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Reactions of phosphorus(III) chlorides with carbonyl compounds

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ABSTRACT. The composition of the products of the interaction of phosphorus(III) chlorides with carbonyl compounds and the pathways leading to their formation are analysed as a function of the structure of the initial reactants and the experimental conditions. The catalytic role in the primary processes of the admixture of hydrogen chloride in phosphorus(III) chlorides is discussed. The influence of the functional group in substituted aldehydes and ketones and of the third reactant on the course of the reactions and on the nature of the final product is demonstrated.

The bibliography includes 231 references.

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I. Introduction

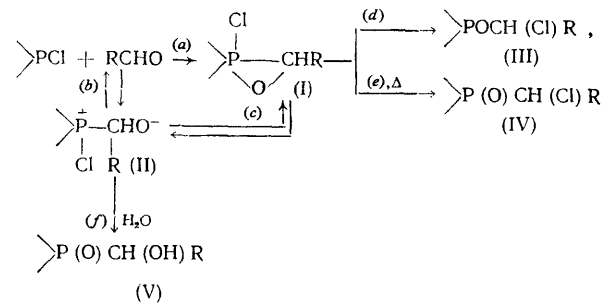
The reactions of phosphorus(III) chlorides with carbonyl compounds have already been discussed in reviews,[1,2] but the later of the two was published 20 years ago. Since then considerable advances have been made in the study of these reactions and a large amount of new scientific data, which have significantly altered many of our ideas about these reactions, has accumulated. The structure of the products of the interaction of phosphorus(III) chlorides with carbonyl compounds and the pathways leading to their formation depend very significantly on whether the reaction is carried out in the presence of a third reactant or in its absence. In the present review, attention is concentrated on the survey of literature data published during the last 20 years. The endeavour to demonstrate the evolution of views on the reactions considered led us to include in the review also certain studies from an early period.

II. Reactions of phosphorus(III) chlorides with carbonyl compounds in the absence of a third reactant

1. Aldehydes

More than 100 years ago, Fossek[3] established for the first time that phosphorus trichloride interacts vigorously with aldehydes to form thick oily adducts. Michaelis[4] attributed to them the structure of cylcophosphorane (I) (Scheme 1, pathway *a*), i.e. he postulated that the interaction proceeds with an increase in the coordination number of phosphorus. Conant[5] initially fully supported Michaelis's scheme but on the basis of kinetic studies he assumed the initial formation of a dipolar product (II) (pathway *b*)[6] capable of being converted into the phosphorane (I) (pathway *c*).

Scheme 1



Page,[7] Kabachnik,[1] and Atherton et al.[8] held a different view on the nature of the primary process. They assumed that phosphorus(III) chloride is an electrophile and that the coordination number of the phosphorus atom does not change in the primary process.

$$\text{>PCl} + \text{RCHO} \rightarrow \underset{\text{(III)}}{\text{>POCH (Cl) R}}.$$

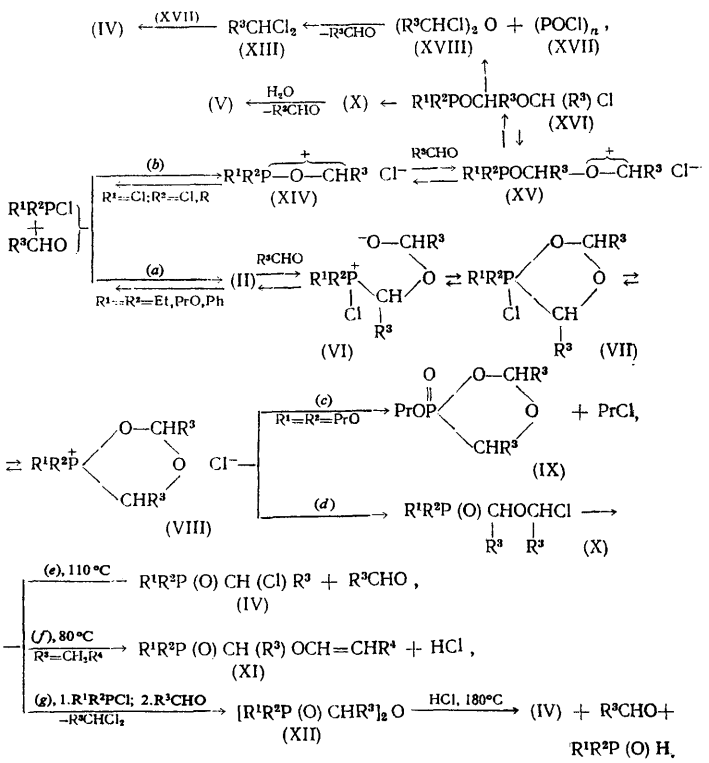
Pudovik and Khairullin[2] maintained the view that phosphorus(III) chlorides behave as nucleophiles in the primary step of the interaction and, taking into account new data,[1,7,8] supplemented the Michaelis–Conant mechanism by introducing into it the new pathways *d* and *e*. If the product of the direct interaction of phosphorus(III) chloride with an aldehyde is pyrolysed (pathway *e*) or is treated with water (pathway *f*), then stable α-chloroalkyl derivatives [compounds (IV)] and α-hydroxyalkyl derivatives [compounds (V)] of phosphorus(IV) are formed.[1,2,9–15]

On the basis of the structures of compounds (IV) and (V), the investigators assumed that only one aldehyde molecule is consumed in the formation of the product in the reaction of phosphorus(III)

chloride with aldehydes. However, since the 1970's, studies have been published indicating the consumption of two aldehyde molecules per P–Cl bond.[16–21] From the character of the effect of the nature of the substituents in phosphorus(III) chlorides and aldehydes on the rate of reaction, it was concluded that PCl_3 and $RPCl_2$ exhibit electrophilic[16–19,22–24] reactivity, while R^1R^2PCl and $(R^1O)(R^2O)PCl$ exhibit nucleophilic activity.[16,17,20] Thus the interaction of secondary chlorophosphines with benzaldehydes affords the salts (VIII), which are then converted via the Arbuzov reaction into compounds (X) (Scheme 2, pathways *a* and *d*),[24] while the interaction of chlorodiphenylphosphine with aliphatic polyfluoroaldehydes gives rise to the stable phosphoranes (VII).[20] The phosphorane (VII) with $R^1 = R^2 = PrO$ is stabilised as a result of the elimination of propyl chloride with retention of the 1,4,2-dioxaphospholan ring (IX) (pathways *a* and *c*). The formation of compounds (VII) and (VIII) can probably be represented in the following way: as a result of the nucleophilic attack by the lone pair of phosphorus(III) on the carbon atom of the carbonyl group, the dipolar ion (II) is formed and combines with a second aldehyde molecule, being converted into a new dipolar ion (VI). The latter is sterically more favourable for the formation of the phosphorane structure (VII) compared with the ion (II).

At 80 °C, compound (X) is dehydrochlorinated to the product (XI) (pathway *f*),[18] while at 110 °C it splits off an aldehyde molecule and is converted into the familiar compound (IV) (pathway *e*).[23] The phosphine oxide (X) also readily reacts with chlorodiphenylphosphine and an aldehyde, affording the alkylidine chloride (XIII) and the ether (XII) (pathway *g*). The pyrolysis of the latter in the presence of HCl leads, as in the case of the product (X), to compound (IV).[16]

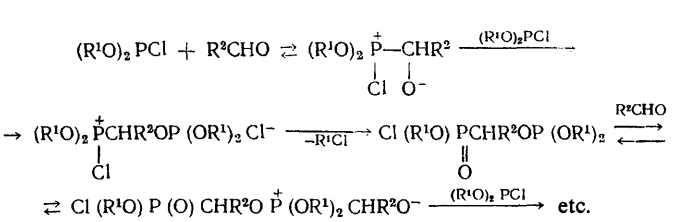
Scheme 2



In the case of phosphorus(III) chlorides exhibiting electrophilic properties, the primary products apparently arise from the exchange of chlorine atoms at the phosphorus(III) for a new group[16] and are formed as a result of the nucleophilic attack by the oxygen atom of the carbonyl group on the phosphorus(III) atom, which leads to the ion pair (XIV) (pathway *b*). The cation (XIV), whose stability is enhanced by the delocalisation of the charge, combines with the next aldehyde molecule, affording the new ion pair (XV). Compounds (XV) and (XVI) are converted into the product (X) via a stage involving the formation of a quasi-phosphonium salt of type (VIII). Compound (X) readily gives rise to the α-hydroxyalkyl derivative (V) of phosphorus(IV) on treatment with water and can also react chemically via pathways *e* and *f*.[18]

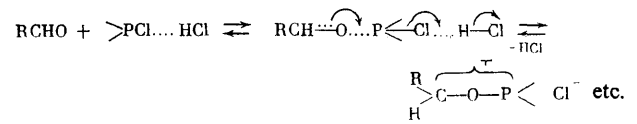
In later studies,[22,23] the isolation of compounds (XIII) and (XVIII) after the reaction of PCl_3 with benzaldehyde led to the hypothesis that the phosphorus-containing product (XVII) is formed and reacts with benzylidene chloride (XIII) via the mechanism of the Arbuzov reaction. The structure of compound (XVII) was not demonstrated rigorously and it is also difficult to postulate the interaction of a compound having a P(III)–Cl bond with a weak electrophile such as benzylidene chloride. It has still not been elucidated from what intermediate are the ethers (XVIII) formed directly under mild conditions. However, it is entirely possible that it is a compound containing one or several 1-(1'-chloroalkoxy)-alkoxy-groups at the phosphorus atom. One should also note that, in the interaction of formaldehyde (paraformaldehyde) with phosphorus(III) chloride, the formation of organophosphorus compounds with $POCH_2OCH_2Cl$ and $P(O)CH_2OCH_2Cl$ structural fragments has not so far been confirmed experimentally, although the detection or isolation of the ether (XVIII, $R^3 = H$) after this reaction has been frequently reported.[9,25–27]

The manifestation by dialkyl phosphorochloridites of both nucleophilic and electrophilic properties at different stages of the reaction with aldehydes has been assumed in some investigations:[27,28]

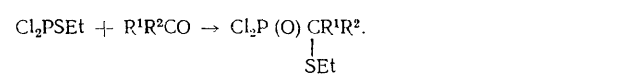


The demonstration of the catalytic effect of the HCl impurity in phosphorus(III) chlorides on the course of the reactions considered is extremely important.[29,30] It was found that phosphorus(III) chloride freed from the HCl impurity by treatment with alkyl vinyl ethers (AVE) does not interact with an aldehyde at 20 °C. The process begins only after the introduction of HCl into the reaction mixture. The catalytic effect of the HCl impurity had been detected previously in the reaction of phosphorus(III) chlorides with alkene oxides,[31,32] carboxylic acids,[33] and acetals.[34,35] The catalytic role of the HCl impurity in phosphorus(III) chlorides in exchange reactions is also emphasised in a recent review.[36] The catalytic role of HCl in the interaction of aldehydes with phosphorus(III) chlorides can be

reflected by a mechanism analogous to that of the reactions of the latter with alkene oxides and acetals:

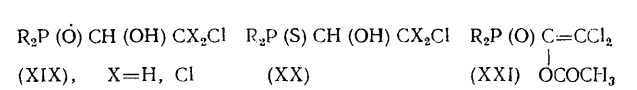


The nature of the phosphorus(III) chloride can alter radically the mode of its interaction with carbonyl compounds. It has been shown recently that ethyl phosphorodichloridothioate reacts with benzaldehyde and acetone via the P–S bond and not with participation of the P–Cl bond.[37,38]



The interaction of phosphorus(III) chlorides with aldehydes containing functional groups as substituents has also been investigated. Thus mercurated acetaldehyde reacts with phosphorus(III) chlorides to form *O*-derivatives, i.e. the reaction takes place with transfer of the reaction centre.[39]

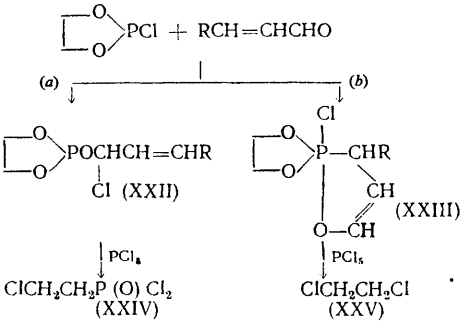
It has been suggested that secondary chlorophosphines exhibit nucleophilic reactivity in their reactions with α-chloroaldehydes and that an adduct having the betaine structure (II) is formed.[2,40,41] In order to obtain the individual compounds (XIX)–(XXI), the R_2PCl + $X_2ClCCHO$ reaction mixture is treated with proton-donating compounds or acetic anhydride.



However, one should note that the possibility of the initial interaction of various secondary chlorophosphines with chloroaldehydes has not been confirmed experimentally, while the products (XIX)–(XXI) can be formed as a result of the initial hydrolysis of the chlorophosphines to the corresponding acid and the addition of the latter to the carbonyl group of the aldehyde. A structure analogous to that that of compound (III) has been attributed[42] to the product of the interaction of chloral with 2-chloro-1,3,2-dioxaphospholan, but adequate evidence for this has not been adduced.

2-Chloro-1,3,2-dioxaphospholan reacts vigorously with acroleine and crotonaldehyde to form oligomers (Scheme 3).[43] On the basis of the structure of the products (XXIV) and (XXV) obtained after treating the oligomers with phosphorus pentachloride, the authors concluded that the 1,2-addition of the chloride to the carbonyl group with dissociation of a P–Cl bond mainly takes place, i.e. a chlorine atom at the phosphorus(III) atom is exchanged for a new group [pathway *a*, compound (XXII)]. The partial 1,4-addition of the phosphorus atom to the conjugated system without the rupture of a P–Cl bond and with increase in the coordination number of phosphorus from 3 to 5 has also been postulated [pathway *b*, compound (XXIII)].

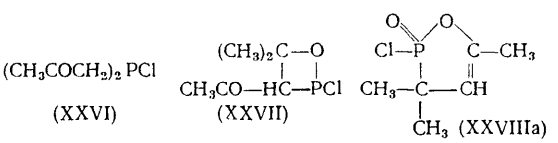
Scheme 3



It seems to us that the interaction of phosphorus(III) chlorides with unsaturated aldehydes has still been studied inadequately and that more far reaching studies are necessary to establish the real reaction mechanism.

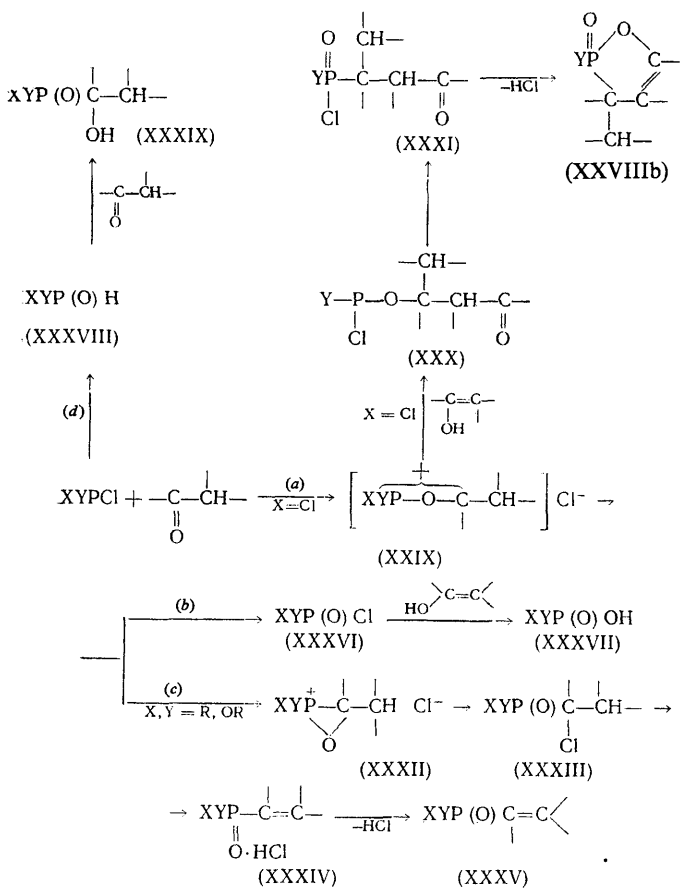
2. Ketones

In the past century, Michaelis[1,2] already established that in the presence of aluminium trichloride PCl_3 and $RPCl_2$ condense with acetone in proportions of 1 : 2. The acyclic structure (XXVI) was attributed initially to the reaction product, which has come to be called "the Michaelis chloride" in the literature. Later the cyclic structure (XXVII) was assigned to it. Much later, in the study of the reactions of phosphorus(III) chlorides with unsaturated ketones, it was possible to show that the product has the structure of 2-chloro-2-oxo-1,2-oxaphospholene (XXVIIIa).[44]



During the last 15 years, it has been found that aliphatic and aliphatic-aromatic ketones react with phosphorus(III) chlorides also in the absence of $AlCl_3$ but on heating. The products of the reactions of PCl_3 and phosphorus(III) dichlorides are derivatives of 1,2-oxaphospholene (XXVIIIb) (Scheme 4, pathway *a*).[13,45–50]

Scheme 4

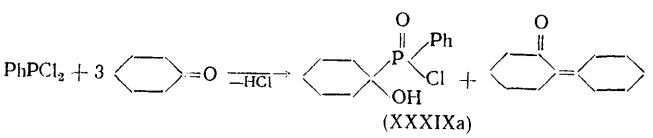


The authors suggest that the primary process is the exchange of a chlorine atom at the electrophilic phosphorus(III) atom (Scheme 4, pathway *a*). The ion pair (XXIX) reacts with the enolic form of the ketone, affording a γ-ketoester chloride of phosphorus or phosphonous acid (XXX), which isomerises to the phosphorus(IV) derivative (XXXI) capable of cyclisation, with elimination of HCl, to the final product (XXVIIIb). If cyclohexanone is used as the ketone, then a polycyclic compound is formed and this too is a substituted 1,2-oxaphospholene.[51]

The formation of the intermediate compound (XXXI) was confirmed by IR spectroscopy and NMR. In the studies indicated, the question of the pathways leading to the transition (XXX) → (XXXI) was not discussed. It is entirely possible that compound (III) decomposes into partial phosphorus acid chloride and an unsaturated ketone, which interact, affording the product (XXXI). HCl probably favours such decomposition.

Chlorodiethyl- and chloroethylphenyl-phosphines and phosphorochlorodites react with ketones,[50–53] including cyclic ketones,[53–56] in proportions of 1:1 to form α-chloroalkyl derivatives of phosphorus(IV) (XXXIII) (Scheme 4, pathways *a* and *c*), which split off HCl on heating or on treatment with a base and are converted into the unsaturated compounds (XXXIV) and (XXXV). It has been noted[53–57] that, in the interaction of secondary chlorophosphines with cyclohexanone, it was possible to detect by NMR the intermediate (XXXII) and to convert it into the more stable tetraphenylborate derivative. In the case of secondary chlorophosphines, the initial nucleophilic attack by the oxygen atom of the carbonyl group on the phosphorus(III) atoms has also been postulated. This entails the formation of the exchange product (XXIX), which is rapidly converted into compound (XXXII). However, one should note that, as for the reactions with aldehydes, there is a possibility that the secondary chlorophosphines may manifest nucleophilic properties, i.e. compound (XXXII) may be formed from the dipolar ion (II).

In contrast to other phosphorus(III) chlorides, chlorodiphenylphosphine reacts with acetone via pathway *b* (Scheme 4). When acted upon by the enolic form of the ketone, the acid chloride (XXXVI) is converted into the acid (XXXVII).[57] It reacts with cyclohexanone in an even more complex manner—via the three pathways *b*, *c*, and *d*—and compounds (XXXIII), (XXXVII), and (XXXIX) are isolated from the reaction mixture. The interaction of dichlorophenylphosphine with cyclohexanone also proceeds via pathway *d*. In this reaction, the initial reactants are consumed in proportions of 1:3.[58]



The reactions of cyclopentanone with dichlorophosphines and of cyclohexanone with phenyl phosphorodichloridite and dichloro-*p*-fluorophenylphosphine proceed via pathway *c* and the reaction products are cyclopentenyl and cyclohexenyl derivatives of phosphorus(IV) (XXXV).[13,59,60]

The reactions of phosphorus(III) chlorides with ketones having a second functional group have also been studied. For example, they interact in a fairly complex way with the hydroxyketones (XL). The structure of the final reaction product depends significantly both on the experimental conditions and on the nature of the substituents in the initial reactants. Whether or not triethylamine is present in the reaction mixture is an important factor.

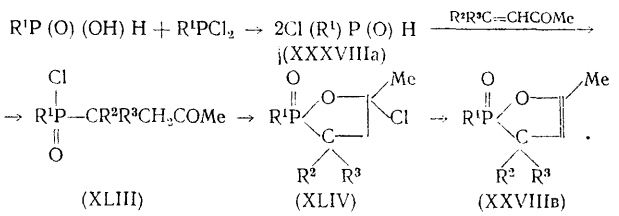
In the absence of a base, all the phosphorus(III) chlorides induce the rapid catalytic decomposition of β-ketoalcohols into αβ-unsaturated ketones (XLI) and water.[61–69]

$$\underset{\text{(XL)}}{CH_3C(O)CH_2CR^1R^2OH} \xrightarrow{>PCl} \underset{\text{(XLI)}}{CH_3C(O)CH{=}CR^1R^2} + H_2O.$$

Further reactions, leading to the final products, are therefore treated within the framework of reactions of unsaturated ketones with phosphorus(III) chlorides in the presence of water. The latter hydrolyses the phosphorus(III) chlorides to the corresponding acids XYPHO (XXXVIII) (X = Y = R, RO, Ar; X = OH, Y = R, RO, Ar; X = Y = OH). Acetic acid acts similarly on phosphorus(III) chlorides,[69,70] but the process is reversible. The acids (XXXVIII) exhibit different reactivities in relation to ketones (XLI); phosphinous acids add to the double bond, forming tertiary phosphine oxides (XLII), while the remaining acids are fairly inert under the conditions of the reaction considered.

$$\underset{\text{(XLI)}}{R^1R^2P(O)H} + \underset{}{R^3R^4C{=}CHC(O)CH_3} \rightarrow \underset{\text{(XLII)}}{R^1R^2P(O)CR^3R^4CH_2C(O)CH_3}.$$

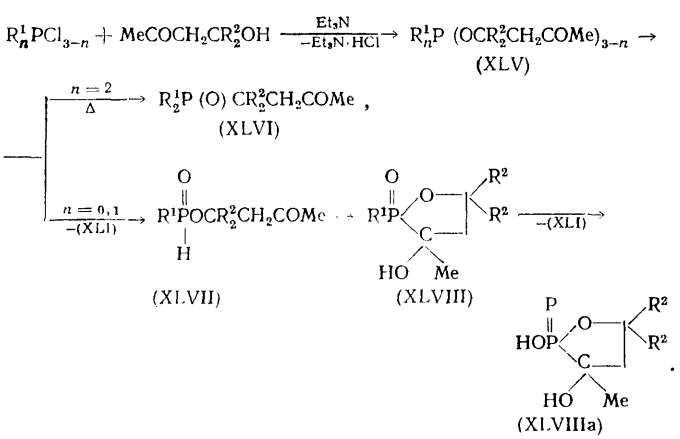
Dialkylphosphorous acids can be isolated in a pure form. Alkylphosphorous, phosphonous, and phosphorous acids react readily with phosphorus(III) chlorides, forming chemically extremely reactive partial acid chlorides (XXXVIIIa). The interaction of the latter with ketones (XLI) leads to Δ^4-1,2-oxaphospholenes (XXVIIIc). The formation of the intermediates (XLIII) and (XLIV) was demonstrated not only by spectroscopic methods but also by isolating them, for certain substituents R^1, R^2, and R^3, in a pure form. The claim that the 1,2-oxaphospholene systems are formed as a result of intermolecular and intramolecular nucleophilic substitution at the phosphorus(III) atom[71] in the reactions considered is controversial.



(XLIII) (XLIV) (XXVIIIв)

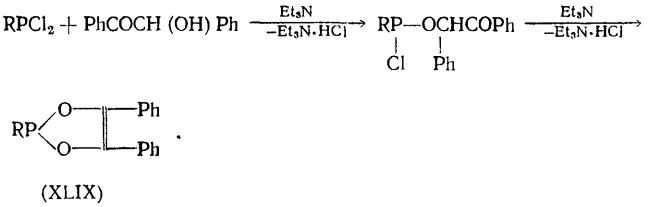
Without exaggeration, one can now claim that the idea of the chemists of the Kazan School that β-ketoalcohols undergo catalytic decomposition to an unsaturated ketone and water and that the phosphorus(III) chloride interacts initially with water and not with the carbonyl compounds, as well as the idea that the partial acid chlorides (XXXVIIIa) are formed as intermediates were fully confirmed in subsequent studies[70] and constitute a major contribution to the theory of the reactions of phosphorus(III) chlorides with all aldehydes and ketones in the presence of proton-donating compounds, whose investigation was initiated more than a century ago.

In the presence of triethylamine, the character of the reaction of phosphorus(III) chlorides with hydroxyketones is completely different: the primary process involves the hydroxy-group without altering the coordination number of the phosphorus atom.[69,72–78] If the exchange products (XLV) contain only one γ-ketoalkoxy-group, then on heating they rearrange to the phosphorus(IV) derivatives (XLVI);[73,77] if there are two such groups, then an unsaturated ketone is split off and the acid (XLVII) cyclises to the oxaphospholan (XLVIII).[69,72–76,79] If there are three such groups, then yet another ketone (XLI) molecule is eliminated[69] and the oxaphospholanol (XLVIIIa) is formed:



(XLVII) (XLVIII) (XLVIIIa)

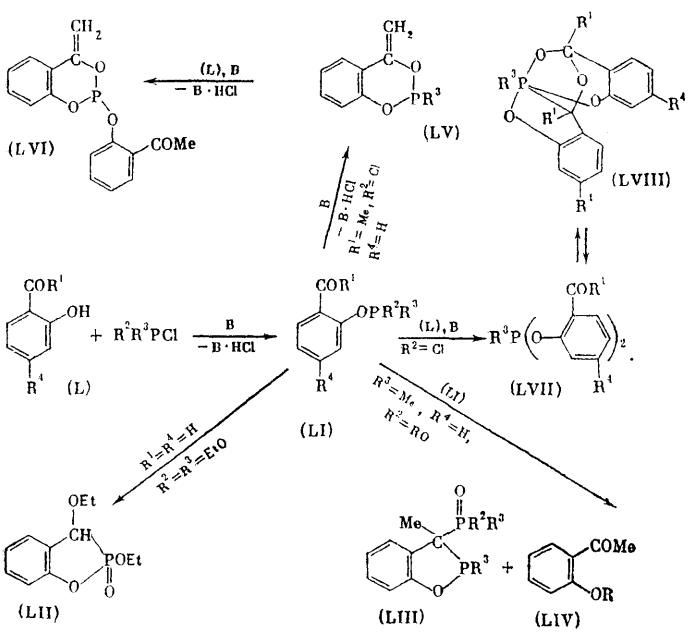
The products of the reactions of benzoin with phosphorus(III) di- and tri-chlorides are unsaturated phosphorus(III) derivatives (XLIX) formed as a result of the primary exchange and subsequent cyclisation.[80,81]



(XLIX)

Phosphorus(III) chlorides interact in a very complex manner with *o*-carbonylphenols (L). The subsequent reactions of the primary products (LI) depend on the nature of the groups R^1, R^2, R^3, and R^4 and the experimental conditions. The products are the most stable in the case of phosphorus(III) monochlorides.[82,83] However, when R^1 = H, heterocyclisation proceeds readily as a result of the attack by the lone pair the phosphorus(III) atom on the carbon atom of the carbonyl group and compound (LII) is formed (Scheme 5).[84]

Scheme 5



Compounds (LIII) and (LIV) are the products of the slow interaction of two (LI, R^1 = Me) molecules. In the presence of a base (B), compound (LI, R^2 = Cl) is converted into the products (LV) and (LVII) as a result of intramolecular (R^3 = RO, Cl)[82,83,85] or intermolecular (R^3 = alkyl, aryl)[82,85–88] nucleophilic substitution. When R^3 = Cl, the product (LV) can enter into an exchange reaction with formation of compound (LVI).[85] Compounds (LVII)

are entirely stable if R^4 is the sterically bulky 2,4,5,6-tetramethylphenyl group or if the electrophilicity of the carbonyl group is reduced (R^1 = OMe).[86] In the absence of these factors, compounds (LVII) are converted into the cyclic phosphoranes (LVIII) as a result of oxidative cyclisation.[85–88] When R^1 = 2,4-$Me_2C_6H_3$ and R^4 = OMe, the phosphorane (LVIII) is in equilibrium with the phosphonous form.[86]

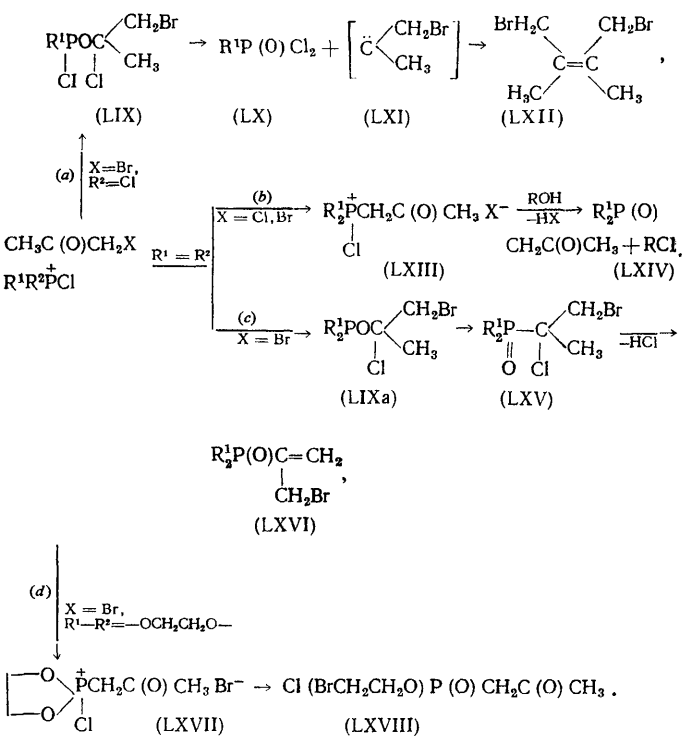
The interaction of salicylaldehyde with PCl_3 under severe conditions (high temperatures) leads to 2,3-dichloro-2-oxo-4,5-benzo-1,2-oxaphospholan.[89,90]

Metal derivatives of ketones react readily with phosphorus(III) chlorides. Thus the latter react with α-mercurated ketones with transfer of the reaction centre and the formation of unsaturated esters.[91]

The influence of the nature of the substituents at the phosphorus(III) on the mode of interaction can be traced in relation to the reactions of phosphorus(III) chlorides with trialkylstannylacetone:[91] PCl_3 and the secondary chlorophosphines react without transfer of the reaction centre, phosphorochloridites and phosphorodichloridites react with transfer of the reaction centre, while phosphonous ester chlorides afford a mixture of *O*- and *C*-phosphorylated products.

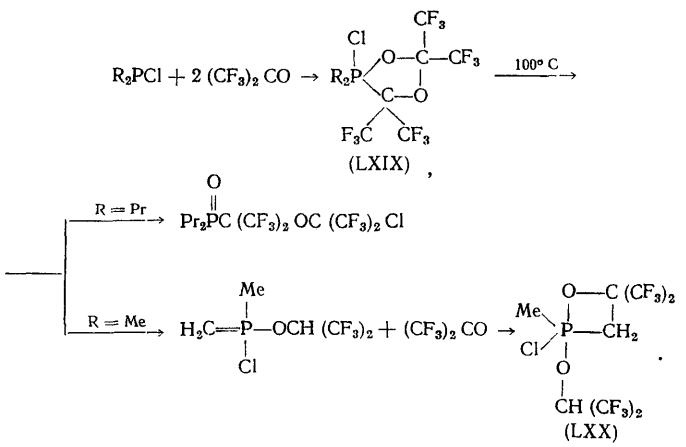
Depending on the nature of the substituents at the phosphorus(III) atom, phosphorus(III) chlorides can interact with α-monohalogenoketones both at the α-carbon atom and at the carbonyl group.[92–95] The reaction of phosphorus(III) dichlorides with bromoacetone results in the formation of phosphorus(IV) dichlorides (LX) and the dibromoalkene (LXII) (Scheme 6).[92] It has been suggested that phosphorus(III) dichlorides exhibit electrophilic properties and that initially a chlorine atom at the phosphorus(III) atom is substituted by a new group [pathway *a*, compound (LIX)]. Compound (LIX) then decomposes at the C–O bond with formation of the dichloride (LX) and the carbene (LXI), which dimerises to the alkene (LXII). Secondary chlorophosphines react with α-halogenoketones via two pathways:[93–95] in the first pathway, phosphorus(III) combines with halogenoacetone (nucleophilic properties) to form the phosphonium salt (LXIII), which can be isolated in a pure form[94] or can be converted into the phosphine oxide (LXIV) on treatment with alcohols,[93,95] water, or acetaldehyde[95] (pathway *b*); in the other pathway, a chlorine atom at the phosphorus(III) atom is substituted by a new group (electrophilic properties) with formation of the intermediate (LIXa), which subsequently isomerises to the phosphorus(IV) derivative (LXV); the latter is dehydrochlorinated, affording the product (LXVI) (Scheme 6, pathway *c*). 2-Chloro-1,3,2-dioxaphospholan (R^1–R^2 = $-OCH_2CH_2O-$) exhibits nucleophilic properties, combining with bromoacetone and affording the quasi-phosphonium salt (LXVII), which is converted into the product (LXVIII) via the Arbuzov reaction.[93]

Scheme 6

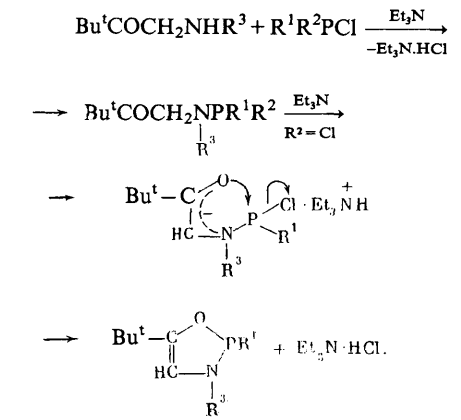


Hexafluoroacetone reacts with secondary chlorophosphines similarly to polyfluoroaldehydes[20] in proportions of 2:1 to form the phosphorane (LXIX) with the 1,2,4-dioxaphospholan ring.[96–98]

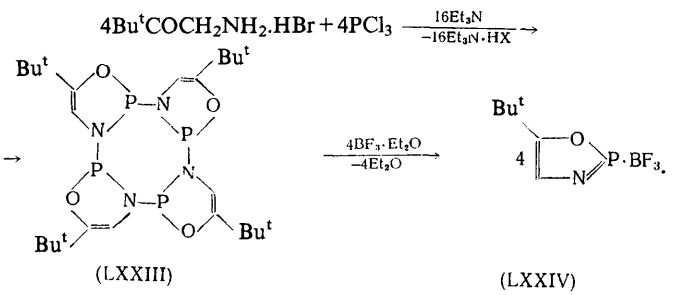
Compound (LXIX, R = Pr) undergoes the Arbuzov reaction[96] at 100 °C, while the corresponding compound with R = Me is converted into the cyclic compound (LXX). It is suggested that the reaction proceeds via the intermediate formation of an ylide.[98]



α-(*N*-Alkyl)aminoketones interact with phosphorus(III) chlorides with dissociation of an N–H bond. When there is a chlorine atom at the phosphorus(III) atom, the exchange products (LXXI) readily undergo intermolecular cyclisation to the product (LXXII).[99–104]

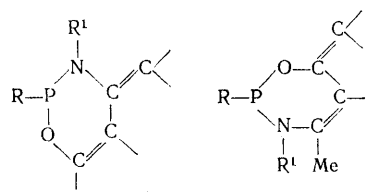


The salt of the unsubstituted aminoketone reacts with PCl_3 to produce the complex polycyclic compound (LXXIII) which is converted into a product with a two-coordinated phosphorus atom (LXXIV) on treatment with boron trifluoride etherate. Compound (LXXIV) was identified as a complex with BF_3.[105]



(LXXIII) (LXXIV)

The reactions of phosphorus(III) dichlorides with *N*-monosubstituted enaminoketones lead to 1,3,2-oxazaphosphorinanes with a diene system of C=C bonds [compounds (LXXV)], their exocyclic C=C bond adjoining the nitrogen atom.[106] Their product with the exocyclic C=C bond at the oxygen atom [compound (LXXVI)] has not been detected.

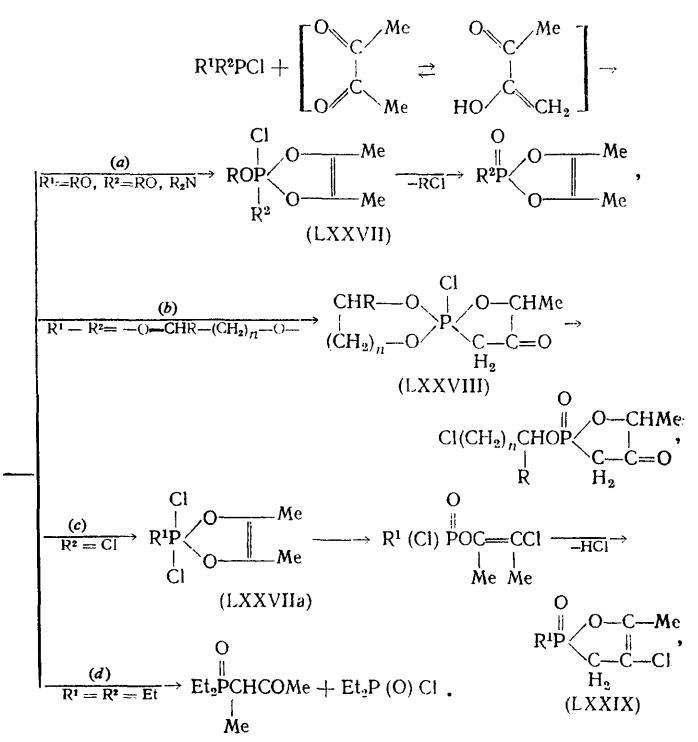


(LXXV) (LXXVI)

Although phosphorus(III) chlorides react with saturated aminoketones[99–104] and the nitrogen analogues of acetylacetone and acetoacetic ester[107] exclusively at the nitrogen atom, the conclusion that the enaminoketones are initially phosphorylated at the O or N atom must be reached with much caution, since there is a possibility of prototropic interactions between the primary exchange products and also compounds (LXXV) and (LXXVI).

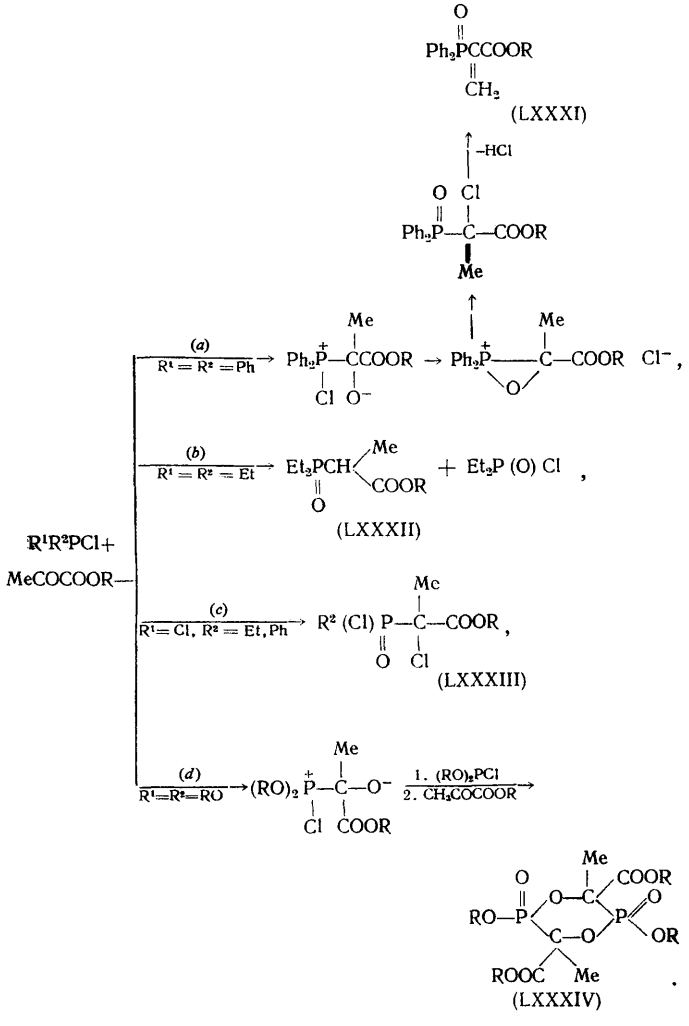
The reactions of phosphorus(III) chlorides with α- and β-dicarbonyl compounds (diacetyl, acetylacetone, and pyruvic and acetoacetic esters) have been investigated. Diacetyl reacts exothermically with all phosphorus(III) chlorides. The structure of the reaction product depends on the nature of the substituents at the phosphorus(III) atoms. It is believed that acyclic phosphoromonochloridites react with the ketone form of diacetyl (Scheme 7, pathway *a*),[108–111] while cyclic phosphorochloridites react with the enolic form (Scheme 7, pathway *b*).[112] The adducts (XXVII) and (XXVIII) are converted into phosphorus(IV) derivatives via the mechanism of the second stage of the Arbuzov reaction. The formation of the phosphorane (XXVII) has been confirmed by ^{31}P NMR.[111] The adduct (XXVIIa) formed in the first stage of the reactions of dichlorophosphines is subsequently converted into the 1,2-oxaphospholene (XXIX), i.e. the reaction proceeds with formation of a new P–C bond (Scheme 7, pathway *c*).[113,114] The reaction of chlorodiethylphosphine with diacetyl produced the tertiary phosphine oxide (XXX) and the chloride of diethylphosphinic acid (Scheme 7, pathway *d*).[115] The authors assumed the possibility of the involvement in the reaction of the enolic form of diacetyl and the formation of diethylphosphinous acid as an intermediate. Although it follows from mechanisms *a*, *b*, and *c* that the phosphorus atom exhibits biphilic properties, there is no unanimous view in the literature about the character of the primary step of the interaction. Whereas the role of phosphoromonochloridites in the primary step of the reaction remains unelucidated,[108–111] the role of nucleophiles is attributed to the more electrophilic primary dichlorophosphines.[113,114] At the same time, the possibility of a donor–acceptor interaction of the oxygen atom of diacetyl with the phosphorus(III) atom of chlorodiethylphosphine[115] (electrophilic properties)—the most nucleophilic of phosphorus(III) chlorides—has been postulated. It follows from the data presented that the role of the phosphorus(III) chloride in the primary step of the interaction has not been clearly defined and that additional studies are necessary in order to throw light on this problem.

Scheme 7



According to literature data, pyruvate esters react, in contrast to diacetyl, with phosphorus(III) chlorides exclusively in the ketone form and the structure of the reaction products depends significantly on the nature of the substituents at the phosphorus(III) atom. Thus the product of the reaction of chlorodiphenylphosphine (Scheme 8, pathway *a*) is the unsaturated phosphine oxide (LXXXI),[116] while the product of the reaction of chlorodiethylphosphine (Scheme 8, pathway *b*) is the unsaturated phosphine oxide (LXXXII).[115–117]

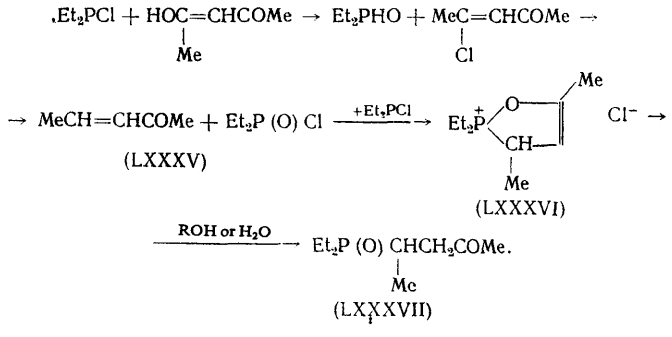
Scheme 8



The reaction of pyruvate esters with primary dichlorophosphines (Scheme 8, pathway *c*) gives rise to the chlorides of phosphinic acids (LXXXIII) with functional-group substituents,[116,118] while their reaction with dialkyl phosphorochloridites (Scheme 8, pathway *d*) affords 2,5-dialkoxy-3,6-dialkoxy-carbonyl-3,6-dimethyl-2,5-dioxo-1,4-dioxa-2,5-diphosphorinanes (LXXXIV).[119]

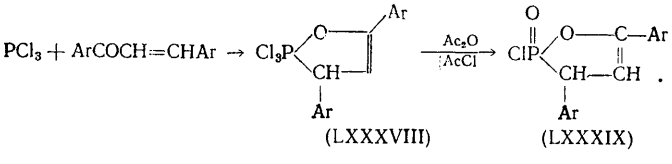
It is believed that in the reactions described, chlorodiphenylphosphine exhibits nucleophilic reactivity,[116] while dialkyl phosphorochloridites exhibit nucleophilic reactivity in the first stage and electrophilic reactivity in the second.[119]

The interaction of chlorodiethylphosphine with acetylacetone in the absence of a base is completed by the formation of the chloride of diethylphosphinic acid and the phosphonium salt (LXXXVI), which is converted into the tertiary phosphine oxide (LXXVII) on treatment with alcohols or water.[57,115] The authors believe that the reaction proceeds with participation of the enolic form of the β-diketone via the intermediate formation of diethylphosphinous acid and the unsaturated ketone (LXXXV). The product of the reaction of the latter with the initial phosphine is the salt (LXXXVI).



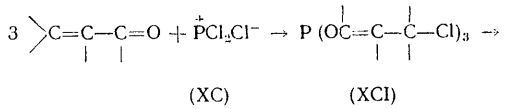
A similar scheme has been postulated also for the reaction of chlorodiethylphosphine with acetoacetic ester.[115]

The study of the reactions of phosphorus(III) chlorides with ketones containing an alkylidene group as a second substituent was initiated by Conant as early as 1917.[1,2] He suggested that the reaction proceeds via the 1,4-addition of phosphorus(III) to the ends of the conjugated system with formation of the phosphorane (LXXXVIII),[120] which is converted into the oxaphospholene derivative of phosphorus(IV) (LXXXIX) on treatment with acetic anhydride.

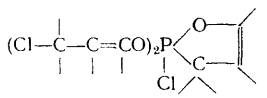


Later Drake and marvel[44] established that the 1,4-addition of PCl_3 to alkyl- and aryl-substituted unsaturated ketones is a general feature although in the study of more complex systems such universality was questioned.[121,122]

In view of the difficulty of alkylating PCl_3 and the results of his own studies of the interaction of this chloride with five- and six-membered cyclic unsaturated ketones, Kabachnik[1] criticised the 1,4-addition mechanism proposed by Conant. He suggested instead a mechanism involving the 1,4-addition of the charged $P^+Cl_2Cl^-$ fragments to the ends of the conjugated system of the ketone, which results in the formation of the γ-chlorinated unsaturated phosphite ester (XCI). The latter is converted via the mechanism of the first stage of the Arbuzov reaction into compound (XCII) with the 1,2-oxaphospholene ring.



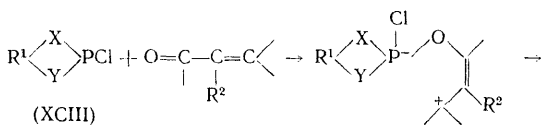
(XC) (XCI)



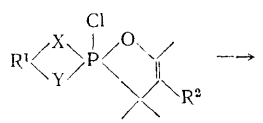
(XCII)

Thus, as for unsubstituted aldehydes, the nucleophilic substitution of a chlorine atom at the electrophilic phosphorus(III) by a new group is postulated. The interaction of PCl_3 with complex ketones such as 4-cholest-3-ynone and 10-methyl-2-oxo-$\Delta^{1,9}$-octalin has been interpreted similarly.[123] However, the manifestation of biphilic properties by phosphorus(III) and its 1,4-addition to the end of the conjugated system of the unsaturated ketones are generally acknowledged.[2,43,124–129]

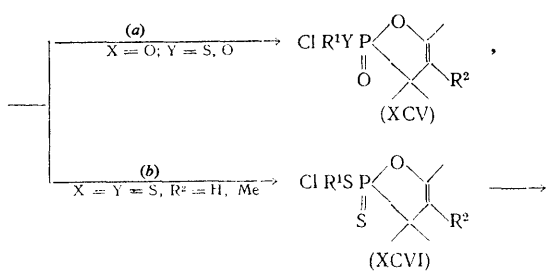
The reactions of unsaturated ketones with cyclic phosphorus(III) halides (XCIII) have been studied in detail. It has been suggested that cyclic phosphorus(III) chloride exhibit electrophilic reactivity in the primary step of the interaction.[128]



(XCIII)

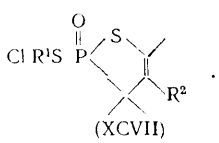


(XCIV)



(XCV)

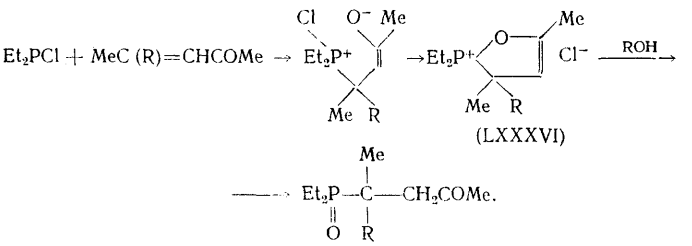
(XCVI)



(XCVII)

The 1,4-adduct (XCIV) is stable when R^1 = arylene,[128] whereas in the case where R^1 = alkylene the adduct (XCIV) is converted into compounds (XCV) and (XCVI) via the mechanism of the second stage of the Arbuzov reaction.[2,43,124,125] When R^2 = H, compound (XCVI) isomerises to compound (XCVII) via Pishchimuka's mechanism.[126]

Important results were obtained in a study of the interaction of chlorodiethylphosphine with unsaturated ketones.[57] In this case, the 1,4-adduct was isolated in a pure form and some of its reactions were investigated. On the basis of the chemical shift of the phosphorus atom (126–128 p.p.m.), the structure of the quasi-phosphonium salt (LXXXVI) was attributed to it. Furthermore, chlorodiethylphosphine proved to be more reactive than phosphorus trichloride and phosphorus(III) dichlorides, whence it it possible to conclude that it manifests nucleophilic properties in the primary step of the interaction.

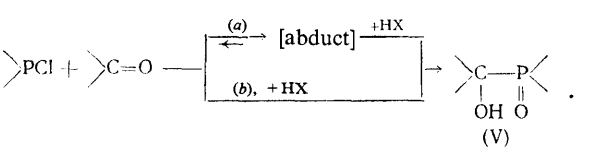


(LXXXVI)

The data described above show that during the last 15–20 years important information has been obtained about the reactions of phosphorus(III) chlorides with carbonyl compounds in the absence of a third reactant: the involvement in the role of the catalyst of the HCl impurity in the phosphorus(III) chloride and the consumption of two aldehyde molecules, in some cases also ketone molecules, for each P–Cl bond were established and new pathways in the reactions of ketones were discovered.

III. The reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of a third reactant

The reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of hydrolysing agents (water, acetic acid, and acetic anhydride with subsequent treatment of the reaction mixture with water) leads to 1-hydroxyalkylphosphonic and 1-hydroxyalkylphosphinic acid (V).[1,2] Under these conditions, it is possible to obtain initially the product of the addition of the phosphorus(III) chloride to the carbonyl compound and it can then be treated by the hydrolysing agent[6,130–132] (pathway *a*) or the initial reactants can be mixed in the presence of water, acetic acid, or acetic anhydride[132] (pathway *b*).

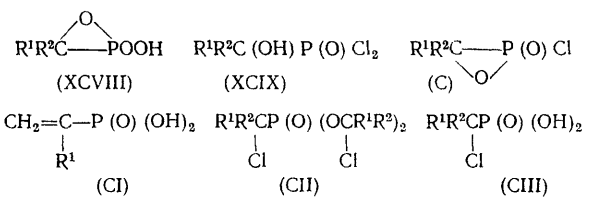


(V)

Approximately 15 years ago, it was assumed that whatever the pathway (*a* or *b*) followed in the synthesis, the mechanism of the formation of compounds (V) is the same: the interaction of the phosphorus(III) chloride with the carbonyl compound leads initially to an adduct, which is then acted upon by the hydrolysing agent.

However, the mechanisms of the interaction of these reactants via pathways *a* and *b* are fundamentally different.

We shall deal briefly with the evolution of views on the reaction of phosphorus(III) chlorides with carbonyl compounds involving the subsequent employment of hydrolysing agents (pathway *a*). According to Michaelis, the adduct (I) hydrolyses directly to the acid (V) (see Scheme 1).[4] Conant assumes the intermediate formation of phosphonic acid (XCVIII).[130,131,133] Careful kinetic studies led him to the conclusion that the hydrolysable reactants interact with the dipolar adduct (II).[6] When acetic acid is employed, the acid chlorides (XCIX) and (C) are formed initially and are converted into the acid (V) on treatment with water. The reaction with ketones is complicated by the formation of the unsaturated acids (CI).[130,132] The mechanism of the interaction of phosphorus(III) chlorides with unsaturated ketones is treated similarly.[6,120,130,131,133]

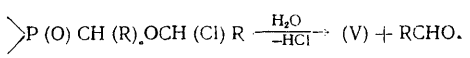


(XCVIII) (XCIX) (C)

(CI) (CII) (CIII)

According to the ideas of Page[7] and Kabachnik,[1] the primary product (III) containing phosphorus(III) isomerises to compound (CII), which subsequently hydrolyses to the acids (CIII) and (CV). In later investigations, Kabachnik[90,134] rejected the possibility of the transition (CIII) → (V) under mild conditions.

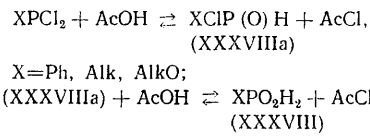
At the present time, the views described above on the reaction pathway *a* are apparently of only historical value. In reality, 1-(1-chloroalkoxy)alkyl derivatives of phosphorus(IV) (X) are formed initially and are subsequently hydrolysed to the acid (V).



(X)

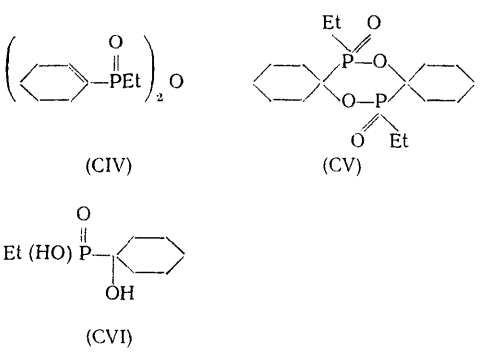
Ketones, which are less reactive than aldehydes, react sluggishly with phosphorus(III) chlorides under mild conditions: in the course of 20–40 h at room temperature.[56,57] Therefore, even if the hydrolysing agent is added to the mixture of phosphorus(III) chloride and the ketone several hours after they have been mixed, pathway *a* hardly makes a decisive contribution to the overall reaction mechanism. Furthermore, in contrast to aldehydes, the interaction of phosphorus(III) chlorides with ketones leads to the formation of different organophosphorus compounds depending on the structure of the ketones: (XXXIII), (XXXV), (XXXVII), and (XXXIX) (Scheme 4), which are entirely stable in relation to hydrolysing agents. On the other hand, in the presence of the latter, the reaction is very rapid (pathway *b*) with formation of compounds (XXXIX) in high yields. Hence it follows that in the case of ketones the adducts (I) and (II) and compound (CII) are not the direct objects of the action of hydrolysing agents.

Mainly as a result of the work of Soviet chemists, it can now be regarded as demonstrated that pathway *b* involves the primary interaction of phosphorus(III) chlorides with the hydrolysing agent and the intermediate formation of hydrophosphoryl compounds (XXXVIII) [in particular, the extremely reactive partial chlorides of phosphonous and phosphorous acids (XXXVIIIa)].[59,61–64,69,70,135–150] When carboxylic acids are used as hydrolysing agents,[70,142] the phosphorus(III) chloride is initially converted into the partial acid chloride (XXXVIIIa), which is capable of hydrolysing further to the acid (XXXVIII). The latter interacts both with the initial phosphorus(III) chloride and with the acyl chloride to form compound (XXXVIIIa). When water is used, the reactions are irreversible.



(XXXVIIIa) (XXXVIII)

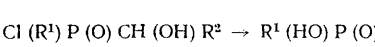
Carbonyl compounds constitute a kind of trap for active hydrophosphoryl compounds, especially the partial acid chlorides (XXXVIIIa). Cyclohexanone proved to be the most successful carbonyl compound, which made it possible to isolate the product (XXXIXa) in a pure form as a result of its direct interaction with compound (XXXVIIIa, X = Ph).[58,59,139,140] When Ph is replaced by Et in compound (XXXIXa), its stability falls and after the removal of the solvent only the organophosphorus compounds (CIV)–(CVI) are produced.[140,145]



(CIV) (CV)

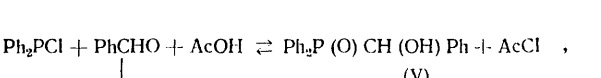
(CVI)

It has been shown recently that compounds (XXXIX) change after a time, being converted into the acid (CIII) containing a 1-chloroalkyl group.[151–153]



(XXXIX) (CIII)

There are also literature data showing that even compounds without a labile P–Cl bond may be modified, for example, compound (V). Thus Miller and Stewart,[154] who repeated Conant's experiments on the interaction of chlorodiphenylphosphine with benzaldehyde in the presence of acetic acid, established that the expected product (V) is initially formed rapidly (5 min) but after three days the final reaction product is not compound (V) but the acetate (CVII) and the diphosphorylated ester (XII):



(V)

(CVII) (XII)

The substance characterised by Conant as compound (V)[135] turned out to be the ester (XII).

The reaction of aryldichlorophosphines with ketones in the presence of monothioacetic acid takes place in a somewhat unusual manner:[155] instead of the expected 1-hydroxyalkylphosphinomonothioic acids, 1-mercaptoalkylphosphinic acids (CVIII) are obtained. Since the coordination number of phosphorus remains unaltered in the initial stage of the reaction, the following reaction mechanism has been proposed:

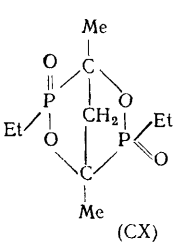
$$PhPCl_2 + CH_3COSH \xrightarrow{HCl} PhP(Cl)SCOCH_3 \xrightarrow{R^1R^2C=O} \rightarrow R^1R^2C(Cl)P(O)(SCOCH_3)Ph \xrightarrow{H_2O} \underset{(CVIII)}{R^1R^2C(SH)P(O)(OH)Ph}.$$

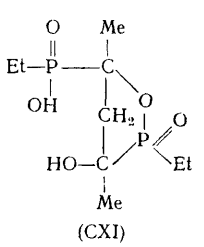
The interaction of phosphorus(III) chlorides with aldehydes and ketones in the presence of mercaptans is a new convenient method of synthesis of α-alkylthioalkylphosphonates and the corresponding phosphinates (CIX).[156]

$$R^1R^2PCl + R^3R^4C=O + R^5SH \xrightarrow{-HCl} R^1R^2P(O)\underset{SR^5}{\underset{|}{C}}R^3R^4.$$
(CIX)

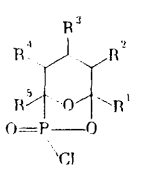
The reactions of phosphorus(III) chlorides with unsaturated ketones in the presence of hydrolysing agents also includes a stage involving the formation of hydrophosphoryl compounds (XXXVIII).[69,157] If hydrogen sulphide is used instead of acetic acid or water, products with the thiophosphoryl group are obtained.[158]

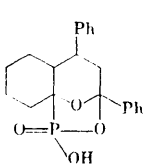
The reactions of diketones with phosphorus(III) chlorides in the presence of acetic acid have also been investigated.[159–163] The reaction of chloroethylphosphine and actylacetone leads to the formation of the bicyclic diphosphorus compound (CX), which hydrolyses very readily to the monocyclic derivative of 2-oxa-1,2-oxaphospholan (CXI).[159]

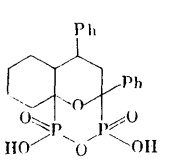

(CX)


(CXI)

Monophosphorylated [compounds (CXII) and (CXIII)] and diphosphorylated [compound (CXIV)] derivatives of tetrahydropyran are formed from PCl_5 and 1,5-diketones:[160–163]

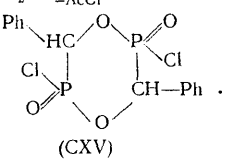

(CXII)


(CXIII)


(CXIV)

A hydrolysing agent, can also be used in the synthesis of polyfunctional organophosphorus compounds from a phosphorus(III) chloride, a carbonyl compound, and a dialkylamine[164,165] or the amides of carboxylic and carbonic acids.[166–176] It is suggested that the reactions proceed via a stage involving the formation of hydrophosphoryl compounds.[172]

New data have also been obtained in the study of the reactions of phosphorus(III) chlorides with aldehydes in the presence of acetic anhydride.[8,177] The authors were able to isolate the cyclic product (CXV), which is assumed to be a precursor of compound (V), obtained by the hydrolysis of the adduct of the aldehyde with the phosphorus(III) chloride. A mechanism including the initial interaction of PCl_3 with the aldehyde was postulated initially:[8]

$$PhCHO + PCl_3 \rightleftarrows PhCH(Cl)OPCl_2 \xrightarrow[-AcCl]{Ac_2O} \rightarrow PhCH(OCOCH_3)P(O)Cl_2 \xrightarrow{-AcCl}$$

(CXV)

This mechanism is incorrect, because, as shown above (see Section II), not one but two aldehyde molecules should be consumed per P–Cl bond.[16–18,22–24] It was later established that aldehydes react initially with acetic anhydride to form the diacetate (CXVI), PCl_3 functioning as the process catalyst.[177,178] The subsequent reaction of the diacetate with PCl_3 leads to compound (CXV). It was obtained by unambiguous synthesis from compound (CXVI) and PCl_3 and also from compounds (XVII) and (CXVII):

$$PhCHO + Ac_2O \xrightarrow{PCl_3} \underset{(CXVI)}{PhCH(OAc)_2} \xrightarrow{PCl_3} \underset{(CXVII)}{PhCH(OAc)Cl} + AcOPCl_2 \rightarrow$$
$$\rightarrow \underset{(XVII)}{(POCl)_n} + AcCl + (CXVII) \rightarrow (CXV).$$

However, not everything is clear in this mechanism. The structure of the product (XVII) has not been established and it has not been shown what are the essential features of the catalysis and whether or not compound (XVII) does really react on treatment with compound (CXVII) in accordance with the mechanism of the Arbuzov reaction (since α-chloroalkyl carboxylate esters are weak electrophiles). The mechanism of the interaction of phosphorus(III) chlorides with ketones, including unsaturated ketones, in the presence of acetic anhydride has not been finally elucidated, although in the case of unsaturated ketones we have an important general method of synthesis of compounds with the 1,2-oxaphospholene ring[2,179–183] and the latter can be used to synthesise ketoalkyl esters of phosphorus acids.[2,184–187]

The procedure in which the reactions of phosphorus(III) chlorides with carbonyl compounds are carried out in the presence of phosphorus(III) acid esters proved to be fruitful.[40] Such reactions were first achieved by Birum.[188] Organic compounds containing several phosphorus atoms different coordination numbers have been obtained by this procedure. It is believed that the phosphorus(III) acid ester initially adds to the carbon atom of the carbonyl group with formation of the dipolar ion (CXVIII),[40] whose interaction with the phosphorus(III) chloride leads to the polyfunctional compounds (CXIX):

$$(3-n)\ R^1R^2POR^3 + (3-n)\ R^4R^5C{=}O \rightarrow (3-n)\ R^1R^2\overset{+}{P}(OR^3)-\underset{R^5}{\overset{R^4}{C}}-O^- \xrightarrow{+R^6_nPCl_{(3-n)}} \rightarrow$$

(CXVIII)

$$\rightarrow R^6_nP[OCR^4R^5P(O)R^1R^2]_{3-n} + (3-n)\ R^3Cl.$$

(CXIX)

In recent years, these reactions were used to obtain acetals containing two phosphorus atoms with different coordination numbers[189,190] and the monophosphorylated [compound (CXX)] and diphosphorylated [compound (CXXI)] alkyl phosphorodichloridites:[191,192]

$$R^1CHO + P(OR^2)_3 + PCl_3 \rightarrow (R^2O)_2P(O)CHR^1OPCl_2 + R^2Cl,$$

(CXX)

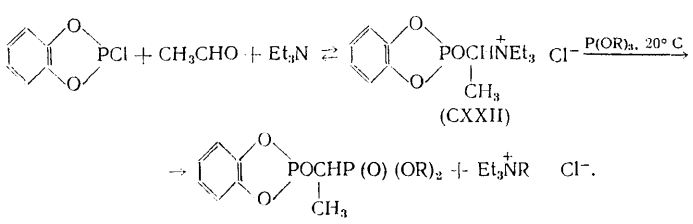
$$(R^1O)_2P(O)COCH_3 + P(OR^2)_3 + PCl_3 \rightarrow (R^1O)_2P(O)\underset{O{=}P(OR^2)_2}{\overset{O\ \ CH_3}{\overset{\|\ \ |}{C}}}OPCl_2 + R^2Cl.$$

(CXXI)

The replacement of trialkyl phosphites in this process by their thioanalogues alters fundamentally the character of the reaction:[193]

$$(R^1S)_3P + R^2R^3C{=}O + PCl_3 \rightarrow Cl_2P(O)\underset{SR^1}{CR^2R^3}.$$

Fairly numerous studies have been devoted to the reactions of phosphorus(III) chlorides with carbonyl compounds in the presence of triethylamine in order to synthesise unsaturated organophosphorus compounds. The synthesis of vinyl esters of phosphorus(III) acids by the reaction of *o*-phenylene and ethylene phosphorochloridites with acetaldehyde in the presence of triethylamine was reported as early as 1957.[194] The salt (CXXII) is formed initially in these reactions, its vacuum heat treatment affording the vinyl ester. However, further study of this reaction showed that, under conditions described in the above study,[194] the salt (CXXII) decomposes into the initial compounds, *o*-phenylene phosphorochloridite being isolated in a satisfactory yield. In the presence of trialkyl phosphite, the salt (CXXII) decomposes under mild conditions with formation of compounds (CXXIII) containing two phosphorus atoms:[29]



(CXXII)

(CXXIII)

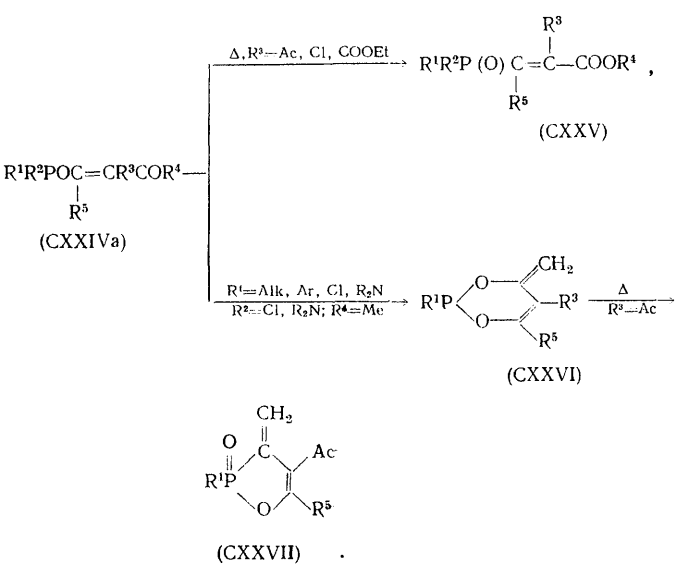
It has been established that electron-accepting substituents at the phosphorus(III) atom and the α-carbon atom of the ketone favour reactions involving the formation of a wide variety of unsaturated organophosphorus compounds (CXXIV):[81,82,91,100,195–224]

$$R_nPCl_{3-n} + (3-n)\ O{=}CCHYZ \xrightarrow[-(3-n)Et_3N\cdot HCl]{(3-n)Et_3N} R_nP(OC{=}CYZ)_{3-n}.$$

(CXXIV)

Base catalysis apparently operates in this instance and the intermediates are triethylammonium enolates. This has been confirmed indirectly by the interaction of both phosphorus(III) and phosphorus(IV) chlorides with ketones exhibiting an enhanced CH acidity under comparable conditions. For comparison, one should note that, depending on the structure of the ketone and the nature of the substituents at the phosphorus(III) atom and the solvent, sodium enolates give rise not only to unsaturated compounds but also to *C*-phosphorylated derivatives as well as *OC*-diphosphorus compounds.[225–228]

In the case of β-dicarbonyl compounds, the substitution products (CXXVIa) can be isolated in a pure form,[82,210–219,222] while in the presence of a base many of them are converted into the cyclic derivatives (CXXVI).[80,206–212,215,216] On heating, compounds (CXXIVa) and (CXXVI, R^3 = Ac) undergo the vinyl phosphite–vinyl phosphonate rearrangement with formation of compounds (CXXV) and (CXXVII):[214,215,218,223]



(CXXIVa)

(CXXV)

(CXXVI)

(CXXVII)

In the case of thiocyanatoacetone, the substitution product (CXXIVb) cyclises to 1,3,2-oxathiaphospholene (CXXVIII) with elimination of propionitrile:[209]

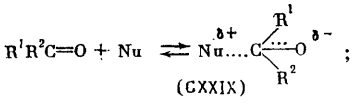
$$(EtO)_2POC(Me){=}CHSCN \rightarrow \text{(CXXVIII)} + EtCN.$$

(CXXIVb)

(CXXVIII)

Important results have been obtained using as the third reactant an alkyl vinyl ether (AVE), which is a weaker nucleophile than trialkyl phosphites and triethylamine. The latter activate the carbonyl compound and enter unchanged into the composition of the final products (CXXII) and (CXXIII), forming a new C–E bond (E = P, N).[188,194] In contrast to them, alkyl vinyl ethers

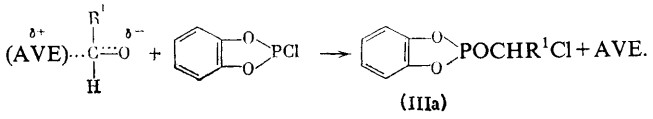
activate only the carbonyl group in aldehydes, without forming a new C–C bond and do not enter into the composition of the reaction product.[29,30,229] The fact that all the nucleophiles enumerated block the carbon atom of the carbonyl group as a result of the formation of the donor–acceptor complex (CXXIX) and hence also the carbonium ion centre in the intermediate adduct (XIV) is also an important feature. This is apparently in fact the cause of the consumption of only one molecule of the carbonyl compound per P–Cl bond in the presence of these nucleophiles.



(CXXIX)

Nu = $P(OR)_3$, Et_3N, AVE.

Only by creating special conditions has it been possible to achieve the synthesis of one of the representatives of the primary adducts of phosphorus(III) chlorides with aldehydes (IIIa),[29,30,229–231] the possibility of the formation of which had been predicted at an early stage by Page[7] and then by Kabachnik[1] and Atherton.[8]



(IIIa)

In the absence of an alkyl vinyl ether, the product (IIIa) decomposes slowly into the initial compounds, the latter forming an adduct in proportions of 1 : 2.

IV. Conclusion

The main conclusion arising from the data described is that, in the case of PCl_3 and phosphorus(III) dichlorides, the primary process in the interaction with carbonyl compounds can be characterised as catalytic nucleophilic substitution at the electrophilic phosphorus(III) atom, the admixture of HCl in the phosphorus(III) chlorides playing the role of the catalyst under these conditions. In various secondary processes, the coordination number of phosphorus rises to 4. Depending on the nature of the carbonyl compound, the roles of both a nucleophile and an electrophile are attributed to secondary chlorophosphines and phosphorochloridites. However, additional studies are required for a more correct solution of this problem.

Ketones are less reactive than aldehydes, but their reactions with phosphorus(III) chlorides are more varied. More far reaching studies are required to establish the true nature of the processes leading to specific compounds. In the presence of a secondary functional group in the ketone, the more reactive group reacts with the phosphorus(III) chloride and subsequently the primary product participates in various intramolecular and intermolecular interactions with formation of important polyfunctional organophosphorus compounds. The reactions of phosphorus(III) chlorides with aldehydes and ketones in the presence of hydrolysing agents are characterised by the conversion of phosphorus(III) chlorides into hydrophosphoryl compounds and the addition of the latter to the carbonyl group. Tertiary amines, trialkyl phosphites, and alkyl vinyl ethers, used as the third reactant, do not increase the coordination number of the phosphorus atom linked initially to the chlorine atom. Depending on the structure of the carbonyl compound, base or nucleophilic catalysis operates. An alkyl vinyl ether makes it possible to synthesise the primary products of the interaction of phosphorus(III) chlorides with aldehydes in proportions of 1 : 1. The question of the synthesis of intermediates with phosphorus(III) and two aldehyde fragments per P–Cl bonds still remains open.

A satisfactory answer cannot be found in the literature for all the questions raised. In view of both the theoretical importance of these reactions and their importance in the development of preparative syntheses of organophosphorus compounds with functional group substituents, there has been an increasing growth of interest in these processes. The present review surveys the advances in the development of this field and is also designed to draw the attention of investigators to a number of problems which are still unsolved.

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