It was interesting to synthesize and to study the properties of esters of acids of phosphorus containing a hetero-atom in the $\beta$-position of the alkyl group, in connection with the studies of tautomerism of organophosphorus compounds. For the first object of this type, we selected the di-(8-ethylmercaptoethyl) hydrogen phosphite (II). We failed to isolate this substance under the conditions of the usual synthesis of dialkyl hydrogen phosphites [1]:

$$\text{PCl}_3 + 3\text{ROH} \rightarrow \text{HPO(OR)}_2 + \text{RCI} + 2\text{HCl}$$

the sole isolated product was $\beta$-chlorodiethyl sulfide. Later we proposed to prepare di-(8-ethylmercaptoethyl) hydrogen phosphite by cleavage of one alkoxy group from tri-(8-ethylmercaptoethyl) phosphite (I). The latter was synthesized by the action of phosphorus trichloride on $\beta$-hydroxydiethyl sulfide in the presence of a tertiary base [2]:

$$3\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{OH} + \text{PCl}_3 + 3\beta \rightarrow 3\beta \cdot \text{HCl} + (\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{O})_2\text{P},$$

where $\beta$ - dimethylaniline, triethylamine or pyridine. However, the cleavage of the neutral ester (I) with a calculated amount of acid led only to a difficulty separable mixture of substances.

We accomplished the synthesis of di-(8-ethylmercaptoethyl) hydrogen phosphite by modification [3] of the above-cited reaction, according to the following equation:

$$\text{PCl}_3 + 3\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{OH} + 2\text{C}_2\text{H}_4\text{N} (\text{CH}_3)_2 \rightarrow 2\text{C}_2\text{H}_4\text{N} (\text{CH}_3)_2 \cdot \text{HCl} +$$
$$+ \text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{Cl} + (\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{O})_2\text{POH}$$

Here, a mixture of 2 moles of dimethylaniline and 2 moles of $\beta$-hydroxydiethyl sulfide was added with cooling to a solution of phosphorus trichloride in benzene, after which the remaining $\beta$-hydroxydiethyl sulfide was added. Similar results were obtained also from another variant of the synthesis [4] by the following scheme:

$$\text{PCl}_3 + 2\text{C}_2\text{H}_4\text{SC}_2\text{H}_4\text{OH} + 2\text{C}_2\text{H}_4\text{N} (\text{CH}_3)_2 \rightarrow (\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{O})_2\text{PCl} +$$
$$+ 2\text{C}_2\text{H}_4\text{N} (\text{CH}_3)_2 \cdot \text{HCl} \rightarrow (\text{C}_2\text{H}_5\text{SC}_2\text{H}_4\text{O})_2\text{POH} + \text{HCl}.$$
2HPO (OC₂H₄SC₂H₅)₂ → P (OC₂H₄SC₂H₅)₃ + HPO (OH) (OC₂H₄SC₂H₅)

(the corresponding trialkyl phosphite was isolated).

Ethyl β-ethylmercaptoethyl hydrogen phosphite was prepared similarly to di-(β-ethylmercaptoethyl) hydrogen phosphite:

\[
\text{C}_6\text{H}_5\text{OPCl}_2 + \text{C}_6\text{H}_5\text{SC}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{N} (\text{CH}_3)_2 \rightarrow \text{C}_6\text{H}_5\text{SC}_6\text{H}_5\text{O} \quad \text{(III)}
\]

\[
\text{H}_2\text{O} \quad \text{H}
\]

\[
\rightarrow \text{C}_6\text{H}_5\text{N} (\text{CH}_3)_2 \cdot \text{HCl} + \text{HCl} + \text{P}
\]

Some properties of the resulting β-ethylmercaptoethyl phosphites were studied. Thus, like the usual dialkyl hydrogen phosphites [5], these substances form sodium derivatives. The sodium salt of di-(β-ethylmercaptoethyl) hydrogen phosphite readily adds sulfur [6]:

\[
\text{NaO} \quad \text{P}
\]

\[
\rightarrow \text{OC}_2\text{H}_4\text{SC}_2\text{H}_5 + \text{S} \rightarrow \text{Na}^+ \quad \text{NaO} \quad \text{P}
\]

\[
\rightarrow \text{P} + \text{S} \rightarrow \text{P}
\]

\[
\rightarrow \text{OC}_2\text{H}_4\text{SC}_2\text{H}_5 \quad \text{S} \quad \text{OC}_2\text{H}_4\text{SC}_2\text{H}_5
\]

forming the well crystallizable di-(β-ethylmercaptoethyl) sodium thiophosphate.

Sodium di-(β-ethylmercaptoethyl) phosphite also readily reacts in the Michaelis-Becker reaction [7]:

\[
\text{OC}_2\text{H}_4\text{SC}_2\text{H}_5
\]

\[
\text{NaO} \quad \text{P}
\]

\[
\rightarrow \text{OC}_2\text{H}_4\text{SC}_2\text{H}_5 + \text{CH}_3\text{I} \rightarrow \text{Na}^+ \quad \text{NaO} \quad \text{P}
\]

\[
\rightarrow \text{OC}_2\text{H}_4\text{SC}_2\text{H}_5 \quad \text{CH}_3\text{PO} (\text{OC}_2\text{H}_4\text{SC}_2\text{H}_5)_2
\]

forming di-(β-ethylmercaptoethyl) methylphosphonate (V). The latter was also synthesized by the Arbuzov reaction from tri-(β-ethylmercaptoethyl) phosphite and methyl iodide:

\[
P (\text{OC}_2\text{H}_4\text{SC}_2\text{H}_5)_3 + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{PO} (\text{OC}_2\text{H}_4\text{SC}_2\text{H}_5)_2 + \text{IC}_2\text{H}_5\text{SC}_2\text{H}_5.
\]

In addition, it was also prepared by the action of β-hydroxydiethyl sulfide on methylphosphonic dichloride in the presence of dimethylaniline:

\[
\text{CH}_3\text{POCl}_2 + 2\text{HOCH}_2\text{H}_2\text{SC}_2\text{H}_5 + 2\text{C}_6\text{H}_5\text{N} (\text{CH}_3)_2 \rightarrow \text{(VI)}
\]

\[
\rightarrow \text{CH}_3\text{PO} (\text{OC}_2\text{H}_4\text{SC}_2\text{H}_5)_2 + 2\text{C}_6\text{H}_5\text{N} (\text{CH}_3)_2 \cdot \text{HCl}.
\]

The constants of di-(β-ethylmercaptoethyl) methylphosphonate, prepared by three different methods, are given in the table.

It is possible to prepare similarly di-(β-ethylmercaptoethyl) methylthiophosphonate, (VI)* by starting with methylthiophosphonic dichloride. The di-(β-ethylmercaptoethyl) methylphosphonate readily adds two molecules of methyl iodide or dimethyl sulfate, forming the methiodide (VII) or the methyl methosulfate (VIII) which are readily soluble in water and insoluble in organic solvents.

*Eq. is not given in original (Ed.).