SYNTHESIS OF SOME DERIVATIVES OF BIS-2-CHLOROETHYL 2,2,2-TRICHLORO-1-HYDROXYETHYLPHOSPHONATE

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In previous investigations we have carried out reactions between dialkyl 2,2,2-trichloro-1-hydroxyethylphosphonates and lower alkanoyl chlorides, ethyl chloroformate, and dialkyl phosphorochloridates with formation of the corresponding dialkyl 1-(acyloxy)-2,2,2-trichloroethylphosphonates [1-3]. Tests showed that some of these compounds have an appreciable fungicidal activity, while others have high toxicity to various insects coupled with low toxicity to warm-blooded animals [4].

In continuation of these investigations we have synthesized bis-2-chloroethyl 2,2,2-trichloro-1-hydroxyethylphosphonate and brought it into reaction with lower carboxylic acid chlorides and with acetic anhydride. The starting substance — bis-2-chloroethyl 2,2,2-trichloro-1-hydroxyethylphosphonate (I) — was prepared by reaction between chloral and bis-2-chloroethyl hydrogen phosphite [5]. Preparatively the reaction is simple: chloral is added to bis-2-chloroethyl hydrogen phosphite, and the mixture is then stirred at 70-80°C for 2-3 h. Recrystallization gives pure bis-2-chloroethyl 2,2,2-trichloro-1-hydroxyethylphosphonate (I). The synthesis of derivatives of bis-2-chloroethyl 2,2,2-trichloro-1-hydroxyethylphosphonate was conducted in accordance with the equation

\[
\text{CICH}_2\text{CH}_2\text{O})_2\text{P}--\text{CHOH} + \text{ClCOR} + (\text{C}_2\text{H}_4\text{H}_2\text{N})\rightarrow (\text{CICH}_2\text{CH}_2\text{O})_2\text{PCHOCOR} + (\text{C}_2\text{H}_4\text{H}_2\text{N} \cdot \text{HCl})
\]

\[\text{R} = \text{C}_2\text{H}_5, \quad \text{C}_3\text{H}_7-n, \quad \text{C}_3\text{H}_7-i, \quad \text{OC}_2\text{H}_5, \quad \text{CH}_2\text{Cl}, \quad \text{CHCl}_2, \quad \text{CCl}_3.\]

By this reaction we obtained satisfactory yields of alkanoyl, chloraecetyl, and ethoxycarbonyl derivatives of bis-2-chloroethyl 2,2,2-trichloro-1-hydroxyethylphosphonate. Bis-2-chloroethyl 1-(acyloxy)-2,2,2-trichloroethylphosphonate was prepared by the reaction of bis-2-chloroethyl 2,2,2-trichloro-1-hydroxyethylphosphonate with acetic anhydride by the method proposed in [1]. The yields of the products, their main physical constants, and their analyses are given in Table 1.

EXPERIMENTAL

Synthesis of Bis-2-chloroethyl 2,2,2-Trichloro-1-hydroxyethylphosphonate (I). 32 g of chloral was added with stirring in the course of 10 min to 44.7 g of bis-2-chloroethyl hydrogen phosphite in a four-necked round-bottomed flask. Reaction was slightly exothermic (the temperature rose from 20 to 60°C). To complete the reaction the flask was heated at 80°C for 2 h. The thick, but quite clear colorless liquid was then poured into a beaker, in which it crystallized out completely as a snow-white mass (72 g). By recrystallization from a mixture of benzene and cyclohexane we isolated 61.2 g (79.3%) of product, m.p. 88-89°C.

Synthesis of Bis-2-chloroethyl 1-Acetoxy-2,2,2-trichloroethylphosphonate (II). 20 g of (I) was introduced into a round-bottomed flask fitted with stirrer, and 11.5 g of acetic anhydride containing three drops of concentrated sulfuric acid was added in one portion. Reaction was slightly exothermic (the temperature rose from 20 to 28°C). After 10-15 min the crystalline (I) had gone into solution. The mixture was left for 12 h at room temperature, and the acetic acid formed in the reaction and the excess of acetic anhydride were distilled off at the water pump. The residue was a clear thick colorless liquid. We obtained 17 g (75.5%) of (II), b.p. 158-159°C (0.012 mm).

Synthesis of the Bis-2-chloroethyl 1-(Acyloxy)-2,2,2-trichloroethylphosphonates (III)-(IX). The esters were prepared by reaction between (I) and the corresponding carboxylic

<table>
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<th>No.</th>
<th>Compound</th>
<th>Yield, %</th>
<th>B.p., °C (p. mm)</th>
<th>M.p., °C</th>
<th>$n_D^2$</th>
<th>$d_2^0$</th>
<th>$MR$</th>
<th>Found, %</th>
<th>Calculated, %</th>
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<td>(CICH$_2$CH$_2$O)$_2$P—CH$_2$OH</td>
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<td>(CICH$_2$CH$_2$O)$_2$P—CHOOCOCH$_3$</td>
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