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Abstract

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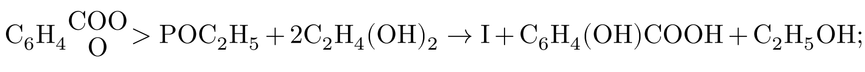
β-HYDROXYALKYL ALKYLENE PHOSPHITES—A NEW TYPE OF ESTERS OF PHOSPHOROUS ACID

(Presented by Academician A. E. Arbuzov on 12 VII 1962)

1,2-Glycol derivatives of phosphorous acid have been described in large numbers. Most often these are compounds with a closed five-membered dioxaphospholane ring and, very rarely, unstable derivatives of dialkylphosphorous acids, in which two acid residues are connected by a glycol bridge (^{1}). The latter diphosphites readily redistribute radicals and are converted into more stable cyclic phosphites. In the literature there is only one mention of a derivative of 1,2-glycol and phosphorous acid in which one alcoholic hydroxyl remains unesterified; however, we believe that this compound—β-hydroxyethylethylene phosphite—was in fact not obtained by the authors (^{2}) and is reported erroneously, since both the method of preparation and its physical constants (a liquid, b.p. 134-136° at 12 mm) have nothing in common with our data presented below.

We previously found a method for preparing mixed phosphites under mild conditions by alcoholysis of the ester of salicylphosphorous acid (^{3}). In attempting to obtain β,β'-dioxytriethyl phosphite by this method, we treated 1 mole of the ethyl ester of the named acid with 2 moles of ethylene glycol. Instead of the expected product, we obtained β-hydroxyethylethylene phosphite (2-(2′-hydroxyethoxy)-1,3,2-dioxaphospholane) (I)—the first representative of a new type of phosphites. This is a crystalline substance with a faint unpleasant odor, m.p. 50°, distills in vacuo without decomposition, b.p. 86° at 9 mm, soluble in alcohol, dioxane, and warm ether, poorly soluble in benzene, gasoline, and cold ether, and decomposes with water. It is best purified by recrystallization from a warm ethereal solution after cooling to $-85°$. It reacts with copper(I) halides and sulfur with self-heating.

To leave no doubts concerning the structure of I, we synthesized it by seven different methods:

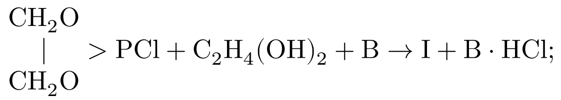


$$C_6H_4\genfrac{}{}{0pt}{}{COO}{O}> POC_2H_5 + 2C_2H_4(OH)_2 \rightarrow I + C_6H_4(OH)COOH + C_2H_5OH; \quad (1)$$

$$PCl_3 + 2C_2H_4(OH)_2 + 3B \rightarrow I + 3B \cdot HCl; \quad (2)$$

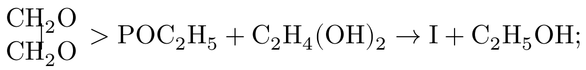
$$\mathrm{ROPCl_2 + 2C_2H_4(OH)_2 + 2B \rightarrow I + ROH\,2B \cdot HCl}, \tag{3}$$

$$\mathrm{R = C_2H_5 \text{ or } C_4H_9};$$

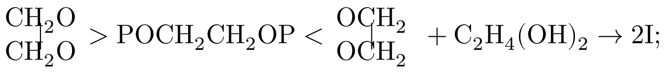


$$\begin{array}{c}\mathrm{CH_2O}\\ |\\ \mathrm{CH_2O}\end{array} > \mathrm{PCl + C_2H_4(OH)_2 + B \rightarrow I + B \cdot HCl}; \tag{4}$$

$$\mathrm{(C_2H_5O)_3P + 2C_2H_4(OH)_2 \rightarrow I + 3C_2H_5OH}; \tag{5}$$



$$\begin{array}{c}\mathrm{CH_2O}\\ \mathrm{CH_2O}\end{array} > \mathrm{POC_2H_5 + C_2H_4(OH)_2 \rightarrow I + C_2H_5OH}; \tag{6}$$



$$\begin{array}{c}\mathrm{CH_2O}\\ \mathrm{CH_2O}\end{array} > \mathrm{POCH_2CH_2OP} < \begin{array}{c}\mathrm{OCH_2}\\ \mathrm{OCH_2}\end{array} \mathrm{+ C_2H_4(OH)_2 \rightarrow 2I}; \tag{7}$$

B—triethylamine or pyridine.

Some variants of reactions ((2), (3), and (4)) were carried out in the presence of a large excess of ethylene glycol; however, in all cases only I was isolated. Apparently, compounds of the types β, β'-dioxytrialkyl phosphite and β, β', β''-trioxytrialkyl phosphite, whose possible formation we investigated, cannot exist at temperatures above −20° (the minimum temperature of our experiments) and, with elimination of an alcohol molecule or, respectively, glycol, are converted into the most stable under these conditions β-oxyalkylalkylene phosphite.

$$\mathrm{ROP(OCH_2CH_2OH)_2 \rightarrow I + ROH}, \qquad \mathrm{P(OCH_2CH_2OH)_3 \rightarrow I + C_2H_4(OH)_2}.$$

The most convenient and rapid method for obtaining I is reaction (7). It is sufficient to mix equimolecular amounts of ethylene glycol and triethylene diphosphite, and the reaction, with self-heating, is completed in a few minutes and gives a quantitative yield of the pure product.

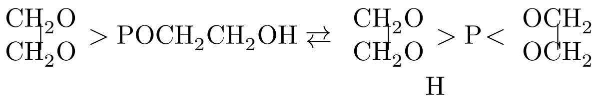
By a scheme analogous to (6), homologues of compound I were obtained: β-oxy-α, α, β-trimethylpropylene pinakonylene phosphite* (2-(2′-oxy-1′,1′,2′-trimethylpropyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane) (II) from pinacol, and β-oxy-α-methylpropylene pseudobutylene phosphite* (2-(DL-erythro-2′-oxy-1′-methylpropyloxy)-cis-4,5-dimethyl-1,3,2-dioxaphospholane) (III) from meso-butanediol-2,3 (b.p. 179–181°, m.p. 32°). III was also obtained by scheme (5). II and III are crystalline substances with m.p. 88–89° and

82–85°, respectively; they dissolve in organic solvents better than I and are decomposed by water.

The alcoholic hydroxyls in I, II, and III are readily determined by the Chugaev–Terevitinov method. In compound I the alcoholic hydroxyl was acylated with three different acid residues. The acetyl group could be introduced only by the action of ketene; reactions with acetyl chloride or acetic anhydride did not lead to the desired result. β-Acetoxyethyl ethylene phosphite is a liquid with b.p. 119–120.5° at 9 mm, n_D^{20} 1.4580, d_4^{20} 1.2573, obtained in 43.5% yield. Reactions proceed smoothly with ethylene phosphorous acid chloride anhydride in the presence of base, and also with phenyl isocyanate. Triethylene diphosphite was obtained in 50% yield. It is a quite stable liquid with b.p. 126° at 0.7 mm, n_D^{20} 1.4906, d_4^{20} 1.3755; literature data (^{4}) for the unpurified substance: n_D^{25} 1.49325, d_4^{25} 1.3200. β-(Phenylcarbamoyloxy)-ethylene phosphite is a crystalline substance with m.p. 138–142°, obtained in quantitative yield.

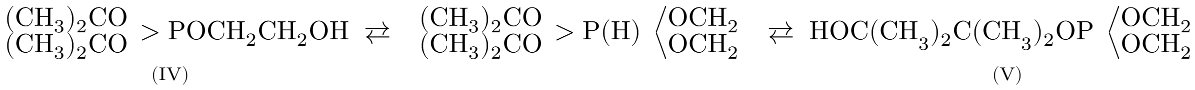
The structure of the acyl derivatives was confirmed by reverse syntheses from ethylene phosphorous acid chloride anhydride and the corresponding monoacylated glycols. An attempt to methylate the hydroxyl group in I with diazomethane was unsuccessful.

The supposition of the possibility of tautomerism (8)



$$\begin{matrix}CH_2O\\CH_2O\end{matrix}>POCH_2CH_2OH \rightleftarrows \begin{matrix}CH_2O\\CH_2O\end{matrix}>\underset{H}{P}<\begin{matrix}OCH_2\\OCH_2\end{matrix} \qquad (8)$$

in β-oxyalkylalkylene phosphites was disproved by the synthesis of two isomeric substances—β-oxyethyl pinakonylene phosphite (2-(2′-oxyethyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (IV) and β-hydroxy-α,α,β-trimethylpropylethylene phosphite (2-(2′-hydroxy-1′,1′,2′-trimethylpropyloxy)-1,3,2-dioxaphospholane) (V). Both were synthesized analogously to schemes (4) and (6). If the tautomeric equilibrium (8) took place, then IV and V would be identical as a result of the reaction



$$\underset{(IV)}{\begin{matrix}(CH_3)_2CO\\(CH_3)_2CO\end{matrix}>POCH_2CH_2OH} \rightleftarrows \begin{matrix}(CH_3)_2CO\\(CH_3)_2CO\end{matrix}>P(H)\left\langle\begin{matrix}OCH_2\\OCH_2\end{matrix}\right. \rightleftarrows \underset{(V)}{HOC(CH_3)_2C(CH_3)_2OP\left\langle\begin{matrix}OCH_2\\OCH_2\end{matrix}\right.}$$

However, IV and V proved to be different substances. IV is a viscous liquid that does not distill without decomposition and does not crystallize at temperatures above −40°; below −40° it solidifies into a glassy mass. V is also a viscous

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* We call the divalent radical $-C(CH_3)_2C(CH_3)_2-$ pinakonylene, and the radical $-CH(CH_3)CH(CH_3)-$ pseudobutylene.

liquid, but at 0° it crystallizes completely and melts again at 20°. Seeding with crystals of V does not cause crystallization of IV at lowered temperatures.

Elemental analysis of all the compounds obtained gave satisfactory results.

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

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