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Thermal or "Pseudo-Claisen" Rearrangements of Allylic and Propargylic Esters of Phosphorous Acid

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As is known, a necessary condition for the occurrence of the Claisen rearrangement is the presence in the compound of the following groupings of atoms:

$$>C{=}C{-}O{-}C{-}C{=}C<, \quad >N{=}C{-}O{-}C{-}C{=}C<, \quad -N{=}C{-}S{-}C{-}C{=}C<.$$

This condition is satisfied by allylic ethers of enols and phenols, iminoallylic ethers, and allyl rhodanides, which rearrange at elevated temperatures into C-derivatives. A characteristic feature of these rearrangements is the "inversion" of the allyl radical in the course of the rearrangement. Many other types of compounds having formally similar groupings,

$$>C{=}C{-}N{-}C{-}C{=}C<, \quad >C{=}C{-}O{-}C{-}C{\equiv}N, \quad >C{=}C{-}O{-}C{-}C{\equiv}O,$$

are incapable of rearrangement; rearrangement is also absent in the case where the double bond in the allylic part of the system is replaced by a triple bond ([1]). In 1959 we showed ([2]) that, on heating, unsaturated esters of thiophosphorous acid undergo a rearrangement of the Claisen type,

$$S{=}P{-}\underset{\displaystyle OR}{\overset{\displaystyle OR}{O\overset{|}{C}H_2}}CH{=}CH_2 \longrightarrow O{=}P{-}\underset{\displaystyle OR}{\overset{\displaystyle OR}{S\overset{|}{C}H_2}}CH{=}CH_2.$$

In the presence of substituents at the α- and γ-carbon atoms of the allyl group, the rearrangement is accompanied by inversion.

In studying the properties of tetrathylbutynediol diphosphite, we found that even at room temperature it undergoes an exothermic rearrangement, leading to the formation of 2,3-di(diethylphosphono)-butadiene-1,3 ([3])

$$(C_2H_5O)_2POCH_2C{\equiv}CCH_2OP(OC_2H_5)_2 \longrightarrow CH_2{=}C{-}C{=}CH_2$$

$$O{=}P(\overset{|}{O}C_2H_5)_2 \quad O{=}P(\overset{|}{O}C_2H_5)_2.$$

This observation served as the starting point for a systematic study of thermal rearrangements of unsaturated esters of phosphorous acid containing a β,γ-multiple bond in one or several ester radicals ([4]). Allylic and substituted allylic esters of phosphorous acid undergo thermal rearrangement when heated to 175-180°; in the latter case the rearrangement is accompanied by inversion of the radicals, which was established on the basis of a comparison of the properties of these compounds and their IR spectra.

$$(RO)_2POCH_2{-}CH{=}CH{-}CH_3 \longrightarrow (RO)_2P(=O){-}CH(CH_3){-}CH{=}CH_2$$

$$(RO)_2POCH(CH_3){-}CH{=}CH_2 \longrightarrow (RO)_2P(=O){-}CH_2{-}CH{=}CH{-}CH_3.$$

We further showed that dialkyl propargyl esters of phosphorous acid also undergo analogous rearrangements (5). The rearrangement proceeds in two stages: the allenylphosphine esters formed in the first stage, under the reaction conditions, undergo a prototropic transformation with formation of α,β-propynylphosphine esters.

$$(RO)_2POCH_2C \equiv CH \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}{-}CH = C = CH_2 \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}{-}C \equiv C{-}CH_3.$$

However, in the majority of the experiments carried out it was not possible to effect the two stages separately; as a result of rapidly successive rearrangements, the α,β-propynylphosphine ester is usually obtained directly. Only in one experiment, when di-*n*-propyl chlorophosphite was allowed to react with propargyl alcohol in the presence of triethylamine, was a small amount of the allene isomer obtained alongside the α,β-propynylphosphine ester. The products were identified from their constants and IR spectra.

The prototropic isomerization of an allenylphosphine ester into an α,β-propynylphosphine ester apparently proceeds under the action of an organic base present in catalytic amounts in the reaction medium. In contrast to allyl esters of phosphorous acid, propargyl esters of phosphorous acid undergo rearrangements much more readily, at temperatures close to room temperature,

and with the evolution of a large amount of heat. Thus, in these rearrangements there occurs an acetylene–allene–acetylenic isomerization of propargyl radicals, accompanied by the simultaneous transition of phosphorus from the trivalent to the pentavalent state. A partial acetylene–allene rearrangement of propargyl esters of phosphinous and phosphorous acids, as we have recently learned, was observed almost simultaneously, but independently of us, by American investigators (6). In this case they isolated only the allene isomers. We have shown that the rearrangement of γ-substituted propargyl esters of phosphorous acid is accompanied by inversion of the radicals. Study of the IR spectra and properties of the compounds showed that, as a result of isomerization of diethyl γ-methyl- and diethyl γ-phenylpropynylphosphites, products are formed with the methyl and, respectively, phenyl group at the α-carbon atom.

$$(C_2H_5O)_2POCH_2C \equiv C\text{—}R \rightarrow (C_2H_5O)_2\overset{\overset{O}{\|}}{P}\text{—}\underset{R}{C} = C = CH_2,$$

where $R = CH_3$ or C_6H_5.

In this case the rearrangement stops at the stage of the allene isomer, which is explained by the absence of a labile hydrogen atom at the carbon bonded to the phosphine group; the prototropic transformation becomes impossible. Exclusively the allene isomer is also formed in the rearrangements of dialkyl α,α-dimethylpropargyl phosphites.

$$(RO)_2POC(CH_3)_2\text{—}C \equiv CH \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}\text{—}CH = C = C\begin{matrix}CH_3\\CH_3\end{matrix}.$$

Obviously, owing to the inductive influence of two methyl groups in the γ-position relative to the phosphine group, the hydrogen in the allene system becomes less mobile in comparison with an unsubstituted allene radical. The presence of two methyl groups located in the allene system in a state of hyperconjugation with the double bond apparently makes it also thermodynamically more stable than the acetylenic isomer.

by heating. Heating dialkyl-γ,γ-dimethylallenylphosphonates in the presence of basic catalysts (sodium ethoxide and triethylamine) does not cause a prototropic transformation, but only leads to dimerization of the product. Upon addition of an alcoholic solution of sodium alcoholate, addition of the alcohol to the dialkyl-γ,γ-dimethylallenylphosphonate proceeds smoothly. The latter reactions are of independent interest and are currently being studied by us.

As a result of the interaction of 1 mole of ethyldichlorophosphine with 2 moles of propargyl alcohol in the presence of triethylamine, we obtained a product close in constants to the product described in (7) as the dipropargyl ester of ethylphosphinous acid. However, study of the chemical properties and infrared

spectral data showed that this product contains a pentavalent phosphorus atom, allene and acetylene bonds, and, consequently, is the propargyl ester of ethylallenylphosphinic acid.

$$C_2H_5PCl_2 + 2HOCH_2C \equiv CH \rightarrow C_2H_5P(OCH_2C \equiv CH)_2 \rightarrow C_2H_5P(=O)(OCH_2C \equiv CH)(CH = C = CH_2).$$

The second stage of the rearrangement—the prototropic transformation—does not occur under the reaction conditions. This is probably associated with a decrease in the mobility of the prototropic system, caused by the increased electron-donor properties of the phosphine group (when OC_2H_5 is replaced by C_2H_5). However, under the action of basic catalysts (triethylamine on heating and sodium ethoxide at room temperature), the propargyl ester of ethylallenylphosphinic acid is rearranged into the propargyl ester of ethyl-α,β-propynylphosphinic acid.

$$CH{\equiv}C{-}CH_2O{-}P(=O)(C_2H_5){-}C(H){=}C{=}CH_2 \longrightarrow CH{\equiv}C{-}CH_2O{-}P(=O)(C_2H_5){-}C{\equiv}C{-}CH_2 \longrightarrow CH{\equiv}C$$

The first phase of the rearrangement of propargyl and allyl esters of phosphorous acid, in its character and results, very closely resembles Claisen rearrangements. They, like Claisen rearrangements, are thermal rearrangements and are accompanied by inversion of unsaturated radicals. We believe that the rearrangements of β,γ-unsaturated esters of phosphorous acid proceed through a five-membered cyclic transition state; the role of the double bond in the nonallylic part of the molecule is performed by the trivalent phosphorus atom with its P-electrons.

$$(RO)_2\ddot{P} - O - CH_2 - CH = CH - CH_3 \longrightarrow (RO)_2P(=O) - CH(CH_3) - CH = CH_2$$
$$(RO)_2\ddot{P} - O - CH_2 - C{\equiv}CH \longrightarrow (RO)_2P(=O) - C(H) = C = CH_2 \longrightarrow (RO)_2P(=O) - C{\equiv}C - CH_3$$

The first phases of these rearrangements, which may be represented in the form of the general equations

$$> \ddot{P} - O - C - C = C < \leftrightarrow > P(=O) - C - C = C <$$

$$> \ddot{P} - O - C - C \equiv C - \longrightarrow > P(=O) - C = C = C <,$$

may be assigned to rearrangements of the S_{Ni} type and, as it seems to us, may be regarded as rearrangements of the "pseudo-Claisen" type. The somewhat greater rate of these rearrangements in comparison with ordinary Claisen rearrangements can be explained by the increased nucleophilicity of the trivalent

phosphorus atom in comparison with the carbon-carbon double bond. The special ease of the acetylene-allene rearrangement is evidently due to the combination of the nucleophilic properties of the trivalent phosphorus atom with the considerable electrophilicity of the triple bond. Although the occurrence of inversion of the allyl or propargyl radicals in the rearrangements studied would seem to confirm the course of the reaction by a mechanism of cyclic electron transfer, it cannot serve as direct proof of the intramolecular character of the rearrangement. The formation only of the oxide of γ,γ-dimethylallenyldiphenylphosphine in the rearrangement of the α,α-dimethylpropargyl ester of diphenylphosphinous acid likewise, in our opinion, is not proof of the intramolecular character of its course and cannot exclude an ionic mechanism. Indeed, in the event that the reaction proceeds by an ionic mechanism, owing to the influence of two methyl groups, the equilibrium between the resulting positive ions will probably be completely or almost completely shifted toward the ion with an allenic structure. To prove the intramolecular mechanism of the rearrangement, we carried out the joint rearrangement of diphenyl propargyl phosphite and diethyl γ-phenylpropargyl phosphite, obtained in crude (undistilled) form in the reactions of the chloranhydrides of diphenylphosphorous and diethylphosphorous acids with propargyl and γ-phenylpropargyl alcohols, respectively.

$$(C_6H_5O)_2POCH_2{-}C\equiv CH \rightarrow (C_6H_5O)_2\overset{O}{P}CH=C=CH_2 \rightarrow (C_6H_5O)_2\overset{O}{P}{-}C\equiv C{-}CH_3.$$

$$(C_2H_5O)_2POCH_2-C\equiv C-C_6H_5 \rightarrow (C_2H_5O)_2\overset{O}{P}-\underset{C_6H_5}{C}=C=CH_2.$$

It had been established in advance that both esters undergo rearrangement when heated in benzene solution. Upon gradual heating of a mixture of these esters in benzene solution, when the reaction mixture reached 50°, a further spontaneous rise in temperature to 60° was observed, which indicated that the rearrangements were taking place. As a result of distillation of the reaction mixture, only two products were obtained, identified by their constants and IR spectra: the diethyl ester of α-phenylallenylphosphinic acid and the diphenyl ester of α,β-propynylphosphinic acid. Since the formation of "mixed" products—the diphenyl ester of α-phenylallenylphosphinic acid and the diethyl ester of α,β-propynylphosphinic acid (the latter could have been detected especially easily)—was not observed, it may be assumed that the rearrangement proceeded not by an ionic mechanism but entirely intramolecularly, i.e., through a five-centered cyclic transition state. A description of the experimental data relating to the present investigation will be given by us in a separate communication.

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Note: Figure translations are in progress. See original paper for figures.