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Abstract

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On the Rearrangement of α-Oxyphosphinic and α-Oxythiophosphinic Esters into Phosphinates and Thiophosphates

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Previously we showed that the α-oxyethyldiphosphinates formed as a result of the reaction of dialkylphosphorous acids with vinyl acetate undergo, under the reaction conditions in the presence of alkaline agents, a "phosphonate-phosphate" rearrangement with formation of dialkyl α-(dialkylphosphon)ethyl phosphates (^{1,2}). An analogous rearrangement is undergone by the dialkyl esters of α-cyano-(^{3}), α-carbethoxy-(^{4}), α-aceto-(^{5}) or α-phenyl-(^{6}), α-oxyalkylphosphinic acids. All these derivatives of α-oxyphosphinic esters are products of the addition of dialkylphosphorous acids to the corresponding carbonyl compounds. As is known, oxyphosphinic esters formed upon addition of dialkylphosphorous acids to the simplest aldehydes and ketones are, in most cases, highly unstable compounds, decomposing on heating, especially in the presence of alkaline catalysts, into the initial products (^{7}). In general form these reactions may be represented by the following scheme:

$$\mathrm{R{-}C(OH)(X){-}P(=O)(OR')_2} \xrightarrow{\mathrm{AlkO^-}} \mathrm{R{-}C(O^-)(X){-}P(=O)(OR')_2} \underset{\mathrm{B}}{\overset{\mathrm{A}}{\rightrightarrows}}$$

$$\mathrm{A:}\quad \mathrm{R{-}C(X){-}O{-}P(=O)(OR')_2} \xrightarrow{\mathrm{AlkOH}} \mathrm{RCH(X){-}OP(=O)(OR')_2}$$

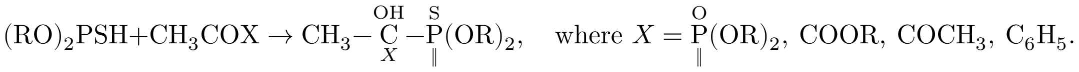
$$\mathrm{B:}\quad \mathrm{R{-}C(X){-}P(=O)(OR')_2} \xrightarrow{\mathrm{AlkOH}} \mathrm{RCOX + (R'O)_2P(=O)H}$$

where $\mathrm{R = alkyl,\ X = CN, COOR, P(=O)(OR')_2, COCH_3, alkyl, aryl;}$
$\mathrm{R' = alkyl.}$

Our study of the kinetics of the "phosphonate-phosphate" rearrangement of the tetraethyl ester of α-oxyethyldiphosphinic acid (scheme A) showed that its rate does not depend on the presence in the reaction mixture of peroxide compounds or inhibitors and increases considerably with an increase in the concentration of sodium ethoxide or diethylamine. Reactions of decomposition of α-oxyphosphinic esters (scheme B) also proceed readily in the presence of alkaline catalysts (^{8}). These observations confirm the ionic mechanism of the reactions proceeding according to schemes A and B under conditions of alkaline catalysis. The course of reactions according to A or B depends on the structure of the radicals surrounding the carbonyl carbon, and first of all on the nature of the substituent group X. When electronegative groups are present as X, the latter draw the electrons binding the carbon and phosphorus atoms toward the carbon atom, thereby creating favorable conditions for the reaction to proceed according to scheme A. We have recently shown that also in the case of a phenyl group, which possesses weak electron-withdrawing properties, the reaction likewise proceeds according to scheme A. When alkyl groups, which displace the electrons of the carbon-phosphorus bond toward the phosphorus atom, are present as X, the reactions proceed according to scheme B. Our attempts, by changing the conditions for carrying out the reactions (heating α-oxyphosphinic esters in sealed tubes at different temperatures and in the presence of different quan-

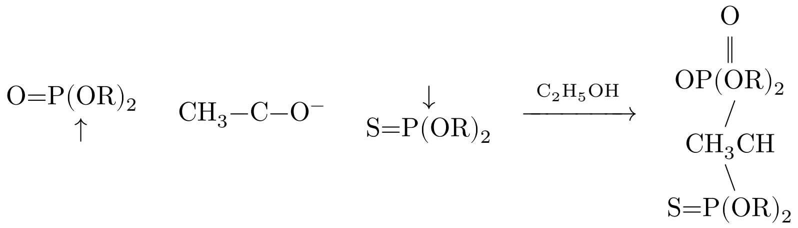
···the presence of catalysts) to direct these reactions, at least partially, according to scheme A did not lead to positive results.

It seemed highly interesting to trace the influence of the structure of the phosphorus-containing group on the course of the reactions under consideration. For this purpose we studied the behavior, under conditions of alkaline catalysis, of derivatives of esters of α-hydroxyethylthiophosphinic acids. It might have been expected that replacement of the phosphinic group by a thiophosphinic group, which—owing to the lower electronegativity of sulfur as compared with oxygen—has a smaller inductive effect, could weaken the tendency for the reactions to proceed according to scheme A. We carried out reactions of acetophosphinic and pyruvic esters, diacetyl, and acetophenone with diethyl thiophosphorous acid in the presence of sodium ethoxide. All the reactions are accompanied by an exothermic effect. Under mild conditions, in the absence of catalysts or in the presence of diethylamine, at a temperature not exceeding 80-100°, the corresponding derivatives of α-hydroxythiophosphinic esters were obtained

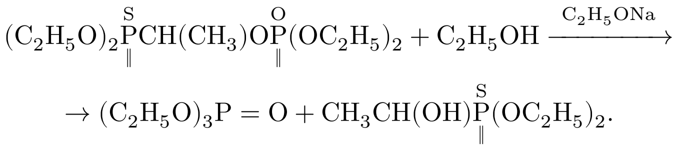


$$(RO)_2PSH+CH_3COX \rightarrow CH_3-\underset{X}{\overset{OH}{C}}-\underset{\|}{\overset{S}{P}}(OR)_2, \quad \text{where } X=\underset{\|}{\overset{O}{P}}(OR)_2,\ COOR,\ COCH_3,\ C_6H_5.$$

In a number of cases they can be distilled in a high vacuum without decomposition. In their IR spectra an absorption band characteristic of the hydroxyl group was found (3400-3550 cm^{-1}). On heating in the presence of sodium ethoxide they behave differently. Dialkyl esters of α-carbethoxy-, α-diethylphosphon-, and α-acetyl-α-hydroxyethylthiophosphinic acids are completely rearranged into the corresponding phosphates or thiophosphates, whereas dialkyl esters of α-hydroxy-α-phenylethylthiophosphinic acid decompose on heating into acetophenone and dialkyl thiophosphorous acid. Evidently, in the latter case the presence of the phenyl group is already insufficient to create a sufficient positive charge on the phosphorus atom; as a result (in contrast to the analogous reactions of α-hydroxy-α-phenylethylphosphinic esters), the reactions proceed not according to scheme A, but according to scheme B. In studying the rearrangement of the diethyl ester of α-hydroxy-α-(diethylphosphon)-ethylthiophosphinic acid it was shown that insertion of oxygen occurs between the carbon and the phosphorus located in the phosphinic, and not in the thiophosphinic, group, which is also consistent with the ideas developed regarding the difference in electronegative properties of phosphinic and thiophosphinic groups.



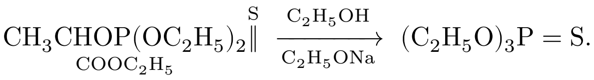
Upon transesterification of the rearrangement product of α-hydroxy-α-(diethylphosphon)-ethylthiophosphinate with ethyl alcohol in the presence of sodium ethoxide, triethyl phosphate was obtained in good yield



$$(C_2H_5O)_2\overset{S}{\underset{\|}{P}}CH(CH_3)O\overset{O}{\underset{\|}{P}}(OC_2H_5)_2 + C_2H_5OH \xrightarrow{C_2H_5ONa}$$
$$\rightarrow (C_2H_5O)_3P = O + CH_3CH(OH)\overset{S}{\underset{\|}{P}}(OC_2H_5)_2.$$

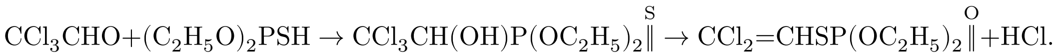
We have also shown that the rearrangements studied are not accompanied by thione-thiol isomerization. In the IR spectra of the rearrangement products of α-hydroxy-α-(carbethoxy)-ethyl- and α-hydroxy-α-(aceto)-ethylthiophosphinates, no absorption characteristic of the P=O group was observed. In the Raman spectra of these compounds, bands at 630 and 660 cm^{-1} were found, indicating

on the presence in them of a P=S group. In the transesterification of diethyl carbethoxyethyl thiophosphate, only triethyl thiophosphate was obtained.



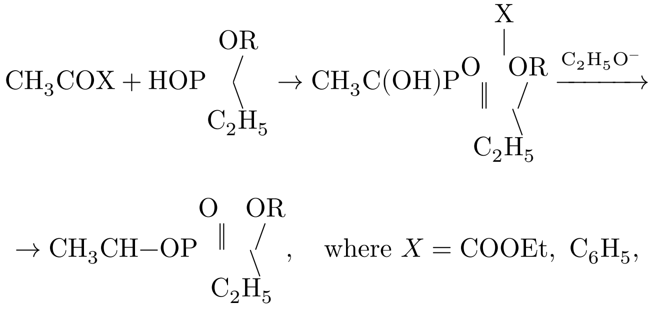
$$\underset{COOC_2H_5}{CH_3CHOP(OC_2H_5)_2}\overset{S}{\|} \xrightarrow[C_2H_5ONa]{C_2H_5OH} (C_2H_5O)_3P = S.$$

In the light of the results we have obtained, Pelkhovich' s assertion (^{9}) about an extremely facile thione-thiol isomerization, proceeding simultaneously with rearrangement and elimination of hydrogen chloride from diethyl-α-hydroxy-α-trichloromethyl thiophosphinate, seems somewhat unexpected:



$$CCl_3CHO+(C_2H_5O)_2PSH \to CCl_3CH(OH)P(OC_2H_5)_2\overset{S}{\|} \to CCl_2{=}CHSP(OC_2H_5)_2\overset{O}{\|}+HCl.$$

The conclusions concerning the structure of the rearrangement product, drawn by him solely on the basis of consideration of the IR absorption spectrum, appear to us not yet sufficiently convincing and require additional confirmation. We also studied the reactions of pyruvic ester and acetophenone with partial esters of alkyl- and phenylphosphinous acids. As a result of the reactions with partial esters of alkylphosphinous acids, the corresponding esters of alkylphosphonic acids were isolated, i.e., the reactions proceed with rearrangement



$$CH_3COX + HOP\left\langle\begin{matrix}OR\\ C_2H_5\end{matrix}\right. \to CH_3C(OH)P\overset{O}{\|}\overset{\overset{X}{|}}{}\left\langle\begin{matrix}OR\\ C_2H_5\end{matrix}\right. \xrightarrow{C_2H_5O^-}$$

$$\to CH_3CH{-}OP\overset{O}{\|}\left\langle\begin{matrix}OR\\ C_2H_5\end{matrix}\right., \quad \text{where } X = COOEt,\ C_6H_5,$$

$$R = C_2H_5,\ n\text{-}C_3H_7,\ iso\text{-}C_3H_7.$$

In the case of the reaction of the ethyl ester of ethylphosphinous acid with acetophenone, an addition product was obtained and characterized—the ethyl ester of ethyl-(α-hydroxy-α-phenyl)-ethylphosphinous acid. The reactions of the acidic ethyl and isopropyl esters of phenylphosphinous acid with acetophenone also proceed in the presence of sodium ethoxide and are accompanied by an exothermic effect; however, on distillation of the reaction mixtures only the starting products are isolated.

Evidently, in this case decomposition occurs of the initially formed hydroxyphosphinous esters into acetophenone and an ester of phenylphosphinous acid. Such a sharp difference in the behavior of esters of alkyl- and phenyl-(α-hydroxy-α-phenyl)-ethylphosphinous acids may be explained by the presence, in the latter, of conjugation of the phenyl group with the P=O group, leading to a decrease in the positive charge on the phosphorus atom. This, as in the case of replacement in the phosphinic group of the O atom bonded to P by an S atom, leads to the fact that the reactions proceed not according to scheme A, but according to scheme B.

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