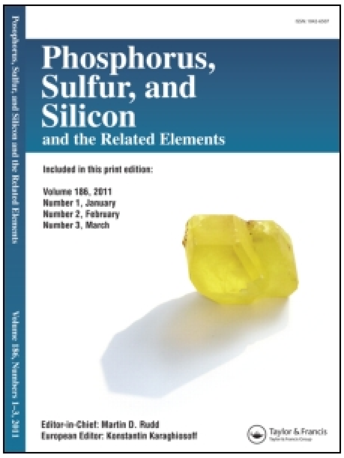

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Selective Phosphorylation of α,β-Unsaturated Carbonyl Compounds

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SELECTIVE PHOSPHORYLATION OF α,β-UNSATURATED CARBONYL COMPOUNDS

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Elaboration of effective methods of selective phosphorylation of α,β-unsaturated carbonyl compounds containing simultaneously C=C and C=O bonds, which may compete with each other or react consistently one after another, is one of the most complex problems in the modern organophosphorus synthesis. On the basis of our previous systematic investigations of kinetics and mechanism of the Pudovik and Abramov reactions in the series of α,β-unsaturated carbonyl compounds we have suggested three possible ways to solve this problem: a) soft reaction conditions, regulated by solvent, catalyst and temperature; b) interface catalysis; c) metallocomlex catalysis (reaction in the coordination sphere of transition metal).

Experimental verification show, that all three approaches give enough satisfactory results and permit to obtain corresponding α-hydroxyphosphonates (products of the Abramov reaction) with a good yield even for a such "unsuitable" subsrate as benzylideneacetophenone (chalcone) which in common conditions always gives the adducts on the C=C bond (product of the Pudovik reaction).

Thus suitable methods of selective phosphorilation of α-enones C=O bond have been elaborated. α-Hydroxyphosphonates obtained may be easily isomerized into corresponding γ-ketophosphonates by heating or alkoholate action.