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## Abstract

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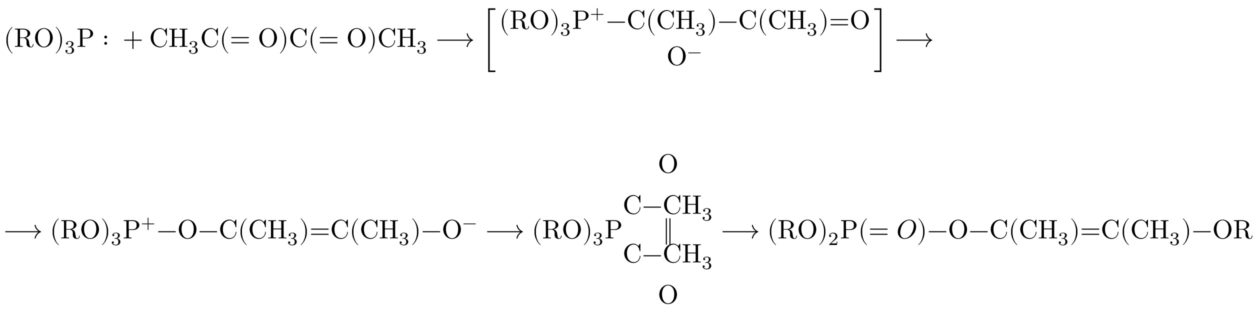
## ON SOME NEW TYPES OF THE ARBUZOV REARRANGEMENT

*(Presented by Academician B. A. Arbuzov, March 14, 1958)*

In the works of G. Kamai and V. A. Kukhtin published recently, some new cases of the Arbuzov rearrangement have been described, occurring under the action of various electrophilic reagents on trialkyl phosphites ($^{1-8}$). Most of these works are devoted to the study of the interaction of esters of phosphorous and phosphinic acids with C=C−C=O-conjugated systems ($^{3-8}$).

Continuing the study of reactions of $\pi\pi$-conjugated systems with trialkyl phosphites, we found that the latter readily enter into interaction with diacetyl, the final product of this reaction being dialkoxy-(dimethylalkoxyvinyl)-phosphate (III). By analogy with the reactions studied earlier ($^{3-4}$), its formation evidently proceeds according to the following scheme:



$$(RO)_3P: + CH_3C(=O)C(=O)CH_3 \longrightarrow \left[\begin{matrix}(RO)_3P^{+}{-}C(CH_3){-}C(CH_3){=}O \\ O^{-}\end{matrix}\right] \longrightarrow$$

$$\longrightarrow (RO)_3P^{+}{-}O{-}C(CH_3){=}C(CH_3){-}O^{-} \longrightarrow (RO)_3P\begin{matrix}O\\ C{-}CH_3\\ \| \\ C{-}CH_3\\ O\end{matrix} \longrightarrow (RO)_2P(=O){-}O{-}C(CH_3){=}C(CH_3){-}OR$$

(I) (Ia) (II) (III)

The product (I) formed in the nucleophilic attack by phosphorus on the carbon atom is readily rearranged into product (Ia), with formation of the more stable P−O bond. Such a scheme for this stage of the reaction is given by Bengelsdorf ($^{9}$) for the case of the interaction of phosphites with $\alpha$-halocarbonyl compounds. The constants of the alkoxyvinyl phosphates obtained are given in Table 1. On complete saponification these substances give phosphoric acid; on careful saponification with a 2% solution of hydrochloric acid, they form the corresponding ketophosphates (Table 1).

$$\mathrm{(RO)_2P(=}O\mathrm{)-O-C(CH_3)=C(CH_3)-OR} \xrightarrow[2\%\,\mathrm{HCl}]{\mathrm{H_2O}} \mathrm{(RO)_2P(=}O\mathrm{)-O-CH(CH_3)-C(=}O\mathrm{)CH_3}$$

(IV)

When carrying out the reaction of addition of trialkyl phosphites to diacetyl under milder conditions (20-30°, in ethereal solution), we were able, as a result of distillation, to isolate in pure form the intermediate reaction product (II). In its properties it is in many respects analogous to the intermediate products, previously studied by us in the pure state, of addition of trialkyl phosphites to $\alpha, \beta$-unsaturated acids ($^{3-8}$). It reacts with water with considerable self-heating (up to 50-70°), thereby forming the ketophosphate (IV). On heating and spontaneously on standing, it is converted into the final

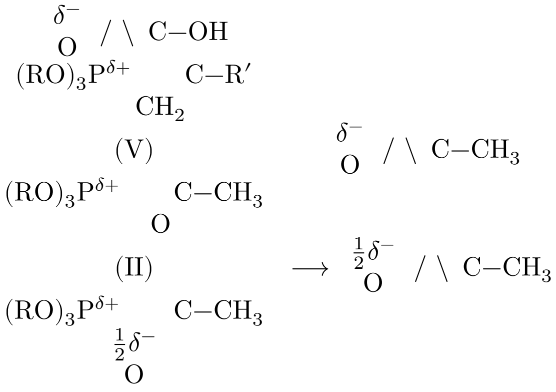
Table 1

| Formula | B.p., °C mm Hg | $n_D^{20}$ | $d_4^{20}$ | P, % found | P, % calc. | Yield, % |
|---|---|---|---|---|---|---|
| $(C_2H_5O)_2P(=O)-OC(CH_3)=C(CH_3)-OC_2H_5$ | 127–130/10 | 1.4250 | 1.1061 | 12.32 | 12.30 | 23.3 |
| $(n\text{-}C_3H_7O)_2P(=O)-OC(CH_3)=C(CH_3)-OC_3H_7\text{-}n$ | 140–142/10 | 1.4230 | 1.0752 | 11.17 | 10.51 | 46.7 |
| $(n\text{-}C_4H_9O)_2P(=O)-OC(CH_3)=C(CH_3)-OC_4H_9$ | 148–150/10 | 1.4240 | 1.0192 | 9.83 | 9.63 | 42.6 |
| $(C_2H_5O)_2P(=O)-OCH(CH_3)-C(=O)CH_3$ | 132–134/12 | 1.4230 | 1.1122 | 13.78 | 13.84 | 30.7 |

| Formula | B.p., °C mm Hg | $n_D^{20}$ | $d_4^{20}$ | P, % found | P, % calc. | Yield, % |
|---|---|---|---|---|---|---|
| cyclic P compound: $(C_2H_5O)_3P$ with an $O{-}C(CH_3) = C(CH_3){-}O$ ring | 104–105/10 | 1.4290 | 1.0825 | 12.42 | 12.30 | 47.2 |
| cyclic P compound: ([[*unclear*]]-$C_3H_7O$)P with an $O{-}C(CH_3) = C(CH_3){-}O$ ring | 127–130/10 | 1.4305 | 1.0256 | 10.92 | 10.51 | 37.1 |

alkoxyvinyl phosphate (III). When several drops of product (II) are added to acrylic acid, a telomerization reaction proceeds vigorously ($^8$).

The reason for the greater stability of the trialkoxyphospho(dimethylethene) dioxides (II) isolated by us, in comparison with the intermediate products of addition of phosphites to acids, becomes clear from a comparison of their formulas:



(V)

(II)

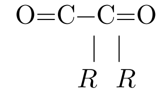
As shown in our papers ($^7$, $^8$), the P–O bond in the ring of product (V) is ionic in character, and if it is not completely ionic, then in any case it is very strongly polarized and unstable. In product (II) the molecule is symmetrical; both P–O bonds in the ring are evidently equivalent, and the polarization is distributed uniformly between both bonds, which accounts for the stability of the molecule. However, at the moment of reaction the polarization is probably concentrated on the bond being attacked; therefore product (II), in its chemical activity, is not inferior to product (V).

The isolation in chemically pure form of the intermediate product of the addition of trialkyl phosphites to diacetyl once again confirms that the interaction of $\pi\pi$-conjugated systems with esters of trivalent phosphorus acids is a new type of Arbuzov rearrangement. True, as a result of addition to diacetyl, not an alkylphosphinic ester but a phosphate is formed. However, the almost complete analogy in the course of this reaction with the action of C=C—C=O-conjugated systems compels one to regard it likewise as one of the types of the Arbuzov rearrangement.

In recent years the reactions of $\alpha$-halocarbonyl compounds with phosphites have been studied by many authors (9–14). In our papers we have already expressed the idea that the reaction of $\sigma\pi$-conjugated systems with phosphites, likewise,

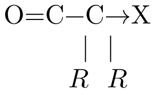
as well as reactions of $\pi\pi$-conjugated systems, may be regarded as a particular case of the Arbuzov rearrangement (3,4). The conjugation system in halocarbonyl compounds is, in character, analogous to the conjugation system of $\alpha$-diketones.

Therefore, the formation of an intermediate product of the Arbuzov rearrangement under the action of diacetyl on trialkyl phosphites is,



$$\mathrm{O{=}\underset{\substack{|\\ R}}{C}{-}\underset{\substack{|\\ R}}{C}{=}O}$$

$\pi\pi$-conjugation



$$\mathrm{O{=}\underset{\substack{|\\ R}}{C}{-}\underset{\substack{|\\ R}}{C}{\rightarrow}X}$$

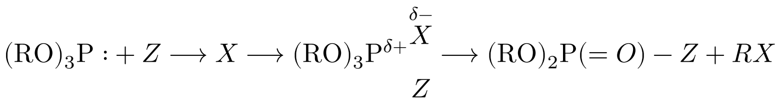
$\sigma\pi$-conjugation

in our opinion, an indirect confirmation of our assumption concerning the course of the reactions of halocarbonyl compounds with phosphites according to the scheme of the Arbuzov rearrangement. It should also be noted that, independently of us, A. I. Razumov (15) came to the conclusion that it is necessary to broaden the concept of the Arbuzov rearrangement. In connection with the foregoing, we consider it necessary and timely to propose a new, broader definition of the Arbuzov rearrangement. It seems to us that, on the basis of our experimental data, of works on $\alpha$-halocarbonyl compounds (9–14), and also of certain other works (16–19), the definition of the Arbuzov rearrangement may be formulated as follows.

The Arbuzov rearrangement is the transformation of esters of trivalent phosphorus acids into derivatives of pentavalent phosphorus, occurring under the action of electrophilic reagents and accompanied by the formation of a new $P$—$Z$ bond ($Z = C, O, N$, etc.). It proceeds by an initial attack by the nucleophilic atom of trivalent phosphorus on the most electrophilic part of the molecule; then an addition intermediate is formed, which is converted into the final product through the elimination of one ester radical from the nucleophilic part of the molecule that has added.

The cases of the Arbuzov rearrangement known at the present time may be divided into three types:

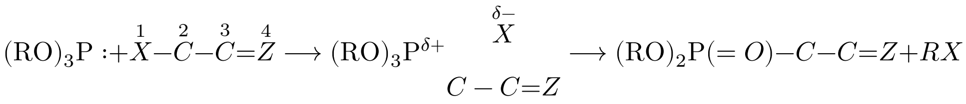
1. Rearrangement under the action of unconjugated (or $\sigma\sigma$-conjugated) electrophilic systems:



$$(\mathrm{RO})_3\mathrm{P} : + Z \longrightarrow X \longrightarrow (\mathrm{RO})_3\mathrm{P}^{\delta+}\begin{matrix}\overset{\delta-}{X}\\ \\ Z\end{matrix} \longrightarrow (\mathrm{RO})_2\mathrm{P}(=O) - Z + RX$$

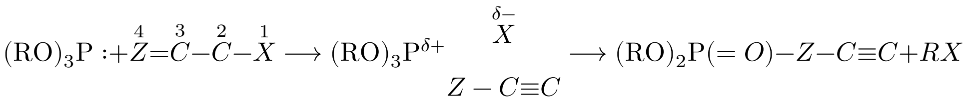
2. Rearrangement under the action of $\sigma\pi$-conjugated systems. It may proceed in two directions:

a) according to scheme 2—1 (without transfer of the reaction center):



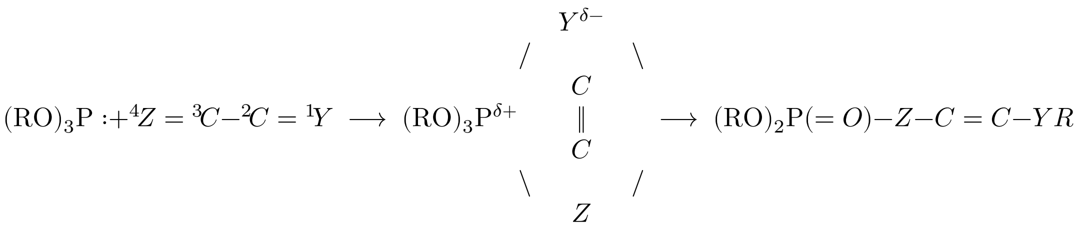
$$(\mathrm{RO})_3\mathrm{P} :+\overset{1}{X}-\overset{2}{C}-\overset{3}{C}=\overset{4}{Z} \longrightarrow (\mathrm{RO})_3\mathrm{P}^{\delta+}\begin{matrix}\overset{\delta-}{X}\\ \\ C-C=Z\end{matrix} \longrightarrow (\mathrm{RO})_2\mathrm{P}(=O)-C-C=Z+RX$$

b) according to scheme 4—1 (or (3)—4—1, if the initial attack at $C_3$ followed by formation of a $P$—$Z$ bond is assumed), i.e., with transfer of the reaction center:



$$(\mathrm{RO})_3\mathrm{P} :+\overset{4}{Z}=\overset{3}{C}-\overset{2}{C}-\overset{1}{X} \longrightarrow (\mathrm{RO})_3\mathrm{P}^{\delta+}\begin{matrix}\overset{\delta-}{X}\\ \\ Z-C\equiv C\end{matrix} \longrightarrow (\mathrm{RO})_2\mathrm{P}(=O)-Z-C\equiv C+RX$$

3. Rearrangement under the action of $\pi\pi$-conjugated systems. It always proceeds with transfer of the reaction center, according to scheme 4–1 (or (3)–4–1).



$$(\mathrm{RO})_3\mathrm{P} :+{}^4Z = {}^3C-{}^2C = {}^1Y \longrightarrow (\mathrm{RO})_3\mathrm{P}^{\delta+}\begin{matrix} & Y^{\delta-} & \\ / & & \backslash \\ & C & \\ & \| & \\ & C & \\ \backslash & & / \\ & Z & \end{matrix} \longrightarrow (\mathrm{RO})_2\mathrm{P}(=O)-Z-C = C-YR$$

Further study and discussion of these interesting reactions will undoubtedly make it possible to supplement and refine the definition proposed by us.

K. M. Orekhova took part in carrying out the experimental part of this work, for which the author considers it necessary to express his gratitude to her.

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