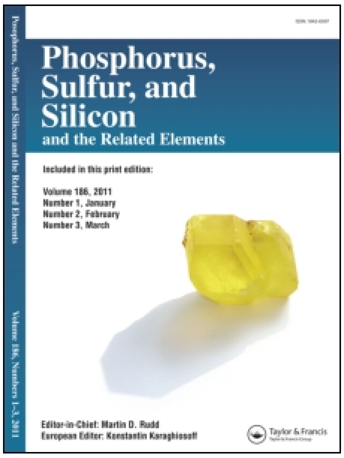

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Novel Methods for the Synthesis of Phosphonate Esters on the Solid Surface

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NOVEL METHODS FOR THE SYNTHESIS OF PHOSPHONATE ESTERS ON THE SOLID SURFACE

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Phosphonate esters are versatile intermediate in organic synthesis. These compounds have found a wide range of application in the areas of industrial, agricultural, and medicinal chemistry owing to their physical properties as well as their utility as synthesis intermediates. The synthesis of some phosphonate esters under solvent free condition was described. These methods are easy, rapid, and high-yielding reactions for the synthesis of phosphonate esters.

Keywords: Alumina; diethylphosphite; magnesia; microwave; phosphonate esters

In recent years, considerable interest has been focused on the synthesis of phosphonic acids, particularly the α-substituted analogs that are an important class of compounds with applications as antibiotics, antiviral agents, and enzyme inhibitors.[1] Among the α-functionalized phosphonic acids, α-aminophosphonic acid derivatives are gaining in interest in medicinal chemistry. A number of synthetic methods for the synthesis of 1-aminophosphonates has been developed during the past two decades.[2] Of these methods, the Kabachnik-Fields[3] synthesis of 1-aminophosphonates, catalyzed by a base or an acid, is the most convenient. The key step in the Kabachnik-Fields synthesis of 1-aminophosphonates is the nucleophilic addition of an amine to a carbonyl compound followed by the addition of a dialkyl or diaryl phosphite to the resulting imine. The formation of 1-hydroxyphosphonates or a product of its rearrangement frequently accompanies the formation of 1-aminoalkyl phosphonates.[4] Lewis acids, such as $SnCl_2$, $SnCl_4$, $BF_3 \cdot Et_2O$, $ZnCl_2$, $MgBr_2$, and $InCl_3$, have been used as catalysts; however, these reactions cannot be carried out in a one-step operation with the carbonyl compound, amine and dialkyl phosphite, because the

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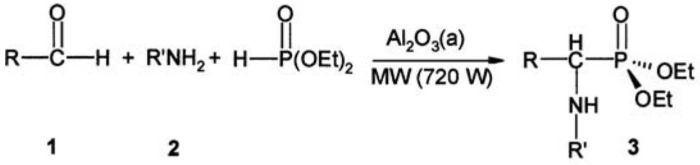
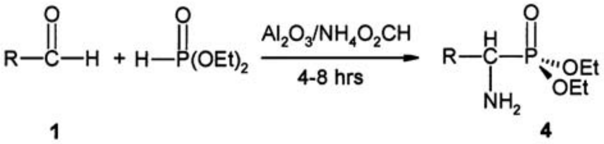
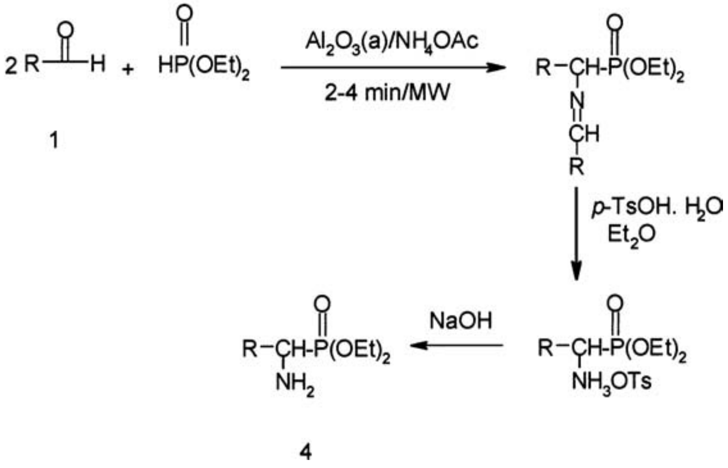
amines and water that exist during imine formation can decompose or deactivate the Lewis acids.[5] Surface-mediated solid-phase reactions are of growing interest because of their advantages of ease of set up, mild conditions, rapid reactions, selectivity, increased yields of the products, and low cost compared with their homogeneous counterparts. Acceleration of organic reactions by microwave dielectric heating has been widely exploited. Microwave irradiation using solvent-free conditions has also shown its utility in organic synthesis. As a part of our efforts to explore the utility of surface-mediated reactions for the synthesis of organophosphorus compounds,[6] herein some new methods for the synthesis of 1-aminophosphonates on the solid surface are described.







The reactions were clean with no tar formation, and, interestingly, no product from the 1-hydroxyphosphonate was observed. Indeed, a wide range of aldehydes and amines was converted into the corresponding 1-aminophosphonates using this reaction procedure.

Using solid-phase synthesis also was successful in the synthesis of 1-hydroxyphosphonates, acylphosphonates, alkylphosphonates, and phosphorylation of phenols.

In summary, a simple work-up, low consumption of solvent, relatively fast reaction rates, mild reaction conditions, good yields, and the selectivity of the reactions make these methods an attractive and useful contribution to present methodologies.

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