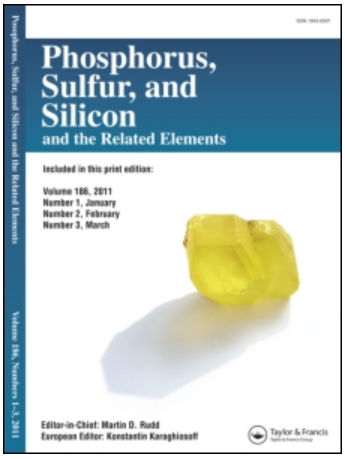

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α,β-Unsaturated Derivatives of Trivalent Phosphorus in Reactions with Activated Carbonyl Compounds

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α,β-UNSATURATED DERIVATIVES OF TRIVALENT PHOSPHORUS IN REACTIONS WITH ACTIVATED CARBONYL COMPOUNDS

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Dialkyl alkynylphosphonites (I) react with esters and nitriles of α-oxocarboxylic acids to give phosphorylated alkanoates, 1,3,2-dioxaphospholanes and 1-phosphabicyclohept-4-enes, depending on the nature of the reagent and conditions of the reaction. The reaction of dialkyl alkenylphosphonites (II) with esters and nitriles of α-oxocarboxylic acids predominantly leads to dioxaphospholane derivatives.

The reaction of I with α-bromoketones occurs in three directions: the Perkov reaction, the Arbuzov reaction and heterocyclization. The reactions of I with diphenylcarbodiimide (III) lead to the formation of phosphabicycloheptenes exclusively.

Unlike I and II dialkoxyisocyanatophosphines (IV) react with III to give stable cycloadducts 1:1 - 1,3,4-diazaphospholines. The reactions of trifluoropyruvic acid esters with IV proceed with the formation of 1,3,4- and 1,3,2-oxaazaphospholines.

Bis(2,2,3,3-tetrafluoropropoxy)- and diphenoxyisocyanatophosphines with IV form crystalline dimers, substituted diphosphatricyclodecanes.