ESTERS OF "GLYCOLPHOSPHOROUS ACIDS"

COMMUNICATION I. COMPOUNDS HAVING FIVE-, SEVEN, AND EIGHT-MEMBERED RINGS

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The cyclic esters of phosphorous acid have received practically no study until recently. In the literature there are to be found only the reports by Carré [1] of his preparation in 1902 of the acid chloride of "ethylene-glycolphosphorous acid" \(\text{CH}_2\text{O} - \text{P} - \text{Cl}\) (ethylene phosphorochloridite) by the action of phosphorus trichloride on ethylene glycol and of the "ethylene-glycolphosphorous acid" itself (ethylene hydrogen phosphite) \(\text{CH}_2\text{O} - \text{P} - \text{OH}\), the barium salt of which was analyzed. Neither compound was isolated in a chemically pure form.

More detailed investigations into cyclic derivatives of phosphorous acid were commenced in our laboratory in 1945 [2]. In the present communication we give the results that we have obtained in a study of compounds containing five-, seven-, and eight-membered rings. By the action of phosphorus trichloride on ethylene glycol, 1,4-butanediol, and diethylene glycol in presence of substances that bind hydrogen chloride, we have synthesized the following phosphorochloridites (Table 1).

Ethylene phosphorochloridite (Compound 1) is a colorless liquid that fumes in air; it is similar in properties to diethyl phosphorochloridite. The phosphorochloridites derived from glycols in which the OH groups are separated by a chain of four or of five atoms (Compounds 2 and 3) contain seven- and eight-membered rings. They are very unstable; they fume strongly in air and, in a thin layer, ignite spontaneously and burn with a blue flame. In the pure state they are colorless liquids, but they rapidly polymerize, even in closed vessels, giving a colorless gelatin-like mass, which later becomes yellow with separation of red phosphorus.

By the action of alcohols in presence of pyridine or of dimethylaniline on cyclic phosphorochloridites, mixed cyclic esters are formed:

\[
\text{CH}_2\text{O} - \text{P} - \text{Cl} + \text{HOR} \xrightarrow{\text{(Dimethylaniline or pyridine)}} \text{CH}_2\text{O} - \text{P} - \text{OR} + \text{HCl}.
\]

Cyclic esters of phosphorous acid may be obtained also by the action of glycols on Menshutkin's acid chloride in presence of the same acid-binding media:

\[
\text{CH}_2\text{OH} + \text{Cl}_4\text{POR} \xrightarrow{\text{(Dimethylaniline or pyridine)}} \text{CH}_2\text{O} - \text{P} - \text{OR} + \text{HCl}.
\]

Esters having a seven-membered ring were obtained by the latter method. We did not succeed in obtaining a mixed ester having an eight-membered ring. Six esters, obtained by one or other of the above methods, are listed in Table 2.
The physical and chemical properties of the esters obtained depend to a considerable extent on molecular size and structure: the compounds of low molecular weight are in many ways similar to trimethyl phosphate. The mixed cyclic esters of phosphorous acid are extremely reactive compounds. They react vigorously with cuprous halides, giving complex compounds. The CuI complexes of ethylene methyl phosphite and of ethyl ethylene phosphite were obtained in a crystalline form (Compound 1, m.p. 132-133°C; Compound 2, m.p. about 90°C). The cyclic esters react with sulfur with formation of thio esters. They react with water with evolution of much heat, and on coming into contact with concentrated nitric acid they burst into flame. One of the most interesting properties of cyclic phosphorous esters is their ability to react with many substances with opening of the ring. The reaction may be represented as follows:

\[
\begin{align*}
\text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{Br} & \rightarrow \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5 \quad \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5 \\
\end{align*}
\]

and is a special case of the Arbuzov rearrangement.

By the action of CH₃I on \( \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5 \) there was obtained ethyl 2-idoethyl methylphosphonate: b.p. 138-139°C/10 mm; \( n^\circ_D \) 1.6783; found MRD 48.54; calculated MRD 48.45. On hydrolysis with 10% hydrochloric acid it yielded methylphosphonic acid. The product of the reaction of CH₃I with ethylene methyl phosphate decomposed when distilled.

The action of C₂H₅Br on \( \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5 \) yielded 2-bromoethyl ethyl ethylphosphonate, b.p. 129-139°C/11 mm (dec.); \( n^\circ_D \) 1.3726; found MRD 48.98; calculated MRD 48.17.

The reactions of the mixed ethylene-methyl, ethyl-ethylene, and butyl-ethylene esters of phosphorous acid with bromotriphenylmethane led also to rupture of the five-membered ring. The following reaction products were obtained:

\[
\begin{align*}
\text{CH}_2\text{Br} \cdot \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5, \text{b.p.} \ 153-155°C; \ 
\text{CH}_2\text{Br} \cdot \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5, \text{b.p.} \ 99-101°C; \ 
\text{CH}_2\text{Br} \cdot \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5, \text{b.p.} \ 108-110°C. \\
\end{align*}
\]

In the cases that we examined of reactions between the cyclic esters and halogen compounds, the yields were generally low, and they were never quantitative. It cannot therefore be asserted that the reaction proceeds exclusively in one direction, i.e., with rupture of the ring. The mixed ethylene-methyl and ethyl-ethylene esters of phosphorous acid were found to react energetically with acetyl chloride, but we did not succeed in isolating individual compounds owing to decomposition of the reaction products when vacuum-distilled. The analytical figures for chlorine in the fractions separated differed from the calculated values by 2-3%.

By treatment with water, ethyl ethylene phosphate yielded a product corresponding in analysis to

\[
\begin{align*}
\text{CH}_2\text{OH} \cdot \text{CH}_2\text{O} \cdot \text{POC}_2\text{H}_5, \text{b.p.} \ 142-143°C/11 \text{ mm}; \ n^\circ_D \ 1.4825. \text{ It was a very viscous, colorless liquid.}
\end{align*}
\]