Chemistry

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Abstract

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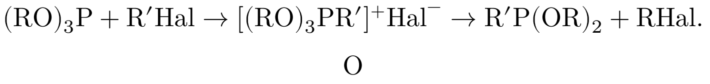
On the Mechanism of the Reactions of Esters of Acids of Trivalent Phosphorus with Silicon- and Tin-Alkyl Halides

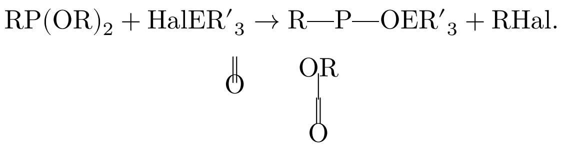
(Presented by Academician B. A. Arbuzov, March 9, 1964)

As is known, as a result of the reactions of esters of acids containing trivalent phosphorus with alkyl halides and their derivatives, proceeding according to the general scheme of the Arbuzov rearrangement, esters of alkylphosphonic acids containing a phosphorus-carbon bond are formed



$$(RO)_3P + R'Hal \rightarrow [(RO)_3PR']^+Hal^- \rightarrow R'P(OR)_2 + RHal.$$
$$O$$

The reactions of esters of phosphorous and phosphonous acids with silicon- and tin-alkyl halides, as was shown (1), proceed differently and lead to the formation of esters of phosphinic acids containing the bond P—O—E. To explain the mechanism of these reactions it was assumed that esters with trivalent phosphorus first isomerize into esters of phosphinic acids, which then enter into reaction with halogen-containing compounds. Evidence for the correctness of this view was the formation of the same compounds in the reaction of silicon- and tin-containing halides with esters of phosphinic acids.



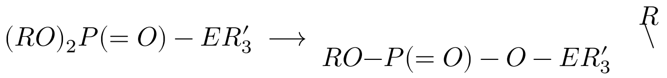
$$RP(OR)_2 + HalER'_3 \underset{\substack{\| \\ O}}{\rightarrow} R\text{—}\underset{\substack{OR \\ | \\ \| \\ O}}{P}\text{—}OER'_3 + RHal.$$

The reactions proceed under rather mild conditions. Thus, for example, triethylbromosilane reacts with triethyl phosphite already at 70°, and the reaction takes place within a short time. The reaction between triethoxychlorosilane and triethyl phosphite at 120—130° is completed in 30 min (2). The isomerization of phosphites into esters of phosphinic acids in these and analogous reactions would most simply be admitted as a result of the action on them of alkyl halides liberated at the initial moment in accordance with the scheme of the Arbuzov rearrangement.

The possibility of such an anomalous course of Arbuzov rearrangement reactions was indicated earlier by us (3) and by other authors (4). It is possible in those cases in which the alkyl halide liberated is more reactive in comparison with the main reagent. However, in the reactions under consideration such a possibility is unlikely, since the activity of brominated and especially chlorinated alkyls in Arbuzov rearrangement reactions is low. Thus, according to the data of A. E. Arbuzov, half of the triethyl phosphite taken into the reaction in the presence of 0.2 molar amount of ethyl bromide at 110° isomerizes in 10 h 35 min (5). According to our data, triethyl phosphite, when heated with ethyl chloride at 120—130° for 2 h, remains unchanged. Still less probable is the thermal rearrangement of phosphites in the course of the reaction, which, as is known, can proceed only at temperatures above 200° (6).

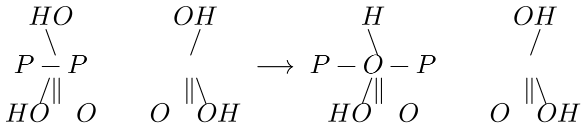
It could be assumed that the formation of compounds with the bond P—O—E, in the interaction of esters of trivalent phosphorus with halogen derivatives of silicon, tin, and phosphorus, may also take place by another mechanism. In the first stage, the reactions proceed according to the Arbuzov scheme–

and then, as a result of intramolecular rearrangement of the reaction product having a P–E bond, compounds with P–O–E bonds are formed.



$$(RO)_2P(=O)-ER'_3 \longrightarrow RO{-}P(=O)-O-ER'_3 \quad \overset{R}{\diagdown}$$

It is known that hypophosphoric acid spontaneously, under mild conditions, undergoes rearrangement into isohypophosphoric acid (7).



To study the mechanism of the above-described reactions, as the objects of investigation we chose esters of dialkylphosphinous acids, which, as it seemed to us, are the most suitable for this purpose. If the reactions proceed in accordance with the first mechanism, with preliminary isomerization of the phosphinite into the oxide of a trialkylphosphine, the reactions should stop at this stage.

$$R_2POR + HalER'_3 \xrightarrow{\text{slight}} R_2P(=O)ER'_3 + RHal \xrightarrow[\text{cat. } RHal]{R_2POR} R_3P = O + RHal.$$

If the reactions proceed by the second mechanism, a product with a P–E bond should be formed, since further intramolecular isomerization proves impossible owing to the absence of alkoxyl groups at the phosphorus:

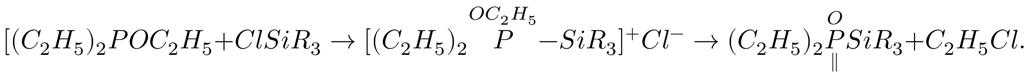
Figure 1: IR spectrum of the intermediate complex obtained in the interaction of ethyl diethylphosphinite with tri-n-propylchlorosilane

Figure 1: Figure 1: IR spectrum of the intermediate complex obtained in the interaction of ethyl diethylphosphinite with tri-n-propylchlorosilane

$$R_2POR + HalER'_3 \to R_2P(=O)ER'_3 + RHal.$$

Fig. 1. IR spectrum of the intermediate complex obtained in the interaction of ethyl diethylphosphinous acid ester with tri-*n*-propylchlorosilane

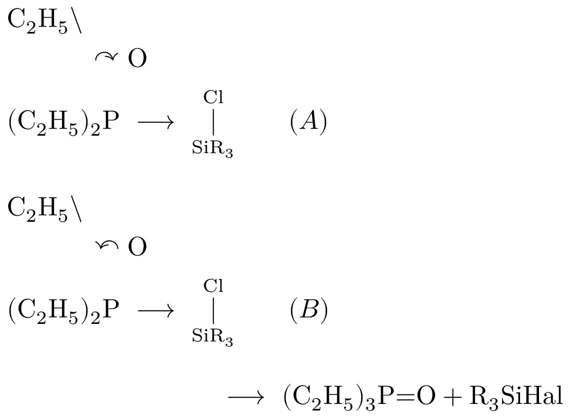
We studied the reactions of ethyl diethylphosphinous acid ester with trimethyl-, triethyl-, tri-*n*-propyl-, tri-*n*-butylchlorosilanes and dimethyldichlorosilane. The results of the experiments proved very interesting. In all cases, when the initial reagents, previously cooled to 0°, were mixed, the temperature of the reaction mixtures rose to +5—+27°, and abundant precipitation of a crystalline precipitate occurred. The crystalline precipitates are quite stable in a nitrogen atmosphere at a temperature of about 0°. Under these conditions they remain unchanged for several days; at room temperature they rapidly melt into a liquid. It could be assumed that the crystalline compounds formed are intermediate products of the Arbuzov rearrangement. In their IR spectra there was an absorption band in the region 1020—1060 cm^{-1}, characteristic of the P—O—C bond, with no absorption in the region of the phosphoryl group (Fig. 1)



$$[(C_2H_5)_2POC_2H_5 + ClSiR_3 \to [(C_2H_5)_2\overset{OC_2H_5}{P}-SiR_3]^+Cl^- \to (C_2H_5)_2\overset{O}{\underset{\|}{P}}SiR_3 + C_2H_5Cl.$$

However, this assumption was not confirmed. When the precipitates were heated to 120° with subsequent distillation in vacuum, instead of the expected compounds with a P—Si bond, the initial trialkylchlorosilanes and the oxide of triethylphosphine were isolated. No ethyl chloride evolution was observed. Special-

experiments it was shown that, under the conditions of decomposition of the crystalline intermediate products, i.e., at 110-120°, alkyl chlorides do not isomerize the ethyl ester of diethylphosphinous acid. Thus, from the experimental data obtained it follows that the reactions proceed neither by the first nor by the second proposed mechanisms, and that the crystalline products formed are not compounds of a phosphonium or pentacovalent structure. We believe that they are complexes formed through donor-acceptor interaction of the unshared electron pair of the phosphorus or oxygen atom with the unfilled 3*d* orbitals of the silicon atom. The presence in silicon of vacant 3*d* orbitals gives it an electron-deficient character and creates favorable possibilities for the formation of various complex compounds ([8]). In the complex compound formed, owing to displacement of the electron pair from phosphorus or oxygen to silicon, conditions are created that are favorable for intramolecular rearrangement in the phosphinite molecule, associated with transition of the phosphorus atom from a trivalent to a pentavalent



$$\begin{matrix} C_2H_5\backslash \\ \curvearrowright O \\ (C_2H_5)_2P \longrightarrow \overset{Cl}{\underset{SiR_3}{|}} \quad (A) \end{matrix}$$

$$\begin{matrix} C_2H_5\backslash \\ \curvearrowleft O \\ (C_2H_5)_2P \longrightarrow \overset{Cl}{\underset{SiR_3}{|}} \quad (B) \end{matrix}$$

$$\longrightarrow (C_2H_5)_3P{=}O + R_3SiHal$$

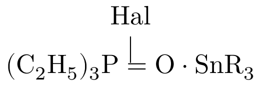
state (^{9}). Unfortunately, at present there are not sufficient grounds to make a final choice between the possible structures of the complex compounds (A) and (B).

The formation of complex compounds of analogous structure between esters of acids of trivalent phosphorus and alkyl halides, and various carbon compounds containing, in addition to a halogen atom, other functional groups, appears less probable, since tetravalent carbon has no free orbitals in the outer *L* quantum shell. Therefore alkyl halides are capable of forming, with phosphorous and phosphinous esters, depending on the reaction conditions (t, nature of the solvent), intermediate products of phosphonium or pentacovalent structure, which upon thermal decomposition, in accordance with the scheme of the Arbuzov rearrangement, lead to esters of phosphinic acids or to oxides of tertiary phosphines.

$$R_2POR + HalR' \longrightarrow \begin{bmatrix} O{-}R \\ \overset{+}{R_2P}{-}R' \end{bmatrix} Hal^- \longrightarrow R_2P(=O)R' + HalR$$

$$\begin{bmatrix} O{-}R \\ \overset{+}{R_2P}{-}R' \end{bmatrix} Hal^- \rightleftarrows \begin{matrix} OR \\ R_2P{-}Hal \\ R' \end{matrix}$$

When reactions of the ethyl ester of diethylphosphinous acid with trialkyltin halides were carried out, it was not possible to isolate intermediate products in crystalline form (^{10}). However, the formation of intermediate complex compounds through donor-acceptor interaction of the unshared electron pair of the phosphorus atom with the vacant 5*d*-orbital of the tin atom in these reactions also raises no doubt ([11,12]). Apparently, the intermediate complexes formed under the experimental conditions are liquid products. At 90-110° an intensive reaction, in the course of which no alkyl halide is eliminated. As a result of distillation, products were obtained which, according to analysis and IR spectra, corresponded to complex compounds of the composition

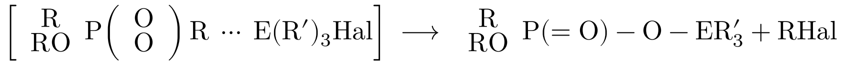


$$\begin{array}{c}\text{Hal}\\ (C_2H_5)_3P \overset{|}{=} O \cdot SnR_3\end{array}$$

These same complex compounds are also formed upon direct interaction of triethylphosphine oxide with triethyltin iodide. The absence of analogous complex compounds in the case of trialkylchlorosilanes is probably explained by the lower tendency of the silicon atom toward complex formation as compared with tin ([8,11]).

In the present investigation we studied the reactions of trialkylsilicon and trialkyltin halides with the ethyl ester of diethylphosphinous acid. The preliminary data obtained by us make it possible to consider that the formation of intermediate complex compounds with a donor-acceptor bond also occurs in the reactions of alkyltin and alkylsilicon halides with esters of monoalkylphosphinous and phosphorous acids.

Thus, upon careful heating to 120°, triethyl phosphite with triethyltin iodide gives a crystalline product which, upon further heating to 140-150°, undergoes further transformation with elimination of ethyl iodide. Upon prolonged heating of triethyl phosphite with triethyltin iodide at 75°, a gradual increase in the viscosity and refractive index of the reaction mixture occurs, which also indicates the formation of an intermediate complex. The reaction connected with decomposition of the complex and elimination of ethyl iodide proceeds only at 150° ([13]). Esters of phosphorous and phosphinous acids that are part of the intermediate complexes, as a result of an intramolecular rearrangement taking place in the complex, form esters of phosphinic acids, which apparently then react with halogen derivatives of tin and silicon by a mechanism of cyclic electron transfer.



$$\left[\begin{array}{c}R\\RO\end{array} P\left(\begin{array}{c}O\\O\end{array}\right)R \cdots E(R')_3Hal\right] \longrightarrow \begin{array}{c}R\\RO\end{array} P(=O)-O-ER'_3+RHal$$

As a result, esters of phosphinic acids are formed with $P—O—E$ bonds, where $E = \mathrm{Sn}, \mathrm{Si}$.

Thus, the results obtained by us as a whole confirm Malatesta's conception of the mechanism of the reactions under consideration. As was already noted, Malatesta, assuming in the first stage a preliminary isomerization of the phosphite, substantiates the causes of the latter neither experimentally nor theoretically. We believe that in the first stage of the reaction there occurs the formation of an intermediate unstable complex of a silicon or tin alkyl halide with an ester of an acid of trivalent phosphorus, in which the intramolecular rearrangement of the phosphite into the corresponding ester of phosphinic acid takes place.

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named after V. I. Ulyanov-Lenin

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