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Abstract

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ADDITION OF TRIALKYL PHOSPHITES TO α,β-UNSATURATED ALDEHYDES

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In an earlier published paper ([1]), we reported on the ability of trialkyl phosphites to add to α,β-unsaturated acids. This reaction probably proceeds according to the scheme:

$$(RO)_3P : +CH_2{=}CH{-}C(=O)OH \longrightarrow (RO)_2P(OR){-}CH_2{-}CH{=}C(O^-){-}OH \longrightarrow$$
$$\longrightarrow (RO)_2P(=O){-}CH_2{-}CH{=}C(OR){-}OH \longrightarrow (RO)_2P(=O){-}CH_2{-}CH_2{-}C(=O){-}OR$$

It could be supposed that certain other compounds possessing a π,π-conjugated system are also capable of this reaction.

Studying the action of trialkyl phosphites on acrolein and crotonaldehyde, we established that they enter into a very active interaction with phosphites. Thus, for example, triethyl phosphite reacts with acrolein almost as actively as with acrylic acid; the reaction proceeds with self-heating, the temperature rising to 70° upon slow addition of acrolein to triethyl phosphite. However, isolating the interaction product is considerably more difficult than in reactions with α,β-unsaturated acids. Distillation of the reaction products at 3-4 mm is accompanied by signs of strong decomposition and takes place with considerable overheating in the bath (to 80-100°). The addition product obtained does not give the characteristic reactions for an aldehyde group; the action of bromine water reveals the presence of a double bond. In accordance with the chemical properties of the product obtained, and also on the basis of analytical data, two possible formulas may be proposed for it:

$$\underset{\text{I}}{(RO)_2P{-}CH_2{-}CH{=}CHOR \quad \| \; O} \qquad \underset{\text{II}}{(RO)_2P{-}CH(OR)CH{=}CH_2 \quad \| \; O}$$

Formula II corresponds to the product of addition at the carbonyl group; formula I corresponds to addition through the conjugated system $C{=}C{-}C{=}O$ in the 1-4 position. To resolve the question of the structure of the product obtained, it

was subjected to saponification with a 15% solution of hydrochloric acid. The syrupy product obtained upon saponification gives characteristic reactions for the carbonyl group with fuchsine-sulfurous acid and with an alkaline solution of sodium nitroprusside. Subsequently, upon saponification of the product of addition of tributyl phosphite to acrolein with a 2% solution of sulfuric aci-

at a temperature of 80-90°, we succeeded in isolating β-(dibutylphosphono)propionaldehyde. The aldehyde obtained was proved by the formation of its 1,4-dinitrophenylhydrazone with m.p. 101°. The aldehyde group can be obtained only upon saponification of the vinyl ether group of compound I:

$$(RO)_2P\,CH_2\underset{\underset{O}{\|}}{C}H = CHOR \xrightarrow[-ROH]{+H_2O} (RO)_2P\,CH_2CH_2\underset{\underset{O}{\|}}{C}H$$

On the basis of the results obtained it may be considered that the products of the addition of trialkyl phosphites to α,β-unsaturated aldehydes have structure I; consequently, this reaction proceeds by addition of trialkyl phosphite to the α,β-unsaturated aldehyde through the conjugated system of double bonds in the 1-4 position. Like acrolein, crotonaldehyde also reacts with trialkyl phosphites. In this case the interaction proceeds less vigorously, with slight self-heating (by 4-5°), and requires heating of the reaction mixture at 100-150° for 2-3 hours for completion of the reaction. The constants of the products obtained are given in Table 1. The mechanism of the reaction of addition of trialkyl phosphites

Table 1

No.	Formula	B.p., °C (mm Hg)	n_D^{20}	d_0^{20}	MR_D calc.	MR_D found	P, % calc.	P, % found	Yield, %
1	$(C_2H_5O)_2P(=O)CH_2CH(OC_2H_5)CHOC_2H_5$	132–133 (3)	1.4442	1.0602	55.75	55.81	13.95	13.9	16.6
2	$(n\text{-}C_3H_7O)_2P(=O)CH_2CH(OC_3H_7\text{-}n)CHOC_3H_7\text{-}n$	153–155 (5)	1.4426	1.0089	69.67	69.34	11.7	11.4	11.0
3	$(n\text{-}C_4H_9O)_2P(=O)CH_2CH(OC_4H_9\text{-}n)CHOC_4H_9\text{-}n$	156–157 (3)	1.4460	0.9806	83.52	82.94	10.1	10.4	40.6*
4	$(C_2H_5O)_2P(=O)CH(CH_3)CH(OC_2H_5)CHOC_2H_5$	138–139 (3)	1.4506	1.0436	60.43	60.89	13.1	12.8	17.1
5	$(n\text{-}C_3H_7O)_2P(=O)CH(CH_3)CH(OC_3H_7\text{-}n)CHC_3H_7\text{-}n$	152–153 (3)	1.4496	1.0046	74.28	74.29	11.1	11.0	12.9

No.	Formula	B.p., °C (mm Hg)	n_D^{20}	d_0^{20}	MR_D calc.	MR_D found	P, % calc.	P, % found	Yield, %
6	(n-$C_4H_9O)_2P(=O)CH_2CH_2CHO$	130–132	1.4406	1.0129	63.88	65.16	12.4	12.0	30.8

* Yield after treatment of the addition product with butanol.

to α,β-unsaturated aldehydes can be expressed by the following general scheme:

$$(RO)_3P: + {}^{+}CH_2 = CH - C\overset{O^{-\delta}}{\underset{H}{}} \longrightarrow (RO)_2P\overset{O}{\underset{CH_2CH = CHOR}{}}$$

Some facts obtained by us in the course of the investigation indicate that the first stage of the reaction is the formation of an intermediate product to which the formula

$$(RO)_3P\begin{matrix} O - CH \\ \| \\ CH_2 - CH \end{matrix}$$

may be assigned, and the possibility is not excluded that the P—O bond in the ring is ionic in character. The following facts speak in favor of this assumption.

1. **Action of high temperatures on the addition product.** As was already stated above, the first distillation of the addition product proceeds very unevenly: signs of strong decomposition are noticeable, and the distillation proceeds with considerable overheating in the bath. A secondary distillation proceeds more smoothly, with only slight resinification of the product. The yield of esters of γ-alkoxyallylphosphonic acid increases if the addition product is heated before distillation to 180–200°. Such heating of the addition product of tributyl phosphite to acrolein increased the yield of the butyl ester of γ-butoxyallylphosphonic acid from 18 to 31.1%.
2. **Action of alcohol on the addition product.** When butanol acts on the undistilled addition product (containing no residues of acrolein and tributyl phosphite), the temperature rises by 5–6° and remains elevated for a long time. The yield of the butyl ester of γ-butoxyallylphosphonic acid in this case increases to 40.6%. The phosphinate obtained does not give a rise in temperature when alcohol acts on it.
3. **Action of water on the addition product.** When water acts on the undistilled addition product with tributyl phosphite, the temperature rises

by 11°. The odor of butanol appears, as well as a sharp odor of phosphonaldehyde—after some time the product is almost completely converted into phosphonaldehyde. The pure butyl ester of γ-butoxyallylphosphonic acid does not react with water under the same conditions.

All these facts can be explained by the formation of an intermediate product of cyclic structure, which under the action of high temperature or alcohol is converted into an ester of γ-alkoxyallylphosphonic acid, and under the action of water into phosphonaldehyde:

$$\text{I.}\quad (\mathrm{RO})_3\mathrm{P}\begin{matrix}\mathrm{O}-\mathrm{CH}\\ \mathrm{CH_2}-\mathrm{CH}\end{matrix}+\mathrm{ROH}\rightarrow(\mathrm{RO})_2\mathrm{P}\begin{matrix}\mathrm{RO}\\ \mathrm{CH_2}-\mathrm{CH}=\mathrm{CHOR}\end{matrix}\begin{matrix}\mathrm{OH}\\ \|\end{matrix}\rightarrow$$
$$\rightarrow(\mathrm{RO})_2\mathrm{P}(=\mathrm{O})\,\mathrm{CH_2}-\mathrm{CH}=\mathrm{CHOR}+\mathrm{ROH}$$

$$\text{II.}\quad (\mathrm{RO})_3\mathrm{P}\begin{matrix}\mathrm{O}-\mathrm{CH}\\ \mathrm{CH_2}-\mathrm{CH}\end{matrix}+\mathrm{HOH}\rightarrow(\mathrm{RO})_2\mathrm{P}\begin{matrix}\mathrm{RO}\\ \mathrm{CH_2}-\mathrm{CH}=\mathrm{CHOH}\end{matrix}\begin{matrix}\mathrm{OH}\\ \|\end{matrix}\rightarrow$$
$$\rightarrow(\mathrm{RO})_2\mathrm{P}(=\mathrm{O})\,\mathrm{CH_2}-\mathrm{CH_2C}(=\mathrm{O})\mathrm{H}+\mathrm{ROH}$$

On the basis of the foregoing one may conclude that the interaction of trialkyl phosphites with the conjugated system C = C − C = O probably occurs in two stages, according to the Arbuzov rearrangement scheme ([2]):

$$\text{I.}\quad (\mathrm{RO})_3\mathrm{P}:+{}^{\delta+}\mathrm{CH_2}=\mathrm{CH}-\overset{\delta-}{\mathrm{C}}(=\mathrm{O})\mathrm{H}\longrightarrow(\mathrm{RO})_3\mathrm{P}^{+}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{C}(\mathrm{O}^{-})\mathrm{H}$$
$$\longrightarrow\ \text{cyclic intermediate}$$

$$\text{II.}\quad \text{cyclic intermediate}\longrightarrow(\mathrm{RO})_2\mathrm{P}(=\mathrm{O})\mathrm{CH_2}-\mathrm{CH}=\mathrm{CHOR}.$$

The action of alkyl halides on trialkyl phosphites is probably only a special case of the Arbuzov rearrangement. As we have shown earlier, anhydrides of organic acids ([3]), σ, π-unsaturated acids ([1]), α, β-unsaturated aldehydes and, in all probability, a number of other π, π-conjugated systems are capable of this reaction.

In the light of the results obtained by us, we consider it possible to express certain considerations concerning the Perkow reaction ([4]). He described the reaction:

$$(\mathrm{RO})_3\mathrm{P}:+\mathrm{CCl_3C}\begin{matrix}\mathrm{O}\\ \|\\ \mathrm{H}\end{matrix}\longrightarrow(\mathrm{RO})_2\mathrm{POCH}=\mathrm{CCl_2}+\mathrm{RCl}$$

The author gives a rather complicated explanation of this reaction, attempting to explain its abnormal course from the point of view of the Arbuzov rearrangement. It seems to us that such a course of the reaction is readily explained

if chloral is regarded as a σ,π-conjugated system with an electrophilic carbon. By analogy with π,π-conjugated systems, chloral should enter into the Arbuzov rearrangement according to the scheme:

$$Cl_3C{-}CHO + P(OR)_3 \longrightarrow \begin{array}{c} CCl_2{=}CH \\ | \\ O{-}P(OR)_2 \\ | \\ [Cl \cdots OR] \end{array} \longrightarrow (RO)_2P(=O){-}OCH{=}CCl_2{+}RCl.$$

Almost the same scheme is given by A. N. Pudovik and N. M. Lebedeva ([5]) for the interaction of chloro- and bromoacetone with trialkyl phosphites; it is only unclear why the authors assume, at the intermediate stage, the separate existence of a phosphonium ion and a neutral halogen atom.

Allen and Jonson ([6]), besides reactions with haloketones, also studied the action on trialkyl phosphites of other σ,π-conjugated systems; moreover, Arbuzov rearrangement reactions in many cases also proceed with transfer of the reaction center.

Probably, the interaction of trialkyl phosphites with conjugated systems in the 1—4 position, with the formation of an intermediate complex, is a general rule both for π,π- and for σ,π-systems.

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