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Halogenophilic Reactions Involving Derivatives of Four- and Five-coordinate Phosphorus

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The general aspects of halogenophilic reactions of phosphorus compounds have been examined. Examples of the reactions of the halides of four- and five-coordinate phosphorus with readily polarisable nucleophiles, taking place with the transfer of formally positive halogen, have been reviewed.
The bibliography contains 140 references.

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I. INTRODUCTION

In the light of the general problem of nucleophilic reactions at a tetrahedral phosphorus atom, the transformations of its halides are of particular interest. The reason is that, because of their accessibility and high reactivity in nucleophilic reactions, phosphorus halides are the compounds on which the organic chemistry of this element is based.

The view is now generally held that in the reaction of phosphorus halides with nucleophilic reagents, the decisive step is the attack on the central atom, and the result is the formation of the products of halogen replacement.[1,2] At the same time there is a fairly large amount of experimental material on the reactions of the halides of four- and five-coordinate phosphorus with a number of nucleophilic reagents, leading to a decrease in the coordination number of the phosphorus atom. Their results cannot be interpreted in terms of replacement reactions. It is apparently for this reason that they have hardly ever been discussed in the theoretical examination of nucleophilic reactions with P^{IV} and P^{V} halides, and have not been reviewed before. In this respect, the situation that has arisen resembles that for nucleophilic reactions in organic halides. These processes have been studied in detail, and are generally interpreted in terms of replacement reactions at a carbon atom. It is found fairly frequently, however, that in spite of a high positive charge on the carbon atom, created by the negative inductive effect of the halogen atoms, for example in polyhalogenomethanes, nucleophilic attack at this atom is hindered. Usually, in these systems, it is directed to a peripheral atom, that is an S_{N^2Hal} reaction, or halogenophilic reaction, takes place, the result of which appears as the transfer of formally positive halogen.[3,4] The prerequisites for this reaction are shielding of the carbon atom by substituents and stability of the carbanion as the leaving group.[4] The ease of nucleophilic attack on the halogen increases in the order Cl ≪ Br < I,[5-8] and its probability increases with increase in the softness and volume of the nucleophile.[6,9,10] It has been established that these reactions on the whole are characteristic of compounds in which the halogen atom is joined to a carbon atom carrying strong electron-acceptor substituents (ester, carbonyl, nitro-, and sulpho-groups).[5-9] Halogenophilic reactions are also assumed in the reactions of nucleophilic reagents with compounds containing N–Hal,[10-13] O–Hal, and S–Hal bonds.[10]

Comparison of the values of the constants σ_I, σ_m, and σ_n for phosphorus-containing substituents and for groups facilitating the manifestation by the halogen of the properties of an electropositive atom shows that the acceptor characteristics of the phosphorus fragments are similar to or even greater than the latter (see Table). This suggests that halogenophilic reactions should also be possible for compounds having a P–Hal bond. The halides of four-coordinate phosphorus should apparently show the greatest tendency to undergo these reactions. Unfortunately, the acceptor properties have not been determined quantitatively for halogenophosphonium cations, but spectroscopic studies of intramolecular interactions in four-coordinate phosphorus chlorides containing unsaturated groups have shown that the fragment PCl_3^+, for example, has a stronger action than the $POCl_2$ and $PSCl_2$ groups.[15-17]

Values of the constants σ_I, σ_m, and σ_n for different acceptor fragments.[14]

Group	σ_I	σ_m	σ_n	Group	σ_I	σ_m	σ_n
CCl_3	0.41	0.40	0.46	$PSCl_2$	0.59	0.70	0.80
COMe	0.23	0.36	0.47	PF_4	0.45	0.63	0.80
CN	0.57	0.56	0.66	$^+PMe_2PhI^-$	—	0.71	0.83
NO_2	0.68	—	—	$^+PPh_3Cl^-$	0.76	—	—
SO_2Ph	0.57	0.59	0.70	$^+PBu_3Cl^-$	0.60	—	—
PCl_2	0.45	0.53	0.61	$^+PMe_3I^-$	—	0.74	—
$POCl_2$	0.65	0.78	0.90	$^+PMePhI^-$	—	0.71	0.83

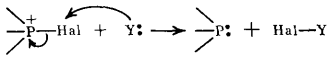
Useful information on the electron density distribution in the P–Cl bond in compounds of four-coordinate phosphorus can be obtained by ^{31}P NMR and ^{35}Cl NQR, which make it possible to characterise the electron environment of the two partners forming the bond.[18] Analysis of the relationship between the ^{35}Cl NQR frequencies and the ^{31}P NMR chemical shifts for R_nPOCl_{3-n}, R_nPSCl_{3-n}, and $R_nPCl_{4+n}^+$ showed that with increase in the electron-acceptor properties of the substituent in the compounds of each series,

the NQR frequency increases, and the NMR signal is displaced to a higher field. This is interpreted as a decrease in the polarity of the P–Cl bond. On going from phosphoryl to thiophosphoryl compounds and then to the chlorophosphonium analogues, the NQR frequency increases, and the shielding of the phosphorus nucleus decreases. Judging from the ^{35}Cl NQR spectra, the electron density on the chlorine atom decreases. Evidence in support of this explanation is provided by the recently measured asymmetry parameters of the electric field gradient at ^{35}Cl nuclei in chlorine-containing phosphorus compounds.[19] It was shown for the case of $POCl_3$, $PSCl_3$, and $PCl_4^+.AlCl_4^-$ that the asymmetry parameters of these four-coordinate phosphorus compounds are close to zero, possibly indicating that there is practically no interaction of the unshared electron pairs of the chlorine atom with the phosphorus atom.

A decrease in the polarity of the P–Cl bond may be indicated by the decrease in its length on going from phosphoryl and thiophosphoryl chlorides[20] to the tetrachlorophosphonium cation.[21]

Thus halogenophilic reactions among P^{IV} derivatives should be expected with the highest probability for halogenophosphonium compounds. The reactions of five-coordinate phosphorus halides involving the formation of these quasiphosphonium salts may take place similarly.

In these cases, in the reaction with soft bases,[22] the appearance of the products of the reduction of phosphorus to the three-coordinate state may be accompanied by the simultaneous oxidative chlorination of the nucleophile:



These reactions may not be heterolytic. A possible alternative is one-electron transfer processes. Their examination, however, is outside the scope of the present review, the aim of which was to summarise the reactions of four- and five-coordinate phosphorus halides, taking place with the transfer of formally positive halogen, which have not previously been systematised.

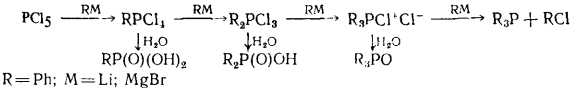
II. REACTIONS WITH ORGANOMETALLIC COMPOUNDS

A large number of reactions of phosphorus halides with organometallic compounds (OMC) are generally regarded as processes of nucleophilic substitution at the phosphorus atom.[23] At the same time, there are data indicating that a whole range of reactions of P^{IV} and P^{V} halides with OMC give products of the reduction of phosphorus to the three-coordinate state.

The first example of a reaction of this kind is the reaction of phosphorus pentachloride with phenylmagnesium bromide,[24] which gives triphenylphosphine in good yield. Reduction of PCl_5 is also observed in its reaction with *para*-trimethylsilylphenylmagnesium bromide.[25] The formation of the corresponding tertiary phosphine was detected in the reaction of phosphorus pentachloride with $PhC{\equiv}CMgBr$.[26]

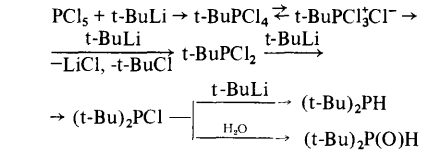
Comparatively recently, more thorough studies of these reactions were carried out, their synthetic possibilities were demonstrated, and a probable mechanism proposed. It was found that tertiary phosphines are obtained only by using an excess of OMC,[27,29,30] and that the yields of the reduction products increases with increase in the volume of the organic group in the OMC.[30] A detailed study of the products of the reaction of PCl_5 with an excess of phenyl-lithium showed that in addition to triphenylphosphine, an equivalent quantity of chlorobenzene is formed.[30] Decrease in the PCl_5 : PhLi ratio to 1 : 3 produces a fundamental change in the nature of the final product. Instead of the tertiary phosphine, its oxide is formed (after hydrolysis). Further decrease in this ratio leads to the formation of a mixture of the corresponding phosphonic and phosphinic acids.[31]

The results indicate that the reaction of five-coordinate phosphorus with phenyl derivatives of lithium and magnesium involve initially the successive replacement of halogen in the pentachloride molecule as far as the triorganodichlorophosphorane structure, whose ionised state makes possible a reduction process in subsequent reaction with the OMC:[31]



R = Ph; M = Li; MgBr

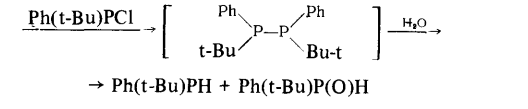
Increase in the volume of the group in the OMC molecule has a significant influence on the result of the reaction. The branching at the α-carbon atom in the isopropyl-lithium molecule leads to a marked increase in the yield of the reduction product.[29] The change to the t-butyl derivative leads to the formation of not the corresponding tertiary phosphine but a mixture of di-t-butylphosphine and di-t-butylphosphinous acid.[30] The presence of these products indicated that the reduction of five-coordinate phosphorus chloride takes place not at the triorganodichlorophosphorane stage but at an earlier stage, and is associated with the appearance of a chlorophosphonium intermediate:



The data obtained are consistent with the fact that it is impossible to replace directly all the chlorine atoms in the P^{III} compound by a t-butyl group, because of steric crowding at the phosphorus.[32,33] In this case the reaction of di-t-butylchlorophosphine, as reduction product, with an excess of the lithium alkyl gives a secondary phosphine, probably by a scheme including the transfer of a hydride ion from the lithium alkyl to the organophosphorus molecule.[32] Hydrolysis of the di-t-butylchlorophosphine remaining gives the secondary phosphine oxide (dialkylphosphonous acid).

Similar conclusions were reached in a study of the reaction of organic derivatives of phosphorus pentachloride with OMC.

The reactions of organyltetrachlorophosphoranes with an excess of an organolithium compound or Grignard reagent also give tertiary phosphines.[34–36] Increase in the volume of the group in the OMC increases the yield of reduction product.[36] The reaction of phenyltetrachlorophosphorane with t-butyl-lithium is influenced by steric and electronic factors. The expected di-t-butylphenylphosphine is not detected, and a mixture of t-butylphenylphosphine and its oxide appears.[30] The reaction probably takes place with the intermediate formation of t-butylphenylchlorophosphine, which subsequently reacts with the lithium alkyl to give the mixture of products indicated, by a scheme analogous to that proposed by Hoffmann for Grignard reagents:[33]



In this case the reduction of the five-coordinate structure at the phosphorus atom takes place at the t-butylphenyltrichlorophosphorane stage, which is different from the results

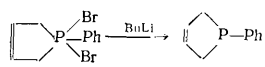
obtained in a detailed study of the reaction of phenyltetrachlorophosphorane with phenyl-lithium.[36] In the last case it was shown that the reduction and the formation of the equivalent quantity of chlorobenzene accompanying it take place at a reagent ratio of 1 : 3, that is at the stage of triphenyldichlorophosphorane formation.

In a study of the reaction of diphenyltrichlorophosphorane with phenyl-lithium in different proportions it was found that with equimolar quantities of the reagents, reduction of the phosphorane is not observed.[37] The hydrolysis of the reaction mixture gives triphenylphosphine oxide. The tertiary phosphine is formed only in a two-fold excess of the lithium aryl. The formation of chlorobenzene shows directly the halogenophilic character of the reaction. Reduction of Ph_2PCl_3 is also observed in the reaction with lithium alkyls. The yield of diphenylalkylphosphines increases with increase in the volume of the alkyl group in the organolithium compound.

The reactions of triorganotrihalogenophosphoranes with OMC have been studied in more detail. It was previously considered[38,39] that the reaction of triphenyldihalogenophosphoranes with alkylmagnesium halides gives triphenylalkylphosphonium salts. It was later established, however, that they are formed only with methylmagnesium iodide.[40] In other cases triphenylphosphine and the corresponding organic halide are obtained. Metallated derivatives of amines, pyrrole, and indole react with triphenyldihalogenophosphoranes to give aminotriphenylphosphonium salts.[41] The authors suggest that halogen transfer takes place at an intermediate stage:

$$Ph_3PHal_2 + RNHMgX \xrightarrow[-MgXHal]{} [Ph_3P + RNHHal] \rightarrow Ph_3P^+—NHR\ Hal^-$$

The reduction of cyclic dihalogenophosphoranes to the corresponding phospholenes under the influence of a lithium alkyl has been detected:[42]



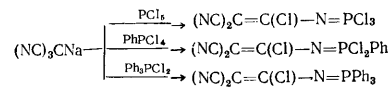
In a study of the reactions of organometallic compounds with chlorophosphoranes it was shown that the species responsible for the reduction of the phosphorus atom to the three-coordinate state are chlorophosphonium structures, either forming the basis of the chlorophosphorane structure or formed during the reaction.[27,36,37] To confirm this, the reactions were carried out between organolithium compounds and chlorophosphoranes shown by ^{31}P NMR,[43,44] ^{35}Cl NQR,[43–46] and ultraviolet spectroscopy[15–17] to be in the ionised state $R_nPCl_4^+{}_{-n}Cl^-$ in solution and in the solid state. For the reactions of $Ph_3PCl^+Cl^-$, $Ph_2EtPCl^+Cl^-$, *iso*-$Pr_3PCl^+Cl^-$, $Et_3PCl^+Cl^-$, *t*-$Bu_2PCl_2^+Cl^-$, and *iso*-$Pr_2PCl_2^+Cl^-$ it was shown that the presence of the chlorophosphonium cation in these compounds makes reduction possible under the influence of organic derivatives of lithium at the first stage of the reduction.[47] The organic halide is formed in quantities equivalent to the reaction product. The process was therefore interpreted in terms of halogenophilic attack on a chlorine atom in the phosphonium cation by the potential carbanion of the organometallic compound. Similar conclusions were reached in a study of the reactions of organolithium and organomagnesium compounds with organylchlorophosphonium hexachlorophosphates having a structurally fixed chlorophosphonium cation:[48,49]

$$R_nPCl_{4-n}^+\ PCl_6^- + R'Li \rightarrow R_nPR'_{3-n} + R'_3P + RCl + LiCl$$

R = Ph, p-ClC_6H_4, p-MeC_6H_4, p-$MeOC_6H_4$, PhCH=CH; R′ = Ph, Alk; n = 1—3

The absence of a chlorine atom in the phosphonium cation of the adduct $Ph_4P^+PCl_6^-$ makes its reduction by phenyllithium in the initial stages of the reaction impossible.[48]

Halogenophilic reactions apparently take place in the reaction of the sodium salt of tricyanomethane with phosphorus pentachloride and its organic derivatives:[50]



This is indicated by the formation of the same compounds by an independent method. Thus the expected products of the halogenophilic reaction of phosphorus pentachloride with $(NC)_3CNa$, namely PCl_3 and tricyanochloromethane, gave the same 1-trichlorophosphazo-1-chloro-2,2-dicyanoethylene.[50] An analogous reaction takes place between $(NC)_3CCl$ and triphenylphosphine.[51] Thus the first stage of the reaction of $(NC)_3CNa$ with P^V chlorides apparently involves halogen transfer:

$$R_nPCl_{5-n} + NaC(CN)_3 \rightarrow NaCl + [R_nPCl_{3-n} + ClC(CN)_3]$$

It is extremely probable that a similar process also takes place in the reaction of organyltetrachlorophosphoranes with malonodinitrile,[52] which is a strong CH acid (pK_a 11.0 [53]):

$$CH_2(CN)_2 + RPCl_4 \rightarrow HCl + [ClCH(CN)_2 + RPCl_2] \rightarrow NC—CH=C(Cl)—N=PCl_2R$$

Halogenophilic reactions can also be assumed in other cases with ionisation of CH acids:[54–56]

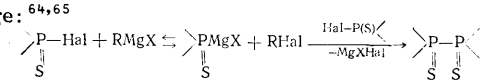
$$Ph_nPCl_{5-n} + CH_2X_2 \xrightarrow{Et_3N} Ph_nPCl_{3-n}=CX_2 + Et_3N\cdot HCl$$

X = COOEt, CN, SO_2Ph; n = 2, 3

The halogenophilic nature of the reaction is also indicated by result of the reaction of PCl_5 with a carbanion stabilised by resonance, such as phosphorus ylid:[57]

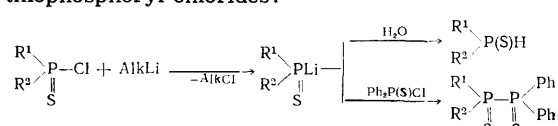
$$Ph_3P^+—\bar{C}(CH_2C_6H_4NO_2\text{-}n)COR + PCl_5 \rightarrow Ph_3P^+—C(Cl)\cdot(CH_2C_6H_4NO_2\text{-}n)COR$$

Among other reactions of OMC with P^{IV} derivatives, the transformations of the phosphoryl chlorides $R_nP(O)Cl_{3-n}$ have been most fully studied. They provide a familiar method for making a phosphorus–carbon bond, interpreted as nucleophilic replacement at the phosphorus atom.[23] The analogous reactions of thiophosphoryl chlorides have been less extensively studied. Work in this direction has established that phosphorus sulphide chlorides and arylthiophosphoryl dichlorides react with aryl-,[58] vinyl-,[59,60] and arylethynylmagnesium halides[60,61] to give tertiary phosphine sulphides. With lower alkylmagnesium halides, an "anomalous" Kabachnik reaction takes place[62,63] to give compounds with a phosphorus–phosphorus bond. The same products are formed with Grignard reagents and thiophosphoryl tribromide.[64] It has been suggested that the most probable scheme for this unusual reaction involves metal–halogen exchange:[64,65]



This scheme is confirmed by the formation of organic halides[49,65] and secondary phosphine sulphides (by hydrolysis of the exchange products).[66]

Organolithium compounds, which have an even greater tendency to undergo exchange reactions, react similarly with thiophosphoryl chlorides:[67]



R^1 = Cl, R^2 = Et, Ph, Cl; Alk = Et, Bu

This metal–halogen exchange reaction possibly takes place by a mechanism involving nucleophilic attack on the halogen. This model, for example, represents one probable scheme for the exchange reactions of organic halides.[68]

A curious feature is that increase in the concentration of the organolithium compound in the above reaction leads to the formation of tertiary phosphines.[69] This may be related to the reduction of the product of exchange by the lithium alkyl, the possibility of which was demonstrated by Trippett.[70]

Thus a soft base such as the potential carbanion of an OMC brings about reactions with various four- and five-coordinate phosphorus halides, whose results cannot be explained in terms of nucleophilic attack at phosphorus. A logical explanation of these reactions is provided by schemes including a halogenophilic reaction.

III. REACTIONS WITH COMPOUNDS OF THREE-COORDINATE PHOSPHORUS

Compounds of three-coordinate phosphorus are soft bases. It is evidently this property of P^{III} compounds that makes possible the unique reactions with polyhalogenohydrocarbons (Appel, Todd–Atherton, etc. reactions) and also with compounds containing an N–Hal or S–Hal bond. The large number of studies in this field have been summarised in several reviews,[10,71,72] where the preferred direction of these reactions, namely attack on the three-coordinate phosphorus compound at the halogen atom, is emphasised.

Similar reactions should naturally be expected for halides of four- and five-coordinate phosphorus.

Thus P^{III} compounds are fairly frequently used to reduce various halogenophosphonium derivatives.

For example, under the influence of phenyldichlorophosphine in the presence of phosphorus oxide chloride, methyldichlorophosphine is formed from the corresponding adduct of the Clay–Kinnear–Perren reaction:[73]

$$MePCl_3^+\,AlCl_4^- + PhPCl_2 \xrightarrow{POCl_3} MePCl_2$$

The use of tributylphosphine instead of $PhPCl_2$ lowers slightly the yield of desired product. The reaction of $PCl_4^+SbCl_6^-$ with Bu_3P gives phosphorus trichloride and tributyldichlorophosphorane.[74] The reduction of the adducts $t\text{-}Bu_3PX^+MX_3^-$ (X = Cl, Br; M = Ge, Sn) by the action of $t\text{-}Bu_3P$ has been demonstrated;[75] the products are $t\text{-}Bu_3P.MX_2$ and $t\text{-}Bu_3PX^+X^-$. Another reaction between compounds of three-coordinate phosphorus and compounds containing a chlorophosphonium cation was discovered recently:[76]

$$Ph(R^1)PClX\,AlCl_4^- + (R^2O)_2PR^3 \xrightarrow{H_2O} Ph(R^1)P(O)R^3$$

R^1 = Me, Et, s-Alk, CH_2OBu; R^2 = Et, Bu; R^3 = OR, OH, Cl; X = Cl, Br

It is suggested that the main stage of the reaction is halogen transfer:

$$\rangle P\text{–}Hal + (R^2O)_2PR^3 \rightarrow \rangle P: + HalP(OR^2)_2R^3$$

The reaction of the products of the Clay–Kinnear–Perren reaction with P^{III} compounds was recently studied in detail.[77] It was shown that these adducts can be reduced by triarylphosphines, triarylphosphites, and diethylaminodichlorophosphine. Chlorination of the reagent to give the corresponding chlorophosphonium salt takes place simultaneously:

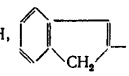
$$RPCl_3^+AlCl_4^- + R'_nPCl_{3-n} \rightarrow RPCl_2 + R'_n\,PCl_{4-n}^+\,AlCl_4^-$$

R = Cl, iso-Pr, CCl_3; R′ = Ph, PhO, *p*-MeOPhO (n = 3), Et_2N (n = 1)

Comparison of the results with data on the reaction of chlorophosphonium cations with nitrogen bases[78] shows that on going from hard compounds, for example pyridines, to soft compounds (P^{III} compounds) there is a fundamental change in the direction of attack by the base. Thus the phosphorus atom shows acceptor properties with respect to the unidentate pyridines, giving stable complexes $PCl_4^+.2Py$, whereas with three-coordinate phosphorus compounds the reaction centre is the chlorine atom, covalently bonded to phosphorus.

Salts of diethyl hydrogen phosphite exist predominantly in the form $(EtO)_2\overset{\cdot\cdot}{P}\text{–}O^-$ with three-coordinate phosphorus, and have been used to reduce various chlorophosphonium compounds.[79] The products of this reaction also correspond to the halogenophilic reaction scheme:

$$RPCl_3^+\,PCl_6^- + 2(EtO)_2P\bar{O}\,\overset{+}{H}NEt_3 \rightarrow RPCl_2 + 2(EtO)_2P(O)Cl + PCl_3 + 2Et_3N\cdot HCl$$

R = PhCH=CH, PhOCH=CH, 

$RP(O)Cl_2$ and $(EtO)_2PCl$ are formed simultaneously in low yields, and this is attributed to the ambidentate character of the diethyl phosphite anion. In this case the oxygen atom, as a hard basic centre, attacks the phosphorus in the phosphonium cation:

$$RPCl_3^+\,PCl_6^- + 2\,(EtO)_2P\text{–}O^- \rightarrow RP(O)Cl_2 + 2(EtO)_2PCl + 2Cl^- + POCl_3$$

The appearance of diethylchlorophosphite in the reaction mixture leads to the competing reaction involving the reduction of the original chlorophosphonium compounds under the influence of this tervalent phosphorus derivative:

$$RPCl_3^+\,PCl_5^- + (EtO)_2PCl \rightarrow RPCl_2 + 2EtOP(O)Cl_2 + PCl_3 + 2EtCl$$

The presence of ethyl dichlorophosphate in the reaction products confirms that this reaction takes place.

This reaction of salts of diethyl hydrogen phosphite with chlorophosphonium derivatives is directly analogous to the familiar Todd–Atherton reaction, in which the main stage is halogen transfer:

$$CCl_4 + (RO_2)P\text{–}O^-\ \overset{+}{H}NR_3 \rightarrow CCl_3^-\overset{+}{H}NR_3 + (RO)_2\overset{Cl}{\overset{|}{P}}{=}O$$

It has been reported[80] that PH_3 reduces the products of the phosphorylation of alkenes by phosphorus pentachloride, which have a quasiphosphonium salt structure, to the corresponding dichlorophosphines in good yield. AsH_3 reacts analogously:[81]

$$3RPCl_3^+PCl_6^- + EH_3 \rightarrow 3RPCl_2 + 3PCl_3 + 6HCl + 2ECl_3$$

R = EtOCH=CH, BuOCH=CH, PhCH(Cl)–CH_2, BuCH(Cl)–CH_2; E = P, As

Methyldichlorophosphite is used fairly successfully to reduce unsaturated chlorophosphonium derivatives:[82,83]

$$\begin{matrix}R^1\\R^2\end{matrix}\!\!\rangle C{=}CHPCl_3^+\,PCl_6^- \xrightarrow{CH_3OPCl_2} \begin{matrix}R^1\\R^2\end{matrix}\!\!\rangle C{=}CHPCl_2 + CH_3Cl + POCl_3$$

R^1 = Me, Et; R^2 = H, Me, Cl

Compounds of three-coordinate phosphorus are widely used to reduce phosphorus pentahalides and their organic derivatives.

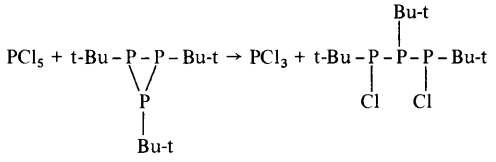
Conductometric[84] and ^{31}P NMR spectroscopic[74] studies of the reaction of phosphorus pentachloride with tertiary phosphines have shown that in the first stage of the reaction at a reagent ratio of 1 : 1, PCl_3 and the triorganyldichlorophosphorane are formed. The use of a two-fold excess of the pentachloride leads to the appearance of the triorganylchlorophosphonium hexachlorophosphate:

$$PCl_5 + R_3P \rightarrow PCl_3 + R_3PCl_2$$
$$R_3PCl_2 + PCl_5 \rightarrow R_3PCl^+\,PCl_6^-$$

R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-$EtOC_6H_4$, Bu

The same result was obtained using phenyl- and diphenylchlorophosphines.[74]

Phosphorus pentachloride and pentabromide bring about the rupture of the phosphorus–phosphorus bond in tri-t-butylcyclotriphosphane:[85]

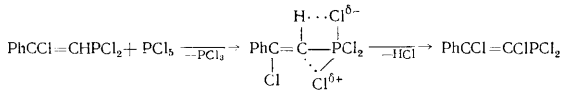


The chlorination of tri-*p*-cyclohexylphenyl phosphite to the corresponding dichlorophosphorane under the influence of phosphorus pentachloride takes place fairly readily.[86]

Unsaturated dichlorophosphines on treatment with PCl_5 give tetrachlorophosphoranes:[87,88]

$$PCl_5 + RCH{=}CHPCl_2 \rightarrow RCH{=}CHPCl_4 + PCl_3$$

The reaction of α-chlorostyryldichlorophosphine with the pentachloride, however, does not give a P^V derivative, because of the ease of the intramolecular chlorination at the vinyl carbon atom.



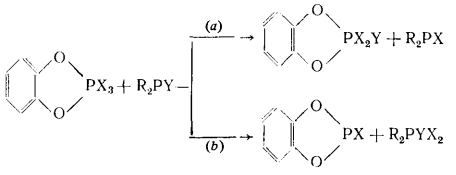
Methyl dichlorophosphite is used to reduce halogenophosphoranes:[89,90]

$$RPCl_4 + CH_3OPCl_2 \rightarrow RPCl_2 + CH_3Cl + POCl_3$$
$$R = Me,\ CCl_3,\ p\text{-}ClC_2H_4C_6H_4$$

Its use to convert distyryl- and tristyrylchlorophosphoranes into the three-coordinate state did not give satisfactory results. In this case, phosphoryl derivatives are obtained.[91]

The reduction of trihalogenophospholenes by triphenylphosphine, which is converted into the triphenyldihalogenophosphorane in the process, has been noted.[92]

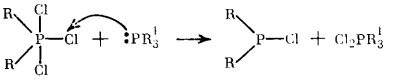
A series of studies of the reaction of P^V halides with compounds of three-coordinate phosphorus was carried out by Gloede and co-workers.[93–96] It was shown for the case of trihalogenodioxaphospholenes that cyclic halogenophosphoranes can undergo ligand exchange (*a*) and halogen transfer (*b*) with P^{III} derivatives:



R = Y = OEt, OPh; R = OPh, Y = Cl; X = Cl, Br

It is emphasised that the redox reactions (*b*) become preferred on going from the chlorides to the bromides of five-coordinate phosphorus.[94] This is consistent with the application of the principle of hard and soft acids and bases (HSAB) to halogenophilic reactions.

It has been suggested that the reduction of halides of five-coordinate phosphorus can take place not only with the participation of their halogenophosphonium form. Unionised trigonal bipyramidal halogenophosphoranes can also take part in halogenophilic reactions, and the reduction takes place as a result of attack on the halogen atom in the equatorial position by the soft base.[97] The electrophilic properties of this atom apparently arise as a result of the reaction of its unshared electron pairs with the phosphorus atom.[19] A similar intramolecular reaction has been assumed for other equatorial ligands.[98] This has been used to explain the reactions of various chlorophosphoranes with tertiary phosphines.[97] Phenyl- and diphenylchlorophosphoranes, which in weakly polar solvents have a trigonal bipyramidal structure with the organic substituents in the equatorial positions, are rapidly reduced by triphenyl- and tributylphosphines to the corresponding chlorophosphines. The reducing agent is converted into the triorganodichlorophosphorane:

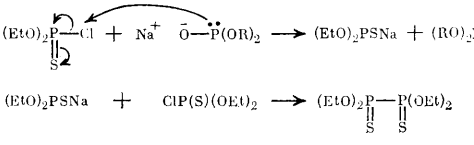


The reaction takes place analogously with CCl_3PCl_4 and $(CCl_3)_2PCl_3$, whose trichloromethyl substituents are in the apical positions.

Tertiary phosphines do not react, however, with triphenyldichlorophosphorane, which in non-polar solvents is probably present in the unionised form.[99] According to the apicophilicity rules,[100] the phosphorane in this form should have a trigonal bipyramidal structure with all the organic substituents in equatorial positions, which structurally excludes the appearance of Cl_{eq} and makes halogenophilic reactions impossible.

The successful use of white phosphorus to reduce P^{IV} and P^V halides can be explained in terms of halogenophilic reactions; the P_4 molecule can be regarded as a derivative of tervalent phosphorus. White phosphorus can reduce triorganodichloro-,[101] diorganotrichloro-,[102] and organotetrachlorophosphoranes,[103] trihalogenophospholenes,[104] and compounds containing a chlorophosphonium cation.[105–107]

Halogen transfer reactions under the influence of P^{III} derivatives are also observed in a number of thiophosphoryl halides. For example, unlike diethyl chlorophosphate, its thio-analogue reacts with sodium diethyl phosphite to give tetraethyl dithiohypophosphate:[108]



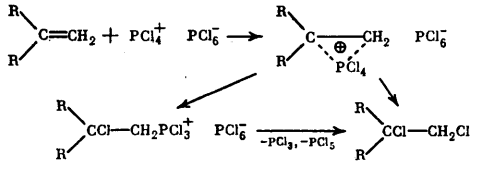
IV. REACTIONS WITH ALKENES AND ARENES

According to the HSAB principle, alkenes and arenes are regarded as soft bases, so that they can be expected to undergo reactions involving attack on a halogen atom in halogenophosphonium compounds or in derivatives of five-coordinate phosphorus.

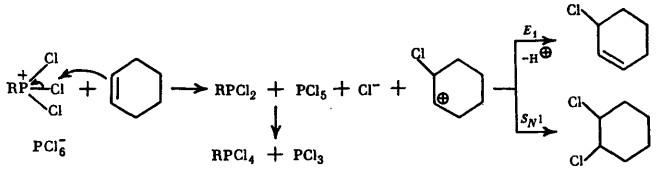
Thus phosphorus pentachloride and its organic derivatives have a chlorinating action on organic compounds of many classes, including various arenes.[109] In addition to the homolytic chlorination of alkylaromatic compounds in the side chain, a heterolytic reaction is also observed. This is indicated for example, by the chlorination of mesitylene to 2,4,6-trimethylchlorobenzene under conditions in which radical processes are inhibited.[110] An attempt was made to explain the chlorinating action of PCl_5 and its derivatives in terms of halogenophilic reactions at the chlorophosphonium cation, present in the crystalline pentachloride.[111] It was found that the model quasiphosphinium salts $PCl_4^+X^-$, where $X = AlCl_4$, BF_3Cl, $SbCl_6$, and PCl_6, and $Ph_nPCl_{4-n}^+PCl_6^-$ can, like PCl_5, chlorinate substituted benzenes in the ring. The ease of chlorination increases with increase in the electron-donor properties of the substituent in the arene. It was shown for the case of anisole that the formation of the chlorination product (*p*-chloranisole) is accompanied by the

simultaneous reduction of the phosphonium salt to three-coordinate phosphorus compounds. A necessary condition for the chlorination of the arene is the presence of chlorine in the phosphonium cation; thus the adduct $Ph_4P^+PCl_6^-$ cannot chlorinate anisole even under severe conditions.

Many authors[110,112,113] report a side reaction giving 1,2-dichloroalkanes in the phosphorylation of alkenes by phosphorus pentachloride. Moderate heating of the products of the phosphorylation of unsaturated compounds with an excess of an alkene in donor solvents (toluene, acetonitrile) also gives these dichlorides.[114] Increase in temperature and the polarity of the medium increases the chlorinating power of PCl_5 with respect to alkenes.[113] It is suggested that in polar media, phosphorus pentachloride ionises, and the resulting tetrachlorophosphonium cation reacts with the unsaturated compound.[110,113] The concerted opening of the epiphosphorane transition state leads to the production of a mixture of chlorination and phosphorylation products.



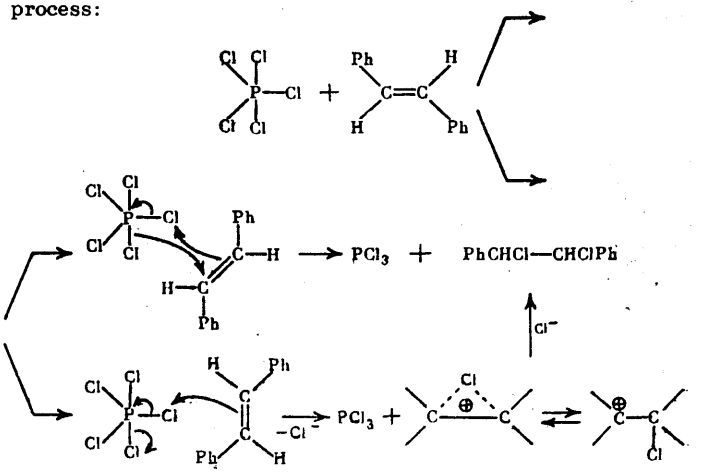
It has been shown for the case of the reactions of chlorophosphonium compounds with cyclohexene that the cation in $R_nPCl_{4-n}^+PCl_6^-$ (R = Ph, PhCH = CH; n = 1–3) is in fact responsible for the formation of alkene chlorination products.[115] Dephosphorylation of the original phosphorus-containing compound is not observed, however, and the corresponding chlorophosphoranes and phosphorus trichloride are formed. This fact, and also the presence of *trans*-dichlorocyclohexane and 3-chlorocyclohexene as alkene halogenation products provide evidence in support of a scheme involving halogenophilic attack by the alkene on the chlorine atom in the phosphonium cation:



Further evidence is provided by the increase in the difficulty of chlorinating cyclohexene with increase in the number of organic substituents in the cation, and by the fact that tetraphenylphosphonium hexachlorophosphate does not react.

It should be emphasised, however, that the formation of dichloroalkanes from alkenes and phosphorus pentachloride in weakly polar media (benzene, dichloroethane) as a result of the production of the halogenophosphonium cation in the reaction sphere does not agree with data on the state of PCl_5 in these solvents. Ultraviolet spectroscopy has shown convincingly that it is present in the unionised form.[116,117]

In a study of the chlorination of *trans*-stilbene by phosphorus pentachloride[118] it was suggested that this reaction be regarded as a halogenophilic reaction involving the unionised form of the phosphorus halide. The attack by the alkene takes place at the halogen atom in the equatorial plane of the trigonal bipyramidal PCl_5. The reaction can take place either as a concerted *anti*-addition or as a stepwise process:



V. REACTIONS WITH HALIDE ANIONS

From the above ideas about the preference of reactions with soft nucleophiles for achieving halogenophilic reactions, processes of this kind should be expected when halogenophosphonium compounds are treated with iodide and bromide anions:

$$\equiv\overset{+}{P}\text{—Hal} + \text{Hal}'^- \rightleftarrows \equiv P: + \text{Hal—Hal}'$$

The hard chloride anion should not be capable of bringing about these transformations.

Thus crystalline phosphorus pentachloride $PCl_4^+PCl_6^-$ is reduced to phosphorus trichloride by hydrogen iodide,[119] R_4NI,[120] and a mixture of KI and $R_4N^+Cl^-$.[121] PBr_5, which is also ionised in the solid state ($PBr_4^+Br^-$), reacts with tetraorganylammonium iodides to form PBr_3.[122] Analogous reactions take place with phosphorus pentaiodide.[123] All these transformations can be represented by the general scheme:

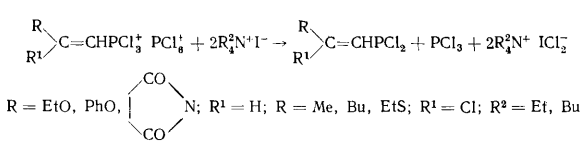
$$PX_5 + R_4N^+I^- \rightarrow PX_3 + IX + R_4N^+X^-$$
$$R_4N^+X^- + IX \rightarrow R_4N^+IX_2^-$$

In this case, tetraorganylhalogenoiodates are formed by the reaction of the interhalogen compound with the ammonium halide.

A similar scheme was observed for the reactions of phosphorus pentahalides with bromide anion donors.[120,122] As expected, the reaction of the chloride anion with chlorophosphonium compounds does not involve reduction. Derivatives of five-coordinate phosphorus are formed,[122,124] corresponding to attack by Cl^- on the phosphorus atom in the phosphonium cation.

It has been noted that the above equilibrium can be displaced towards the formation of reduction products not only by binding the interhalogen compound in a trihalide anion but also by complex formation with p-donors such as cyclic ethers and tertiary amines.[122] This makes it possible to carry out the reduction using potassium iodide.

The reduction of chlorophosphonium derivatives by tetraorganylammonium iodides has been extended to alkene phosphorylation products having a quasiphosphonium structure:[124]



Similar donors of soft halide anions reduce the adducts obtained by the Clay–Kinnear–Perren reaction:[122]

$$R_nPCl_{4-n}^+\ AlCl_4^- + R_4^1N^+\ Hal^- \rightarrow R_nPCl_{3-n} + R_4^1N^+\ HalCl_2^- + AlCl_3$$

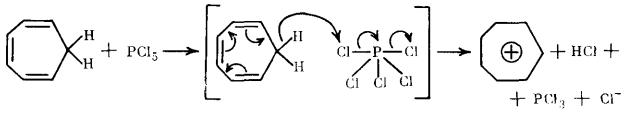
R = iso-Pr, iso-Bu, CCl_3, $n = 0,1$; R^1 = Et, Bu; Hal = I, Br

Here, however, it should be noted that if this reaction is carried out using alkyl iodides, spontaneous reduction of the products is observed;[125] this probably involves the I^- ion formed by the ionisation of the organic halide. The formation of triphenylmethylphosphonium salts by the action of methyl iodide on triphenyldihalogenophosphoranes[126] also involves halogen transfer.

VI. REACTIONS WITH OTHER READILY POLARISABLE BASES

The hydride ion, as a soft base, should reduce phosphorus halides capable of halogenophilic reactions. This explains the reduction of triphenyldichlorophosphorane by lithium hydroaluminate[127] and of the adducts $RPCl_3^+AlCl_4^-$ by sodium and calcium hydrides.[128] The formation of tertiary phosphines in the hydrogenation of a large number of triorganodichlorophosphoranes by hydrogen in pyridine takes place for the same reason.[129]

The reaction of phosphorus pentachloride with cycloheptatriene to give tropylium chloride and phosphorus trichloride is explained by the transfer of a hydride ion to the halogen atom:[130,131]



Silicon hydrides readily reduce the products of the phosphorylation of alkenes by phosphorus pentachloride:[132,133]

$$RCH{=}CHPCl_3^+\ PCl_6^- + 2Me_nCl_{3-n}SiH \xrightarrow[-2Me_nCl_{4-n}Si,\ -2HCl]{} RCH{=}CHPCl_2 + PCl_3$$

$n = 0–3$

The reducing power of the silanes decreases with increase in the number of chlorine atoms in the molecule of the silicon-containing reagent. An analogous conclusion was reached in a study of the chlorination of silanes by phosphorus pentachloride.[134]

Sulphur-containing bases such as diorgano sulphides, thiols, the thiocyanate ion, and the thiosulphate ion are soft bases.[22] These reagents should also undergo halogenophilic reactions with phosphorus halides. Thus triphenyl- and tributyldichlorophosphoranes can be reduced by thiophenol and alkanethiols in the presence of triethylamine:[135]

$$R_3PCl^+\ Cl^- + RSH \xrightarrow[-20^\circ]{R_3N} R_3P + R_3N{\cdot}HCl + RSSR$$

Only small quantities of thiophosphoryl derivatives were formed. This last direction becomes preferred, however, in the reaction of chlorophosphonium derivatives with ethanethiol in the absence of a tertiary amine or with potassium thiocyanate.[136]

Sodium thiosulphate reacts with crystalline phosphorus pentachloride to give $POCl_3$, $PSCl_3$, and PCl_3 in the ratio 5 : 1 : 1. The formation of the last compound involves halogenophilic attack by the $S_2O_3^{2-}$ anion.[137]

The reduction of halogenophosphonium derivatives by carbon monoxide may be noted:[138]

$$RPCl_3^+\ AlCl_4^- \xrightarrow[KCl]{CO} RPCl_2 + COCl_2 + KAlCl_4$$

Carbon monoxide is also chlorinated by triphenyldichlorophosphorane.[139] These data agree with the suggestion that the soft base carbon monoxide is capable of halogenophilic reactions.

Halogen transfer is also observed in the reaction of diphenyltrichlorophosphorane with tin(II) chloride.[140]

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The above experimental data show that halogen transfer processes are widely encountered in the chemistry of phosphorus halides. Although it is at present difficult to reach an unambiguous conclusion about the mechanism of these reactions, it can be seen that they are described fairly accurately by halogenophilic transformation schemes. In addition to the appearance of products of the reduction of the phosphorus halide, oxidative chlorination of the reagent is also generally observed. It can also be clearly seen that the decisive factor in these reactions is the softness of the base, and the application of the HSAB principle makes it possible to predict the final result fairly confidently.

The type of reaction examined above naturally should not be limited to the examples given, and the future appearance of new transformations which will extend even further the synthetic possibilities of halogen derivatives of phosphorus, an important preparative base in organophosphorus chemistry, can be expected.

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