. Musierowicz, Roczniki Chem., 36, 1655 (1962).
197. J. Michalski and S. Musierowicz, Chem. and Ind., 565 (1959).
198. D. William, U. S. P. 2 864 740 (16.12.1958); Ref. Zhur. Khim., 49106 (1960).
199. A. N. Pudovik and E. A. Ishmaeva, Zhur. Obshch. Khim., 36, 2080 (1965).

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The Concept of Electronegativity. Conclusions and Prospects†

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The principal methods for the determination of the electronegativity (EO) of the elements and radicals are examined—thermochemical, structural, spectroscopic, quantum-chemical, and a method based on ionisation potential. Particular attention is drawn to the necessity of taking into account the characteristic features of the chemical bond—its multiplicity and degree of hybridisation. The problems of the dimensions of the electronegativity of the elements are discussed. A compilation of the recommended electronegativities of atoms, radicals, and ions is given.
The principal applications of the concept of electronegativity are discussed: the determination of the atomic charges in molecules and crystals (good agreement between experimental and theoretical values is demonstrated); an estimate of the multiplicity of chemical bonds in inorganic ions and compounds, which agrees with the determination from the geometrical or spectroscopic characteristics of these substances; the principal physicochemical properties and the behaviour of inorganic substances as a function of the ionic character of their bonds and the difference between the electronegativities of the constituent atoms have been examined (semiconductor and molecular-physical characteristics, acid-base relations, specific features of the trans-effect of atoms in the inner sphere of platinum compounds, the possibility of the synthesis of new inorganic substances). The controversial questions of the nature and limits of applicability of the concept of electronegativity in general chemistry are briefly discussed.

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I. INTRODUCTION

More than one hundred years ago Berzelius[1] put forward the brilliant hypothesis concerning the electrical nature of chemical forces and divided all atoms into electropositive and electronegative. Lewis's theory gave rise to a concrete concept of polarity—regarded as the result of the displacement of the centre of gravity of the electron cloud of the bond towards one of the atoms, which is in fact electronegative in the given molecule.

More intensive experimental studies on polar molecules by various physical methods created the conditions for a new important scientific theory, whose author was Pauling[3]. The latter introduced into chemistry the concept of electronegativity (EO) defined as the capacity of the atom in a molecule (or in general in a compound) to attract valence electrons, and indicated an experimental method for its quantitative determination. This study gave rise to many other attempts to determine empirically the electronegativities of elements with the aid of geometrical, spectroscopic, and energy characteristics of atoms in molecules.

However, towards the beginning of the 1950's it became clear that the electronegativity of the element is not in most cases a constant property of the latter, but depends on the valence and degree of hybridisation of the bonds. Therefore special experimental and quantum-chemical investigations were begun in order to determine the electronegativity of atoms in various valence states and to find the electronegativities of whole groups of atoms (radicals).

The history of the development of the concept of electronegativity (up till 1961) is described in the present author's monograph[4] and the present review therefore considers mainly recent studies, which have made the greatest contributions to the theory and practical application of electronegativity in chemistry. Here too the principal conclusions following from the controversy on the meaning and limits of applicability of the concepts of electronegativity, which took place in recent years in the Soviet Union and to some extent abroad, will be described.

† In publishing this article, the Editorial Board consider it necessary to inform the readers that, although they do not agree with some of the author's views, the publication of the review is useful, since it will enable a wide circle of chemists to become familiar with the present state of the problem.