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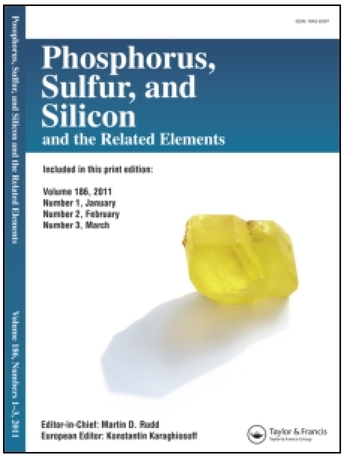

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Kinetics and Mechanism of the Pudovik Reaction

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KINETICS AND MECHANISM OF THE PUDOVIK REACTION

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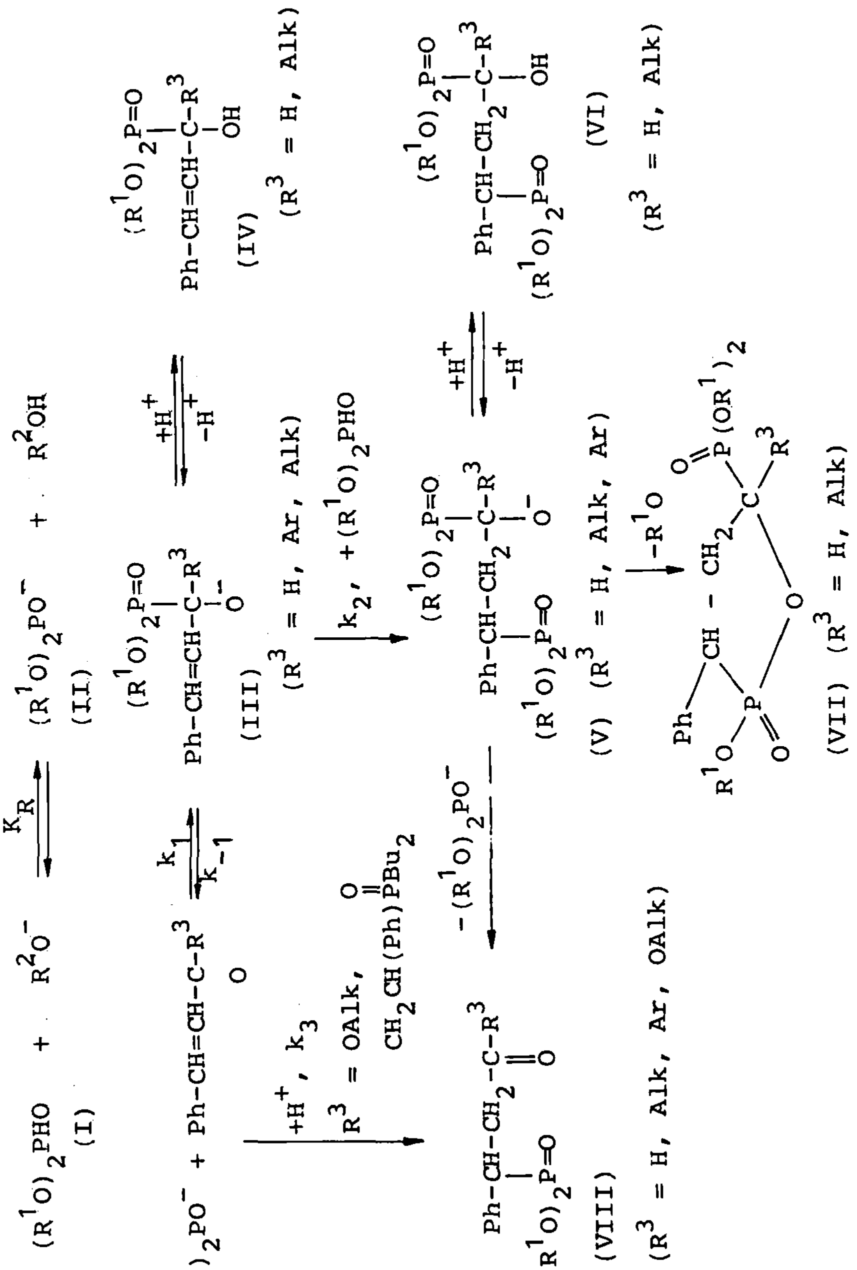
Abstract The kinetics and the mechanism of the Pudovik reaction for the series of α,β-unsaturated carbonyl compounds have been studied. The factors which determine the addition locoselectivity and the reactivity of the hydrophosphoryl and unsaturated compounds in this process are established. The qualitative and quantitative relationships obtained allow to predict the reaction rate and its direction depending on the reagents structure and also on the nature of catalyst and solvent used.

The Pudovik reaction concerning hydrophosphoryl compounds (HPC) addition to electrophilic unsaturated substances is one of the most interesting reactions in phosphorus chemistry both in theoretical and practical aspects. At the same time, kinetic investigations of the Pudovik reaction have not been carried out. There are no systematic data about the reaction mechanism and reactivity of addends. The paper is devoted to the results of kinetic investigation of the Pudovik reaction for the series of α,β-unsaturated carbonyl compounds and their analogs in the alcohol medium under alcoholate catalysis.[1-4] On the basis of kinetic results obtained and the literature data the united mechanism of the reaction has been suggested[3] which is in a good agreement both with the kinetic manifestations and literature data on HPC addition to α,β-unsaturated aldehydes and ketones (see scheme). On the first reversible stage the dialkylphosphite anion is formed, which, as a rule, attacks the carbon atom of the carbonyl group as the most electrophilic center of the α-enone molecule. The following direction of the reaction depends on the stability of the intermediate (III) which is generally conditioned by the nature of substituent R^3. If intermediate (III) is


(R1O)2PHO (I)
R2O-
KR
(R1O)2PO- (II)
R2OH
(R1O)2PO- + Ph-CH=CH-C-R3
k1
k-1
(III)
(R3 = H, Ar, Alk)
+H+
-H+
(IV)
(R3 = H, Alk)
+H+, k3
R3 = OAlk,
CH2CH(Ph)PBu2
k2, +(R1O)2PHO
-(R1O)2PO-
(V) (R3 = H, Alk, Ar)
(VI)
(R3 = H, Alk)
-R1O
(VII) (R3 = H, Alk)
(VIII)
(R3 = H, Alk, Ar, OAlk)

Scheme

quite basic (R^3 = H, Alk), it quickly captures proton from the medium with the formation of hydroxyphosphonate (IV) (product of the kinetic control). It is in a good agreement with the literature data[5,6], according to which the same substrates (unsaturated aldehydes, benzylideneacetone) are inclined to the formation under low conditions of adducts on carbonyl group. When the stability of (III) is high enough because of delocalization of anion charge by electron accepting substituents (R^3 = Ph, Ar, CH=CH-Ph) or (for R^3 = H, Alk) in presence of a large amount of catalyst, which creates obstacles to the formation of (IV) from (III), then addition of one more molecule of dialkylphosphites to C=C bond is carrying out to give the intermediate (V). The following stabilization of (V) is also determined by its basicity, i.e. by the nature of R^3. If R^3 = H, Alk, the basicity of (V) is high enough. In this case it may be stabilized by three different ways: protonation with the formation of bis-adduct (VI); intramolecular substitution to give phospholane (VII), and at last elimination of the phosphite anion with γ-ketophosphonate (VIII) formation. As known[7] in the case of benzylideneacetone, for instance, all three directions are realized under respective conditions. Similarly the reactions of dialkylphosphites with some unsaturated aldehydes[7,8] are carried out. It is obvious that in the case of intermediate's (V) low basicity, as it takes place in reactions of chalcone (R^3 = Ph) and cinnamon (R^3 = = CH=CHPh), it looses the ability to protonation and intramolecular cyclization and the single way of its stabilization is phosphite anion elimination with the formation of ketophosphonate (VIII).[6]

The mechanism suggested with the primary attack on the C=O group well explains many qualitative manifestations of the Pudovik reaction, such as a higher stability of hydroxyphosphonates (IV) in the cases of electron donating substituents at phosphorus or smaller amounts of alcoholate or less basic catalysts[5,6,9], and so on. However it does not mean that the direct attack of phosphite anion on the C=C bond is impossible in principle. It may be supposed that such an attack would be realized when carbonyl group participation is impeded by strong electronic or steric interaction. Our kinetic investigations actually show that the very reaction way takes place for cinnamylic esters[4] and also for sterically loaded 1:1 adduct of cinnamon with dibutylphosphinite. It is shown that the dialkylphosphites reactivity in the reactions investigated is controlled by the steric effect of the substituents at phosphorus.[10]

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