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Phosphorohalidites and Phosphoropseudohalidites in the Arbuzov Reaction with Halogen-containing Compounds

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The literature data on the reactions of phosphorohalidites and phosphoropseudohalidites with various halogen-containing compounds are surveyed and described systematically.
The bibliography includes 133 references.

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I. INTRODUCTION

In his studies of the structure of phosphorous acid and its esters as long ago as the beginning of the present century, Arbuzov established that fully esterified phosphorous acids readily rearrange to esters of alkylphosphonic acids under the influence of alkyl halides.[1,2] Subsequently the reaction was extended to fully esterified phosphonous and phosphinous acids:

$$RR^1POR^2 + R^3X \rightarrow R^3P(O)RR^1 + R^2X\ .$$

In contrast to the full esters, phosphorohalidites and phosphonohalidites are less reactive and in most cases do not interact with alkyl halides under the usual conditions of the Arbuzov reaction. It appears that phosphorohalidites and phosphonohalidites because of their weak nucleophilic properties were made to undergo the Arbuzov rearrangement only after more than 50 years elapsed. Apart from its theoretical importance, this reaction is also of considerable practical interest, since with its aid it is possible to obtain extremely reactive derivatives of tetracoordinate quinquevalent phosphorus which may serve as the starting compounds in the synthesis of a wide variety of derivatives of phosphoric, phosphonic, and phosphinic acids. Several extensive reviews and review reports have been published[2-23] on reactions of the full esters, thioesters, and amidoesters of tervalent phosphorus acids with organic compounds both containing and not containing a halogen. In these publications there are only individual examples of reactions of phosphorohalidites and phosphoropseudohalidites. Certain aspects of the reactions of these phosphorus derivatives with halogen-containing compounds were described in somewhat greater detail in monographs,[24,25] in a report,[26] and in a review.[27] There are no complete reviews on the Arbuzov reaction involving phosphorohalidites and phosphoropseudohalidites.

We felt it of interest and timely to survey the available literature data on the reactions of these phosphorus derivatives with halogen-containing compounds.

II. REACTIONS OF PHOSPHOROMONOHALIDITES AND PHOSPHONOMONOHALIDITES WITH ALKYL HALIDES

It has been found during the last decades that the most reactive phosphorohalidites and phosphonohalidites are the monofluoro-derivatives: di-isopropyl phosphorofluoridite, alkyl methylphosphonofluoridites, and alkyl *NN*-dimethylphosphoramidofluoridites react with methyl iodide to form the products of the Arbuzov reaction:[28-30]

$$AlkOP(X)F + MeI \rightarrow MeP(O)(X)F + AlkI\ ;$$
$$X = AlkO,\ Me,\ Me_2N\ .$$

Dialkyl phosphorofluorofluoridites react analogously with carboxylic acid chlorides:[31]

$$(AlkO)_2PF + RCOCl \rightarrow RCOP(O)(OAlk)F + AlkCl\ .$$

It was established subsequently that compounds containing an activated carbon–halogen bond enter into the reaction with dialkyl phosphorohalidites under fairly mild conditions:

$$-\ddot{O}-\overset{|}{\underset{|}{C}}-Cl(Br, I), \quad -\ddot{S}-CH_2Cl \quad =\ddot{N}-\overset{|}{\underset{|}{C}}-Cl(Br)$$

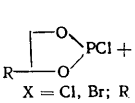
Alkyl α-chloroethyl ethers readily react with dialkyl phosphorochloridites to form alkyl α-alkoxyethylphosphonochloridates,[32,33] while alkyl -chloromethyl and alkyl αα-dichloromethyl ethers enter into the Arbuzov reaction only in the presence of a catalyst ($FeCl_3$):[34]

$$(RO)_2PX + R^1OCH(R^2)Cl \xrightarrow{(FeCl_3)} R^1OCH(R^2)P(O)(OR)X + RCl\ ;$$
$$X = Cl;\ R = Et, Bu, Am;\ R^1 = Et, Bu;\ R^2 = Me\ ;$$
$$X = Cl, F;\ R = Et;\ R^1 = Me, Et;\ R^2 = H, Cl\ .$$

The esters of chloro- and dichloro-acetic acids do not react with dialkyl phosphorohalidites. In contrast to them, the esters of alkoxychloroacetic acids do interact with dialkyl phosphorochloridites and phosphorofluoridites in the presence of catalysts (Lewis acids) and in their absence, while the esters of alkoxydichloroacetic acids react only in the presence of a catalyst:[34-37]

$$(EtO)_2PX + ClC(R^2)(COOR)OR^1 \xrightarrow{(FeCl_3)} R^1O(ROCO)C(R^2)P(O)(OEt)X + EtCl\ ;$$
$$X = Cl, F;\ R \text{ and } R^1 = Me, Et;\ R^2 = H, Cl\ .$$

When cyclic alkyl phosphorochloridites react with alkyl chloromethyl, alkyl bromomethyl, and alkyl dichloromethyl ethers, the Arbuzov reaction always proceeds with the rupture of the C–O bond at the unsubstituted carbon atom:[38-42]

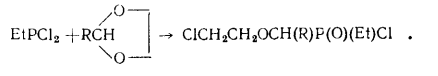


$$PCl + XCH(R^1)OR^2 \rightarrow R^2OCH(R^1)P(O)(Cl)OCH(R)CH_2Cl\ ;$$
$$X = Cl, Br;\ R = H, Me;\ R^1 = H, Cl;\ R^2 = Alk(C_1 - C_4)\ .$$

It has been shown[43-49] that the following are formed initially when phosphorus trichloride, alkyl phosphorodichloridites, and dichloroethyl- and dichlorophenylphosphines react with acetals, α-chloroethers and also dialkyl phosphorochloridites and alkyl ethyl(phenyl)phosphonochloridites among other tervalent phosphorous acid esters which enter into the Arbuzov reaction:

$$R^1CH(OR)_2 + R^2PCl_2 \rightarrow R^2(RO)PCl + R^1CHClOR \rightarrow ROCH(R^1)P(O)(R^2)Cl\ ;$$
$$PCl_3 + 2R^1CH(OR)_2 \rightarrow (RO)_2PCl + 2R^1CHClOR\ ;$$
$$(RO)_2PCl + R^1CHClOR \rightarrow ROCH(R^1)P(O)(OR)Cl\ ;$$
$$R = Alk;\ R^1 = H,\ Me;\ R^2 = AlkO,\ Et,\ Ph\ .$$

Dichloroethylphosphine reacts similarly with 2-alkyl-1,3-dioxolanes:[50]



$$EtPCl_2 + RCH(OCH_2CH_2O) \rightarrow ClCH_2CH_2OCH(R)P(O)(Et)Cl\ .$$

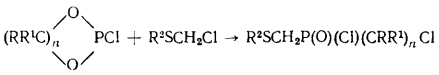
The reactions of dialkyl phosphorochloridites with acylals lead to the formation of α-chloroethers, which interact with the initial dialkyl phosphorochloridites:[51]

$$(RO)_2PCl + MeCH(OR^1)OCOMe \rightarrow (RO)_2POCOMe + MeCHClOR^1\ ;$$
$$(RO)_2PCl + MeCHClOR^1 \rightarrow R^1OCH(Me)P(O)(OR)Cl\ .$$

Alkylacetyl phosphorochloridites and acetyl phosphonochloridites, formed when phosphorodichloridites or dichlorophosphines are treated with acetic anhydride or an acetic acid acylal, react with α-chloroethers analogously to dialkyl phosphorochloridites and alkyl phosphonochloridites.[52-57] A reaction of the same type occurs between phosphorus trichloride and a mixture of acetic anhydride and its acetal:[58]

$$RPCl_2 + (MeCO)_2O \rightarrow RP(Cl)OCOMe \xrightarrow{MeCH(OR^1)Cl} R^1OCH(Me)P(O)(R)Cl\ ;$$
$$R = AlkO,\ Et,\ Ph\ .$$

The reaction of cyclic phosphorochloridites with alkyl chloromethyl sulphides has been patented:[59]



$$(RR^1C)_n(O_2)PCl + R^2SCH_2Cl \rightarrow R^2SCH_2P(O)(Cl)(CRR^1)_nCl\ ;$$
$$n = 2,\ 3;\ R \text{ and } R^1 = H,\ Me\ .$$

III. REACTIONS OF PHOSPHORODIHALIDITES WITH ALKYL HALIDES

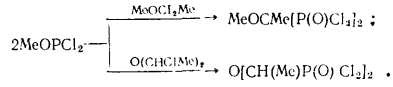
Arbuzov showed that neither methyl iodide nor benzyl chloride act upon the "Menshutkin acid chloride" ($MeOPCl_2$) even on heating at 200 °C for 12 h.[3] However, according to patent data,[60,61] the products of the Arbuzov rearrangement are formed on heating (in a sealed tube at 260–325 °C) methyl phosphorodichloridite with MeI, MeCl, or CCl_4 in the presence of catalysts ($FeCl_3$, ZnI_2, NiI_2, etc). Under milder conditions in the absence of a catalyst, methyl phosphorodichloridite reacts with allyl iodide[62] and ethyl phosphorodichloridite reacts with 4,5-methylenedioxy-2-propylbenzyl iodide.[63]

Methyl and ethyl phosphorodichloridites[64-70] and also butyl phosphorodifluoridite[69-71] enter into the Arbuzov reaction much more readily (than into the reaction with methyl iodide) on treatment with α-chloroalkyl ethers containing[69,70] or not containing[66-68,71] an electronegative alkoxycarbonyl group or three methyl groups at the α-carbon atom.

When alkyl phosphorodichloridites[71-73] and butyl phosphorodifluoridite[71,73] react with dichloromethyl methyl and di(chloromethyl) ethers[72] or with the alkyl esters of alkoxydichloroacetic acids,[71,73] only one chlorine atom is involved in the reaction even in the presence of a large excess of the phosphorodihalidite, while in the reaction of methyl phosphorodichloridite with di(α-chloroethyl) ether or αα-diiodoethyl methyl ether both halogen atoms are substituted:[27]

$$ROCR^1R^2Cl + R^3OPX_2 \rightarrow ROCR^1R^2P(O)X_2 + R^3Cl\ ;$$
$$X = Cl,\ F;\ R = Alk(C_1 - C_4),\ ClCH_2;$$

$$R^1 = H,\ CCl_3,\ COOMe,\ COOEt;\ R^2 = H,\ Cl;$$
$$R^3 = Me,\ Et,\ Bu\ ;$$



$$2MeOPCl_2 \xrightarrow{MeOCl_2Me} MeOCMe[P(O)Cl_2]_2\ ;$$
$$2MeOPCl_2 \xrightarrow{O(CHClMe)_2} O[CH(Me)P(O)Cl_2]_2\ .$$

The reaction of dialkyl formals with an excess of phosphorus trichloride in the presence of $ZnCl_2$ results in the formation of α-chloroethers and alkyl phosphorodichloridites, which react with one another via the mechanism of the Arbuzov reaction:[47,48,74]

$$PCl_3 + (RO)_2CH_2 \rightarrow ROPCl_2 + ROCH_2Cl \rightarrow ROCH_2P(O)Cl_2\ .$$

Alkyl chloromethyl and aryl chloromethyl sulphides react with alkyl phosphorodichloridites analogously to α-chloroethers:[75,76]

$$RSCH_2Cl + R^1OPCl_2 \xrightarrow{FeCl_3} RSCH_2P(O)Cl_2\ ;$$
$$R = Et,\ Pr,\ iso\text{-}Pr,\ Bu,\ Ph\ .$$

IV. PHOSPHOROHALIDITES IN REACTIONS WITH α-CHLORO- AND α-BROMO-ALKYL ISOCYANATES

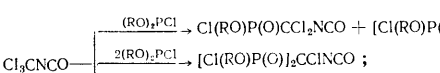
Dialkyl phosphorochloridites and dialkyl phosphorofluoridites undergo the Arbuzov rearrangement very readily on reaction with α-chloro- and α-bromo-alkyl isocyanates, forming α-alkoxychlorophosphonylalkyl and α-alkoxyfluorophosphonylalkyl isocyanates:[24,26,77-85]

$$(RO)_2PX + YCH(R^1)NCO \rightarrow X(RO)P(O)CH(R^1)NCO + RY\ ;$$
$$X = Cl,\ F;\ Y = Cl,\ Br;\ R = Et,\ iso\text{-}Pr;\ R^1 = H,\ Cl,\ Ph,\ BrCH_2,\ CCl_3\ .$$

The reaction of dichloromethyl isocyanate with two moles of dialkyl phosphorofluoridite produces bis(alkoxyfluorophosphonyl)methyl isocyanate:[26,80,81]

$$2(RO)_2PF + Cl_2CHNCO \rightarrow [F(RO)P(O)]_2CHNCO\ .$$

The reaction of trichloromethyl isocyanate with one mole of dialkyl phosphorochloridite affords a mixture of alkoxychlorophosphonyldichloromethyl and bis(alkoxychlorophosphonyl)chloromethyl isocyanates, while the reaction with two moles of the reagent gives rise to the bisphosphorylated isocyanate only. Whatever the proportions of trichloromethyl isocyanate and dialkyl phosphorofluoridite, it is possible to isolate only bis(alkoxyfluorophosphonyl)chloromethyl isocyanate:[26,86]



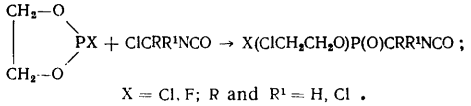
$$Cl_3CNCO \xrightarrow{(RO)_2PCl} Cl(RO)P(O)CCl_2NCO + [Cl(RO)P(O)]_2CClNCO\ ;$$
$$Cl_3CNCO \xrightarrow{2(RO)_2PCl} [Cl(RO)P(O)]_2CClNCO\ ;$$
$$Cl_3CNCO \xrightarrow[n=1,\ 2,\ 3]{n(RO)_2PF} [F(RO)P(O)]_2CClNCO\ .$$

Dialkyl phosphorochloridites react also with dichlorophosphonyl dichloromethyl isocyanate to form a mixed bisphosphorylated chloromethyl isocyanate:[26,86]

$$(RO)_2PCl + Cl_2P(O)CCl_2NCO \rightarrow Cl(RO)P(O)[Cl_2P(O)]CClNCO\ .$$

Cyclic phosphites (2-chloro- and 2-fluoro-phospholans) react with chloro-, dichloro-, and trichloro-methyl isocyanates via the mechanism of the Arbuzov rearrangement

involving ring opening and the formation of the corresponding β-chloroethoxychloro- and β-chloroethoxyfluorophosphonylalkyl isocyanates:[26,87]



$$X = Cl, F;\ R \text{ and } R^1 = H, Cl\ .$$

When alkyl phosphorodichloridites and phosphorodifluoridites react with α-chloro- or α-bromo-alkyl isocyanates, dichlorophosphonyl- and difluorophosphonyl-alkyl isocyanates are formed. The reaction proceeds only in the presence of Lewis acids as catalysts:[24,26,77-79,81-84,86,88-90]

$$R^2OPX_2 + YCRR^1NCO \rightarrow X_2P(O)CRR^1NCO\ ;$$
$$X = Cl, F;\ Y = Cl, Br;\ R = H;\ R^1 = H, Cl, CCl_3, CH_2Cl,;$$
$$CH_2Br, Ph \text{ or } R = R^1 = Cl\ .$$

α-Bromobenzyl isothiocyanate reacts with alkyl phosphorodichloridites and phosphorodifluoridites analogously to α-halogenoalkyl isocyanates:[91]

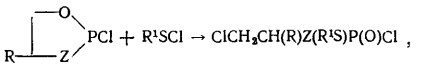
$$ROPX_2 + PhCHBrNCS \rightarrow X_2P(O)CH(Ph)NCS\ ;$$
$$X = Cl, F\ .$$

V. PHOSPHOROHALIDITES IN REACTIONS WITH SULPHENYL CHLORIDES

Dialkyl phosphorochloridites and phosphorofluoridites react very readily with alkane- and arene-sulphenyl chlorides via the mechanism of the Arbuzov rearrangement to form the alkyl and aryl esters of phosphorohalidothiolates:[25,92-95]

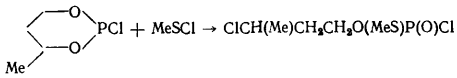
$$(RO)_2PX + R^1SCl \rightarrow R^1S(RO)P(O)X\ .$$

Five-membered cyclic phosphorochloridites, namely 2-chloro-1,3,2-dioxaphospholans, 2-chloro-1,2,3-oxathiaphospholans, and 2-chloro-1,3,2-oxazaphospholans, react with alkane- and arene-sulphenyl chlorides with ring opening at the C—O bond (at the unsubstituted carbon atom in 1,3,2-dioxaphospholans:[96-98]

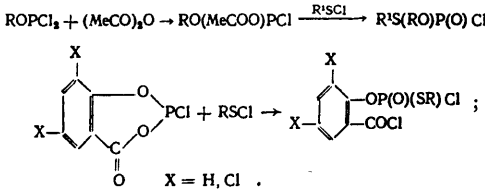


$$Z = O,\ R = H, Me, ClCH_2;\ Z = S, NAlk,\ R = H\ .$$

The C—O bond at the substituted carbon atom is ruptured in six-membered cyclic phosphorochloridites:[98]



When a mixture of an alkyl phosphorodichloridite and acetic anhydride or acetic acid is treated with alkane- and arene-sulphenyl chlorides, acetyl alkyl phosphorochloridites are apparently formed initially and undergo the Arbuzov rearrangement with formation of acetyl chloride.[99,100] The cyclic "salicyl phosphorochloridite" reacts similarly:[101]



$$X = H, Cl\ .$$

Alkane- and arene-sulphenyl chlorides are more reactive than alkyl halides; they enter into the Arbuzov reaction with alkyl phosphorodichloridites and phosphorodifluoridites in the absence of catalysts:[93,94,102-108]

$$ROPX_2 + R^1SCl \rightarrow R^1SP(O)X_2\ .$$

The Arbuzov reaction probably proceeds also when a mixture of phosphorus trichloride and acetic anhydride is treated with alkane- and arene-sulphenyl chlorides:[100]

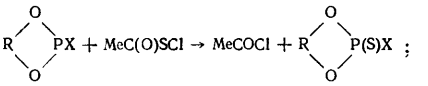


Selenyl chlorides react with alkyl phosphorodichloridites analogously to sulphenyl chlorides, but the reaction proceeds only in the presence of catalysts ($SbCl_5$, BCl_3):[108,109]

$$ROPCl_2 + CF_3SeCl \rightarrow CF_3SeP(O)Cl_2\ .$$

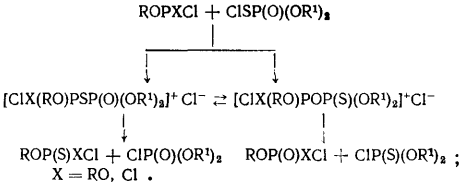
Acetyl-, dialkylphosphono-, and dialkylamino- or *N*-alkyl-*N*-(dialkyl phosphonoamino)-sulphenyl chlorides also react readily with dialkyl phosphorohalidites and alkyl phosphorodihalidites, but the products of the Arbuzov rearrangement are not formed.

Thus cyclic phosphorochloridites, phosphorobromidites, and phosphorofluoridites react with acetylsulphenyl chloride to form acetyl chloride and phosphorohalidothionates:[110-112]



$$R = -(CH_2)_2-,\ -CH_2CH_2CH(Me)-;\ X = Cl, Br, F\ .$$

When dialkyl phosphonosulphenyl chlorides are treated with dialkyl phosphorochloridites and alkyl phosphorodichloridites, either sulphur or oxygen is split off:[25,113]



$$X = RO, Cl\ .$$

Dialkyl phosphorochloridites and alkyl phosphorodichloridites react with dialkylamino- and *N*-methyl-*N*-dialkoxyphosphonylamino-sulphenyl chlorides in proportions of 2 : 1 to form an alkyl chloride, an alkyl phosphorodichloridate, or phosphoryl chloride and amides of phosphorothionic acids, while dialkyl phosphorofluoridites and alkyl phosphorodifluoridites are converted into mixtures of phosphorofluoridothionates and phosphoramidofluoridates. It has been suggested that the products of the Arbuzov rearrangement, namely alkoxyhalogenophosphonyl- or dihalogenophosphonyl-sulphenyl amides, are formed initially and then react in different ways with a second molecule of the corresponding phosphorohalidite:[25,114-118]

$$ROPXY + R^1R^2NSCl \rightarrow [XY(RO)PSNR^1R^2]^+Cl^- \rightarrow RCl + [XYP(O)SNR^1R^2]\ ;$$
$$X = Cl, F, OR;\ Y = Cl, F;\ R^1 = Me,\ R^2 = P(O)(OEt)_2 \text{ or } R^1 \text{ and } R^2 = Alk\ ;$$
$$[XClP(O)SNR^1R^2] + ROPXCl \rightarrow [XClP(O)SP(NR^1R^2)(OR)XI^+Cl^- \rightarrow$$
$$\rightarrow XP(O)Cl_2 + R^1R^2NP(S)(OR)X\ ;$$
$$X = Cl, OR\ ;$$
$$[XFP(O)SNR^1R^2] + ROPXF \rightarrow [XFP(O)S(NR^1R^2)P(OR)FX] \rightarrow XFP(O)NR^1R^2 + ROP(S)FX;$$
$$X = F, OR\ .$$

Dichloromethyleneiminosulphenyl chloride reacts with alkyl phosphorodichloridites analogously to dialkylaminosulphenyl chlorides:[119,120]

$$2ROPCl_2 + Cl_2C{=}NSCl \rightarrow Cl_2C{=}NP(S)(OR)Cl + POCl_3 + RCl\ .$$

VI. REACTIONS OF PHOSPHOROHALIDITES WITH *N*-CHLORO-COMPOUNDS

Dialkyl phosphorochloridites and phosphorofluoridites as well as alkyl phosphorodichloridites and phosphorodifluoridites react very readily with esters of *N*-chloroamidocarboxylic acids [*N*-chloroimidic acids? (Ed.of Translation)] via the mechanism of the Arbuzov reaction:[121]

$$ROPXY + R^1(R^2O)C{=}NCl \rightarrow R^1(R^2O)C{=}NP(O)XY ;$$
$$X = RO, Cl, F;\ Y = Cl, F;\ R^1 = Me, R^2O;\ R^2 = Me, Et .$$

The reactions of dialkyl phosphorochloridites with the esters of *N*-alkyl-*N*-chlorocarbamic acids also yield the products of the Arbuzov rearrangement:[122]

$$(RO)_2PCl + R^1OCON(R^2)Cl \rightarrow R^1OCON(R^2)P(O)(OR)Cl .$$

When phosphorus trichloride reacts with glycols and esters of *N*-alkyl-*N*-chlorocarbamic acids, the initial products are apparently cyclic phosphorochloridites, which then react with the *N*-chloro-compounds:[123]



$$R = (CH_2)_2,\ (CH_2)_3,\ CH(Me)CH(Me) .$$

Alkyl phosphorodichloridites react with the alkyl esters of *N*-alkyl-*N*-chlorocarbamic acids in the presence of the catalyst ($FeCl_3$):[124]

$$ROPCl_2 + R^1OCON(R^2)Cl \xrightarrow{FeCl_3} R^1OCON(R^2)P(O)Cl_2 .$$

When butyl phosphorodifluoridite is heated with *N*-chloro-*NN'*-dimethylbenzamidine, *N*-difluorophosphonyl-*NN'*-dimethylbenzamidine is obtained.[125]

VII. REACTIONS OF PHOSPHOROPSEUDOHALIDITES WITH ALKYL HALIDES AND *N*-CHLORO-COMPOUNDS

Dialkyl phosphorocyanidites enter into the Arbuzov reaction with alkyl iodides on prolonged heating in a sealed tube at 160 °C:[126]

$$(RO)_2PCN + R^1I \rightarrow R^1P(O)(OR)CN ;$$
$$R = Et, Pr;\ R^1 = Me, Et, Pr .$$

The esters of *N*-chlorimidocarboxylic acids [*N*-chloroimidic acids? (Ed.of Translation)] react with dialkyl phosphorocyanidites and alkyl phosphorodicyanidites in benzene:[121]

$$ROP(X)CN + R^1(R^2O)C{=}NCl \rightarrow R^1(R^2O)C{=}NP(O)(X)CN ;$$
$$X = RO, CN;\ R^1 = Me, R^2O;\ R^2 = Me, Et .$$

On prolonged refluxing, diethyl phosphoroisocyanatidite reacts with alkyl iodides via the mechanism of the Arbuzov rearrangement to form *O*-ethylalkylphosphonyl isocyanates:[127,128]

$$(EtO)_2PNCO + RI \rightarrow RP(O)(OEt)NCO ;$$
$$R = Me, Et, Bu, C_8H_{17} .$$

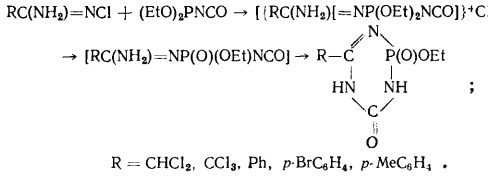
α-Chloroalkyl ethers react with diethyl phosphoroisocyanatidite much more readily than alkyl iodides, whilst αα-dichloroalkyl ethers react only in the presence of the catalyst ($FeCl_3$):[24,129]

$$(EtO)_2PNCO + ROCR^1R^2Cl \rightarrow ROCR^1R^2P(O)(OEt)NCO ;$$
$$R = Me, Et;\ R^1 = H, Cl;\ R^2 = H, COOMe, COOEt .$$

Ethyl phosphorodi-isocyanatidite reacts with α-chloro- and αα-dichloroalkyl ethers only in the presence of the catalyst:[129,130]

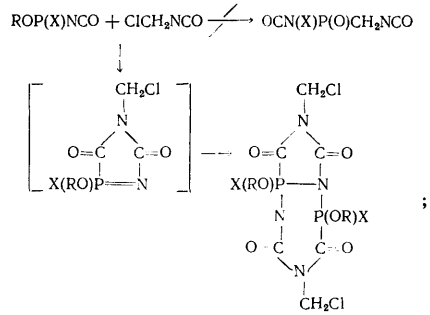
$$EtOP(NCO)_2 + ROCR^1R^2Cl \xrightarrow{FeCl_3} ROCR^1R^2P(O)(NCO)_2 ;$$
$$R = Me, Et;\ R^1 = H, Cl;\ R^2 = H, CCl_3, COOMe, COOEt .$$

The reactions of diethyl phosphoroisocyanatidite with *N*-chloroamidines yield the corresponding phosphonium salts, which readily split off ethyl chloride and are converted into *N*-(*O*-ethylisocyanatophosphonyl)amidines. The latter cyclise to 2-ethoxy-2,4-dioxo-6-R-2,3,4,5-tetrahydro-1,3,5,2-triazaphosphorinanes:[127,131]



$$R = CHCl_2,\ CCl_3,\ Ph,\ p\text{-}BrC_6H_4,\ p\text{-}MeC_6H_4 .$$

When diethyl phosphoroisocyanatidite and alkyl phosphorodi-isocyanatidites are treated with chloromethyl and *p*-chloromethylphenyl isocyanates, it is not possible to obtain the products of the rearrangement—the reaction proceeds via a different pathway. The [3 + 2] -cycloaddition initially results in formation of a substituted 3,5-dioxo-Δ^1-1,4,2-diazaphospholine, which dimerises very readily to the tricyclic 1,3,2λ^5,4λ^5-diazadiphosphetidine:[24,132,133]



$$X = NCO,\ R = Me, Et, Pr, Bu \text{ or } X = RO = EtO .$$

It follows from the data presented in this review that a new development has arisen in recent years in the Arbuzov reaction, whose 80th anniversary occurs in 1985, consisting in the fact that phosphorohalidites, phosphoropseudohalidites, phosphonohalidites and phosphonopseudohalidites, which exhibit reduced nucleophilic properties, are also capable of undergoing the rearrangement on reaction with various halogen-containing electrophiles. The extension of the Arbuzov reaction to phosphorohalidites, phosphoropseudohalidites, phosphonohalidites, and phosphonopseudohalidites made it possible to obtain directly the mono- and di-halides and the mono- and di-isocyanates of tetracoordinate phosphorus acids, as well as their other highly reactive derivatives, which have found extensive applications in the synthesis of a wide variety of organophosphorus compounds possessing useful properties.

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