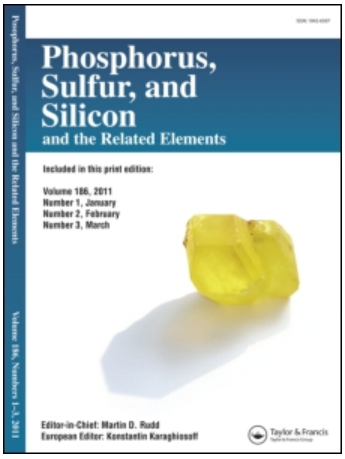

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New Method for the Synthesis of α-Amino Substituted Benzyl Phosphonic Acids and their Derivatives

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New Method for the Synthesis of α–Amino Substituted Benzyl Phosphonic Acids and their Derivatives

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A new method for the synthesis of α-amino-substituted benzylphosphonic or phosphinic acid (5) was descrided. By reaction of phosphoramides (1) with substituted benzaldehydes (2) and phosphite (3) in the presence of BF_3, α-(N-phosphorylamino)-substituted benzylphosphonates or phosphinates (4) was obtained in moderate to good yield. This method distinguished itself by the simple manipulation and higher purity of the product resulted in both steps of the reaction sequences. Meanwhile, aminophosphonic esters are useful intermediated in the phosphorus peptide synthesis. The influence of variation in structure of 1, 2 and 3 on the yield of 5 was evaluated on the basis of sturcture-reactivity studies.

Since the presence of BF_3 is essential in this reaction due to the weak nucleophilicity of 1, the reaction mechanism involving the attack of latter by reactive complex formed via the coordination of BF_3 with 2 was postulated. The electrophility of the carbonyl carbon was thus enhanced. If chlorophosphite (3,R'=Cl) was utilized as phosphorus component, $ZnCl_2$ should be used as catalyst. An oxygen-transfer phosphorylation mechanism was proposed.

Kinetic measurement of acidolysis of compound 4 was performed by HPLC for the mechanistic and structure-reactivity stueies. Both K and Ea correlated linearly with σ constants of the nuclear substituents. The dialkylphosphoryl or thiophosphoryl group behaves itself as protective group for amino-function.

A corralation analysis between ^{31}P NMR chemical shifts and constants was also encounted.