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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 benzyl-phosphonic or phosphinic acid (5) was described. 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 intermediates 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 structure-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 electrophilicity of the carbonyl carbon was thus enhanced. If chlorophosphite (3, $\text{R}'=\text{Cl}$) 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 studies. Both k and E_a correlated linearly with σ constants of the nuclear substituents. The dialkylphosphoryl or thiophosphoryl group behaves itself as protective group for amino-function.

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