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Abstract

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Addition of Trialkyl Phosphites to Acetylenecarboxylic Acids

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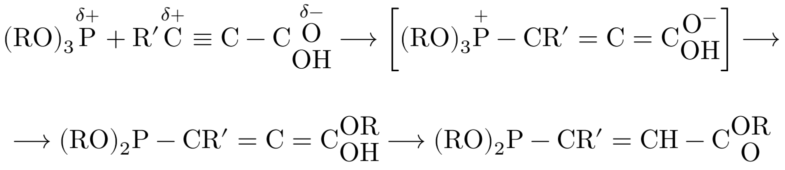
Gilm Kamai and V. A. Kukhtin (^{1}) established that trialkyl phosphites react actively with α, β-unsaturated acids, adding to the conjugated system $C = C - C = O$ in the 1-4 position with subsequent migration of the hydrogen atom; as a result of the reaction, the corresponding esters of β-phosphonocarboxylic acids are formed as the final product. It seemed of interest to us to study the action of trialkyl phosphites on acetylenecarboxylic acids possessing the $C \equiv C - C = O$ conjugation system, in particular on propiolic and tetrolic acids.

Propiolic acid enters very actively into reaction with trialkyl phosphites. Reactions with it were carried out in ether solution with careful dropwise addition of propiolic acid to the phosphite. Tetrolic acid, on the contrary, requires some heating (to 50—60°) for the reaction to begin, after which the temperature of the reaction mixture spontaneously rises sharply. The products we obtained by addition of trialkyl phosphites to acetylenecarboxylic acids are colorless liquids with specific gravity greater than unity, readily soluble in water, and give qualitative reactions for a double bond. In the IR spectrum of the product of addition of triethyl phosphite to tetrolic acid there is an absorption band at 1648 cm^{-1}, characteristic of a double bond. On the basis of these data it may be assumed that the products of addition of trialkyl phosphites to acetylenecarboxylic acids are esters of the corresponding phosphonacrylic acids. In contrast to the reactions of trialkyl phosphites with α, β-unsaturated acids (^{1}), we have so far been unable to establish the formation of intermediate addition products in the interaction of trialkyl phosphites with acetylenecarboxylic acids. The addition reaction probably proceeds according to a scheme analogous to that proposed for the reaction with acrylic acids:



$$(RO)_3\overset{\delta+}{P} + R'\overset{\delta+}{C} \equiv C - C\substack{\overset{\delta-}{O}\\ OH} \longrightarrow \left[(RO)_3\overset{+}{P} - CR' = C = C\substack{O^-\\ OH}\right] \longrightarrow$$

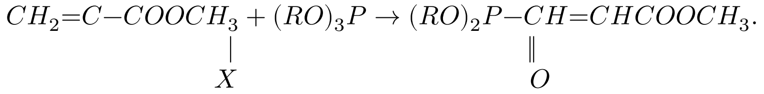
$$\longrightarrow (RO)_2P - CR' = C = C\substack{OR\\ OH} \longrightarrow (RO)_2P - CR' = CH - C\substack{OR\\ O} \qquad (1)$$

To confirm the structure of the products obtained, we carried out a counter synthesis of the methyl ester of β-phosphonacrylic acid by the method of Kuver (^{2}), by the action of methyl α-bromoacrylate on trimethyl phosphite. An identical product was obtained. The constants and analytical data of the products obtained are given in Table 1, from which it is seen that the found values of molecular refractions are somewhat higher than the calculated value. This discrepancy is evidently associated with the presence in the esters obtained of conjugation of the system $O = P - C = C - C = O$, not taken into account by the exaltation.

Table 1

Compound	b.p., °C (mm Hg)	n_D^{20}	d_4^{20}	P, % calculated	P, % found	Molecular refraction calculated	Molecular refraction found
$(CH_3O)_2\underset{\underset{O}{\Vert}}{P}{-}CH{=}CH{-}COOCH_3$	149,5–151 (15)	1,4585	1,2442	15,97	16,35	41,96	42,60
$(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}{-}CH{=}CH{-}COOC_2H_5$	138–142 (5)	1,4500	1,1408	13,14	13,06	55,82	55,68
$(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}{-}\underset{\underset{CH_3}{\vert}}{C}{=}CH{-}COOC_2H_5$	150–151,5 (9)	1,4521	1,1018	12,40	12,35	60,43	61,20
$(n\text{-}C_3H_7O)_2\underset{\underset{O}{\Vert}}{P}{-}\underset{\underset{CH_3}{\vert}}{C}{=}CH{-}COOC_3H_7$	170–172 (6)	1,4545	1,0518	10,61	10,46	74,29	75,26
$(n\text{-}C_4H_9O)_2\underset{\underset{O}{\Vert}}{P}{-}\underset{\underset{CH_3}{\vert}}{C}{=}CH{-}COOC_4H_9$	169–170,5 (2)	1,4565	1,0260	9,28	9,21	88,14	88,57

Küver, McCall, and Dickey were the first to synthesize esters of β-phosphonacrylic acid by the interaction of haloacrylates with trialkyl phosphites (^{2})



$$CH_2{=}\underset{\underset{X}{\vert}}{C}{-}COOCH_3 + (RO)_3P \rightarrow (RO)_2\underset{\underset{O}{\Vert}}{P}{-}CH{=}CHCOOCH_3.$$

On the basis of an analysis of spectral data, these authors conclude that esters of β-phosphonacrylic acid may exist in two isomeric forms (cis and trans). However, in each case they isolated only one product with constant properties. We likewise were unable in any case to isolate two different stereoisomers in pure form. During the first distillation of the reaction products, fractions with very broad boiling-temperature ranges are obtained in most cases, but on repeated distillation products with sharp boiling temperatures are usually obtained. It is possible that the reaction gives two isomeric forms, one of which, less stable, is converted on heating (during distillation) into the more stable configuration. Our work on the study of reactions of esters of trivalent phosphorus with acetylenecarboxylic acids is continuing.

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

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