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THE NEW METHOD FOR THE PREPARATION OF ENOL PHOSPHATES

The Reaction of α-Hydroxy Ketones with Triethyl Phosphite

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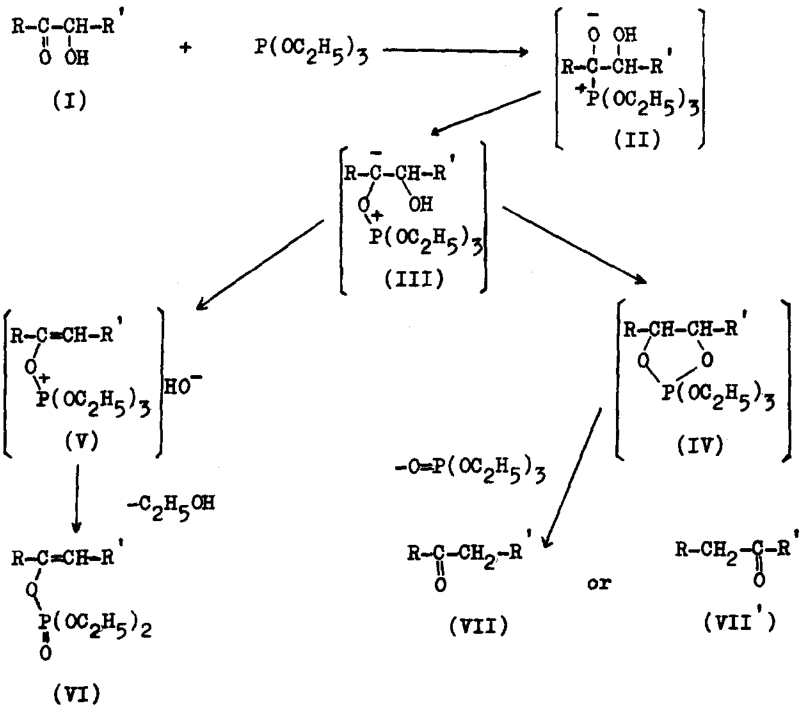
It has recently been found that diaryl diketones and aromatic ketones were deoxygenated by trivalent phosphorus compounds to give diaryl acetylenes or diaryl ketenes[1)] and tetrasubstituted ethylenes[2)], respectively.

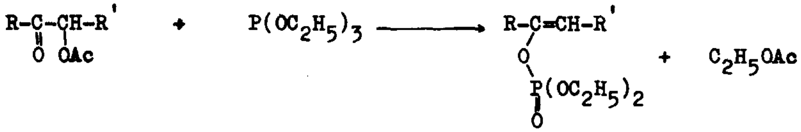
In the present experiment, the deoxygenation[3)] of various α-hydroxy ketones by triethyl phosphite was tried. When benzoin was heated with triethyl phosphite under nitrogen for 10 hr. at 180°C.,desoxybenzoin, triethyl phosphate and diethyl 1,2-diphenylvinyl phosphate were obtained in 42%, 53% and 27% yields, respectively. In a similar way, 4,4'-dimethoxydesoxybenzoin (34%) or desoxyfuroin (35%) was obtained along with triethyl phosphate by the reaction of 4,4'-dimethoxybenzoin or furoin with triethyl phosphite. When 4-methoxybenzoin and triethyl phosphite were heated at 180°C. for 10 hr., a mixture of 4-methoxydesoxybenzoin and 4'-methoxydesoxybenzoin was obtained. (The infra-red spectra of this mixture showed a strong absorption at 1690 cm^{-1}(doublet) attributable carbon-oxygen double bond and no oxygen-hydrogen band.) Therfore, it can be assumed that a probable intermediate of the reaction might be a cyclic-phosphorane (IV) which was produced, by a proton transfer, through the intermediate (II), initially formed by the nucleophilic attack of triethyl phosphite on carbonyl carbon, and the intermediate (III), produced by the intra-molecular rearrangement of phosphorus atom from carbon to oxygen. The decomposition of the intermediate (IV) afforded desoxybenzoin and triethyl phosphate. On the other hand, if the formation of the second phosphonium salt (V) from the



intermediate (III) took place faster than that of intermediate (IV), enol phosphate would result by loosing ethyl alcohol from (V).

Recently, Henning reported that enol phosphate and desoxybenzoin were obtained by heating benzoin with triethyl phosphite in the presence of a catalytic amount of metallic sodium[4]. But the pathway for the formation of the enol phosphate was quite different from the mechanism mentioned in this paper.

In general, it is well known that enol phosphate can be obtained from the reaction of trivalent phosphorus esters and α-halo ketones[5]. Since the formation of enol phosphate from α-hydroxy ketones and triethyl phosphite shown in the present experiment was very interesting, the preparation of enol phosphates from α-acetoxy ketones and triethyl phosphite was further studied. When benzoin acetate was treated with excess triethyl phosphite under nitrogen at 180°C. for 10 hr., diethyl 1,2-diphenylvinyl phosphate (53%) was obtained and benzoin acetate (30%) was recovered. Ethyl acetate was identified by its infra-red spectra.



$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{OAc}{|}}{CH}-R' + P(OC_2H_5)_3 \longrightarrow R-\underset{\underset{\underset{\underset{O}{\|}}{P}(OC_2H_5)_2}{O}}{C}=CH-R' + C_2H_5OAc$$

The infra-red spectra of this enol phosphate showed no C=O or C(O)O band, but C=C band at 1650 cm^{-1} and P=O band at 1285 cm^{-1}. The H^{I} n.m.r. spectra of this compound was in good accodance with the enol phosphate. The ratio of cis isomer to trans isomer was nearly one from H^{I} n.m.r. spectra. When ω-acetoxyacetophenone was treated with triethyl phosphite under nitrogen at 180°C. for 10 hr., diethyl 1-phenylvinyl phosphate (69%) was obtained along with ethyl acetate. The infra-red spectra showed neither C=O band nor C(O)O band, but C=C band at 1640 cm^{-1}, P=O band at 1280 cm^{-1} and C=CH$_2$ band at 840 cm^{-1}. The H^{I} n.m.r. spectra showed terminal methylene protons, aromatic protons, aliphatic methyl and methylene protons.

The corresponding enol phosphate could not be obtained from the reaction of butyroin acetate, aliphatic α-acetoxy ketone, and triethyl phosphite even when they were heated at 180°C. for 10 hr.

Further study on this type of the reaction for the preparation of enol phosphate is now in progress.

Reference

1) T. Mukaiyama, H. Namubu and T. Kumamoto, J. Org. Chem. 29, 2243, (1964).

2) M. Grayson and E. J. Griffith, Topics in Phosphorus Chemistry, vol. I, p. 90, Interscience Publishers, New York (1964).

3) Presented at the 19th Meeting of the Chemical Society of

Japan, Preprint, vol. III, p. 296, Yokohama City, Kanagawa Fri. Apr. 1966.

4) H. G. Henning, *Tetrahedron Letters*, **1966**, 2585.

5) F. W. Lichtenthaler, *Chem. Rev.* **61**, 607 (1961).