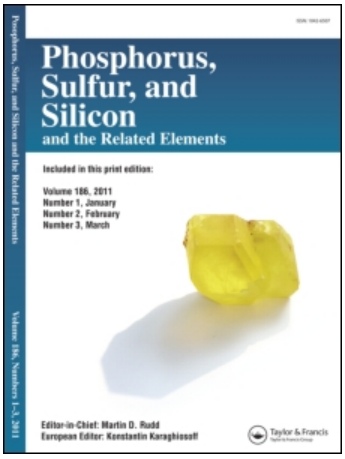

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A Stereospecific Synthesis of Dialkyl(Aryl)-2-Nitroeth-1-Enylphosphonates and their Reactions with Non-Carbon Nucleophiles

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Dialkyl 1-alkyl(aryl)-2-nitroen-1-enylphosphonates (1) are the important intermediate for the synthesis of functionalized phosphonic acids owing to the presence of reactive alkene and nitrogroups. It was expected that nucleophilic addition and subsequent reduction would result 2-aminoalkyl phosphonic acid derivatives. On the other hand, conversion of nitrogroup into silylnitronate as reactive 1,3-dipole provides new synthetic route to phosphoryl isoxazoles. Compounds 1 were prepared by treatment of dialkyl 1-alkyl(aryl)-1-hydroxy-2-nitroalkylphosphonates with thionyl chloride and pyridine. The dehydration process underwent stereospecifically providing exclusive E-ismers. An E2 reaction mechanism is suggested. Direct addition of alkoxide anion to nitroalkene constitute a general method for the preparation of nitroalkylether. As found by Feuer and Markofsky, by reaction of alkali alkoxide with 2-nitroalkene generated in situ from 2-nitroalkyl acetate, the yield of 1-alkoxy-2-nitroalkane was improved markedly. Investigation of the nucleophilic addition of phosphorylated nitroalkene was encouragable. As shown by us, 1-alkyl-2-nitrovinylphosphonates gave normal Michael addition products with alkoxi de anion. Reaction of 1-aryl-2-nitrovinylphosphonates with oxygen and nitrogen nucleophiles afforded unexpected phosphoryl enolate or phosphoryl enamine respectively via NO_2/alkoxy or NO_2/amine substitution. A tentative reaction mechanism was discussed.

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