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Abstract

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A NEW METHOD FOR PREPARING OXYALKYLPHOSPHINIC ACIDS

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In studying boric acid esters, we found that they do not react with phosphorus trichloride even on boiling. Phosphorus oxychloride readily decomposes boric esters when heated on a water bath according to the equation:

$$(\mathrm{AlkO})_3\mathrm{B} + \mathrm{POCl}_3 \rightarrow \mathrm{BPO}_4 + 3\mathrm{AlkCl}.$$

At 0° this reaction proceeds very slowly. Hydrogen chloride does not react with borates of primary and secondary alcohols (1). We therefore assumed that it should be quite possible to phosphorylate boric esters by the reaction of Soborovsky, Zinov' ev, and Englin (2)

$$\mathrm{RH} + \mathrm{PCl}_3 + 0.5\mathrm{O}_2 \rightarrow \mathrm{RPOCl}_2 + \mathrm{HCl}.$$

The reaction was originally proposed for the phosphorylation of hydrocarbons and was later extended to haloalkyls, simple ethers, and certain other compounds.

In the present work we found that boric esters (which we prepared from the corresponding alcohols (3)) readily enter into this reaction. The reaction proceeds successfully only with good cooling of the mixture. Without this, simple oxidation of phosphorus trichloride to oxychloride takes place, and very little of the phosphorylated products is obtained, or none at all. Initially, the phosphorylation reaction was studied using tributyl borate and triisobutyl borate as examples. Schematically it may be represented as follows:

$$(\mathrm{C}_4\mathrm{H}_9\mathrm{O})_3\mathrm{B} + \mathrm{PCl}_3 \rightarrow 0.5\mathrm{O}_2 \rightarrow (\mathrm{C}_4\mathrm{H}_9\mathrm{O})_2\mathrm{POC}_4\mathrm{H}_8\mathrm{POCl}_2 + \mathrm{HCl}.$$

In the optimal variant, 4 moles of phosphorus trichloride are taken per 1 mole of tributyl borate. Evidently, more than one butyl group of tributyl borate is phosphorylated, since the yield of oxybutylphosphinic acid is 60%—if one assumes that theoretically 3 moles of oxybutylphosphinic acid can be obtained from 1 mole of tributyl borate. The directly phosphorylated boric ester proved to be an unstable compound. When an attempt was made to distill off the phosphorus oxychloride obtained during the phosphorylation of triisobutyl borate, it was found that at about 80–100° a vigorous reaction begins and the reaction mass solidifies into a hard colorless resin. On distillation in vacuum at 15 mm, phosphorus oxychloride and a mixture of acid chlorides were distilled off, among them $C_4H_9OPOCl_2$. The residue—a thick, slightly colored mass—was close in chlorine and phosphorus content to $B(OC_4H_8POCl_2)_3$, but with a molecular weight of about 300 (323 and 315 in two determinations) instead of the calculated 578. Apparently, partial cleavage takes place. To isolate and purify the alkyloxyphosphinic acids, after completion of phosphorylation the reaction products were poured into water with ice and evaporated several times to remove hydrochloric and boric acids. Then, by the method proposed by Pedzh (^{4}), phosphoric acid was separated in the form of the magnesium ammonium salt, and from the filtrate the lead salt of the corresponding alkyloxyphosphinic acid was precipitated. Decomposition of the lead salt with hydrogen sulfide gave the free oxyphosphinic acid.

α-Oxyphosphinic acids were obtained by phosphorylation of trimethyl borate and tribenzyl borate. These acids had also been obtained previously (^{4},^{5}) from

of the corresponding aldehydes. The analytical data agreed with those given in the literature. In the phosphorylation of butyl borate, crystalline oxybutylphosphinic acid was obtained, which, unlike the α-oxybutylphosphinic acid described in the literature, does not form an acid chloride with phosphorus pentachloride, but reacts vigorously with formation of a solid white substance, apparently a polycondensation product. From triethyl borate it was possible to obtain oxyethylphosphinic acid in the form of an impure lead salt; it contains phosphorous acid, although beforehand the impurity of phosphorous acid had been separated by us in the form of the magnesium ammonium salt. Evidently a salt is formed of an unstable β-oxyethylphosphinic acid, which, analogously to its ester obtained earlier (^{6}), is readily cleaved with formation of phosphorous acid. The other oxyalkylphosphinic acids were isolated in the form of lead salts; in the free state they are not crystalline and, possibly, are mixtures of isomers. On heating the phosphorochloridates of the borate esters of these acids immediately after phosphorylation, they decompose, and a vigorous reaction occurs with evolution of hydrogen chloride.

In the phosphorylation of isobutyl borate, an experiment was carried out to convert the acid chlorides obtained into ethyl esters by treatment with ethyl alcohol in the presence of pyridine, analogously to the methods for obtaining esters of phosphinic acids published earlier (^{7}).

The resulting mixture of esters was not distilled, and on attempting to distill off triethyl phosphate in vacuo, polymerization even occurred. An experiment was also made to obtain a pyrophosphate by the method of Dvornikov and Morill (^{8}), in order to obtain, according to the overall equation, a pyrophosphate of the type:

$$\mathrm{B(OC_4H_8POCl_2)_3 + 3POCl_3 + 12C_2H_5OH \rightarrow}$$
$$\mathrm{\rightarrow B\,(OC_4H_8P(=O)(OC_2H_5) - O - P(=O)(OC_2H_5)_2)_3 + 3C_2H_5Cl + 12HCl,}$$

The pyrophosphates obtained several times, however, had a molecular weight of 1300—1400, instead of the calculated 963, and evidently were polyphosphates.

The esters obtained, as testing showed, have a very weak insecticidal action on a typical pest of agricultural plants—the granary weevil.

Experimental Part

The phosphorylation reaction of borate esters is carried out in a three-necked conical flask with a reflux condenser (closed with a calcium chloride tube), a thermometer, a dropping funnel, and a capillary through which oxygen, dried over calcium chloride and soda lime, was passed from a cylinder.

Into the flask were placed 0.1 mole of the borate ester; it was cooled with a mixture of ice and salt, and oxygen was passed through the capillary at such a rate that the bubbles could barely be counted; in practice 2—3 liters pass in an hour. At the same time, over the course of 2—2.5 hours, 0.4 mole (55 g) of phosphorus trichloride was added dropwise from the dropping funnel—at first very slowly, since the reaction proceeds vigorously and an undesirable rise in temperature is possible. The reaction temperatures for various esters are given in Table 1. After all the phosphorus trichloride has been added, oxygen is passed until the temperature ceases to rise, and then for another 30 min., after which the process is stopped. Without allowing the reaction mixture to warm up, it is poured in a thin stream with stirring into 1.5 liters of cold water and stirred until dissolution (hydrolysis). The solution is then evaporated several times on a water bath until hydrogen chloride is completely removed (the vapors should not react with Congo paper).

Table 1

Boric ester	Temperature, °C	Oxyalkylphosphonous lead salt, g	Oxyalkylphosphonous lead salt, % theor.	Oxyalkylphosphonic acid, g	Oxyalkylphosphonic acid,% theor.	Analysis *
Methyl	0	57.2	54.4	12	41.7	M.p. 85°; lit. data (4) 85°Found %: P 9.33CH_3PO_4Pb. Calculated %: P 9.41
Ethyl	0	17.0	17.0	–	–	Found %: P 8.95$C_2H_5PO_4Pb$. Calculated %: P 9.35
Propyl	0–7	43	41.6	–	–	Found %: P 8.63$C_3H_2PO_4Pb$. Calculated %: P 8.97
Butyl	4	66.5	60.0	21	51.2	Found %: P 8.48$C_4H_9PO_4Pb$. Calculated %: P 8.65
Isobutyl	0	41	37.4	–	–	Found %: P 8.48$C_4H_9PO_4Pb$. Calculated %: P 8.65

Boric ester	Temperature, °C	Oxyalkylphosphonous lead salt, g	Oxyalkylphosphonous lead salt, % theor.	Oxyalkylphosphonic acid, g	Oxyalkylphosphonic acid,% theor.	Analysis *
Isoamyl	6–12	47	37.8	–	–	Found %: P 8.11$C_5H_{11}PO_4Pb$. Calculated %: P 8.30
Secondary octyl (octanol-2)	5	22	17.0	–	–	Found %: P 8.46; 8.14$C_8H_{17}PO_4Pb$. Calculated %: P 7.51
Cyclohexyl	25	45	39.2	31.6	29.2	M.p. 137°.Found %: P 7.75, 7.98$C_6H_{11}PO_4Pb$. Calculated %: P 8.05
Benzyl	0	31	23.7	–	–	Aniline salt m.p. 200–201°. Lit. data (9) 201 – 202°.Found %: P 7.86; 7.89$C_7H_7PO_4Pb$. Calculated %: P 7.83

* All analyses for P content refer to the lead salts of oxyalkylphosphinous acids.

The mixture is then diluted to a volume of 200–300 ml, ammonia is added until a weakly alkaline reaction is obtained, and phosphoric acid is precipitated with a 10% solution of magnesium nitrate. After 12 hours, the precipitated magnesium ammonium phosphate is filtered off and washed with water.

The filtrate and wash waters are combined and precipitated with a 20% solution of lead acetate or nitrate until precipitation is complete. The lead salt is filtered off, washed several times with hot water, dried in air and, finally, at 110–115° in a drying cabinet. To isolate the free oxyalkylphosphinous acid, the lead salt, without drying, is shaken with 200 ml of water, and then hydrogen sulfide is passed through for 5 hours to precipitate lead sulfide. The precipitate of lead sulfide is filtered off and washed with hot water. The filtrate is tested for completeness of precipitation by passing hydrogen sulfide through it, evaporated on a water bath, and the precipitated oxyalkylphosphinous acid is dried in a desiccator over phosphorus pentoxide. The results are summarized in Table 1.

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named after M. V. Lomonosov

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