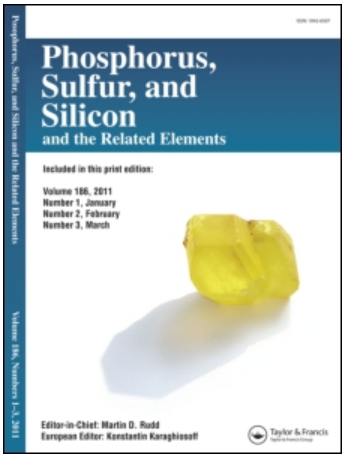

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Synthesis of 4,5-Dihydroisoxazoles Bearing Phosphonate Moiety

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SYNTHESIS OF 4,5-DIHYDROISOXAZOLES BEARING PHOSPHONATE MOIETY

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Introduction of phosphoryl group usually leads to the improvement of biological activity of the parent molecule. A facile synthetic route was introduced based on an intramolecular silylnitronate-olefin cycloaddition (ISOC) reaction. Thus, 3-(β-diethoxyphosphoryl)-ethyl-5-methoxycarbonyl - 4,5 -dihydroisoxazole (1), 3-(α-diethoxyphosphoryl- α-substituted methyl) - 5 - methoxycarbonyl - 4,5 - dihydroisoxazole (2) and 3 - methyl - 4 -alkyl(aryl) - 5 - bisphosphoryl - 4,5 - dihydroisoxazole (3) were prepared from diethyl methylphosphonate, diethylphosphite and methylene bisphosphonate respectively after treatment with BuLi or LDA and appropriate nitroalkene followed by $ClSiMe_3$. Condensation of but - 3 - en - 1 - yl phosphonate with nitroalkene, followed by $ClSiMe_3$, led to the stereoselective synthesis of fused carboisoxazole derivatives (4). In the case of aryl substituted α- nitroalkene, the reaction undergoes stereoselectively due to the formation of transition state of the least steric hindrance during the Michael addition step, which gave rise to the exclusive formation of erythro isomers. With alkyl substituted α- nitroalkenes, the diastereoselectivity was not obvious as the result of minor steric difference of the related groups. It seems necessary to point out that the stereochemistry involved in the ISOC reaction is quite different from an intramolecular nitrile - oxide olefin cycloaddition (INOC) process presumably due to the formation of transition states with diverse steric environments. Since 4,5-dihydroisoxazole derivatives are synthetic equivalent of β- hydroxy ketones, 1,3 - diketones, γ- aminoalcohols, α β- unsaturated ketones, the present contribution should expand the field of applications of 4,5 -dihydroisoxazole derivatives in the natural products synthesis by building block strategy.

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