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# LOWER DIALKYLPHOSPHINOUS ACIDS (SECONDARY PHOSPHINE OXIDES) AND SOME OF THEIR PROPERTIES

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After unsuccessful attempts by Michaelis and his co-workers [1] to synthesize diarylphosphinous acids, the prevailing view in the literature was that such compounds are unstable because of their ready disproportionation into a secondary phosphine and the corresponding phosphinic acid [2].

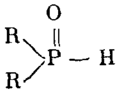
In spite of the fact that a series of higher dialkylphosphinous acids (dialkylphosphine oxides) from dibutylphosphinous and higher [3-6], and also some diarylphosphinous acids [7], have been prepared in recent years, the free lower dialkylphosphinous acids have remained inaccessible, and they have continued to be regarded as substances that are incapable of existence [4, 5]. This opinion has been consolidated by the failures of attempts to synthesize them [4], and particularly to synthesize dimethylphosphinous acid [8, 9]. However, Sander [6] considered that these failures were due to the good solubility of the lower dialkylphosphinous acids in water and the associated difficulties in isolating them, and not to their instability.

This paper describes the syntheses of diethyl-, dipropyl-, diisopropyl- and diisobutyl-phosphinous acids, which were carried out in 80-95% yield by the hydrolysis of the corresponding esters in aqueous dioxane in presence of a catalytic amount of sulfuric acid. The dialkylphosphinous esters were prepared by the method developed by us previously from alkyl phosphorodichloridites and organomagnesium compounds [10]:

$$R'OPCl_2 + 2RMgX \rightarrow R_2POR' + 2MgXCl$$
$$R_2POR' + H_2O \xrightarrow{H^+} R_2PHO + R'OH$$

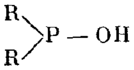
The lower dialkylphosphinous acids were found to be quite stable substances which could be vacuum-distilled without decomposition.

Of the two possible structural formulas of dialkylphosphinous acids (I) and (II), infrared spectrum data confirm the first:



$$R_2P(=O)-H$$

(I)

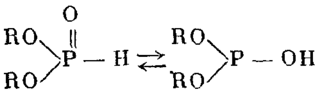


$$R_2P-OH$$

(II)

The infrared spectra (Fig. 1) contain intense absorption bands corresponding to P=O (1179-1196 cm$^{-1}$) and P-H (2278-2304 cm$^{-1}$) valence vibrations. In the neighborhood of 3000 cm$^{-1}$ there are only characteristic C-H vibrations and no signs of absorption bands due to hydroxy groups, which is evidence against formula (II) and also against the presence of appreciable amounts of the form (II) in tautomeric equilibrium with (I). These spectrographic data are in accord with the results of a study of the infrared absorption of dioctylphosphinous acid [11]. Hence, the lower dialkylphosphinous acids, like the higher ones, must be assigned the dialkylphosphine oxide structure (I).

The lower dialkylphosphinous acids may be regarded as organophosphorus analogs of dialkyl hydrogen phosphites, for which the tautomerism III ⇌ IV is extremely probable:



$$(RO)_2P(=O)-H \rightleftarrows (RO)_2P-OH$$

(III) (IV)

It is known from the results of spectrographic and other physical investigations that dialkyl hydrogen phosphites have the structure (III). Their chemical properties are also in accord with this structure: the phosphorus atom in dialkyl hydrogen phosphites does not give some of the addition reactions (with sulfur, cuprous halides) typical for trivalent phosphorus, these substances do not react with phenyl azide, alkyl halides, etc. On the other hand, they are readily oxidized with formation of dialkyl hydrogen phosphates, and they show the dual reactivity that is typical for tautomeric compounds [12] For example, while having the structure (III), by treatment with alkoxides they form salts that correspond in structure to the form (IV). Dual reactivity is characteristic also for these salts: in alkylation and acylation reactions, depending on the nature of the reagent and the reaction conditions, they sometimes form derivatives of the form (III), and sometimes form derivatives of the form (IV) [12]. There are also kinetic proofs of the tautomerism of the dialkyl hydrogen phosphites [13].

In relation to the comparison of dialkylphosphinous acids (I) with dialkyl hydrogen phosphites (III) it was of interest to investigate the ability of dialkylphosphinous acids to undergo addition reactions and to study some of their other properties which would enable us to form an opinion on the tautomerism and dual reactivity of this class of compounds

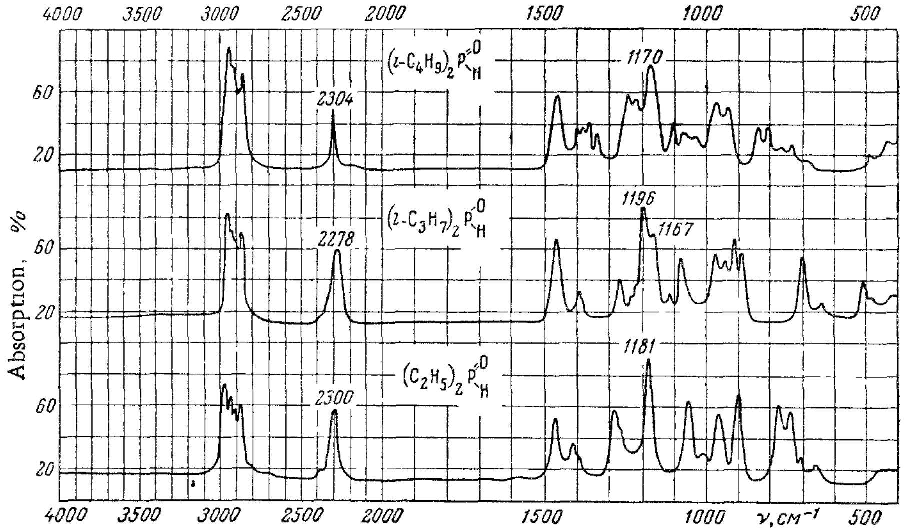


Fig. 1.

It was found that sulfur adds vigorously to dialkylphosphinous acids with evolution of heat and formation of dialkylphosphinothioic acids,* which were identified in the form of their p-phenylenediamine salts:

$$R_2PHO + S \rightarrow R_2PSOH \rightarrow R_2PSOH \cdot H_2NC_6H_4NH_2\text{-}p$$

From dipropylphosphinous acid we prepared the p-phenylenediamine salt of dipropylphosphinothioic acid, which was found to be identical with the product prepared by a method developed by one of us, Mastryukova, and Shipov from a dialkyl hydrogen phosphite and propylmagnesium bromide with subsequent addition of sulfur [14]. One peculiar feature of the addition of sulfur to the lower dialkylphosphinous acids should be noted. The vigorous reaction, to which we refer above, comes to an end after the addition of about one-half of the stoichiometric amount of sulfur. By heating to 100° we may bring up to 60-70% of the calculated amount of sulfur into reaction, but a part of the sulfur always remains undissolved. The lower dialkylphosphinous acids dissolve cuprous iodide, but we were unable to isolate the corresponding complex compounds on account of their instability: on dilution of the solution formed, even with an inert solvent, cuprous iodide is precipitated

Liquid dialkylphosphinous acids are readily oxidized in air (they fume when applied to cotton wool), but for their complete oxidation in air at 20° several days are required.

On reaction with sodium in toluene, diethylphosphinous acid forms the corresponding sodium salt. When this salt is alkylated with an alkyl halide (chloromethyl butyl ether was used) a reaction of the Michaelis-Becker type occurs [16], and the corresponding phosphine oxide [(butoxymethyl)diethylphosphine oxide] is formed:

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* It is shown in [15] that sulfur adds also to dialkylphosphinothious acids (dialkylphosphine sulfides) without catalyst.

$$(C_2H_5)_2PONa + ClCH_2OC_4H_9 \rightarrow (C_2H_5)_2P(O)CH_2OC_4H_9$$

Lower dialkylphosphinous acids react without catalyst at room temperature with benzaldehyde and with methyl acrylate. The normal addition products are formed – the corresponding substituted trialkylphosphine oxides:

$$R_2PHO + C_6H_5CHO \rightarrow R_2P(O)CH(OH)C_6H_5$$
$$R_2PHO + CH_2 = CHCOOCH_3 \rightarrow R_2P(O)CH_2CH_2COOCH_3$$

These reactions are analogous to those of Abramov [17] and B. A Arbuzov and Pudovic [18]. Hence, the chemical properties of the lower dialkylphosphinous acids are similar to those of dialkyl hydrogen phosphites, but with the difference that the former react without catalysts while the latter require the presence of bases.

We must examine the possible explanations of this phenomenon. It may be supposed that the ability of dialkylphosphinous acids to react with the above-mentioned reagents in absence of catalysts is related to their tautomerism, which is like the tautomerism of dialkyl hydrogen phosphites. If it is supposed that the tautomeric equilibrium (I) $\rightleftharpoons$(II) is displaced toward the form containing trivalent phosphorus to a greater extent than in the case of dialkyl hydrogen phosphites, then their higher tendency to undergo addition reactions finds a simple explanation. We consider that this view is not very probable because the attachment of alkyl groups to the phosphorus atom in place of the alkoxy groups of the dialkyl hydrogen phosphites should reduce the acid properties of the form (I) to a greater extent than those of the form (II) and should therefore displace the tautomeric equilibrium still more toward the form containing pentavalent phosphorus than is the case for dialkyl hydrogen phosphites.

A second view is concerned with the formation of the dialkylphosphinite anion. In the absence of bases – proton carriers – the formation of this anion may occur in the course of an autoprotolysis process:

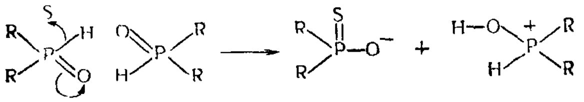
$$2R_2PHO \rightleftarrows R_2PO^- + R_2\overset{+}{P}H(OH)$$

In dialkylphosphinite anions the phosphorus atom has an unshared electron pair, which determines its ability to undergo addition reactions:

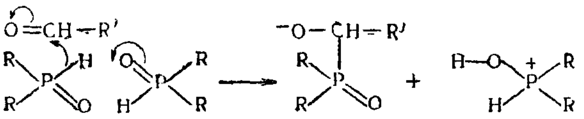
$$R_2PO^- + S \rightarrow R_2P(S)O^-$$

However, this view is also unlikely, for dialkylphosphinous acids are extremely weak acids – undoubtedly weaker than dialkyl hydrogen phosphites – and, although they are stronger bases (all phosphine oxides have basic properties), they can scarcely be expected to have higher autoprotolysis constants than dialkyl hydrogen phosphites

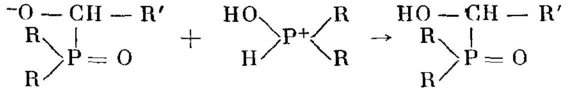
We consider that a third hypothesis is more probable: a trimolecular reaction is assumed, e.g ,



or



The reagent acts directly on the form (I), which contains pentavalent phosphorus; a second molecule of dialkylphosphinous acid acts as a proton acceptor, as a result, in the first case a salt of a strong acid of the phosphinic type with a dialkylphosphine oxide as base is formed, and the reaction stops at this point (with addition of only 50% of the theoretical amount of sulfur, for the protonized dialkylphosphine oxide cannot undergo addition of sulfur). In the second case the process is complete by a new proton transition



and reaction goes to completion. The possibility cannot be excluded that additions to dialkyl hydrogen phosphites, which occur only in presence of bases, proceed by the same mechanism (the catalyst-base plays the part of proton acceptor).

## EXPERIMENTAL

Dialkylphosphinous Acids A solution of 8.7 g of butyl diethylphosphinite in 50 ml of dioxane was mixed in an atmosphere of nitrogen with 2-3 ml of 1-2% sulfuric acid (heat was evolved), the solution was left at 20° for 1-2 days and then vacuum-evaporated The residue was distilled. The yield was 4.23 g (80%). In an analogous way dipropyl-, diisopropyl-, and diisobutyl-phosphinous acids were prepared. Yields, constants, and analytical data are presented in the table.

| Formula | Yield, % | B p., °C (p, mm) | $n_D^{20}$ | $d_4^{20}$ | C, % found | C, % calculated | H, % found | H, % calculated | P, % found | P, % calculated |
|---|---|---|---|---|---|---|---|---|---|---|
| $(C_2H_5)_2PHO$ | 80 | 52—53 (1,5) | 1,4549 | 0,9698 | 45,6<br>45,7 | 45,3 | 10,6<br>10,6 | 10,4 | 28,7<br>29,0 | 29,2 |
| $(C_3H_7)_2PHO$ | 95 | 71—72 (1,5)<br>m p 48—50° | — | — | 53,8<br>53,7 | 53,7 | 11,4<br>11,2 | 11,3 | 22,7<br>22,6 | 23,1 |
| $(i\text{-}C_3H_7)_2PHO$ | 86 | 54—55 (1,5) | 1,4538 | 0,9359 | 53,7<br>53,7 | 53,7 | 11,2<br>11,3 | 11,3 | 23,0<br>22,9 | 23,1 |
| $(i\text{-}C_4H_9)_2PHO$ * | 92 | 74—75 (2)<br>m.p 31—33° | — | — | 59,1<br>59,0 | 59,3 | 11,9<br>11,7 | 11,8 | 19,1<br>19,2 | 19,1 |

* A communication [19] was recently published on the synthesis of diisobutylphosphinous acid, but no constants or analytical data are given for this compound.

p-Phenylenediamine Salt of Dipropylphosphinothioic Acid. In a stream of nitrogen 0.38 g of sulfur was added to 1.6 g of dipropylphosphinous acid. At the end of the exothermic reaction 10-20 ml of dry ether was added to the mixture, unchanged sulfur was separated, and the filtrate was mixed with a saturated ethereal or benzene solution of 0.65 g of p-phenylenediamine. The salt precipitated either immediately or after evaporation of the solution. Yield 1.55 g (47%); m.p. 125 5-127.5° (from benzene). Found: C 53.0; 52.9, H 8.4, 8.5, N 10.5, 10.3, P 11.0; 10.9; S 12.0, 11.7%. $C_{12}H_{23}N_2OPS$. Calculated. C 52.5; H 8.4; N 10.2, P 11.3; S 11.7%.

A mixture with the p-phenylenediamine salt of dipropylphsophinothioic acid [14] had m p. 125-127.5°.

p-Phenylenediamine Salt of Diisobutylphosphinothioic Acid. This was prepared analogously from 1.6 g of diisobutylphosphinous acid, 0 32 g of sulfur, and 0.54 g of p-phenylenediamine. Yield 1.2 g (40%); m.p. 109-110.5° (from benzene). Found: C 56.0, 56.0; H 9.2; 9.1, N 9.5, 9.3; P 10.1; 10.3; S 10.4, 10.8%. $C_{14}H_{27}N_2OPS$. Calculated: C 55.6, H 9.0, N 9.3, P 10 2, S 10.6%

Diethyl(α-hydroxybenzyl)phosphine Oxide. A mixture of 1.06 g of benzaldehyde and 1.06 g of diethylphosphinous acid was allowed to stand in an atmosphere of nitrogen at 20° for 1-2 days The reaction product crystallized out, either spontaneously, or when rubbed Recrystallization from a mixture of dry benzene and petroleum ether gave colorless crystals. Yield 1.8 g (85%), m.p. 87.5-88.5°. Found: C 62.3; 62.2; H 8.1, 8.2, P 14.8, 14.6%. $C_{11}C_{17}O_2P$. Calculated C 62.3, H 8.1, P 14.6%.

(α-Hydroxybenzyl)diisopropylphosphine Oxide. This was prepared analogously from 1.6 g of diisopropylphosphinous acid and 1.28 g of benzaldehyde. Yield 2.6 g (90%); m.p. 112.5-113.5° (from a mixture of benzene and petroleum ether). Found: C 64.8, 64 7; H 8.8; 9.0; P 12.8; 12.7%. $C_{13}H_{21}O_2P$. Calculated: C 65.0, H 8.8, P 12.9%

Diethyl(2-methoxycarbonylethyl)phosphine Oxide. A mixture of 3 g of diethylphosphinous acid, 3 g of freshly distilled methyl acrylate, and a little inhibitor (anthracene, hydroquinone) was allowed to stand for 10-15 days in an atmosphere of nitrogen at 20° Distillation gave 1.3 g of unchanged diethylphosphinous acid and 2.3 g of diethyl(2-methoxycarbonylethyl)phosphine oxide Yield 43% (75% on the amount of the diethylphosphinous acid that reacted), b.p. 123-124° (1.5 mm), b.p. 28-30°; $n_D^{20}$ 1.4710, $d_4^{20}$ 1 0872 Found· C 50.3, 50.2, H 9.1, 8.9; P 15 9; 16.1%; MR 49.41. $C_8H_{17}O_3P$ Calculated: C 50.0; H 8.9, P 16.1%, MR 49.61 ($AR_p$ 5.5 [20]).

Diisobutyl(2-methoxycarbonylethyl)phosphine Oxide. This was prepared analogously from 3.6 g of diisobutylphosphinous acid and 4 g of methyl acrylate (allowed to lie for one month at 20°); yield 2.7 g (49.2%); b p. 173-174° (7 mm); m.p. 42.5-44°. Found: C 57.8; 57.9; H 10.2; 10.2; P 12.5; 12.0%. $C_{12}H_{25}O_3P$. Calculated: C 58.0; H 10.2; P 12.5%.

(Butoxymethyl)diethylphosphine Oxide. 4.8 g of butyl chloromethyl ether was added dropwise with stirring at 60-70° in a stream of nitrogen to the sodium salt of diethylphosphinous acid prepared from 3.9 g of diethylphosphinous acid and a suspension of 0.85 g of sodium in 25 ml of dry toluene. The mixture was heated for 1.5 hours at 100-110° After the usual treatment we obtained 2.5 g (50%) of the phosphine oxide; b.p. 105-105° (2 mm), $n_D^{20}$ 1.4532, $d_4^{20}$ 0.9571. Found· C 56.4; 56.4; H 11.0; 11.0; P 16.2; 16.2%; MR 54.31 $C_9H_{21}O_2P$. Calculated: C 56.2; H 11.0; P 16.1%. MR 54.22.

## SUMMARY

1. Some lower dialkylphosphinous acids were synthesized. According to their infrared spectra, these substances are pentavalent phosphorus derivatives

2. Lower dialkylphosphinous acids combine vigorously with sulfur, dissolve cuprous iodide, and add to benzaldehyde and to methyl acrylate in absence of catalyst.

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