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Abstract

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"PSEUDOALLYLIC" REARRANGEMENTS OF TRI-(CHLOROMETHYL)PHOSPHINE

Tri-(chloromethyl)phosphine was first described in 1930 by Hofmann (^{1}). The chemical properties of this compound, with the exception of oxidation, which was carried out by Hofmann, have not been investigated. We studied the alcoholysis of tri-(chloromethyl)phosphine and found that, instead of the expected replacement of three chlorine atoms by alkoxyl groups, replacement of only two of them takes place, accompanied by an oxidation–reduction reaction leading to the formation of methyl-di-(alkoxymethyl)phosphine oxide.

$$(ROCH_2)_3P \xleftarrow{\text{RONa, ROH}} \times —(ClCH_2)_3P \xrightarrow{\text{RONa, ROH}} CH_3PO(CH_2OR)_2.$$

The interaction of tri-(chloromethyl)phosphine with sodium ethylate in ethyl alcohol proceeds even at room temperature and is complete after two to three days; on boiling, the duration of the reaction is reduced to 4–5 hr. In addition to methyl-di-(ethoxymethyl)phosphine oxide, which was isolated in 83% yield, diethyl ether is also formed in the course of the reaction in 84% yield. The reaction may be represented by the following overall equation:

$$(ClCH_2)_3P+3C_2H_5ONa+C_2H_5OH \rightarrow (C_2H_5OCH_2)_2P(O)CH_3+(C_2H_5)_2O+3NaCl.$$

The structure of methyl-di-(ethoxymethyl)phosphine oxide was proved by its oxidation to methylphosphonic acid on boiling with concentrated nitric acid. Methylphosphonic acid was identified in the form of the monoanilinium salt, which proved identical with the salt of methylphosphonic acid obtained from its dichloroanhydride (^{2}):

$$(C_2H_5OCH_2)_2P(O)CH_3 \xrightarrow[\text{2. } C_6H_5NH_2]{\text{1. } HNO_3} CH_3PO_3H_2 \cdot C_6H_5NH_2 \xleftarrow[\text{2. } C_6H_5NH_2]{\text{1. } H_2O} CH_3POCl_2.$$

Thus, alcoholysis of tri-(chloromethyl)phosphine is accompanied by an oxidation-reduction rearrangement.

This reaction, in our opinion, can be understood on the basis of the ideas of A. N. Nesmeyanov and one of us concerning $\sigma\rho$-conjugation and the analogy in the properties of $\sigma\rho$- and $\sigma\pi$-conjugated (allylic) systems (^{3}).

$$\mathrm{Cl{-}CH_2{-}P:} \qquad \mathrm{Cl{-}CH_2{-}C{=}C.}$$

Tri-(chloromethyl)phosphine is a $\sigma\rho$-conjugated system. The properties of the analogous $\sigma\pi$-conjugated (allylic) system, and in particular its ability to undergo anionotropic rearrangements united under the general name of allylic rearrangements, are well known. Hydrolysis and alcoholysis of allylic halides, as well as various transformations of allylic alcohols and their derivatives, are often accompanied by rearrangement.

On the basis of this analogy, the rearrangement of tri(chloromethyl)phosphine upon alcoholysis becomes understandable; it may be called a "pseudoallylic" rearrangement.

Allylic rearrangement:

$$\mathrm{Cl{-}CH_2{-}CH{=}CH_2 + {}^{-}OR \rightarrow Cl^- + CH_2{=}CH{-}CH_2OR;}$$

"pseudoallylic" rearrangement of a σp-conjugated system:

$$\mathrm{Cl{-}CH_2{-}\ddot{P} + {}^{-}OR \rightarrow Cl^- + CH_2{=}POR \xrightarrow{ROH} CH_3{-}P{=}O + ROR.}$$

In this scheme we do not touch upon the question of the kinetic mechanism of the rearrangement in the sense of the alternative $S_{\mathrm{N}}1'$ or $S_{\mathrm{N}}2'$ in the first stage of the process, nor the question of whether the reaction is two-step (with intermediate formation of phosphinomethylene) or one-step in the second stage or as a whole (this remark also applies to the subsequent schemes).

On the basis of the proposed analogy it may be assumed that the rearrangement of tri(chloromethyl)phosphine will occur not only under the action of alkaline reagents but also of acidic reagents. Indeed, on boiling with concentrated hydrochloric acid, tri(chloromethyl)phosphine is converted into methyl-di(chloromethyl)phosphine oxide, $\mathrm{CH_3P(O)(CH_2Cl)_2}$:

$$\mathrm{Cl{-}CH_2{-}\ddot{P} + Cl^- \rightarrow Cl^- + CH_2{=}P{-}Cl \xrightarrow{HCl,\ H_2O} CH_3{-}P{=}O.}$$

The structure of methyl-di(chloromethyl)phosphine oxide is confirmed by its IR spectrum, which contains a very intense doublet band at 1170-1181 $\mathrm{cm^{-1}}$, corresponding to stretching vibrations of the P=O group in phosphine oxides, as well as characteristic absorption in the region of C—H stretching frequencies, namely at 2984 and 2918 cm^{-1} (CH_3 group) and 2974 and 2906 cm^{-1} (CH_2 group); in the region of deformation vibrations of C—H bonds there is a band of medium intensity at 1412 cm^{-1} and a somewhat more intense doublet in the region of 1386 cm^{-1} (CH_2 and CH_3 groups). It should also be noted that there is a very intense band at 1290 cm^{-1}, always encountered in compounds containing the $CH_3{-}P$ grouping. At the same time, the spectrum lacks absorption bands characteristic of an alcoholic hydroxyl group, which would have to be present in the case of the isomeric structure $HOCH_2P(CH_2Cl)_2$.

The indicated analogy with allylic rearrangements makes it possible to understand, from a general point of view, a number of reactions described in the literature and explained in different ways.

In 1960 Buckler and Epstein (4) showed that, upon interaction of phosphinous hydrogen with ketones in an acidic medium, oxides of primary phosphines are formed, and not α-hydroxyalkylphosphines, as might have been expected. The authors called this transformation an "oxygen-transfer" reaction.

$$\mathrm{RR'CO + PH_3 \rightarrow RR'CHP(O)H_2}.$$

This case is apparently analogous to the rearrangement of allylic alcohols under the influence of acidic reagents.

$$\mathrm{RR'CO + PH_3 + HCl \rightarrow H_2\overset{+}{O}{-}CRR'{-}\ddot{P}H_2 + Cl^- \rightarrow}$$

$$\mathrm{\rightarrow H_2O + RR'C{=}PH_2Cl \xrightarrow{HCl,\ H_2O} RR'CH{-}P(O)H_2}$$

The same scheme can also explain the formation of benzyl-di-(α-oxybenzyl)-phosphine oxide in the reaction of benzaldehyde with phosphorous hydrogen in an acidic medium [5,6], as well as the rearrangement, recently described by Trippett [7], of 1-hydroxy- and 1-methoxyalkylphosphines into the corresponding phosphine oxides under the action of acidic reagents.

$$\mathrm{ROCHR'P(C_6H_5)_2 \longrightarrow R'{—}CH_2{—}P(=O)(C_6H_5)_2 \qquad R = H, CH_3}$$

Recently, Uhing, Rattenbury, and Toy [8] described the hydrolysis of chloromethylphosphinic acid in an alkaline medium, leading to methylphosphonic acid. The authors believe that this process is accompanied by a hydride shift.

$$\mathrm{Cl{—}CH_2{—}P(H)(OH)(=O){—}O^- \longrightarrow CH_3P(=O)(O^-)(OH) + Cl^-}$$

This reaction, too, apparently is one of the cases of “pseudoallylic”rearrangement, but now of a $\sigma\sigma$-conjugated system [3].

$$\mathrm{Cl{-\!\!-}CH_2{-\!\!-}P(=O)(O^-){-\!\!-}H + OH^- \longrightarrow CH_2 = P(=O){-\!\!-}O^- + H_2O + Cl^-},$$

$$\mathrm{CH_2 = P(=O){-\!\!-}O^- \xrightarrow{H_2O} CH_3{-\!\!-}P(=O)(OH){-\!\!-}O^-}$$

Analogously, one can explain the reaction of dicyclohexylchlorophosphine with diazomethane in moist ether, observed by Issleib and Baldauf [8], which leads to methyldicyclohexylphosphine oxide:

$$\mathrm{ClP(C_6H_{11})_2 \xrightarrow{CH_2N_2} Cl{-\!\!-}CH_2{-\!\!-}P(C_6H_{11})_2}$$

$$\mathrm{Cl{-\!\!-}CH_2{-\!\!-}P(C_6H_{11})_2 + OH^- \longrightarrow Cl^- + CH_2 = P(C_6H_{11})_2{-\!\!-}OH \longrightarrow CH_3{-\!\!-}P(=O)(C_6H_{11})_2}$$

Thus, comparison of the literature data with the results obtained by us shows that “pseudoallylic” rearrangements are probably a general phenomenon for a number of α-substituted derivatives of trivalent phosphorus.

Experimental Section

Alcoholysis of tri-(chloromethyl)-phosphine. 15 g (0.084 mole) of tri-(chloromethyl)-phosphine are added dropwise, in a nitrogen atmosphere with stirring, to a heated solution of sodium ethylate in ethyl alcohol (from 7 g ($\sim$ 0.3 g-atom) of sodium and 100 ml of alcohol). After the self-heating has ended, the mixture is boiled in a stream of nitrogen with stirring for 5 hr. The condenser of the apparatus is connected to a trap cooled with dry ice in acetone. After the heating is completed, the alcohol is removed in vacuo; 100 ml of benzene and 5 ml of water are added to the residue, and the mixture is stirred until complete coagulation of the precipitate. The precipitate is filtered off, the solvent is removed in vacuo, and the residue is distilled.

Yield of methyl-di(ethoxymethyl)phosphine oxide 12.5 g (83%); b.p. 97-99° at 2 mm, n_D^{20} 1.4491, d_4^{20} 1.0275. Found MR_D 47.06. Calculated MR_D 46.62*.

Found, %:	C 46.5; 46.4;	H 9.4; 9.6;	P 17.1; 16.9
$C_7H_{17}PO_3$. Calculated, %:	C 46.7;	H 9.5;	P 17.2

The liquid that condensed in the trap is distilled, giving 5.2 g of diethyl ether. The ether is distilled once more over sodium, b.p. 34-34.5°, n_D^{20} 1.3520, d_4^{20} 0.7134. Literature data ([11]): b.p. 34.6°, n_D^{20} 1.3528, d_4^{20} 0.7135.

Rearrangement of tri(chloromethyl)phosphine in acid medium. 6.2 g of tri(chloromethyl)phosphine are boiled with 10 ml of conc. HCl; after 2 hr 10 ml are added, and after 4 hr a further 10 ml of HCl. The mixture is boiled for a total of 8 hr. The tri(chloromethyl)phosphine gradually dissolves completely. The excess hydrochloric acid is removed in vacuo, benzene is added to the residue, the solution is evaporated in vacuo and distilled; 4.45 g (80%) of methyl-di(chloromethyl)phosphine oxide are obtained; b.p. 116-117° at 1.5 mm, m.p. 49-50°.

Found, %: C 22.2; 22.3; H 4.4; 4.3; P 19.1; 19.4; Cl 44.5; 44.7
$C_3H_7POCl_2$. Calculated, %: C 22.4; H 4.4; P 19.2; Cl 44.0

Oxidation of methyl-di(ethoxymethyl)phosphine oxide. 3 g of methyl-di(ethoxymethyl)phosphine oxide are boiled with 10 ml of conc. nitric acid (*d* 1.489) for 5 hr, then another 10 ml of nitric acid are added and the mixture is boiled for a further 9 hr. The excess nitric acid is removed in vacuo, 20 ml of alcohol are added to the residue, the solution is boiled for 30 min, and the alcohol is distilled off in vacuo. The residue—colorless crystals, yield 1.45 g. 0.96 g of the substance is dissolved in 5-6 ml of alcohol and mixed with 0.95 g of aniline. The precipitate that separates is filtered off, yield 1.4 g (74%), m.p. 147-148° (from alcohol).

Found, %: C 44.0; 44.0; H 6.4; 6.4; P 16.3; 16.1; N 7.4; 7.5
$C_7H_{12}NO_3P$. Calculated, %: C 44.4; H 6.4; P 16.4; N 7.4

A mixed sample with the monoanilinium salt of methylphosphinic acid has m.p. 147.5-148.5°.

Monoanilinium salt of methylphosphinic acid. A solution of methylphosphinic acid (obtained from methylphosphinic acid dichloroanhydride (2)) in alcohol is mixed with an equimolecular amount of aniline; the precipitate that separates is filtered off and recrystallized several times from alcohol. M.p. 148-149°.

Found, %: C 44.0; 44.0; H 6.4; 6.6; P 16.4; 16.2; N 7.6; 7.7.

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* In the calculation, the value of the atomic refraction of phosphorus 5.5 was used ([10]).

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

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