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INFLUENCE OF AN ORGANOPHOSPHORUS SUBSTITUENT ON THE NEIGHBORING REACTION CENTER

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 α -Functionalized organophosphorus substances containing P(O)-C-X fragment (where X is a functional group) are not only extremely promising syntones for the synthesis of various types of organophosphorus structures, but present a very convenient objects for the quantitative studies of electronic and steric influence of a complex organophosphorus group on the reactivity of various reaction centers.

In the presented work on the example of our own and literature kinetic investigations with the use of specially elaborated steric and inductive models it is shown, that this influence may be very considerable, realizing in the frame of electronic, steric and stereo-electronic effects each of whom may be dominating depending on the reaction series type and reaction conditions. It is established, that organophosphorus substituent may noticeably alter not only the reaction rate, but also the mechanism of the reaction, as it takes place for instance in the case of α -hydroxyphosphonates which, unlike the non-phosphorylated alkohols and amines, add to phenyl isocyanate by Ad_E (and not by Ad_N) mechanism.

Polar organophosphorus group at the reaction center may show also such specific effects as "the electrostatic umbrella effect", found and studied in the reaction of nucleophilic substitution in the chloromethylphosphine oxides series.