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Abstract

Full Text

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Interaction of Triethyl Phosphite with Hydrogen Sulfide

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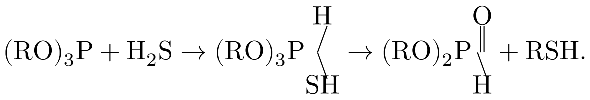
In recent years interest has increased greatly in reactions of organic derivatives of trivalent phosphorus with various sulfur compounds of both inorganic (1–3) and organic character (4,5). In this connection it seemed of interest to study the interaction of trialkyl phosphites with hydrogen sulfide, which is one of the most important and extremely active derivatives of sulfur. There are no data in the literature devoted to this question. It was expected that the reaction would proceed according to the scheme of the Arbuzov rearrangement.



$$(RO)_3P + H_2S \rightarrow (RO)_3P\begin{matrix}H\\ \langle\\ SH\end{matrix} \rightarrow (RO)_2P\begin{matrix}O\\ \|\\ H\end{matrix} + RSH.$$

However, when a stream of dry hydrogen sulfide was passed through triethyl phosphite, prepared by a modified Arbuzov method (6), for 6 hours with vigorous stirring (at room temperature), the reaction did not take place (the triethyl phosphite was quantitatively recovered by vacuum distillation). But when triethyl phosphite, prepared by the method of Milobendzskii and Sakhnovskii (7) in the presence of dimethylaniline, was brought into contact with hydrogen sulfide under the same conditions, a reaction occurred with the formation of a small amount of diethyl thiophosphite. Triethyl phosphite prepared by the modified method of Milobendzskii and Sakhnovskii in the presence of triethylamine showed an even greater tendency toward reactions with hydrogen sulfide. In this case it was possible to isolate diethyl thiophosphorous acid in the form of its lead salt (8).

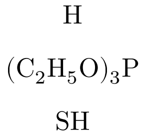
These experiments indicated that traces of organic bases, always present in trialkyl phosphites prepared by the Milobendzskii method, catalyze the reaction of triethyl phosphite with hydrogen sulfide. Special experiments carried out without addition and with prior addition of catalytic amounts of dimethylaniline and triethylamine to chemically pure triethyl phosphite, prepared through magnesium ethylate (6) and containing no traces of either organic bases or diethyl phosphite, also confirmed the assumption of the catalytic action of organic bases on the reaction of triethyl phosphite with hydrogen sulfide. Thus, organic bases are catalysts of the reaction of triethyl phosphite with hydrogen sulfide, with triethylamine, as the stronger organic base, proving to be the more effective catalyst.

The catalytic influence of triethylamine is apparently explained by its ability to form with hydrogen sulfide an unstable quaternary ammonium salt

$$(C_2H_5)_3N + HSH \rightleftarrows [(C_2H_5)_3\overset{+}{N}H]\,\overline{SH},$$

which then interacts with triethyl phosphite. Therefore it seemed that an increase in the concentration of triethylamine would have a positive effect on the reaction rate. A mixture of triethyl phosphite with 30% by weight of triethylamine over

50 h of vigorous stirring in a stream of hydrogen sulfide at a temperature of 10° reacted completely. When separating the reaction products, we encountered a very interesting phenomenon. As a result of vacuum distillation of the reaction mixture at low temperature (not above 90°), diethyl thiophosphite was isolated in 92.5% yield. Alcohol was qualitatively detected in the triethylamine fraction. An attempt to distill off the low-boiling products (triethylamine, ethyl alcohol) from the reaction mixture at a reaction-mixture temperature of 130–140° led to vigorous evolution of ethyl mercaptan with formation of diethyl phosphorous acid (95%). In the interaction of triethyl phosphite with hydrogen sulfide in the presence of triethylamine, an intermediate product of addition of hydrogen sulfide to triethyl phosphite is apparently formed; on rapid heating to 130–140° it decomposes into diethyl phosphorous acid and ethyl mercaptan, while at low temperature (not above 90°) it gives diethyl thiophosphorous acid and ethyl alcohol. Since hydrogen sulfide does not react with chemically pure triethyl phosphite in the absence of organic bases, it is difficult to assign to the intermediate addition product the structure of a quasiphosphonium compound



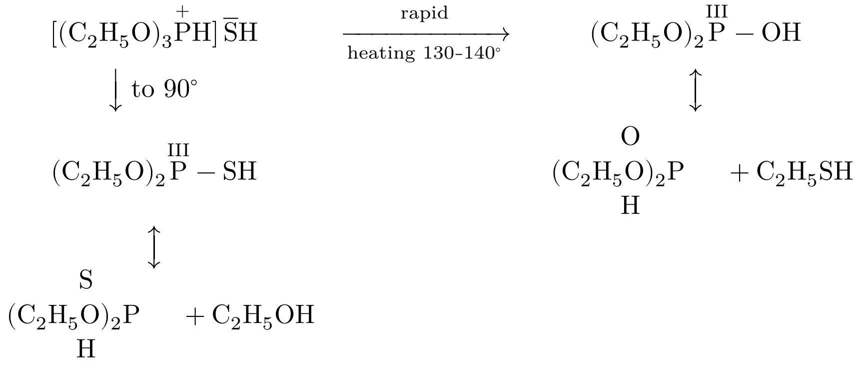
$$\overset{H}{\underset{SH}{(C_2H_5O)_3P}}$$

More likely is an ionic structure of the intermediate addition product, in whose formation triethylamine participates, acting as a kind of ion carrier:

$$(C_2H_5)_3N + H_2S \rightleftarrows [(C_2H_5)_3\overset{+}{N}H]\,\bar{S}H,$$

$$[(C_2H_5)_3\overset{+}{N}H]\,\bar{S}H + \dot{P}(OC_2H_5)_3 \rightleftarrows [(C_2H_5O)_3\overset{+}{P}H]\,\bar{S}H + (C_2H_5)_3N.$$

The decomposition of the phosphonium salt apparently proceeds by two routes:



$$[(C_2H_5O)_3\overset{+}{P}H]\,\overline{S}H \xrightarrow[\text{heating 130-140°}]{\text{rapid}} (C_2H_5O)_2\overset{III}{P}-OH \leftrightarrow (C_2H_5O)_2\overset{O}{\underset{H}{P}} + C_2H_5SH$$

$$[(C_2H_5O)_3\overset{+}{P}H]\,\overline{S}H \xrightarrow{\text{to } 90°} (C_2H_5O)_2\overset{III}{P}-SH \leftrightarrow (C_2H_5O)_2\overset{S}{\underset{H}{P}} + C_2H_5OH$$

It was not possible to isolate the intermediate phosphonium salt, since the reaction products contain a considerable amount of triethylamine, and an attempt to separate it by distillation leads to decomposition of the intermediate product.

Experimental Part

Triethyl phosphite was prepared from magnesium ethylate (6), purified from traces of diethyl phosphite with metallic sodium, and distilled. Hydrogen sulfide was prepared in a Kipp apparatus and dried with calcium chloride and phosphorus anhydride. The reaction was carried out in a three-necked flask equipped with a mechanical stirrer, thermometer, tube for introducing hydrogen sulfide, and a reflux condenser protected by a calcium chloride tube. The course of the reaction was monitored by the change in the refractive index of the reaction mixture.

Experiment 1. Over 50 h of intensive stirring of a mixture of triethyl phosphite (36.0 g, n_D^{20} 1.4130, d_4^{20} 0.9680) and triethylamine (11.0 g) in a stream of hydrogen sulfide ···

hydrogen sulfide; at 10°, the refractive index of the mixture n_D^{20} changed from 1.4110 to 1.4610. When an attempt was made to distill off triethylamine from the reaction mixture at atmospheric pressure (temperature of the reaction mass, 130–140°), ethyl mercaptan and diethyl phosphite containing an admixture of diethyl thiophosphite were isolated. Ethyl mercaptan was obtained in an amount of 6.5 g (50%): b.p. 36–37°, n_D^{20} 1.4330, d_4^{20} 0.8380; according to (9): b.p. 34.7, 37°, n_D^{25} 1.4351, d_4^{25} 0.8315; and 28.5 g (95%) of diethyl phosphite containing an admixture of diethyl thiophosphite: b.p. 74–75° (at 12 mm), n_D^{20} 1.4110, d_4^{20} 1.0706. In order to separate the diethyl and diethyl thio phosphites, the crude product was dissolved in water; from the aqueous solution the diethyl thiophosphite was extracted with *n*-heptane, and the diethyl phosphite with benzene. After drying the extracts and distilling off the solvents, 25.5 g (88.3%) of pure diethyl phosphite was obtained: n_D^{20} 1.4080, d_4^{20} 1.0740 (10), and 1.7 g of diethyl thiophosphite with n_D^{20} 1.4470.

Experiment 2. A mixture of 36.0 g of triethyl phosphite and 10.0 g of triethylamine was treated analogously. The refractive index of the mixture n_D^{20} changed, reaching a constant value over 48 h, from 1.4110 to 1.4590. A portion of the product (25.9 g) was immediately subjected to vacuum distillation at a bath temperature not above 90°. This gave 2.5 g of a fraction: b.p. 25-30° (at 100 mm), n_D^{20} 1.4020, consisting of a mixture of triethylamine and ethyl alcohol. Because of the closeness of their boiling points they could not be separated; ethyl alcohol was detected in the form of sodium ethoxide. The fraction with b.p. 74-76° (at 14 mm) was diethyl thiophosphite with the following constants: 17.5 g (92.5%), n_D^{20} 1.4520, d_4^{20} 1.0798 (10). Found MR_D 38.92, calculated MR_D 39.51.

Found, %:	P 19.91;	S 20.50
$C_4H_{11}O_2PS$. Calculated, %:	P 20.10;	S 20.70

The lead salt of diethyl thiophosphorous acid obtained from this product has m.p. 75-76° and gives no depression of the mixed melting point with a sample obtained from diethyl thiophosphite synthesized by the Michalski method (11), according to (8): m.p. 75-76°. The other portion of the reaction products (20.2 g) was treated as in the first experiment. When the bath temperature reached 130-140°, the products described in experiment 1 were obtained.

As a result of the work carried out, the interaction of triethyl phosphite with hydrogen sulfide in the presence of a catalyst—organic bases—and in their absence has been studied.

It has been established that, in the interaction of triethyl phosphite with hydrogen sulfide in the presence of triethylamine, rapid heating of the reaction mass to 130-140° gives diethyl phosphite (95%), whereas gradual heating to 90° gives diethyl thiophosphite (92.5%). The reaction described is a new method for preparing diethyl thiophosphite.

A scheme for the mechanism of the reaction of triethyl phosphite with hydrogen sulfide has been proposed.

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CITED LITERATURE

1. A. C. Poshkus, J. E. Herweh, L. T. Hass, J. Am. Chem. Soc., **80**, 5022 (1958).
2. J. Michalski, B. Pliszka, Chem. and Ind., 1962, No. 24, 1052.
3. A. C. Poshkus, J. E. Herweh, J. Am. Chem. Soc., **84**, 555 (1962).
4. V. A. Kukhtin, A. N. Pudovik, *Usp. khim.*, **28**, 96 (1959).
5. C. Walling, O. H. Basedow, E. S. Savas, J. Am. Chem. Soc., **82**, 2181 (1960).
6. N. N. Mel' nikov, Ya. A. Mendel' baum, *ZhOKh*, **28**, 2473 (1958).
7. T. Milobendzki, A. Sachnowski, Chem. Polski, **15**, 34, 48 (1917); Chem. Zbl., **1**, 912 (1918).
8. M. I. Kabachnik, G. A. Mastryukova, Acad. Sci. USSR, Institute of Organic Chemistry, *Chemical Reference Book*, 2, Moscow, 1963.
9. Handbook of Chemistry, 2, Leningrad-Moscow, 1963.
10. E. N. Tsvetkov, M. I. Kabachnik, *Reactions and Methods for the Study of Organic Compounds*, Book 13, Moscow, 1964, p. 267.
11. Cz. Krawiecki, J. Michalski, J. Chem. Soc., 1960, 881.

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