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Abstract

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THERMAL DECOMPOSITION OF ADDITION PRODUCTS OF TRIALKYL PHOSPHITES TO DIACETYL

(Presented by Academician A. E. Arbuzov on 8 V 1961)

In our earlier published work ([1]) it was reported that intermediate products of the addition of trialkyl phosphites to α-diketones had been obtained:

$$\begin{matrix}CH_3{-}C{=}O\\CH_3{-}C{=}O\end{matrix} + P(OR)_3 \rightarrow \begin{matrix}CH_3{-}C{-}O\\ \| \quad \backslash\\CH_3{-}C{-}O\end{matrix} P(OR)_3.$$

These compounds, having the structure of 1,3,2-dioxaphospholenes and being derivatives of pentacovalent phosphorus, were isolated by us in a chemically pure state and their properties were characterized ([1], [2]). Recently we discovered another very interesting property of these compounds. When attempting to distill, in an inert atmosphere under vacuum, on an efficient rectification column having 15 theoretical plates, the product of addition of tripropyl phosphite to diacetyl, we found that during its distillation decomposition takes place, with a product distilling off that boils much lower than the starting material. On redistillation of the low-boiling product that separated, it distilled at a constant point and was identified as pure tripropyl phosphite (b.p. 83° at 10 mm, n_D^{20} 1.4265; literature data ([3]), b.p. 83° at 10 mm, n_D^{20} 1.4265). It reacted with cuprous halide on heating, forming a crystalline complex; upon addition of diacetyl to it, the original addition product was again obtained. Tripropyl phosphite was isolated upon decomposition of the addition product in a yield of about 50%.

In analogous fashion, when the product of addition of tributyl phosphite to diacetyl was heated in an inert atmosphere under vacuum in a flask equipped with an efficient rectification column, tributyl phosphite was obtained in 72% yield (b.p. 119–120° at 9 mm, n_D^{20} 1.4320; literature data ([3]), b.p. 119.5–120° at 10 mm, n_D^{20} 1.4321).

Thus, we found that the products of addition of trialkyl phosphites to diacetyl are capable of decomposing in the reverse direction, with liberation of the starting trialkyl phosphite:

$$\begin{matrix} CH_3{-}C{-}O \\ \quad \| \quad \backslash \\ CH_3{-}C{-}O \end{matrix} P(OR)_3 \rightarrow \begin{matrix} CH_3{-}C{=}O \\ CH_3{-}C{=}O \end{matrix} + P(OR)_3.$$

We had already noted earlier ([2]) that the product of addition of triethyl phosphite to diacetyl, when heated in a sealed ampoule, partially decomposes with formation of triethyl phosphate and ethyl ester of ethylphosphinic acid. This addition product is more stable than the addition products obtained from higher phosphites; it distills smoothly on a rectification column at 5-10 mm residual pressure. However, when it is heated in an inert atmosphere to 180-190° in a flask with an efficient column

at a residual pressure of 50-60 mm, it also decomposes completely, with the formation mainly of triethyl phosphate (61%) and small amounts of the ethyl ester of ethylphosphinic acid (6%). We were able to detect only traces of triethyl phosphite: the lower fraction, isolated in a very small amount, gives with cuprous chloride a temperature rise of 15-20°. Evidently, under more severe conditions the decomposition either proceeds mainly by direct elimination of triethyl phosphate, or the eliminated triethyl phosphite is oxidized by diacetyl and is partially isomerized at the moment of isolation into ether to the ethyl ester of ethylphosphinic acid.

The results obtained by us indicate that, in principle, cleavage of the products of addition of electrophilic reagents to esters of trivalent phosphorus into the starting products is possible, i.e., a course of reaction is possible that is the reverse, in its nature, of the first stage of the Arbuzov rearrangement.

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CITED LITERATURE

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