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Abstract

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SPIRODIPHOSPHITES*

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Continuing our investigations in the field of cyclic esters of acids of elements of Group V ([1–3]), we studied several bicyclic diphosphites based on pentaerythritol. In doing so we were able to establish that the transesterification reaction of trialkyl phosphites with pentaerythritol, depending on the manner in which it is carried out, can lead to products of different structure. Thus, on simultaneous heating of two moles of triethyl phosphite with one mole of pentaerythritol, a product possessing a spiro structure is obtained, 3,9-diethoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane—white needles with m.p. 80-82°:

$$2P(OC_2H_5)_3+C(CH_2OH)_4 \rightarrow 4C_2H_5OH+C_2H_5O—P\begin{matrix}OCH_2\\ \\ OCH_2\end{matrix}C\begin{matrix}CH_2O\\ \\ CH_2O\end{matrix}P—OC_2H_5$$

I

However, carrying out this reaction in stages leads to the formation of a bicyclic diphosphite possessing a bridged structure:

$$P(OC_2H_5)_3 + C(CH_2OH)_4 \rightarrow P(OCH_2)_3C—CH_2OH + 3C_2H_5OH$$

$$P—OCH_2\begin{matrix}OCH_2\\ —\end{matrix}C—CH_2OH + P(OC_2H_5)_3 \rightarrow C_2H_5OH + P—OCH_2\begin{matrix}OCH_2\\ —\end{matrix}C—CH_2O—P\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix}$$

II

Unlike its isomer, mono-(1-oxymethyl-3,5,8-trioxa-4-phosphabicyclo-[2,2,2]-octane)-diethyl phosphite (II) is a colorless liquid with b.p. 113-115° (0.5 mm), n_D^{20} 1.4822, $d_4^{20} = 1.2469$, MR_D found 65.01; calculated –65.50

Found %: P 21.78; 22.01

$C_9H_{18}O_6P_2$. Calculated %: P 21.80

Yield 48% of theoretical.

From the point of view of conformational considerations, the spiro structure (in the favorable case, two "chairs" with equatorial substituents) should, in all probability, be energetically more advantageous and correspond to an energy minimum in comparison with the bridged structure (in any case, two adjacent "boats"). Therefore at first there seemed to us possible a thermal isomerization of the spiro diphosphite (I) into the bridged (II), which purely externally could be regarded as an intramolecular disproportionation. In connection with this, we devoted particular attention to the synthesis and study of the properties of spiro diphosphites based on pentaerythritol, especially since by the beginning of the work only two compounds of this kind had been described in the literature. Diethyl pentaerythritol diphosphite (I) was obt—

* After this work had been prepared for publication, we became aware of the patent of Friedman and Gould ([8]), in which the authors propose using certain 3,9-dialkoxy- and 3,9-diaryloxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecanes for obtaining flame-resistant polymers, stabilizers, and plasticizers.

obtained in 79% yield by the reaction of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane with ethanol in the presence of N-ethylmorpholine ([4]). For the synthesis of diphenylpentaerythrityl diphosphite (m.p. 123°), proposed as a stabilizer for polyvinyl chloride and as an antioxidant for lubricating oils and rubbers, the transesterification reaction of triphenyl phosphite with pentaerythritol in the presence of sodium phenolate as catalyst was used ([5]). In our work spirodiphosphites were obtained by two methods:

A —by the simultaneous transesterification reaction of two moles of trialkyl phosphite with one mole of pentaerythritol, both in the presence of metallic sodium (catalyst) and without it:

$$2(RO)_3P + C(CH_2OH)_4 \rightarrow RO—P(OCH_2)_2C(CH_2O)_2P—OR + 4ROH$$

B —by the reaction of two moles of alkyl dichlorophosphite with one mole of pentaerythritol in ethereal solution in the presence of pyridine:

$$2ROPCl_2 + C(CH_2OH)_4 \xrightarrow{C_5H_5N} RO—P(OCH_2)_2C(CH_2O)_2P—OR + 4HCl.$$

Table 1

3,9-Dialkoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecanes

$$RO—P(OCH_2)_2C(CH_2O)_2P—OR$$

R	M.p., °C	B.p., mm	Method	Yield, %	Empirical formula	P, % found	P, % calculated
CH_3	124–127	–	B	48.1	$C_7H_{14}O_6P_2$	24.52; 24.19	24.19
C_2H_5*	80–82	121–124^(1)	A	38.7	$C_9H_{18}O_6P_2$	21.60; 21.65	21.80
n-C_3H_7	71–73	–	A	19.7	$C_{11}H_{22}O_6P_2$	19.82; 19.91	19.84
n-C_3H_7	70–72	135–137^(0.5)	B	30.0	$C_{11}H_{22}O_6P_2$	19.87; 19.90	19.84
iso-C_3H_7	51–53	128–130^(0.5)	A	25.0	$C_{11}H_{22}O_6P_2$	19.90; 19.54	19.84
n-C_4H_9	25–27	139–140^(0.5)	B	15.1	$C_{13}H_{26}O_6P_2$	18.55; 18.50	18.20

* First obtained by Lucas and co-workers ([4]), m.p. 80–82°.

The spirodiphosphites synthesized by us (see Table 1) are white crystalline substances with a characteristic odor; they are very hygroscopic and melt rapidly in air. They are readily soluble in pyridine, ether, alcohol, and water. They are vigorously oxidized by concentrated nitric acid and add sulfur. Dimethyl-, diethyl-, and dipropylpentaerythrityl diphosphites distil well in vacuum at 0.5–1.0 mm. Upon heating for 1.5 hours at 80–90° a mixture of dimethylpentaerythrityl diphosphite with methyl iodide, an Arbuzov isomerization occurs with the formation of 3,9-dimethyl-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane, which after distillation in vacuum is a white crystalline substance with m.p. 239–241°.

Found, %: P 24.35; 24.43

$C_7H_{14}O_6P_2$. Calculated, %: P 24.19

Yield 84.0% of theoretical.

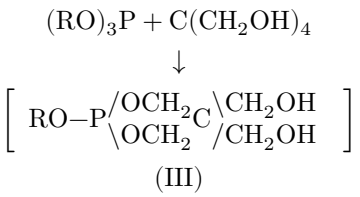
dimethylpentaerythrityl diphosphite $\xrightarrow{CH_3J}$ 3,9-dimethyl-3,9-dioxo-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-

On careful study of the infrared absorption spectra of spiranic diphosphites after melting, distillation, and heating of the latter at 130°, we were unable to detect absorption bands characteristic of bridged

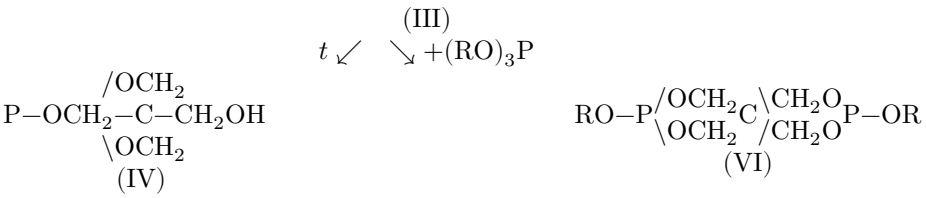
structures. The data obtained indicate the absence, under these conditions, of thermal isomerization of the spirane structure into the bridged one. It is difficult to expect that a further increase in temperature will facilitate this process; most likely, at high temperatures thermal polymerization of spirane

diphosphites will occur, analogously to the known thermal polymerization of cyclic esters of phosphorus acids ([6]). This supposition is consistent with the fact that already during distillation of the obtained spirodiphosphites in vacuo, as a result of their certain overheating, a large amount of nondistilling residue is formed in the form of a yellow brittle resin, slowly soluble in cold water.

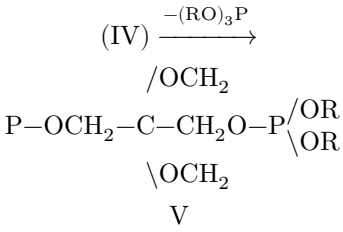
Proceeding from the configuration of the molecule of crystalline pentaerythritol ([7]) and on the basis of the experimental material obtained, it may be assumed that the transesterification reaction of trialkyl phosphite with pentaerythritol proceeds through the intermediate formation of an unstable monocyclic phosphite (III). Further stabilization of the latter occurs either upon heating (distillation) with formation of the thermostable bridged structure of pentaerythrityl phosphite (VI), which is the basis of bicyclic



(III)



(IV) (VI)



V

bridged diphosphite V, or upon interaction with a second molecule of trialkyl phosphite with formation of the energetically more favorable spirane structure VI. Both isomeric structures (V) and (VI) exist quite realistically and, in all probability, independently of one another.

Such a conception of the formation of these structures is consistent with the data obtained by us in the study of pentaerythritol esters of sulfurous acid ([2]).

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