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SUBSTITUTED 1-PHOSPHABICYCLO[3.2.0]HEPT-4-ENES

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Abstract.The interaction between dialkyl alkynylphosphonites and pyruvic acid methyl ester in boiling benzene afforded 1,1-dialkoxy-3,6-dimethyl-3,6-di(methoxycarbonyl)-4R-2,7-dioxa-1-phosphabicyclo[3.2.0]hept-4-enes.

Trialkyl phosphites and dialkyl phosphonites react with pyruvic acid esters to form 1,3,2-dioxaphospholanes at 0 ÷ -10°C and at 100°C the mixtures of 1:1 and 1:2 adducts of the open chain or dioxaphospholane structure respectively [1,2].The interaction between dialkyl isocyanatophosphites, hetero-α,β-unsaturated P(III)compounds, and pyruvic acid esters leads to 1:1 heterocyclic adducts - substituted 1,4,3,λ^5-oxazaphospholidines resulting from the involvment in the reaction both phosphorus atom and isocyanate multiple bond [3].

The results obtained show, that in contrast to isocyanatophosphites,dialkyl phosphonites containing triple C≡C bond react with pyruvic acid methyl ester to form 1:2 adducts - 1,1-dialkoxy-3,6-dimethyl-3,6-di(methoxycarbonyl)-4R-2,7-dioxa-1-phosphabicyclo[3.2.0]hept-4-enes (1-3). The latter are representatives of new type unsaturated heterocycles containing phosphorus.

The reaction are likely to start with the nucleophilic attack of a phosphorus atom to the carbon of a carbonyl group.The resulting bipolar ion (1a-3a) transforms into ion (1b-3b) in a manner of phosphonate-phosphate rearrangement. The carbanion of the bipolar ion (1b-3b) adds to β-carbon atom of the activated C≡C bond to give cyclic ylide (1c-3c). Addition of the second molecule of pyruvic acid ester leads to ylide stabilization.In a similar manner the interaction of diphenylvinylphosphine with hexafluoroacetone is known to occur [4].

The reactions of dialkyl alkynylphosphonites with pyruvic acid methyl ester were conducted under the reagent ratios both 1:1 and 1:2. In either