ESTERS OF TRIVALENT PHOSPHORUS THIOACIDS

COMMUNICATION 12. ESTERS OF ETHYL(PHENYL)-\(\beta\)-CYANOALKYLTHIOL-
PHOSPHINIC AND ETHYL(PHENYL)-\(\gamma\)-KETOALKYLTHIOLPHOSPHINIC ACIDS

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Previously it was shown that the acid chloride-esters of thiophosphonous acids react with \(\alpha,\beta\)-unsaturated acids to give the acid chlorides of \(\beta\)-(alkylthioalkylphosphinoxido)propionic acids [1], and with \(\alpha,\beta\)-unsaturated ketones to give 2-thiono-1,2-oxa-4-phospholene derivatives [2]. In the present paper is discussed the reaction of the acid chloride-esters of thiophosphonous acids with \(\alpha,\beta\)-unsaturated ketones, and the nitriles of acrylic and methacrylic acids, in the presence of the acetic and thioacetic acids and water. The reaction of the acid chloride-esters of thiophosphonous acids with \(\alpha,\beta\)-unsaturated nitriles in the presence of CH\(_3\)COOH or water leads to the formation of the esters of alkyl(aryl)-\(\beta\)-cyanoalkylthiol-
phosphinic acids.

The following frequencies (\(\nu\), cm\(^{-1}\)) are observed in the IR spectra of the obtained compounds: 1190-
1200 (P =O) [3]; 2240-2250 (C=\(\equiv\)N) [4]. The absorption in the 500-600 cm\(^{-1}\) region can be associated with the
P-S-C group [5].

The structure proposed by us for the synthesized compounds is also in agreement with the data of the
\(\text{\textsuperscript{31}}\text{P}\) NMR spectra: a signal in the vicinity of \(-60\) ppm (relative to 85\% H\(_3\)PO\(_4\)), which is characteristic for
compounds containing a phosphoryl group [6]. In addition, the structure of the obtained compounds was
confirmed by counter synthesis from the acid chloride of ethyl-\(\beta\)-cyanoethylphosphinic acid [7].

Besides CH\(_3\)COOH and water, we also used CH\(_3\)COSH as the proton donor in the reaction of the acid
chloride-esters of ethylthiophosphonic acid with acrylonitrile.

On the basis of the data obtained when the reaction of the acid chloride-esters of thiophosphonous
acids with the nitriles of \(\alpha,\beta\)-unsaturated acids was studied in the presence of CH\(_3\)COOH, the theory arose that reaction in the presence of CH\(_3\)COH should lead to obtaining the esters of alkyl-\(\beta\)-cyanoalkylthio-
phosphinic acids, which was corroborated experimentally.

The formation of the esters of alkyl(aryl)-\(\beta\)-cyanoalkyl- or dithiophosphinic acids when the acid
chloride-esters of thiophosphonous acids are reacted with the nitriles of \(\alpha,\beta\)-unsaturated acids in the presence of either CH\(_3\)COOH or CH\(_3\)COSH can be depicted by the scheme that was proposed for the reaction of chlorophosphines with the esters [8] and amides [9] of \(\alpha,\beta\)-unsaturated acids:

\[
\begin{align*}
\text{SR}^1 & \quad \text{R}^3 \\
\text{P} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2=\text{C} & \quad \text{CN} + \text{CH}_3\text{COX} \rightarrow \\
\text{R}^1 & \quad \text{SR}^1
\end{align*}
\]

\[
\begin{align*}
\text{P} & \quad \text{H} \quad \text{COCH}_3 \\
\text{Cl} & \quad \text{R}^1
\end{align*}
\]

(A)

\[
\begin{align*}
\text{R}^1 & \quad \text{SR}^1 \\
\text{P} & \quad \text{CH}_2 \quad \text{CH} \quad \text{CN}
\end{align*}
\]

(B)

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Original article submitted October 25, 1971.

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The ambident ion (A), formed in the first step of the reaction, reacts with either CH₃COOH or CH₃COSH and changes to the intermediate adduct (B), which undergoes the second step of the Arbuzov rearrangement with the cleavage of CH₃COCl and the formation of the esters of alkyl(aryl)-β-cyanoalkylthiol- or dithiophosphinic acids.

Besides the nitriles of α,β-unsaturated acids, we also studied the α,β-unsaturated ketones as the unsaturated compounds in the reaction with the acid chloride-esters of thiophosphonous acids. The reaction of the acid chloride-esters of thiophosphonous acids with α,β-unsaturated ketones in the presence of either CH₃COOH or water gave compounds, the elemental composition of which corresponded to the esters of ethyl(phenyl)-γ-ketoalkylthiophosphinic acids. Intense absorption at 1710-1730 cm⁻¹ (C=O [4]) is observed in the IR spectra of the obtained compounds, and also intense absorption in the 1190-1200 cm⁻¹ region (P=O in the given environment) [3], and in the 500-600 cm⁻¹ region (P-S-C) [5]. The reaction of the acid chloride-esters of thiophosphonous acids with α,β-unsaturated ketones can be depicted by a scheme that is analogous to that given above for the reactions of the same acid chloride-esters with the nitriles of α,β-unsaturated acids.

As regards the reaction of the acid chloride-esters of thiophosphonous acids with α,β-unsaturated ketones and with acrylonitrile in the presence of water, we postulate that hydrolysis of the acid chloride to the corresponding acid occurs in the first step of the reaction. The formed acid adds to either the α,β-unsaturated ketone or the nitrile, respectively, giving the esters of ethyl(phenyl)-γ-ketoalkylthiophosphinic acids or the esters of alkyl-β-cyanoalkylthiophosphinic acids:

\[
\begin{align*}
\text{SR}^1 + \text{R}^2 & \rightarrow \text{SR}^1 \text{R}^2 \\
\text{Cl} + \text{R}^3 + \text{O} & \rightarrow \text{R}^3 \text{R}^4 + \text{O} \\
\text{R}^5 & \rightarrow \text{R}^6 \\
\text{O} & \rightarrow \text{O}
\end{align*}
\]

**EXPERIMENTAL**

Ethyl Ester of Ethyl-β-cyanoethylethylthiophosphinic Acid (I). a) To 11 g of the acid chloride of ethylthioethylphosphonic acid in a CO₂ atmosphere, with stirring, a mixture of 3.72 g of acrylonitrile and 4.2 g of CH₃COOH was added in drops. The next day 3.1 g (56% of theory) of CH₃COCl was distilled off. A double distillation of the residue in vacuo gave 5.8 g (43%) of (I), bp 115-116° (0.3 mm); nD₂₀ 1.5200; δH₂₀ 1.1225. Found: P 13.30; S 16.90%; M 51.28. Calculated: P 16.23; S 16.75%; M 51.28.

b) To a solution of 23.3 g of the acid chloride of ethyl-β-cyanoethylphosphinic acid in 150 ml of absolute benzene was added in drops, with stirring, at -10 to -4°, a mixture of 8.7 g of ethyl mercaptan and 14.4 g of triethylamine. The mixture was stirred at 20° for 1 h, filtered, and the benzene was evaporated in vacuo. After the crude product was distilled twice in vacuo we obtained 21 g (75%) of (I), bp 119-120°