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Abstract

Full Text

CHEMISTRY

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ON THE TAUTOMERISM OF DIPHENYL PHOSPHITE

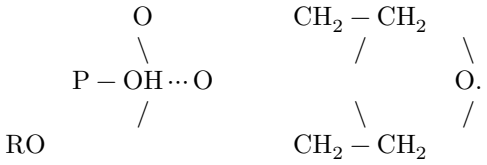
The tautomerism of dialkyl phosphites

$$\begin{array}{ccc} RO & O & RO \\ \backslash & \| & \backslash \\ & P & \rightleftarrows \quad P-OH, \\ / & \backslash & / \\ RO & H & RO \\ & I & II \end{array}$$

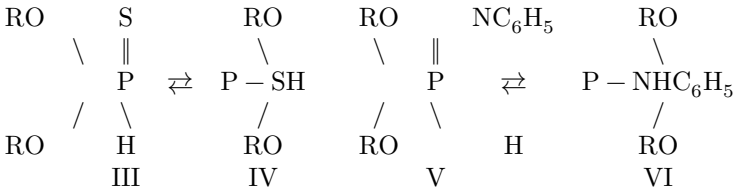
discovered by A. E. Arbuzov ([1]) and Milobendzki ([2]), has been the subject of numerous investigations. On the basis of studies of chemical properties, and of spectroscopic and refractometric data, it may be considered established that the equilibrium position of this tautomeric system is shifted to a considerable extent toward form I. Dialkyl phosphites in the free state do not exhibit the properties characteristic of compounds of trivalent phosphorus; in particular, they do not enter into addition reactions involving the free electron pair of the phosphorus atom of form II. In solutions, dialkyl phosphites likewise do not show the capacity for addition reactions, except in strongly basic media, such as tertiary amines. In these solutions, along with undissociated molecules of dialkyl phosphites, there are salts of the type

$$\left[\begin{array}{l} RO\backslash \\ RO/ \end{array} P-O^{-}\right]\left[HNR_3'^{+}\right],$$

the anion of which readily adds sulfur ([3]), phenyl azide ([4]). M. I. Kabachnik and E. I. Golubeva ([5]) showed that dialkyl phosphites add sulfur comparatively readily also in dioxane medium, in which form II can be stabilized by a strong hydrogen bond



All these data indicate that the equilibrium of dialkyl phosphites is shifted toward form I, and that the action of certain external factors is necessary for the system to be able to manifest the properties of a compound of trivalent phosphorus. If one proceeds from the concepts developed by one of us ([6]), and considers the tautomeric equilibrium of dialkyl phosphites as an acid-base



protolytic equilibrium shifted toward the less acidic form I, then, on passing to analogs of dialkyl phosphites, one may, by changing the structure of the molecule in the corresponding manner, change the ratio of the acidity constants of the forms and thereby obtain systems with different positions of the tautomeric equilibrium. Thus, the equilibrium of dialkyl thiophosphites, as shown by M. I. Kabachnik and T. A. Mastryukova ([7]), is strongly shifted toward form III, and there is reason to believe that it is shifted to an even greater extent than in dialkyl phosphites; while the tautomeric equilibrium of dialkyl anilidophosphites, studied by M. I. Kabachnik and V. A. Gilyarov ([8]), is shifted already toward form VI. This difference in tautomeric relations is explained by a decrease in the ionizability of bonds in the series: SH > OH > NH. In the two examples cited, the change in the position of the tautomeric equilibrium was achieved by a very substantial change in the composition of the dyadic systems.

We set ourselves the task of finding an effect of this kind while preserving the bond dyad system characteristic of dialkyl phosphites, H–P=O. This could be expected when the alkoxy groups of dialkyl phosphites were replaced by more electrophilic groups, whose influence would increase the acidic properties of form I. Diphenyl phosphite was chosen as an example. If the considerations given above are correct, diphenyl phosphite, unlike dialkyl phosphites, should be characterized by typical addition reactions at the unshared electron pair of trivalent phosphorus.

There are two reports in the literature on the synthesis of diphenyl phosphite ([9], [10]). The chemical properties of diphenyl phosphite have not been studied.

We obtained diphenyl phosphite in quantitative yield by cautious hydrolysis of diphenyl chlorophosphite in ether with an equivalent amount of water, followed by removal in vacuo of hydrogen chloride and solvent:

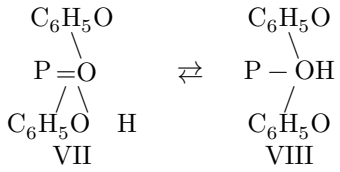
$$(C_6H_5O)_2PCl + H_2O \rightarrow (C_6H_5O)_2POH + HCl.$$

B.p. 100–101° at $3 \cdot 10^{-4}$ mm, n_D^{20} 1.5590, d_4^{20} 1.2318, MR_D found 61.37.

Found, %:	C 61.39, 61.53;	H 4.65, 4.47;	P 13.20, 12.97
$C_{12}H_{11}O_3P$. Calculated, %:	C 61.54;	H 4.73;	P 13.23

In the infrared spectrum of diphenyl phosphite, distinct absorption bands are observed indicating the presence in the molecule of P–H (2420 cm^{-1}) and P=O (1280 cm^{-1}) bonds; in the region characteristic of the hydroxyl group, no appreciable absorption was found (Fig. 1). Thus, the spectroscopic data speak in favor of the structure of diphenyl phosphite with a pentavalent phosphorus atom; the same conclusion is reached by comparison of the molecular refraction found (61.37) with the values calculated for each of the structures separately (MR_D calculated for VII 61.46, for VIII 63.37).

However, the chemical properties of diphenyl phosphite quite definitely indicate the presence of form VIII in appreciable amount in equilibrium with form VII:



VII ⇄ VIII

We found that diphenyl phosphite enters into the following characteristic addition reactions at the free electron pair of trivalent phosphorus.

Addition of phenyl azide. It is known that trialkyl- and triarylphosphines add phenyl azide with the formation of phosphinimines. M. I. Kabachnik and V. A. Gilyarov extended this reaction to complete esters of acids of trivalent phosphorus; dialkyl phosphites do not react with phenyl azide ([12]).

We found that diphenyl phosphite reacts with phenyl azide even in the cold, with formation of diphenyl anilidophosphate:

$$(C_6H_5O)_2POH + C_6H_5N_3 \xrightarrow{-N_2} \left[(C_6H_5O)_2P\begin{matrix}OH\\ \|\\ NC_6H_5\end{matrix}\right] \rightarrow (C_6H_5O)_2P\begin{matrix}O\\ \|\\ NHC_6H_5\end{matrix}$$

A mixture of equimolar amounts of diphenyl phosphite and phenyl azide was left in a sealed ampoule in the dark at room temperature for 4 months. The yield of diphenyl anilidophosphate was 25%, m.p. 128–129° (from aqueous alcohol); a mixed sample with a substance of known structure, obtained

Fig. 1. Infrared spectrum of diphenyl phosphite (below, for comparison, the spectrum of triphenyl phosphite is given (11))

from diphenyl chlorophosphate and aniline, melted without depression. According to the literature data (13), m.p. 129–130°. On heating, the reaction proceeds much more rapidly and with a higher yield (at 100° for 3 hours—50%).

Addition of sulfur. Dialkyl phosphites do not add sulfur without a solvent-base. In contrast to them, diphenyl phosphite reacts with sulfur on heating equimolar amounts of the reagents without a solvent:

$$(C_6H_5O)_2POH + S \rightarrow (C_6H_5O)_2P(O)SH$$

At 120° in 6 hours, 77% of the sulfur enters into reaction. Diphenyl thiophosphate, together with unreacted diphenyl phosphite, was isolated by treating the ethereal solution of the reaction mixture with aqueous alkali and subsequent acidification with hydrochloric acid. Diphenyl thiophosphate was characterized in the form of the cyclohexylammonium salt—colorless needles (from aqueous alcohol), yield 26% (calculated on the sulfur that entered into reaction), m.p. 127–129°. According to the literature data (14), m.p. 127–128°.

Found, %: C 59.29, 59.37; H 6.63, 6.76; P 8.45, 8.42;
S 8.58, 8.38; N 3.76, 3.73;

$$C_{18}H_{24}O_3PSN.$$

Calculated, %: C 59.16; H 6.62; P 8.48;
S 8.76; N 3.83

The addition of sulfur under the indicated conditions is accompanied by evolution of hydrogen sulfide, and along with diphenyl thiophosphate a considerable amount of triphenyl phosphite was isolated from the reaction mixture.

Addition of cuprous chloride. The reaction with monohalide copper salts, leading to the formation of crystalline complexes, was proposed by A. E. Arbuzov (1) as characteristic for compounds of trivalent phosphorus. It was precisely on the basis of the absence of this reaction in dialkyl phosphites that A. E. Arbuzov concluded that the phosphorus atom in the latter is pentavalent.

We have found that cuprous chloride dissolves in diphenyl phosphite with formation of a crystalline complex of composition $(C_6H_5O)_2POH \cdot CuCl$.

After brief heating of equimolar amounts of the reagents, dissolution of the reaction mixture in ether, and removal of the bulk of the resid-

the complex of unreacted cuprous chloride was precipitated with methyl alcohol and reprecipitated from dioxane with petroleum ether. A white powder; on heating to $\sim 120^\circ$ it decomposes.

Found, %: C 43.27, 43.52; H 3.22, 3.19; Cl 10.67, 10.87;
Ash 44.61, 44.88
$C_{12}H_{11}O_3PCuCl$. Calculated, %: C 43.26; H 3.33; Cl 10.64;
Ash 45.17

Reaction of diphenyl phosphite with diazomethane. In contrast to dialkyl phosphites, diphenyl phosphite, having more acidic properties, reacts with diazomethane in ether solution with evolution of nitrogen:

$$(C_6H_5O)_2POH + CH_2N_2 \rightarrow (C_6H_5O)_2POCH_3 + N_2.$$

After removal of excess diazomethane with the solvent and fractionation in vacuo, diphenyl methyl phosphite was isolated. Yield 58%, b.p. 101—103°/2 mm, n_D^{20} 1.5575, d_4^{20} 1.1663, MR_D found 68.56, calculated 68.10. According to the literature data ([15]), b.p. 165.5—166.5°/12 mm, n_D^{23} 1.5528, d_0^{23} 1.1644.

Found, %: C 62.88, 62.82; H 5.36, 5.35; P 12.11, 12.11
$C_{13}H_{13}O_3P$. Calculated, %: C 62.90; H 5.28; P 12.48

The diphenyl methyl phosphite obtained dissolves cuprous chloride on warming; after two reprecipitations from ether with methyl alcohol, the complex $(C_6H_5O)_2POCH_3 \cdot CuCl$ was isolated in almost quantitative yield—a very viscous transparent colorless syrup, which could not be crystallized.

Found, %: C 45.57, 45.44; H 3.77, 3.74; Cl 10.20, 10.38;
Ash 43.00, 42.84
$C_{13}H_{13}O_3PCuCl$. Calculated, %: C 44.97; H 3.77; Cl 10.21;
Ash 43.35

The addition of diazomethane with formation of the complete ester of phosphorous acid may be regarded as one more proof (to the extent of the rigor of Arndt's criterion([16])) of the presence in the equilibrium system of diphenyl phosphite of a tautomeric form with a trivalent phosphorus atom. In this case, in contrast to the preceding addition reactions at the free electron pair of phosphorus, this form was detected by reaction at the hydroxyl group.

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