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Exchange Reactions in the Chemistry of Organophosphorus Compounds

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The results of studies of reactions involving the exchange of alkoxy-, aryloxy-, acyloxy-, phosphorus-containing, amino-, alkylthio-, arylthio-, and hydrocarbon groups between phosphorus compounds are surveyed. The influence of the structure of the organophosphorus compounds, the role of catalysis, and the available information about the mechanisms of these reactions are considered.
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I. INTRODUCTION

Exchange reactions are important in the chemistry of organophosphorus compounds (OPC). Some of them serve as a basis for convenient methods of synthesis of OPC, while others occur in side processes during the preparation, isolation, and storage of OPC. The exchange reactions assume particular importance as a procedure for the introduction of a radioactive label into physiologically active OPC. The study of exchange reactions is also of interest from the standpoint of estimating the stability of OPC and of discovering the pathways in their chemical and metabolic transformations. The exchange reactions with participation of OPC are also of interest from the theoretical standpoint.

The study of exchange reactions involving OPC was developed greatly particularly during recent years, which has been partly reflected in a monograph[1]. However, the reviews on the exchange reactions of OPC [2,3] cover the literature only up to 1968 and are not exhaustive. The intramolecular exchange reactions involving OPC, induced by the migration of substituents in molecular rearrangements, have been adequately surveyed in a number of communications[4-7].

This review deals with intermolecular exchange reactions at the phosphorus atom which proceed without a change in its coordination number.

II. INTERMOLECULAR EXCHANGE OF ORGANIC SUBSTITUENTS IN PHOSPHORUS COMPOUNDS

The tendency of organophosphorus compounds to undergo exchange reactions is determined primarily by the mobility of the bond between phosphorus and the exchanging group, which depends both on the environment of the phosphorus atom and on the structure of the exchanging group; organic substituents linked to phosphorus via heteroatoms exchange more readily. Accordingly, it is useful to consider the OPC exchange reactions after subdividing them in terms of the types of exchanging groups.

1. Exchange of Alkoxy- and Aryloxy-Groups

The reactions involving the exchange of alkoxy-groups between phosphorus compounds and the isotypical reactions in which aryloxy-groups are exchanged have been subjected to most fundamental investigations in the series of derivatives of tricoordinate phosphorus. With rare exceptions, the alkoxy-groups in isotypical OPC exchange more readily than the aryloxy-groups.

Trialkyl phosphites enter into exchange reactions with PCl_3 merely on mixing the reactants[8]. In a mixture of triethyl phosphite with PCl_3 at 20°C, equilibrium is established after two days and faster on heating[9]:

$$(C_2H_5O)_3P + PCl_3 \rightleftarrows (C_2H_5O)_2PCl + C_2H_5OPCl_2 .$$

The kinetic characteristics of this and other exchange reactions of OPC have been published in a review[2].

Alkyl phosphorodichloridites, formed in the reaction of trialkyl phosphites with PCl_3, interact under similar conditions with the initial trialkyl phosphites to form dialkyl phosphorochloridites[10]:

$$(C_3H_7O)_3P + C_3H_7OPCl_2 \rightleftarrows 2(C_3H_7O)_2PCl .$$

The composition of the products of the exchange reactions between trialkyl phosphites and phosphorus trihalides therefore depends on the ratio of the initial reactants. The main products of the reactions of trialkyl phosphites with PCl_3, taken in molar proportions of 2 : 1, are dialkyl phosphorochloridites, which are in fact mainly obtained by this procedure[11-19]:

$$2\,(RO)_3P + PCl_3 \rightarrow 3\,(RO)_2PCl ;$$
$$R{=}CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ C_8H_{17},\ C_{12}H_{25},\ C_3H_5OC(O)CH_2 .$$

The composition of the exchange products and the rate of reaction depend to some extent also on the electron density at the phosphorus atom and on the structure of the ester groups. In the series of trialkyl phosphites the rate of exchange depends little on the length of the alkoxy-groups. Thus the reactions of the lowest trialkyl phosphites with PCl_3 reach completion comparatively rapidly at 20 °C, while the analogous reaction of tridodecyl phosphite is rapidly completed at 50 °C.[15]

The introduction of electron-accepting substituents into the alkoxy-group of the trialkyl phosphite lowers its reactivity in the exchange reactions with PCl_3. The disproportionation of the chloro-substituted phosphites has been noted only on heating[20]. The exchange between tris(perfluoroalkyl) phosphites and PCl_3 is in general difficult[21]. The exchange between tris(trifluoroethyl) phosphites and PCl_3 at 90 °C reaches completion in 4 h:[22]

$$(CF_3CH_2O)_3P + PCl_3 \rightleftarrows (CF_3CH_2O)_2PCl + CF_3CH_2OPCl_2 .$$

Triaryl phosphites enter into exchange reactions with phosphorus trihalides with much more difficulty than trialkyl phosphites. The reactions of triphenyl phosphite with PCl_3

and PBr_3 take place on heating above 150 °C and mixtures of diphenyl phosphorohalidites and phenyl phosphorodihalidites are then formed[23,24]. According to NMR data, the half-exchange period at 160 °C in the reaction of triphenyl phosphite with PCl_3 is 15 h:[10]

$$(C_6H_5O)_3P + PCl_3 \rightarrow (C_6H_5O)_2PCl + C_6H_5OPCl_2 .$$

In the reaction between triphenyl phosphite and PCl_3 at 180 °C, equilibrium is established in 60 h between the initial reactants, diphenyl phosphorochloridite and phenyl phosphorodichloridite[24], but, on raising the temperature to 200° to 230 °C and using an excess of PCl_3, the triaryl phosphites can be fully converted into aryl phosphorodichloridites[25]:

$$(ArO)_3P + 2PCl_3 \rightleftarrows 3ArOPCl_2 ,$$
$$Ar = C_6H_5,\ p\text{-}CH_3C_6H_4,\ m\text{-}CH_3C_6H_4,$$
$$2,4\text{-}(CH_3)_2C_6H_3 .$$

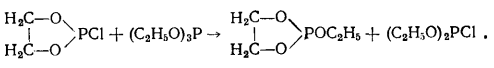
The nature of phosphorus halides exerts a significant influence on the direction and rate of the exchange reactions. Phosphorus trihalides undergo exchange reactions with trialkyl phosphites most vigorously and in terms of their reactivity can be arranged in the sequence[10] $PF_3 < PCl_3 < PBr_3$.

The interaction of trialkyl phosphites with phosphorus iodides leads to the formation of a complete mixture of products even under the conditions of intense cooling. The reactions of trialkyl phosphites with PBr_3 proceed exothermically and, like those with PCl_3, are completed by the formation of exchange products[10]:

$$2(C_3H_7O)_3P + PBr_3 \rightleftarrows 3(C_3H_7O)_2PBr .$$

The reactions between trialkyl phosphites and phosphorus trifluoride proceed with greater difficulty. The reaction between $(CH_3O)_3P$ and PF_3 is completed in 40 h at 80 °C but at a higher temperature it is complicated by the formation of phosphorus(V) derivatives[26].

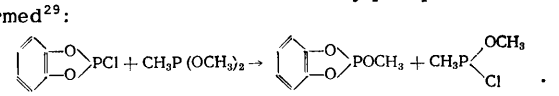
Trialkyl phosphites react with alkyl phosphorochloridites more slowly than PCl_3, but the reactions with ethylene phosphorochloridite and phenylene phosphorochloridite, like those with PCl_3, proceed with evolution of heat, which can be accounted for by the favourable conditions for the formation of the intermediate complex[27]:



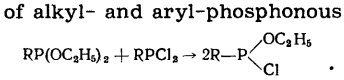
An increase of electron density at the phosphorus atom in phosphorus acid esters increases their reactivity in exchange reactions. Dialkyl phosphonites are more reactive than trialkyl phosphites; the interaction of dialkyl phosphonites with PCl_3 is exothermic and leads to the complete exchange of the alkoxy-groups and the formation of dichlorophosphines[28]:

$$RP(OR')_2 + PCl_3 \rightarrow RPCl_2 + (R'O)_2PCl .$$

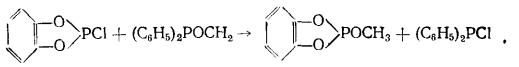
The analogous reaction with PBr_3 leads to a complex mixture of products[10]; the reaction with phosphorochloridites is slower and the ester-chlorides of alkylphosphonous acids are formed[29]:



The reactions of dialkyl phosphonites with dichlorophosphines can serve as a convenient method of synthesis of the ester-chlorides of alkyl- and aryl-phosphonous acids[30,31]:



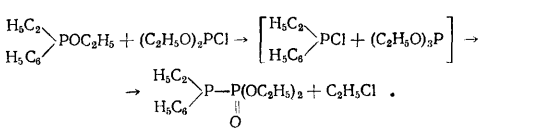
The esters of phosphinous acids react with phosphorus halides even more vigorously. The reactions of dialkyl phosphinites with PCl_3 give rise to a complex mixture of products[10,28], but the reaction with phenylene phosphorochloridite results in the formation of exchange products[29]:



Rapid exchange has also been observed in the reaction of butyl dibutylphosphinite with dipropyl phosphorochloridite[10]:

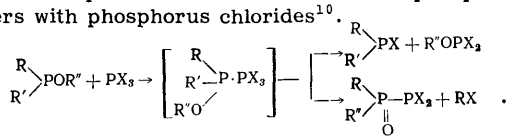
$$(C_4H_9)_2POC_4H_9 + (C_3H_7O)_2PCl \rightarrow (C_4H_9)_2PCl + (C_3H_7O)_2POC_4H_9 .$$

In the reaction of ethyl ethylphenylphosphinite with diethyl phosphorochloridite the products formed initially subsequently condense to form a P–P bond with alteration of the coordination number of one of the phosphorus atoms[32,33]:



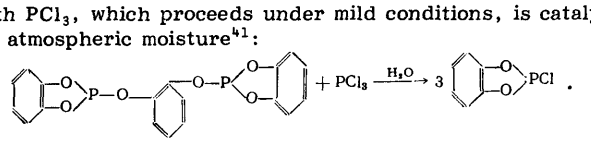
This competing reaction occurs in almost all cases when acid esters of tervalent phosphorus interact with phosphorus chlorides and, depending on the structure of the initial compounds and the exchange products, lead to the formation (in greater or smaller amounts) of side products containing a P–P bond. When trialkyl phosphites react with PCl_3, the exchange reaction is mainly observed and condensation products are formed in insignificant amounts[9]. However, in the reactions of trialkyl phosphites with certain chlorophosphines[29,33,34] and iodophosphines[35,36], the latter pathway becomes the main one, which can be used to synthesise compounds containing a P–P bond[35–40].

The formation of compounds with a P–P bond can be a result of an alternative pathway to the decomposition of the intermediate complex formed in the reaction of phosphorus acid esters with phosphorus chlorides[10].



The available information about the structure of the intermediate complex in the reactions of trialkyl phosphites with phosphorus chlorides is inadequate. The question of the mechanism of these exchange reactions is complicated by catalysis. Both acids and bases have a catalytic effect in reactions involving the exchange of alkoxy- and aryloxy-groups between tricoordinate phosphorus compounds. HCl is a powerful catalyst in the reactions of trialkyl phosphite with PCl_3 and it is extremely difficult to eliminate admixtures of this acid[10]. The acid esters of tervalent phosphorus, which can be formed when the neutral esters are acted upon by HCl or traces of H_2O, are also effective catalysts in these reactions[10]. Boron trichloride and triethylamine have likewise been found to be catalytically active in the exchange reactions of neutral phosphites with phosphorus chlorides[27]. It has been shown by ^{31}P NMR that exchange between tricoordinate phosphorus esters and chlorides catalysed by HCl is preceded by the formation of compounds with a P–P bond[32].

Catalysis can be observed even when the reaction mixture is insufficiently protected from atmospheric moisture. Thus it has been shown that the reaction of phenylene phosphite with PCl_3, which proceeds under mild conditions, is catalysed by atmospheric moisture[41]:



The disproportionation of phenyl phosphorodichloridite when the latter is stored for a month can be accounted for by the catalytic effect of HCl or traces of water[42]:

$$3C_6H_5OPCl_2 \rightarrow (C_6H_5O)_3P + 2PCl_3 .$$

The isotope exchange between phenyl phosphorodichloridite and the radioactive $^{32}PCl_3$ at 20 °C is apparently induced by the same factors[43]:

$$C_6H_5OPCl_2 + {}^{32}PCl_3 \rightleftarrows C_6H_5O{}^{32}PCl_2 + PCl_3 .$$

Nor can one rule out the phenomenon of autocatalysis in reactions involving the exchange of ester groups at the phosphorus atom. Thus aryl phosphorodi-iodites undergo symmetrisation to triaryl phosphites and phosphorus triiodide on storage, the symmetrisation reaction being accelerated by the addition of PI_3:[44]

$$3\,ArOPI_2 \rightarrow [(ArO)_3P + 2PI_3] \rightarrow (ArO)_3PI_2 + P_2I_4 ;$$
$$Ar = C_6H_5,\ o\text{-}CH_3C_6H_4,\ m\text{-}CH_3C_6H_4,$$
$$p\text{-}CH_3C_6H_4,\ o\text{-}ClC_6H_4,\ p\text{-}ClC_6H_4 .$$

Acids and bases can also catalyse the exchange of ester groups between neutral phosphites. In the presence of HCl the reaction between triethyl and trimethylphosphites takes place in 2 h at 20 °C with formation of mixed phosphites[45]

$$(C_2H_5O)_3P + (CH_3O)_3P \overset{HCl}{\rightleftarrows} (C_2H_5O)_2POCH_3 + (CH_3O)_2POC_2H_5 .$$

This reaction is apparently reversible because in the presence of acid reagents, for example, trifluoroacetic acid, rapid symmetrisation of the mixed neutral phosphites is observed at the same temperature[46]. It has been suggested that HCl protonates the oxygen of the alkoxy-group of the phosphite with its subsequent cleavage to dialkyl phosphorochloridite, which then interacts with another phosphite molecule to form the exchange products[32,45].

Under the condition of base catalysis, the exchange of ester groups between neutral phosphites proceeds under much more severe conditions. According to NMR data, the exchange between triethyl and tributyl phosphite is completed in 4 h at 170–180 °C:[47]

$$(C_2H_5O)_3P + (C_4H_9O)_3P \xrightarrow{C_2H_5ONa} (C_2H_5O)_2POC_4H_9 + (C_4H_9O)_2POC_2H_5 .$$

An interesting process involving the exchange of alkoxy-groups for aryloxy-groups has been observed in the presence of alkyl halides. The exchange is accompanied by the Arbuzov reaction, which results in the formation of mixed esters of alkylphosphonic acids[48,49].

The redistribution of ester groups with participation of trialkyl phosphites, triphenyl phosphite, and phosphorous acid takes place at 80–100 °C with formation of mixed acid esters of phosphorous acid[50]:

$$(C_6H_5O)_3P + (RO)_3P + H_3PO_3 \rightarrow 3\ \begin{matrix} RO \\ C_6H_5O \end{matrix}\!\!>\!P(O)H .$$

The marked acidophilic properties of both aliphatic and aromatic neutral esters of tervalent phosphorus promote their involvement in exchange reactions with various phosphorus acids. Neutral phosphites interact with phosphorous acid at 20 °C to form mixtures of acid phosphites[51]:

$$(RO)_3P + H_3PO_3 \rightarrow (RO)_2P(O)H + ROP(O)H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH \quad .$$

The composition of the products of this reaction depends on its conditions and on the ratio of the initial reactants. When a mixture of neutral phosphites and phosphorous acid taken in proportions of 2 : 1 is heated at 100 °C for 2 h, dialkyl or diaryl phosphites are formed as the main products[52–55]:

$$2\,(RO)_3P + H_3PO_3 \rightarrow 3\,(RO)_2P(O)H ;$$
$$R = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ C_5H_{11},\ C_6H_{13},$$
$$C_6H_5CH_2,\ C_6H_5,\ p\text{-}CH_3C_6H_4,\ o\text{-}CH_3C_6H_4,$$
$$m\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4,\ o\text{-}ClC_6H_4 .$$

Under the same conditions, neutral phosphites interact also with acid phosphites, which can result in the formation of mixed acid phosphites. This reaction is particularly convenient for the synthesis of mixed acid phosphites containing alkoxy- and aryloxy-groups[50,56]:

$$(RO)_3P + R'OP\!<\!\begin{matrix}(O)H \\ OH\end{matrix} \rightarrow \begin{matrix} RO \\ R'O \end{matrix}\!\!>\!P(O)H + (RO)_2P(O)H .$$

The exchange reactions of triaryl phosphites with phosphorous acid are apparently reversible, because diaryl phosphites are symmetrised on slow vacuum distillation to triaryl phosphites. This process is accelerated in the presence of bases[57,58]:

$$3\,(C_6H_5O)_2P(O)H \rightarrow 2\,(C_6H_5O)_3P + H_3PO_3 .$$

Such symmetrisation is not characteristic of dialkyl phosphites, but sodium dialkyl phosphorothioites undergo symmetrisation on heating[59]:

$$2(RO)_2PSNa \rightarrow (RO)_3P + ROP(SNa)_2 .$$

When salts of dialkyl phosphites are heated, the products of the Arbuzov rearrangement are usually formed[60], but, when a mixture of di(s-butyl) phosphite was heated with its sodium salt, the exchange products were obtained, which was apparently caused by the steric hindrance to the Arbuzov rearrangement[61]:

$$(s\text{-}C_4H_9O)_2P(O)H + (s\text{-}C_4H_9O)_2PONa \rightarrow$$
$$\rightarrow (s\text{-}C_4H_9O)_3P + (s\text{-}C_4H_9O)P(O)H .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad ONa$$

It is noteworthy that in the reactions of mixed neutral alkyl aryl phosphites with phosphorous acid, the alkoxy-group is more mobile[56]:

$$(C_2H_5O)_2POC_6H_5 + H_3PO_3 \rightarrow \begin{matrix} C_2H_5O \\ C_6H_5O \end{matrix}\!\!>\!P(O)H + C_2H_5OP(O)H .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

The reactions of neutral phosphites with phosphorous acid take place stepwise. The dialkyl phosphite formed initially interacts at a higher temperature with phosphorous acid to form monoalkyl phosphites[62,63]:

$$(RO)_2P(O)H + H_3PO_3 \rightarrow 2\,ROP(O)H .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

Neutral phosphites esterify phosphonous acids at 20 °C with formation of acid phosphonite esters[64]:

$$(RO)_3P + C_6H_5P(O)H \rightarrow (RO)_2P(O)H + C_6H_5P(O)H ;$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\quad OH\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OR$$
$$R = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ iso\text{-}C_4H_9 .$$

Further esterification of phosphonous acid by neutral phosphites takes place at a higher temperature and is complicated by the rearrangement of the neutral phosphonite to the phosphinate[65]. Like phosphites, neutral phosphonites interact with phosphonous acids to form acid phosphonites[66,67]:

$$C_6H_5P(OR)_2 + C_6H_5P(O)H \rightarrow 2\,C_2H_5P(O)H ;$$
$$\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad OH\qquad\qquad\qquad\qquad\qquad\quad OR$$
$$R = C_6H_5,\ iso\text{-}C_8H_{17},\ ClCH_2CH_2 .$$

Alkoxy-groups can be exchanged also between acid phosphites. When a mixture of symmetrical dialkyl phosphites is heated for 15 h at 100–150 °C, asymmetric dialkyl phosphites

are formed in yields from 30 to 70%.[67,68] It has been demonstrated by gas–liquid chromatography (GLC) that the exchange takes place even at 24 °C:[69]

$$(RO)_2P(O)H + (R'O)_2P(O)H \rightleftarrows 2\ \begin{matrix} RO \\ R'O \end{matrix}\!\!>\!P(O)H\ ;$$

$R = CH_3,\ C_2H_5;\ R' = C_2H_5,\ C_3H_7,\ C_4H_9,\ C_5H_{11},\ C_6H_{13},\ C_8H_{17},\ ClCH_2CH_2,\ (ClCH_2)_2CH$.

This reaction is reversible and mixed dialkyl phosphites are gradually symmetrised during storage[70,71]. The symmetrisation is accelerated on distillation[72] and in the presence of bases[70]. Alkylene diphosphites are symmetrised on heating[73]:

$$\begin{matrix} RO \\ H(O) \end{matrix}\!\!>\!POR'OP\!<\!\begin{matrix} OR \\ (O)H \end{matrix} \rightarrow R'\!<\!\begin{matrix} O \\ O \end{matrix}\!\!>\!P(O)H + (RO)_2P(O)H\ .$$

Under the influence of the full esters of tervalent phosphorus acids, the acids of quinquevalent phosphorus are also readily esterified. Thus triethyl phosphite is cleaved by phosphoric acid with the simultaneous formation of monoethyl phosphate[73,74]:

$$(C_2H_5O)_3P + H_3PO_4 \rightarrow (C_2H_5O)_2P(O)H + C_2H_5O\overset{O}{\overset{\|}{P}}(OH)_2\ .$$

The esterification of phosphoric acid by trialkyl phosphites takes place stepwise. Depending on the ratio of the initial reactants, mono-, di-, and tri-alkyl phosphates can be formed on heating in nitromethane[75,76]. The reaction of triphenyl phosphite with phosphoric acid also takes place stepwise under the same conditions:[77,78]

$$(RO)_3P + H_3PO_4 \left|\begin{array}{l} \xrightarrow{1:1} ROP(O)(OH)_2 + (RO)_2P(O)H \\ \xrightarrow{2:1} (RO)_2P(O)OH + 2(RO)_2P(O)H \\ \xrightarrow{3:1} (RO)_3PO + 3\,(RO)_2P(O)H\ . \end{array}\right.$$

The esterification of phosphoric acid by neutral phosphites is a complex process. The study of the mechanism of the esterification of diethyl phosphate showed that the process involves a stage in which the neutral phosphate is protonated and a mixed anhydride is formed[79]:

$$(RO)_3P + (C_2H_5O)_2P(O)OH \left|\begin{array}{l} \rightleftarrows (RO)_3\overset{+}{P}H\overline{O}P(O)(OC_2H_5)_2 \\ \rightleftarrows (RO)_3P(H)\!-\!O\!-\!P(O)(OC_2H_5)_2 \\ \rightleftarrows (RO)_2P(O)P(O)(OC_2H_5)_2 + ROH \end{array}\right. \rightarrow$$

$$\rightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}OR + (RO)_2PHO\ .$$

The reactions of neutral phosphites with phosphonic acids apparently proceed in accordance with an analogous mechanism and here too neutral acid phosphonates can be obtained depending on the reactant ratio[80]:

$$(C_2H_5O)_3P + C_6H_5CH_2\overset{O}{\overset{\|}{P}}(OH)_2 \left|\begin{array}{l} \xrightarrow{1:1} C_6H_5CH_2\overset{O}{\overset{\|}{P}}\!<\!\begin{matrix} OC_2H_5 \\ OH \end{matrix} + (C_2H_5O)_2P(O)H \\ \xrightarrow{2:1} C_6H_5CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + 2(C_2H_5O)_2P(O)H\ . \end{array}\right.$$

The thioacids of quinquevalent phosphorus are readily esterified by the full esters of tervalent phosphorus acids. The reactions of trialkyl phosphites, dialkyl phosphonites, or alkyl phosphinites with dialkyl phosphorodithioates take place with evolution of much heat and trialkyl phosphorodithioates are formed. It has been suggested that the protonation of the tricoordinate phosphorus is an intermediate stage[81,82]:

$$R\!<\!\begin{matrix} R \\ R' \end{matrix}\!\!>\!POR'' + (R'''O)_2\overset{S}{\overset{\|}{P}}SH \rightarrow \left[R\!<\!\begin{matrix} R \\ R'-\overset{+}{P}H\overset{-}{S}\overset{S}{\overset{\|}{P}}(OR''')_2 \\ R''O \end{matrix}\right] \rightarrow (R'''O)_2\overset{S}{\overset{\|}{P}}SR'' + R\!<\!\begin{matrix} R \\ R' \end{matrix}\!\!>\!P(O)H\ .$$

Neutral phosphites and phosphonites react less vigorously with the acid esters of phosphoromonothioic acids. The esterification of *O,O*-dialkylphosphoromonothioic acid by trialkyl phosphites proceeds with evolution of a small amount of heat and is completed by the formation of thiono-isomers[81]:

$$(R'O)_2PR + (R''O)_2POSH \rightarrow (R''O)_2\overset{S}{\overset{\|}{P}}OR' + R\!<\!\begin{matrix} R \\ R'O \end{matrix}\!\!>\!P(O)H\ .$$

We may note that the analogous reaction of triphenyl phosphite with diethylphosphorothioic acid stops at the stage involving the formation of the mixed anhydride[83]:

$$(C_6H_5O)_3P + (C_2H_5O)_2POSH \rightarrow (C_6H_5O)_2\overset{S}{\overset{\|}{P}}O(OC_2H_5)_2 + C_6H_5OH\ .$$

Neutral esters of tricoordinate phosphorus acids also esterify phosphonodithioic acids and the completion of the reaction then requires heating for 1 h at 40–50 °C:[84]

$$(CH_3O)_3P + C_6H_5CH_2\overset{S}{\overset{\|}{P}}\!<\!\begin{matrix} OC_4H_9 \\ SH \end{matrix} \rightarrow C_6H_5CH_2\overset{S}{\overset{\|}{P}}\!<\!\begin{matrix} OC_4H_9 \\ SCH_3 \end{matrix} + (CH_3O)_2P(O)H\ .$$

The esters of quinquevalent phosphorus acids are much more inert in the exchange reactions, which can be explained by their coordination unsaturation, which hinders the formation of the intermediate reaction complex from the exchanging reactants. A competing pathway involving the formation of pyrophosphates occurs preferentially in the reactions of esters of phosphorus(V) acids with phosphorochloridites[85–88]. Pyrophosphoryl compounds are formed preferentially also in the reactions of neutral phosphates with phosphoramidochloridates[89–91], phosphorochlorothioates[92], thiophosphoryl trichloride[93], and phosphorus pentoxide[94]. Only the reaction of phosphorus trichloride with the chloroalkyl esters of phosphonic acids, which may be formed when aldehydes interact with PCl_3 in accordance with the scheme

$$3RCHO + PCl_3 \rightarrow [(RCHClO)_3P \rightarrow RCHClO\overset{O}{\overset{\|}{P}}(OCHClR)_2] \xrightarrow{PCl_3} RCHClO\overset{O}{\overset{\|}{P}}Cl_2\ ,$$

is an exception[95–97].

In contrast to triaryl phosphates[99], trialkyl phosphates[98] undergo the exchange reaction with phosphoric acid, which is catalysed by stronger acids[98]:

$$2(RO)_3PO + H_3PO_4 \rightarrow 3\,(RO)_2P(O)OH\ .$$

Acid catalysis can also explain the incorporation of the radioactive ^{32}P label into neutral phosphates on interaction with labelled iron phosphate[100]:

$$(RO)_3PO + Fe^{32}PO_4 \cdot 2H_2O \xrightarrow{200°C} (RO)_3{}^{32}PO\ .$$

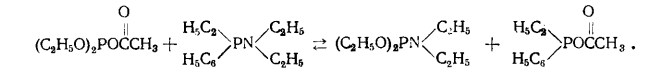
The incorporation of radioactive phosphorus has been observed also on heating tributyl phosphate with radioactive phosphoric acid[101]:

$$2\,(C_4H_9O)_3PO + H_3{}^{32}PO_4 \rightleftarrows (C_4H_9O)_3{}^{32}PO + (C_4H_9O)_2\overset{O}{\overset{\|}{P}}OH + C_4H_9O\overset{O}{\overset{\|}{P}}(OH)_2\ .$$

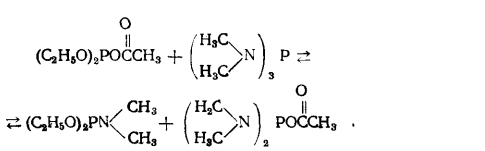
It is noteworthy that the enzyme-catalysed exchange reactions of monophosphates with radioactive phosphoric acid are faster and proceed under milder conditions[102].

2. The Exchange of Acyloxy-Groups

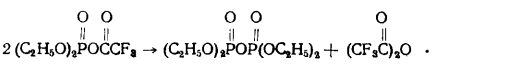
O-Acyl derivatives of phosphorus acids constitute a broad class of mixed anhydrides. Among them, acylphosphites have been studied in greatest detail (the bibliography includes more than 100 items[103]). It has been shown by ^{31}P NMR that, when acetyl diethyl phosphite is heated with the diethylamide of ethylphenylphosphinous acid at 50 °C, a mobile equilibrium is established between these compounds and the exchange products[104]:



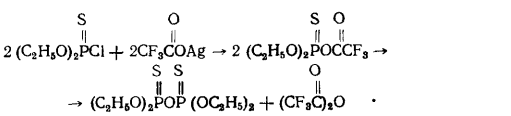
When these reagents are heated at a higher temperature, diphosphine oxide and acetic anhydride are formed. Their formation is most probably associated with the symmetrisation and isomerisation reactions of the mixed anhydrides. There are no data in the literature on the symmetrisation of acyl phosphites, but the formation of pyrophosphites when dialkyl phosphites interact with isocyanates can serve as direct confirmation of the possibility of the occurrence of such reactions[105]. The formation of pyrophosphorous acid derivatives has been observed also in the reactions of acyl phosphites with phosphorous acid triamides[14,106]. It was shown by NMR that under these conditions the formation of pyrophosphoryl compounds is preceded by the exchange of the acyloxy-group between the phosphorus compounds[104]:



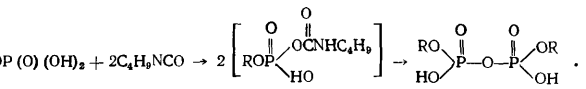
O-Acyl derivatives of phosphorus(V) acids readily undergo symmetrisation as a consequence of their high reactivity. Thus the mixed anhydride of *O,O*-diethylphosphoric and trifluoroacetic acids is wholly converted into tetraethyl pyrophosphate and trifluoroacetic acid anhydride after 24 h at 20 °C:[107]



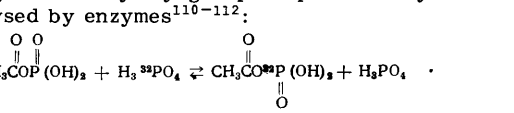
Ethoxycarbonyl diethyl phosphate, which persists for several months, is very stable[107]. The tendency towards analogous reactions has been noted also for *O*-acyl derivatives of phosphoromonothioic acid[108]:



The tendency of the acyloxy-derivatives of phosphorus towards symmetrisation can be used to synthesise pyrophosphoryl compounds which are difficult to obtain. Thus disubstituted pyrophosphates have been prepared by the interaction of phosphoric acid monoesters with butyl isocyanate[109]:

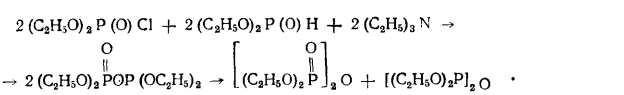


The exchange of the acyloxy-groups is promoted by acids and is catalysed by enzymes[110–112]:

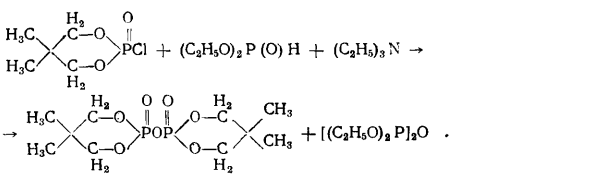


3. The Exchange of Phosphorus-Containing Groups

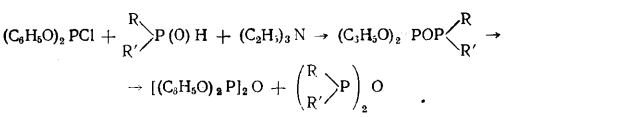
The exchange of phosphorus-containing groups in pyrophosphoryl compounds is formally analogous to the reactions described above. Like the acyloxy-derivatives of phosphorus, mixed pyrophosphoryl compounds readily undergo symmetrisation. In many instances symmetrisation takes place even during the preparation of the mixed anhydrides, for example, the anhydride of *O,O*-diethylphosphoric and *O,O*-diethylphosphorous acids[113–115]:



Only the symmetrical anhydrides have been obtained in the reaction of diethyl phosphite with dimethyl propylene phosphorochloridate[115]:

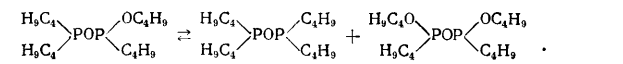


The interaction of acid phosphites[116,117] and phosphonites[118] as well as phosphinous acids[119,120] with the chlorides of tervalent phosphorus acid in the absence of hydrogen chloride acceptors leads to the exchange of the hydroxy-group for chlorine and, in the presence of bases, results in the formation of mixed anhydrides, which then undergo symmetrisation[121–123]:

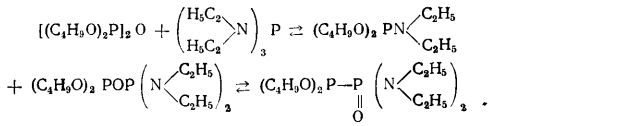


Symmetrical phosphorus acid anhydrides can be obtained also directly by treating the mixed anhydrides of phosphorus acids with the acids themselves[124,125].

We may note that the symmetrisation of the mixed anhydrides of phosphinous and *O*-alkylphosphinous acids is reversible[123]:



The interaction of tetrabutyl pyrophosphite with phosphorous acid tris(diethylamide) leads to the formation of the diethylamide of *O,O*-dibutylphosphorous acid and dibutyl *N,N,N',N'*-tetraethylpyrophosphorodiamidite, which is in tautomeric equilibrium with diphosphine monoxide[126]:



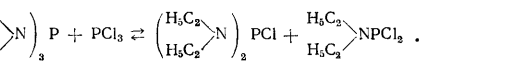
This reaction is of interest also because the exchange of the phosphorus-containing groups proceeds with the cleavage of not only the P–O but also the P–P bonds[127]. Instances of the tautomeric transformation of diphosphine oxides into anhydrides have been examined[128]. A similar preliminary isomerisation has also been postulated in the exchange reaction of diphosphine disulphides with phosphorus-acid chlorides[129]. However, the exchange involving the P–P bond can proceed also without the preliminary isomerisation of diphosphine oxides. Thus dialkyld'phenoxydiphosphine and

dialkyl phosphorochloridite have been obtained by the reaction of diphenyl phosphorochloridite with dialkoxydialkyldiphosphine[129].

The exchange reactions involving the cleavage of the P–P bond have been examined in reviews[131,132].

4. The Exchange of Amino-Groups

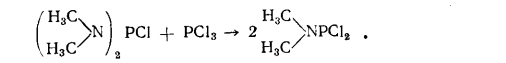
Phosphorus acid amides are more reactive in exchange reactions than their esters. The reaction of phosphorous tris(diethylamide) with PCl_3 takes place almost instantaneously with evolution of much heat and is accompanied by the redistribution of the substituents[9]:



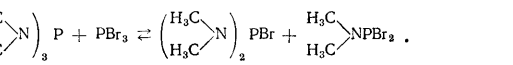
By altering the ratio of the initial reactants, the reaction can be directed towards the preferential formation of phosphorodiamidous chlorides[133–138]:

$$2\,(R_2N)_3\,P + PCl_3 \rightleftarrows 3\,(R_2N)_2\,PCl\ ;$$
$$R=CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9\ .$$

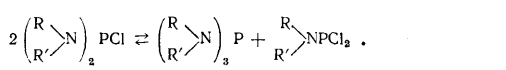
The half-life of this reaction at 20 °C is 30 s.[137] The *N,N,N',N'*-tetra-alkylphosphorodiamidous chlorides formed react in their turn with PCl_3 to produce *N,N*-dialkylphosphoramidous dichlorides[138]:



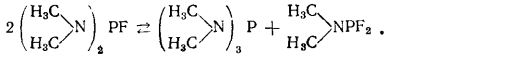
Phosphorus triamides react extremely vigorously also with PBr_3, but the *N,N,N',N'*-tetra-alkylphosphorodiamidous bromides formed are unstable and disproportionate to the initial compounds even on vacuum distillation[134]:



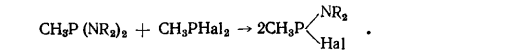
N,N,N',N'-Tetra-alkylphosphorodiamidous chlorides, which disproportionate to the extent of 15% with formation of phosphorous triamides and phosphoramidous dichlorides after storage for 1 month at 20 °C, are also relatively unstable[139]:



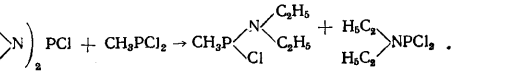
N,N,N',N'-Tetra-alkylphosphorodiamidous fluorides disproportionate even faster and for this reason it is difficult to isolate them in a pure form[140]:



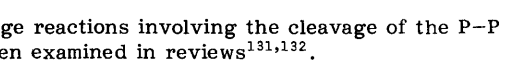
The amino-group attached to the tervalent phosphorus atom is readily exchanged in the reactions of a wide variety of OPC with phosphorus chlorides[27,137,141,142]. The reactions of bis(dialkylamino)phosphorines with dichloro- and dibromophosphines take place at high rates[137,142]:



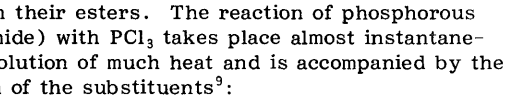
N,N,N',N'-Tetra-alkylphosphorodiamidous chlorides react with alkyldichlorophosphines under mild conditions[137]:



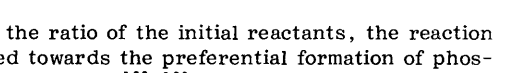
The exchange between phosphorous triamide and diethyl phosphorochloridodithioite is rapid[141]:



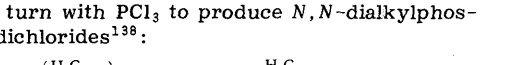
The *N,N,N',N'*-tetra-alkylphosphorodiamidous chloride formed in this reaction reacts under the same conditions with the excess of diethyl phosphorochloridodithioite and *N,N*-diethylphosphoramidous dichloride is formed[141]:



N,N-Diethylphosphoramidous dichloride can also be obtained by the reaction of phosphorous tris(diethylamide) with ethyl phosphorodichloridothioite[141]:

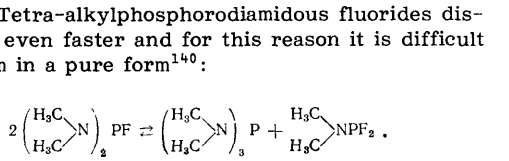


The exchange of the amino-group for chlorine is also observed in the interaction of the ester-amides of phosphorous acid with phosphorochloridites. Ethylene *N,N*-diethylphosphoramidite and diethyl phosphorochloridite have been obtained by the reaction of diethyl *N,N*-diethylphosphoramidite with ethylene phosphorochloridite, which takes place with spontaneous heating[27]:



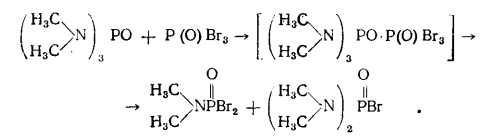
Diethyl *N,N*-diethylphosphoramidite interacts less vigorously with phenylene phosphorochloridite. The catalytic effect of HCl was noted in this reaction[27]:

The exchange of a nitrogen-containing functional group in phosphoramidites and phosphonamidites for chlorine goes to completion and the formation of only a small amount of red condensed products, tentatively assumed to be monomers with a P–P bond, is observed[136]. However, the final product of the reaction of ethylphenylphosphinous diethylamide with diethyl phosphorochloridite is a compound with a P–P bond, which is formed after the completion of the exchange reaction[27]:

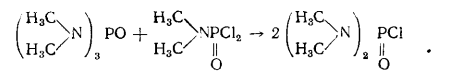


The amides of phosphorus(V) acids enter into exchange reactions with phosphorus chloride under more severe conditions than the analogous derivatives of tervalent phosphorus. Phosphoric triamides react with $POCl_3$ to form stable complexes which withstand heating to 150 °C. At a higher temperature they decompose with formation of phosphoromonoamidic dichloride and phosphorodiamidic chloride, i.e. an exchange reaction takes place[143,144]:

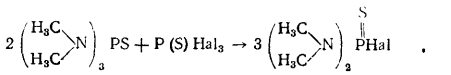
Phosphoryl bromide reacts similarly[144]:



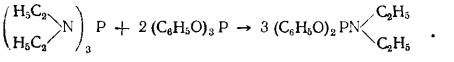
Phosphoric tris(dimethylamide) reacts with *N*,*N*-dimethylphosphoramidic chloride[144]:



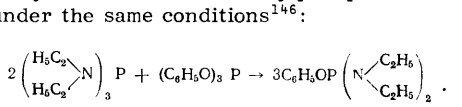
It is noteworthy that the thioamides of phosphorus acids undergo the exchange reaction under milder conditions. Phosphorothioic tris(dimethylamide) reacts with $PSCl_3$ and $PSBr_3$ on refluxing in toluene. The formation of a complex was not observed in these reactions and *N*,*N*,*N'*,*N'*-tetramethylphosphorodiamidothioic halides were obtained in high yields[144]:



Instead of exchange products, pyrophosphoryl compounds and an alkyl halide are formed in the reactions of phosphorus(V) acid chlorides with the ester-amides of the same acids containing at least one alkoxy-group at the phosphorus atom[89–92]. However, in the series of aryloxyamides there is a possibility of the exchange of the amino-groups for chlorine and even for an aryloxy-group. When a mixture of phosphorous tris(diethylamide) is heated with triphenyl phosphite for 5 days at 100 °C, complete exchange takes place with formation of diphenyl *N*,*N*-diethylphosphoramidite in 93% yield[9,145]:

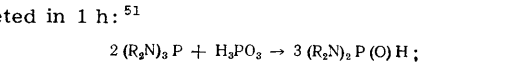


In the presence of an excess of phosphorous tris(diethylamide), phenyl *N*,*N*,*N'*,*N'*-tetra-alkylphosphorodiamidite was obtained under the same conditions[146]:

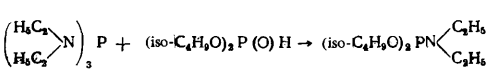


The occurrence of this reaction shows that diaryl phosphoramidites can undergo a reaction involving a redistribution of the amido- and aryloxy-groups at 100 °C and above[145].

The presence of the nitrogen atom in phosphorus acid amides promotes the formation of complexes with proton-donating reagents[27,147–149] and hence the occurrence of exchange reactions between phosphorus acids and their amides. The exchange between phosphorous triamides and phosphorous acid is observed even at 20 °C and at 60 °C is completed in 1 h:[51]

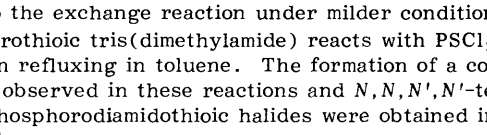


Although the yields of this reaction are approximately 60%, it nevertheless constitutes the most convenient method of synthesis of phosphoramidites[150,151]. On heating for 6 h at 100 °C, the exchange between phosphorous tris(diethylamide) and di-isobutyl phosphite is observed[152]:



The analogous reaction of butyl *N*,*N*,*N'*,*N'*-tetraethylphosphorodiamidite with an acid phosphite stops at the stage involving the formation of a mixed anhydride[152]:

The interaction of tervalent phosphorus acid amides with quinquevalent phosphorus acids is more complex. Together with exchange reactions, pyrophosphoryl compounds are formed and a free amine is liberated in this instance[148]; by removing the amine from the reaction mass, it is possible to drive the reaction fully towards the formation of pyrophosphates and their thio-analogues[153–155]:

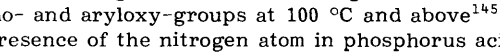


The reactions of phosphorus(V) acids with their amides stop at the stage involving the formation of only pyrophosphoryl compounds and ammonium salts of phosphorus acids[156,157], which is apparently associated with the high stability of these salts. In this connection it is of interest to note that, when phosphoric acid triamides react with carboxylic acid salts, an amino-group is exchanged for a hydroxy-group[158].

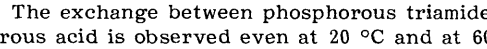
5. The Exchange of Alkylthio- and Arylthio-Groups

As regards their chemical properties, phosphorus acid thioesters differ significantly from their oxygen analogues. The thioesters show a smaller tendency towards being protonated, but their molecules are more polarisable. The sulphur atom in the thioesters of phosphorus(III) acids is capable of competing effectively with the phosphorus atom in reactions with electrophiles[159]. The thiophosphoryl group dissociates more readily than the phosphoryl group. These features have a significant influence on reactions involving phosphorus acid thioesters.

The reaction of trialkyl phosphorotrithioites with PCl_3 proceeds without the liberation of heat, but its completion requires heating[160]:

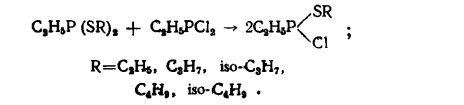


Since the equilibrium in this reaction is established slowly, the exchange products can be separated by vacuum distillation, which makes it possible to use the reaction for the synthesis of dialkyl phosphorochloridodithioites. Thus diethyl phosphorochloridodithioite has been obtained in 74% yield by heating a mixture of triethyl phosphorothioite with a stoichiometric amount of PCl_3 at 110–130 °C for 4 h:[141]

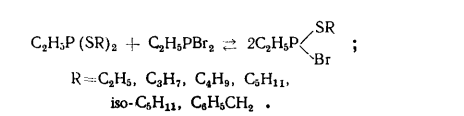


Diethyl phosphorobromidodithioite has been obtained in 70% yield under the same conditions by the reaction of triethylphosphorotrithioite with PBr_3.[141]

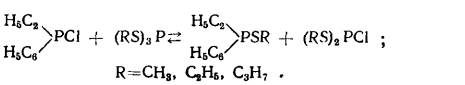
With increase of electron density at the phosphorus atom in the thioesters, the exchange of thiol groups is accelerated. The reactions of alkyl phosphonodithioites with dichlorophosphines are completed in 1 h at 100 °C and constitute a convenient method of synthesising the ester-chlorides of alkylphosphonothious acids[161,162]:



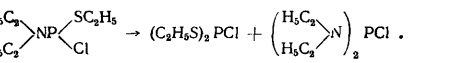
However, with increase of electron density at the phosphorus atom, the mobility of the equilibrium also increases, which can hinder the isolation of the reaction products by distillation. The yield of the ester-bromides obtained by the reaction of the full esters of alkylphosphonodithious acids with alkyldibromophosphines is only 30–60%:[163,164]



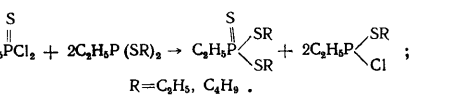
The equilibrium involving chlorophosphines is even more mobile. The reaction of chloroethylphenylphosphine with trialkylphosphorotrithioites is fully reversible and the attempts to isolate the exchange products by vacuum distillations were therefore unsuccessful[141]:



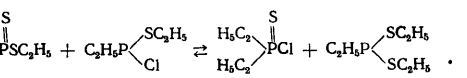
A mobile equilibrium is also established in the interaction of ethyl phosphorodichloridothioite with phosphoramidites; according to NMR data, the reaction of ethyl phosphorodichloridothioite with phosphorous tris(diethylamide) results in the formation of ethyl *N,N*-diethylphosphoramidochloridothioite, but vacuum distillation led to the isolation of only its disproportionation products[141]:



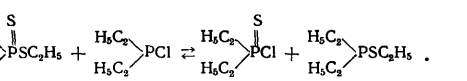
The exchange of alkylthio-groups is observed also in the reactions of dialkyl ethylphosphonodithioites with ethylphosphonothioic dichloride[165]:



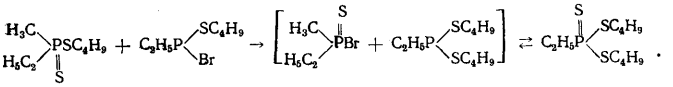
In contrast to their oxygen analogues, the thioesters of phosphorus(V) acids can enter into an exchange interaction with phosphorus halides. The exchange of the thiol group for a halogen then proceeds smoothly only in sulphur-containing compounds without an oxygen atom attached to the phosphorus atom. The exchange between phosphinodithioates and phosphorus chlorides proceeds under the mildest conditions. In a mixture of ethyl diethylphosphinodithioate and the ester-chloride of ethylphosphonothioic acid, the exchange is completed in 3 h at 100 °C. However, the exchange products have been isolated in a low yield apparently owing to the high mobility of the equilibrium[166]:



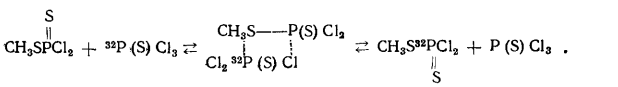
An analogous reaction with chlorodiethylphosphine has been observed on heating in a sealed tube at 140 °C, but the separation of the exchange products by distillation proved to be difficult[167]:



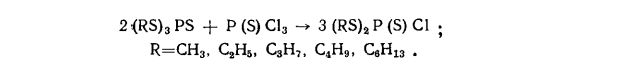
When butyl ethylmethylphosphinodithioate was allowed to react with butyl ethylphosphonobromidothioite, only dibutyl ethylphosphonotrithioate was isolated (in a low yield)[168]:



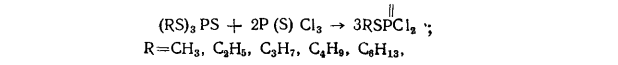
The thiol groups are exchanged for chlorine under more severe conditions in the interaction between the esters and chlorides of phosphorothioic and phosphonothioic acids. The isotope exchange between methyl phosphorodichloridodithioate and $^{32}PSCl_2$ proceeds at an appreciable rate on heating to a temperature above 150 °C and at 200 °C is 50% complete after 5 h. The isotope exchange takes place as a result of the exchange of the methylthio-group for Cl and apparently involves an associative mechanism[43]:



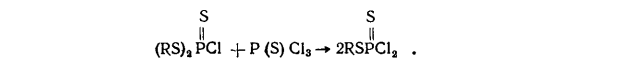
Phosphorotetrathioates react with $PSCl_3$ under the same conditions. Dialkyl phosphorochloridotrithioates have been obtained in 60–70% yield from trialkyl phosphorotetrathioates after 4 h at 180–200 °C:[169]



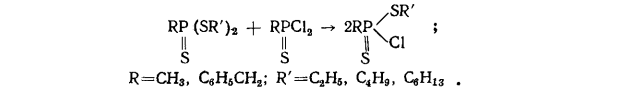
This reaction always results in the formation also of small amounts of alkyl phosphorodichloridodithioates, which become the main reaction products when an excess of thiophosphoryl chloride is used. Triphenyl phosphorotetrathioate has been converted into phenyl phosphorodichloridodithioate by an analogous procedure[169–171]:



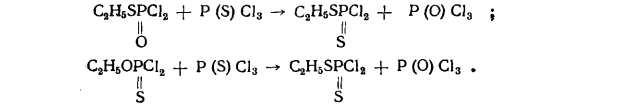
Dialkyl phosphorochloridotrithioates react with $PSCl_3$ under the same conditions to form phosphorodichloridodithioates[170]:



Like the phosphorotetrathioates, phosphonotrithioates react with alkyl- or aryl-phosphonothioic dichlorides, but the completion of the reaction requires in this case heating for ~12 h at 180–200 °C:[172]



Thioesters of phosphorus acids containing an oxygen atom attached to the phosphorus atom form as a rule pyrophosphoryl compounds and not exchange products in the reaction with phosphorus chlorides. The exchange products have been obtained only from certain phosphorodichloridothioates and $PSCl_3$:[173–176]



The thioesters of phosphorus acids also enter into a reaction with thioanhydrides in which the thiol groups are redistributed. When a mixture of phosphorotetrathioates is

heated with P_4S_{10} at 150 °C, an equilibrium is established between the initial compounds and the redistribution products[177]:

$$2\,(RS)_3PS + P_4S_{10} \rightleftarrows 3\,(RSPS_2)_2 \ .$$

A redistribution of alkylthio-groups is observed also in the interaction between unlike trialkyl phosphorotrithioites, the reaction being accelerated by HCl. Heating of a mixture of trimethyl and tributyl phosphorotrithioites in the presence of traces of HCl leads to rapid exchange of the alkylthio-groups[160]:

$$(CH_3S)_3P + (C_4H_9S)_3P \xrightarrow{HCl} (CH_3S)_2PSC_4H_9 + (C_4H_9S)_2PSCH_3 \ .$$

However, phosphorotrithioites and phosphonodithioites are not quite so highly acidophilic as their oxygen analogues and instances of the exchange of thiol groups between phosphorus thioesters and acids have not been described in the literature. It is only known that the acid phosphorus thioesters readily disproportionate. Thus *S,S*-dialkyl phosphorodithioites disproportionate even at room temperature or on slight heating into trialkyl phosphorotrithioites and *S*-alkyl phosphorothioites[178–180]:

$$2\,(RS)_2P(O)H \rightleftarrows (RS)_3P + RSP\begin{matrix}(O)H\\ \diagup\\ \diagdown\\ OH\end{matrix} \ .$$

The monothiol esters of phosphorus acids are unstable in a free state and decompose with liberation of a thiol and phosphorus compounds[181,182].

6. The Exchange of Hydrocarbon Groups

The phosphorus–carbon bond is very strong. Until recently, it was believed that reactions accompanied by the cleavage of the P–C bond are rather anomalous in phosphorus chemistry[183] and that radioactive phosphorus attached to a carbon atom is not involved in isotope exchange[6]. However, careful studies have been carried out recently on a series of OPC with a P–C bond and resulted in the discovery of a number of new reactions involving the cleavage of the P–C bond[43,184–190] and indicating the possibility of the exchange of organic substituents between phosphorus compounds.

The conversion of dichlorophenylphosphine into chlorodiphenylphosphine has been known since the previous century[191]:

$$2\,C_6H_5PCl_2 \rightleftarrows \begin{matrix}H_5C_6\\ \diagdown\\ \diagup\\ H_5C_6\end{matrix}PCl + PCl_3 \ .$$

In the absence of a catalyst, this reaction takes place at 300 °C under pressure[191] or on pyrolysis in a quartz tube[192]. Under the catalytic influence of $AlCl_3$, the reaction is completed faster at a lower temperature and in the absence of pressure[193]. Zinc chloride, tin tetrachloride, slightly moistened $AlCl_3$, and other transition metal chlorides have also been proposed as catalysts of the symmetrisation of aryldichlorophosphines to diarylchlorophosphines[194–196]:

$$2ArPCl_2 \xrightarrow{AlCl_3} Ar_2PCl + PCl_3 \ ;$$
$$Ar = C_6H_5,\ o\text{-}ClC_6H_4,\ n\text{-}ClC_6H_4 \ .$$

We may note that benzyldihalogenophosphines disproportionate to dibenzylhalogenophosphines more specifically in the absence of catalysts and that this process is apparently reversible, since the removal of phosphorus trihalide from the reaction sphere is accompanied by an increase of the yield of the dibenzylhalogenophosphine[197]:

$$2C_6H_5CH_2PHal_2 \rightarrow (C_6H_5CH_2)_2PHal + PHal_3 \ .$$

It was found that $AlCl_3$ catalyses also the reverse reaction involving the redistribution of phenyl groups between the phosphorus compounds; thus ethylenebisdichlorophosphine has been obtained by the reaction of ethylenebisdiphenylphosphine with PCl_3 in the presence of $AlCl_3$ in a closed system at 280 °C:[198]

$$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + 2PCl_3 \xrightarrow{AlCl_3} Cl_2PCH_2CH_2PCl_2 \ .$$

The interaction of phosphines with phosphorus chlorides is a complex process. In the initial stage of the reaction, the C–P bond is not involved and adducts are formed which undergo various reactions depending on the conditions. In the reactions of tertiary phosphines with phosphorus(V) chlorides under mild conditions, dichlorophosphoranes and polymeric products are formed[199–203]; on further heating to 180–200 °C, the initial tertiary phosphines and phosphorus chlorides are reformed[204,205]. Heating of the same reactants at still higher temperatures (220–260 °C) is accompanied by the cleavage of the C–P bond and the exchange of the hydrocarbon groups for Cl:[206]

$$(C_4H_9)_3P + PCl_3 \rightarrow (C_4H_9)_2PCl + C_4H_9PCl_2 \ .$$

The complete conversion of trialkylphosphines into alkyldichlorophosphines requires heating to 280–350 °C and the use of an excess of PCl_3:[206]

$$(C_4H_9)_3P + 2PCl_3 \rightarrow 3C_4H_9PCl_2 \ .$$

Tertiary phosphines interact with PBr_3 under similar conditions, which leads to the formation of dibromophosphines[207]:

$$(C_6H_5)_3P + 2PBr_3 \rightarrow 3C_6H_5PBr_2 \ .$$

The interaction of primary and secondary phosphines with PCl_3 under conditions where the mixture is cooled or slightly heated also does not involve the phosphorus–carbon bond[208–210], but at a higher temperature (~200 °C and above) the phosphorus–carbon bond is ruptured. This has been confirmed by the isotope exchange between alkyl- or aryldichlorophosphines and $^{32}PCl_3$ at 200–250 °C:[43,211]

$$RPCl_2 + {}^{32}PCl_3 \rightleftarrows R^{32}PCl_2 + PCl_3 \ .$$

The reaction is bimolecular, which indicates an associative mechanism, and proceeds at a fairly high rate; at 250 °C the degree of exchange reaches 50% after 5 h.

Isotope exchange has been observed also for phosphonothioic dichlorides[211]:

$$C_6H_5CH_2\overset{\overset{S}{\|}}{P}Cl_2 + {}^{32}PCl_3 \rightleftarrows C_6H_5CH_2{}^{32}\overset{\overset{S}{\|}}{P}Cl_2 + PCl_3 \ .$$

It is noteworthy that phosphonothioic dichlorides are involved in isotope exchange also with the radioactive $^{32}PSCl_3$ under the same conditions[211]:

$$C_6H_5CH_2\overset{\overset{S}{\|}}{P}Cl_2 + {}^{32}P(S)Cl_3 \rightarrow C_6H_5CH_2{}^{32}\overset{\overset{S}{\|}}{P}Cl_2 + P(S)Cl_3 \ .$$

The oxygen analogues do not enter into a similar reaction apparently because the formation of an intermediate complex is difficult for compounds of tetracoordinate phosphorus. The exception, which is observed for phosphonothioic dichlorides, can be accounted for by the fact that on heating they are capable of dissociating into sulphur and tricoordinate dichlorophosphines, which readily enter into an exchange reaction with PCl_3 or $PSCl_3$. This reaction constitutes a convenient method for the introduction of the radioactive ^{32}P label into pesticidal OPC.[212]

The exchange of hydrocarbon groups with phosphoryl chloride is also not observed in the series of oxygen-containing compounds of tetracoordinate phosphorus. Tertiary

phosphine oxides react with $POCl_3$ to form salt-like adducts which dissociate into the initial reactants on heating above the melting point and undergo pyrolytic decomposition[213–216]. The exchange of phenyl groups for Cl has also not been observed in the reaction of triphenylphosphine oxide with PCl_5, but this reaction was carried out under comparatively mild conditions[217–219].

The presence of a hydroxy-group in the hydrocarbon substituent in the α-position relative to the phosphorus atom increases significantly the lability of the phosphorus–carbon bond[185,220]. The exchange reactions involving a series of substituted OPC can also be facilitated in this way. Indeed tetra(hydroxymethyl)phosphonium hydroxide reacts with PH_3 under mild conditions to form tri(hydroxymethyl)phosphine[221]:

$$3\,(HOCH_2)_4\overset{+}{P}\overline{OH} + H_3P \rightarrow 4\,(HOCH_2)_3P + 3H_2O\ .$$

The high reactivity of the hydroxymethyl derivatives of phosphorus is also manifested in the exchange reactions of hydroxymethylphosphonium salts with tertiary phosphines, which results in the transfer of the hydroxymethyl group from the less nucleophilic to the more nucleophilic phosphorus centre[192–195]:

$$(HOCH_2)_4\overset{+}{P}\overline{Cl} + (C_4H_9)_3P \rightarrow (HOCH_2)_3P + (C_4H_9)_3\overset{+}{P}{-}CH_2OHCl^-\ .$$

The exchange of hydrocarbon groups between OPC can be catalysed by alkali metals[225]

$$(C_6H_5)_4\overset{+}{P}\overline{Br} + (p\text{-}CH_3C_6H_4)_2PK \rightarrow (C_6H_5)_3P + (p\text{-}CH_3C_6H_4)\,PC_6H_5\ .$$

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Analysis of published data has shown that organophosphorus compounds can enter into numerous reactions involving the intermolecular exchange of organic substituents at the phosphorus atom. The ability of OPC to participate in these reactions depends significantly on the coordination number of the phosphorus atom. Substituents bound to a tricoordinate phosphorus atom via N, O, and S atoms exchange most readily. The exchange of hydrocarbon groups at the C–P bond (including those at a tricoordinate phosphorus atom) proceeds with much more difficulty. Compounds of tetracoordinate phosphorus enter into exchange reactions under more severe conditions than the analogous derivatives of tricoordinate phosphorus.

There are no literature data concerning the exchange reactions of organic substituents attached to dicoordinate and pentacoordinate phosphorus atoms. Nor have there been any communications about the exchange of substituents bound to phosphorus via heteroatoms such as Se and Si. The exchange reactions of phosphorus isotopes, which are of interest from both practical and theoretical points of view, have been little studied.

It has been shown that the exchange reactions of organic substituents attached to the phosphorus atom can be greatly influenced by acid and basic catalysts; however, the role of the catalysis has been studied thoroughly only in reactions involving compounds of tricoordinate phosphorus[41,45,160,226,227].

Study of the mechanisms of reactions involving the intermolecular exchange of organic substituents attached to the phosphorus atom show that these reactions proceed via stages in which intermediates are produced[9,10,79]. The formation of an unstable intermediate has been established by ^{31}P NMR in reactions involving compounds of both tricoordinate[228] and tetracoordinate[229] phosphorus. Further development of this branch of the chemistry of OPC will be associated with a more profound study of the mechanisms and characteristic features of the exchange reactions.

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