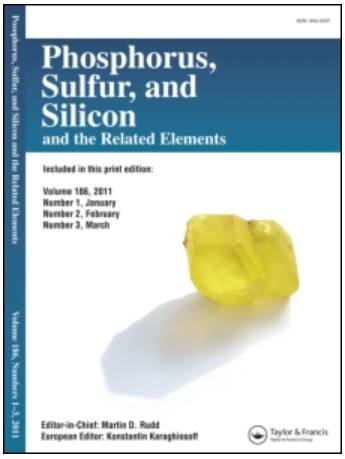

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Synthesis of N-Protected *o*-Hydroxyl-phenyl—α-Aminophosphonic Monoester

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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

$\alpha-$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 $TiCl_4^2$, $InCl_3^3$, $TaCl_5$-SiO_2^4, $Mg(ClO_4)_2^5$ 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 clay[6] and alumina,[7] $BiNO_3 \cdot 5H_2O$[8] in dry media under microwave irradiation have

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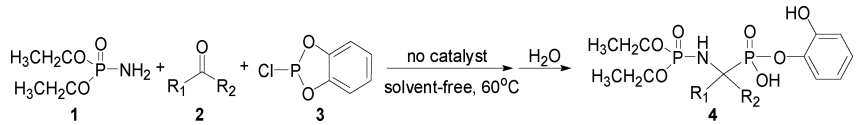
TABLE I Preparation of α-aminophosphonic monoesters 4a–i

4	R_1	R_2	Yield (%)	4	R_1	R_2	Yield (%)
4a	*p*-Cl-C_6H_5	H	80	**4f**	*p*-CH_3O-C_6H_5	H	90
4b	*o*-Cl-C_6H_5	H	92	**4g**	*p*-NO_2-C_6H_5H	H	93
4c	*p*-Br-C_6H_5	H	89	**4h**	$(CH_2)_5$	—	84
4d	*o*-Br-C_6H_5	H	85	**4i**	CH_3	CH_3	87
4e	C_6H_5	H	91	**—**	—	—	—

been reported. In 2002, Ranu[9]reported a more practical green alterative 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).



1 2 3 4

SCHEME 1

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