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Abstract

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A New Reaction for the Preparation of β-Chloroalkyldichlorophosphines from Olefins by an Ionic Mechanism

(Presented by Academician M. M. Shemyakin, May 12, 1964)

According to the general theory of electrophilic agents, their activity is determined by electron affinity and by the coordinative unsaturation of their central atoms, i.e., by their ability to form complexes through interaction with unshared or π-electrons. As examples of the predominant importance of coordinative unsaturation, it has been shown that nitrosyl compounds $\ddot{\mathrm{N}}OX$ often prove to be more reactive than nitryl compounds NO_2X, and thionyl chloride $\ddot{\mathrm{S}}OCl_2$ is more active in hydrolysis reactions and in addition to ethylene than sulfuryl chloride SO_2Cl_2 (1). From this point of view, the comparative ease of exchange of X in mixtures of various trihalides $\ddot{\mathrm{P}}X_3$ and the absence of such exchange in mixtures (2) POX_3, the higher rate of hydrolysis of $\mathrm{R}\ddot{\mathrm{P}}Cl_2$ and $\mathrm{R}_2\ddot{\mathrm{P}}Cl$ than of $RPOCl_2$ and R_2POCl, and similar facts are understandable.

From these ideas and observations it followed that $\ddot{\mathrm{P}}Cl_3$ should add comparatively readily to olefins, like its electronic analogue $\ddot{\mathrm{S}}OCl_2$.

$$\mathrm{R_2C{=}CR_2 + PCl_3 \xrightarrow{AlCl_3} Cl_2P{-}CR_2{-}CR_2{-}Cl}(\sim\text{-bond}). \tag{1}$$

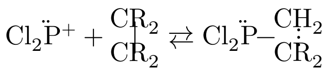
We did in fact succeed in obtaining β-chloroalkyldichlorophosphines by this scheme, as was mentioned earlier (3). This method was, in particular, realized for ethylene, propylene, and cyclohexene*.

By analogy with the reactions of $AlCl_3$ in NOCl and $\ddot{\mathrm{S}}OCl_2$ (1), we assume that $AlCl_3$, $TiCl_4$, etc., aprotonic acids form donor-acceptor adducts in a solution of PCl_3 that are capable of ionization.

$$\mathrm{Cl_3Al + Cl{-}PCl_2 \rightleftarrows I\ Cl_3Al \longleftarrow Cl^- {-}PCl_2^+ \rightleftarrows AlCl_4^- + Cl_2P^+}. \tag{2}$$

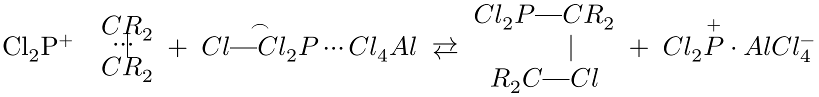
This postulate is confirmed by the existence of complexes of PCl_3 with $AlCl_3$, $TiCl_4$, BCl_3, and BBr_3 (2). They may also occur in forms of the type $\mathrm{Cl_3Al \longleftarrow \leftarrow\!\!-\!:PCl_3}$, I′, tautomeric with I. Adducts of type I, or the cation Cl_2P^+, possess highly electrophilic and coordinatively unsaturated P atoms.

Through their interaction with mobile and peripheral π-electrons of a multiple bond they are capable of forming complexes with unsaturated compounds, which may be represented by scheme (3), in which the distribution of π-electron density over the three-atom orbital is shown by a dotted line:



$$\mathrm{Cl_2\ddot{P}^+} + \begin{matrix}\mathrm{CR_2}\\ |\\ \mathrm{CR_2}\end{matrix} \rightleftarrows \mathrm{Cl_2\ddot{P}}\text{—}\begin{matrix}\mathrm{CH_2}\\ \vdots\\ \mathrm{CR_2}\end{matrix} \quad \text{(II)} \qquad (3)$$

In the complex ion II the positive charge is distributed mainly over the P atom and both C atoms, and to a first approximation II is a 2/3 carbonium cation. According to the general theory of conjugated addition (4), it is capable of reacting rapidly with anions or molecules possessing sufficiently active lone pairs or π-electrons. Thus, in interaction with complex II in the cases studied by us, $AlCl_4^-$ or its solvate $Cl\text{—}Cl_2P \cdots Cl_4Al^-$ could be involved as donors of Cl^-, as well as $\ddot{P}Cl_3$ and $CR_2 = CR_2$, and, finally, reaction products similar to them in chemical character, for example $ClCR_2\text{—}CR_2\text{—}\ddot{P}Cl_2$. According to this theory, the mechanism of formation of β-chloroalkyldichlorophosphine according to equation (1) should be represented as follows:



$$\mathrm{Cl_2P^+} \quad \begin{matrix}CR_2\\ \cdot\!\cdot\!|\\ CR_2\end{matrix} + Cl\text{—}\overset{\frown}{C}l_2P \cdots Cl_4Al \rightleftarrows \begin{matrix}Cl_2P\text{—}CR_2\\ \qquad |\\ R_2C\text{—}Cl\end{matrix} + Cl_2\overset{+}{P} \cdot AlCl_4^- \qquad (4)$$

It is assumed that the reaction proceeds through a transition adduct of II with III, not shown in the scheme. Addition of III occurs from the side opposite to the localization of Cl_2P in cation II.

The reversibility of processes 2–4 is proved by the formation of ethylene on heating chloroethyldichlorophosphine with $AlCl_3$.

$$Cl_3Al \cdots Cl\text{—}CH_2\text{—}CH_2\text{—}PCl_2 \rightleftarrows AlCl_4^- + CH_2 = CH_2 + Cl_2P^+. \qquad (5)$$

To shift equilibria 2–4 in the desired direction, an excess of PCl_3 and olefin was used. The chloroalkyldichlorophosphines formed gave complexes of type 1 of equation (2) with $AlCl_3$, and therefore, when they were isolated from the reaction mixture, KCl was added to decompose the adduct by binding $AlCl_3$ in the form of $K^+AlCl_4^-$.

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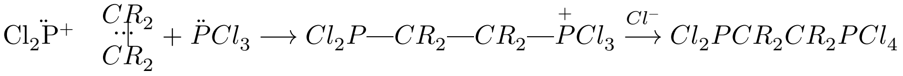
* It is probable that addition of PCl_3 and $SOCl_2$ in the presence of $AlCl_3$ can also be realized for cyclopropane and its derivatives (3).

The β-chloroalkyldichlorophosphines arising according to equation (4) could react similarly to PCl_3, which led, for example in the case of the reaction with ethylene, to the formation of dichlorodiethylchlorophosphine $(ClCH_2—CH_2)_2PCl$. However, owing to the reduced electrophilicity of the cation $R—P^+—Cl$ compared with Cl_2P^+, and also because of the use of a large excess of PCl_3, the yields of dichlorodialkylchlorophosphines were, as a rule, relatively small.

The reaction with vinyl chloride proceeded mainly by the substitution type with elimination of HCl. The orientation in formation of the adduct $\ddot{P}Cl_2—Cl$ to chloroethylenes could occur anomalously, contrary to the generalized Markovnikov rule [3].

In the case of isobutylene, complex II of equation (3), apparently, readily entered into reaction with the olefin, ultimately giving a telomer of type IV $PCl_2—CR_2—CR_2—CR_2—CR_2—Cl$. Along with this, simple polymerization of isobutylene also occurred, which made it difficult to obtain clear results. The formation of chloroalkyldichlorophosphines was proved in this case by treatment with water of the corresponding fractions before and after treatment with Cl_2 and isolation of phenylhydrazine salts of alkylphosphinic or phosphonic acids.

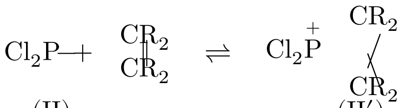
A very interesting possibility of attack on cation II of equation (3) by the $\ddot{P}Cl_3$ molecule, followed by capture of Cl^- from its donors, was not investigated in our work.



$$\mathrm{Cl_2\ddot{P}^+}\ \begin{matrix} CR_2 \\ \vdots \\ CR_2 \end{matrix} + \ddot{P}Cl_3 \longrightarrow Cl_2P—CR_2—CR_2—\overset{+}{P}Cl_3 \xrightarrow{Cl^-} Cl_2PCR_2CR_2PCl_4 \qquad (6)$$

It is not excluded that the product V formed, during distillations with elimination of PCl_3, was converted into chloroalkyldichlorophosphine. Finally, we note that cation II could undergo an intramolecular reaction (7), analogously—

(6), and form II′ could lead to stable cyclic compounds with "pentavalent" phosphorus.



$$\mathrm{Cl_2P—+}\ \begin{matrix} \mathrm{CR_2} \\ | \\ \mathrm{CR_2} \end{matrix} \rightleftharpoons \mathrm{Cl_2\overset{+}{P}}\begin{matrix} \mathrm{CR_2} \\ \mathrm{/} \\ \mathrm{\backslash} \\ \mathrm{CR_2} \end{matrix} \qquad (7)$$

(II) (II′)

Further, $\mathrm{Cl_2P—CR_2—CR_2—Cl}$ may enter, as an alkyl halide, into the Klee reaction (^{6}) and a number of others. The reaction pathways mentioned may be realized, with some modification, also in the interaction of olefins with $\mathrm{SOCl_2}$ (^{1}). There is reason to believe that the results of studying the transformations of $\mathrm{CH_2Cl—CH_2—SOCl}$ (^{1}) are to some extent applicable to analogous reactions of β-chloroalkyldichlorophosphines.

We give a description of several experiments.

1. A mixture of 133.5 g of $AlCl_3$ and 1880 g of PCl_3 was saturated with ethylene, with stirring in a reactor fitted with a reflux condenser, for 30 h at 35°. Then 160 g of finely ground KCl was added, and the mixture was heated on a bath for 2 h at 100°. After cooling, the liquid portion was separated, and the residue was extracted several times in the same way in a stream of ethylene and with heating with PCl_3, etc. From the combined solutions, PCl_3 was distilled off in a stream of N_2, toward the end under vacuum. Fractionation of the residue gave 70-75 g of $CH_2Cl—CH_2—PCl_2$ and 10 g of $(CH_2Cl—CH_2)_2PCl$–in all about 50% based on $AlCl_3$. The distilled-off PCl_3 was reused for the reaction and extraction.

β-Chloroethyldichlorophosphine $CH_2Cl—CH_2—PCl_2$ I is a colorless fuming liquid with b.p. 46° at 7 mm and 169-170° at 754 mm; d_4^{18} 1.4464.

Found, %: C 14.6; H 2.56; P 18.4; Cl 64.4
$C_2H_4Cl_3P$. Calculated, %: C 14.5; H 2.41; P 18.7; Cl 64.5

β-Dichlorodiethylchlorophosphine $(CH_2Cl—CH_2)_2PCl$ II had b.p. 95° at 7 mm:

Found, %: P 16.8; Cl 55.4
$C_4H_8Cl_3P$. Calculated, %: P 16.1; Cl 55.2

Saturation of I with oxygen at 0° and with stirring gave the dichloroanhydride of β-chloroethylphosphinic acid with b.p. 85-87° at 7 mm (see also ([7],[8])).

Found, %: P 16.8; Cl 58.2
$C_2H_4OCl_3P$. Calculated, %: P 17.0; Cl 58.7

On treatment of I with the calculated amount of chlorine, $CH_2Cl—CH_2—PCl_4$ with m.p. 62° was obtained.

2. Under the conditions of experiment 1, propylene gave β-chloropropyldichlorophosphine III with b.p. 55° at 7 mm; d_4^{18} 1.3250; n_D^{18} 1.5172.

Found, %: P 17.0; Cl 58.9
$C_3H_6Cl_3P$. Calculated, %: P 17.3; Cl 59.3

Hydrolysis of III gave a syrupy β-chloropropylphosphinous acid, whose phenylhydrazine salt had m.p. 185°.

On treatment of III with O_2, the dichloroanhydride of β-chloropropylphosphinic acid, $CH_3—CHCl—CH_2POCl_2$, was obtained, with b.p. 92-95° at 10 mm; d_4^{18} 1.404; n_D^{18} 1.4986 (see also ([8])).

Found, %:	C 19.1; H 3.84; Cl 53.9
$C_3H_6OCl_3P$. Calculated, %:	C 18.4; H 3.07; Cl 54.5

3. Cyclohexene (82 g) was added dropwise over 15 h to a mixture of 133.5 g of $AlCl_3$ and 1500 g of PCl_3 at 80-85° and with stirring. After the usual work-up and distillation under vacuum, 18 g of β-chlorocyclohexyldichlorophosphine IV was obtained, with b.p. 117° at 7 mm; d_4^{18} 1.3334; n_D^{18} 1.5525.

Found, %:	P 14.62; Cl 48.0
$C_6H_{10}Cl_3P$. Calculated, %:	P 14.12; Cl 48.6

IV with O_2 was converted into $C_6H_{10}Cl—POCl_2$, b.p. 132–134° at 3 mm; d_4^{18} 1.402; n_D^{18} 1.5300.

Found, %:	C 30.9; H 4.6; Cl 44.6
$C_6H_{10}OCl_3P$. Calculated, %:	C 30.5; H 4.2; Cl 45.3

Hydrolysis led to a syrupy β-chlorocyclohexylphosphinic acid, the phenylhydrazine salt of which crystallized from an alcohol–ether mixture in leaflets, m.p. 218° (amount of N = 13.8%). IV, under the action of Cl_2 at 0°, was converted into the tetrachloride with m.p. 83°, hydrolysis of which gave the same phosphinic acid (see above).

4. The reaction of vinyl chloride under the conditions of experiment 1 was accompanied by evolution of HCl and gave more than 65 g of β-chlorovinylphosphine V, about 40% of theory based on $AlCl_3$; b.p. 64° at 14 mm; d_4^{18} 1.4510; n_D^{18} 1.5364.

Found, %:	C 14.6; H 1.8; Cl 64.9; P 17.9
$C_2H_2Cl_3P$. Calculated, %:	C 14.7; H 1.2; Cl 65.2; P 18.9

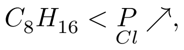
By hydrolysis of V in the cold, chlorovinylphosphinic acid was obtained, whose phenylhydrazine salt had m.p. 163°; with NaOH solution V gave acetylene, and with O_2 it was converted into $CHCl = CHPOCl_2$, b.p. 99–102° at 10 mm; d_{18}^{18} 1.6420; n_D^{18} 1.5202 (see also ([8])).

Found, %:	P 16.8
$C_2H_2OCl_3P$. Calculated, %:	P 17.3

Hydrolysis of the dichloroanhydride gave an acid with m.p. 93° (from dichloroethane); its phenylhydrazine salt had m.p. 196°. The same acid and salt were obtained from $CHCl = CH—PCl_4$ with m.p. 42–46°, synthesized from V and Cl_2.

In obtaining V, higher fractions were isolated, for example with b.p. 95-100° at 5 mm; d_{18}^{18} 1.6421; n_D^{18} 1.5818. By the action of O_2 and then water, a phosphonic acid was obtained whose phenylhydrazine salt had m.p. about 35°; it was not investigated further.

S. I. Pobedimskii, B. G. Gusarov, and V. E. Bogachev took part in the experimental part of the investigation in 1951-1953. In 1962 we became aware of the results of a study by American chemists (^{9}) on the reaction of olefins with an excess of 30-100% PCl_3 and $AlCl_3$ in a CH_2Cl_2 medium. With n-olefins and cycloolefins they did not isolate definite compounds. To the products of reaction with higher isoolefins (isooctene, pentadecene, etc.), after treatment with CH_3OH, they ascribe a structure with "pentavalent" P, for example in the case of isooctene



$$C_8H_{16} < \underset{Cl}{P} \nearrow,$$

containing, according to their data, a four-membered ring involving phosphorus.

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Note: Figure translations are in progress. See original paper for figures.