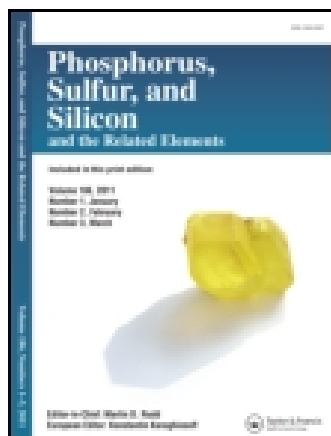




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Synthesis of N-Protected *o*-Hydroxyl-phenyl— α -Aminophosphonic Monoester

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A series of N-protected O-hydroxylphenyl α -aminophosphonic monoesters were synthesized via three-component Mannich-type reactions of phosphoramides, aldehydes (ketones) and 2-chlorobenzo [1,3,2] dioxaphospholes under solvent free and catalyst-free conditions, followed by hydrolysis. It is an efficient and green method to the synthesis of N-phosphoramino O-hydroxyphenyl 1-aminoalkylphosphonic monoesters with high yields.

Keywords α -aminophosphonic monoesters; Mannich-type reaction; no catalyst and solvent-free

α -Aminophosphonic and phosphinic acids are the phosphorous analogues of α -aminocarboxylic acids, and therefore have biological importance both in themselves and as building blocks for peptides.¹ They have acquired great attention in synthetic organic chemistry and a number of synthetic methods have been developed during past two decades. Of these methods, nucleophilic addition of phosphites to imines catalyzed by a base or an acid is the most convenient one. A variety of metal halides such as TiCl_4^2 , InCl_3^3 , $\text{TaCl}_5\text{-SiO}_2^4$, $\text{Mg}(\text{ClO}_4)_2^5$ have been used as Lewis acid catalysts in methylene chloride or other organic solvent to promote this addition. To avoid these disadvantages of the use of organic solvents, a couple of modifications using montmorillonite clay⁶ and alumina,⁷ $\text{BiNO}_3\cdot 5\text{H}_2\text{O}^8$ in dry media under microwave irradiation have

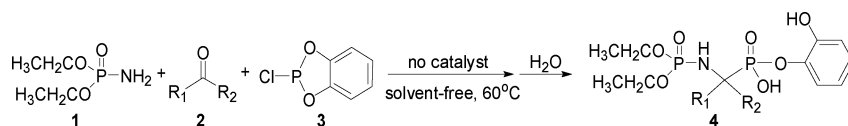
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TABLE I Preparation of α -aminophosphonic monoesters 4a–i

4	R ₁	R ₂	Yield (%)	4	R ₁	R ₂	Yield (%)
4a	<i>p</i> -Cl-C ₆ H ₅	H	80	4f	<i>p</i> -CH ₃ O-C ₆ H ₅	H	90
4b	<i>o</i> -Cl-C ₆ H ₅	H	92	4g	<i>p</i> -NO ₂ -C ₆ H ₅ H	H	93
4c	<i>p</i> -Br-C ₆ H ₅	H	89	4h	(CH ₂) ₅	—	84
4d	<i>o</i> -Br-C ₆ H ₅	H	85	4i	CH ₃	CH ₃	87
4e	C ₆ H ₅	H	91	—	—	—	—

been reported. In 2002, Ranu⁹ reported a more practical green alternative for the synthesis of α -aminophosphonates by a three-component condensation of carbonyl compounds (aldehydes and ketones), amines and diethyl phosphite at 75–80°C in neat without any solvent and catalyst. We would like to disclose a practical and green method for the synthesis of N-protected *o*-hydroxyl-phenyl- α -aminophosphonic monoester under the condition of no catalyst and solvent-free (Scheme 1).

**SCHEME 1**

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