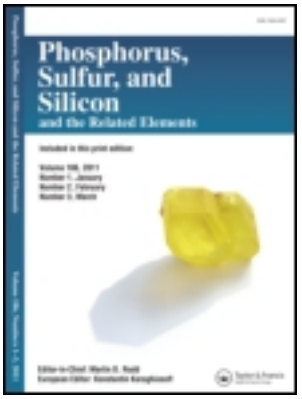

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A PRACTICAL AND EFFICIENT GREEN SYNTHESIS OF β-AMINOPHOSPHORYL COMPOUNDS VIA THE AZA-MICHAEL REACTION IN WATER

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Abstract *Application of water as a solvent (without any cosolvent) promotes the aza-Michael reaction of diethyl vinylphosphonate and diphenylvinylphosphine oxide with a wide range of N-nucleophiles. The solubility of the starting phosphorus substrate in water does not play a crucial role in the reaction course, decreasing to some extent the reaction rate. The reaction can be performed either at room temperature or under reflux to afford the corresponding β-aminophosphonates and β-aminophosphine oxides in excellent yields and of high purity via a simple freeze-drying isolation procedure. Application of basic catalysts makes possible the addition of weak nucleophiles such as α-amino acids and their phosphorus analogues; that is, α-aminophosphonic acids. The aqueous aza-Michael reaction allowed us to easily perform double phosphorylation of primary amines including polyamines using a reactant ratio (phosphorus substrate: amine) of 2:1.*

Keywords β-Aminophosphoryl compounds; aza-Michael reaction; green chemistry; nucleophilic addition; phosphaalkenes; water

INTRODUCTION

The most relevant challenges of modern organic chemistry are atom economy, chirality economy, and performing reactions under environmentally friendly conditions. In the scope of general problems in making chemistry greener, the problem with solvents has become the focus. Theoretically, green chemical processes should be performed under solvent-free conditions, and some organophosphorus reactions, e.g., the Wittig reaction and the Kabachnik-Fields reaction and its two-component version were successfully performed by this way mainly under microwave assistance.[1] However, this approach may be impossible or unprofitable in a variety of cases, dictating the need for design or adaptation of the required technological processes of so-called green solvents such as ionic liquids (ILs), water, and supercritical liquids as the main alternatives to toxic, flammable, and hazardous organic solvents. The importance of this area can be demonstrated by the

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continuous increase in the number of papers and patents in recent decades. Indeed, ionic liquids, due to their ability to dissolve a variety of organic, inorganic, and metal complex materials and promote a great number of chemical transformations, in addition to their nonvolatile nature, low toxicity, and potential for recyclability, are finding their way into a wide variety of industrial applications.[2] Similarly, many chemical and related processes have been developed using the inherent physical and chemical properties of supercritical fluids.[3] Supercritical fluid technology applied to materials processing can play also a great role in materials science.[4] Furthermore, organic reactions in water which is the least expensive, nontoxic solvent (known also as *nature's solvent*) until about decade ago were a mere curiosity for only a few practitioners. Now this area has become very popular and some excellent reviews on this topic may be found in the literature.[5]

Nevertheless, the above-mentioned green solvents enter very slowly into organophosphorus chemistry compared to general organic synthesis, apparently because of common warnings pertaining to the instability of organophosphorus compounds. The known examples of application of ionic liquids and water as alternative media able to promote some principle organophosphorus reactions leading to the substances of practical and research importance were reviewed by us recently.[6]

Among those, our own results dealing with the aza-Michael additions of amines to vinylphosphonates in water (without any catalyst or cosolvent) as an effective, simple, and ecologically friendly approach to biologically active β-aminophosphonates were mentioned. In this article we outline the advantages and limitations of this method for both soluble and insoluble in water substrates. The results have been partially published[7,8] and some are communicated preliminarily in this article.

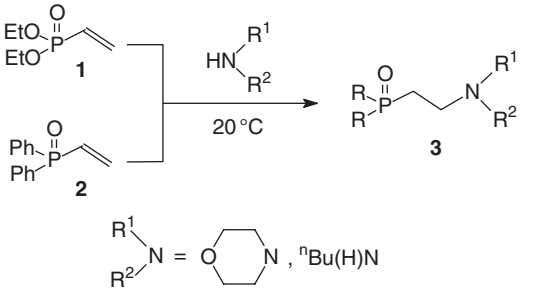
RESULTS AND DISCUSSION

The aza-Michael reaction is one of the most general and widely used methods for building up new carbon–nitrogen bonds, especially in the synthesis of a variety of β-aminocarbonyl compounds and their analogues, which possess biological activity and useful are as intermediates in further synthesis of β-aminoalcohols, amino acids, lactames, etc. In the organophosphorus area, a similar approach using vinylphosphonates as the starting substrates and yielding β-aminophosphonates was firstly applied by A. N. Pudovik in 1951.[9] This methodology provided a wide range of β-aminophosphonates (note that β-aminophosphonic acid is a natural compound isolated from *Celiate protozoa* by Horiguchi and Kandatsu[10] in 1959) possessing diverse biochemical properties such as antibacterial, anti-HIV, and protease-inhibiting activities[11] that are useful as synthetic nonviral vector-mediated gene transfer agents.[12] These compounds also possess complexing properties[13] that are advantageous for selective ionophores or membrane carrier design.[11b] Moreover, β-aminophosphine oxides are useful building blocks in the synthesis of the corresponding P,N-ligands bearing phosphine donor moieties.[14]

In the nonphosphorus version of the aza-Michael addition to α,β-unsaturated carboxylic acid esters, nitriles, or amides, the process was accelerated by a wide range of catalysts including bases,[15] Lewis,[16] or Brønstead[17] acids, coordination compounds of platinum group,[18] tributylphosphine,[19] copper nanoparticles,[20] sugars,[21] *N*-methylimidazole,[22] poly(*N*-vinylimidazole),[23] and so on, as well as via using ionic liquids,[24] biphasic systems IL/water,[25] and water[26] as promoting media. In contrast, before the beginning of our works, the reactions of vinylphosphonates or vinylphosphine oxides were commonly performed using the excess amine (either neat or in combination with a solvent) and basic catalysts,

such as EtONa or metal sodium, under elevated temperatures over prolonged reaction times. Therefore, such severe conditions do not avoid the polymerization of the starting vinyl substrates, substantially decreasing the yields of the desired products. The known attempts to optimize the synthesis of β-aminophosphoryl compounds were limited by using MeOH[14b] as a protic solvent and a combination of the excess amine with water (closed ampoule, 110°C, 7 days),[13b] which were performed in both cases using diphenylvinylphosphine oxide as a starting substrate.

In order to develop an efficient green synthesis of β-aminophosphoryl compounds of doubtless practical importance, first of all, we estimated the possibility to use imidazolium ILs as the promoting media for the aza-Michael reaction since nucleophilicity of amines in ionic liquids are known to increase comparing with that in common organic solvents.[27] The reactions of diethyl vinylphosphonate **1** and diphenylvinylphosphine oxide **2** with morpholine and butylamine were used as a model (Scheme 1). The difference in chemical shifts of the phosphorus substrates (17.2 and 24.3 ppm for **1** and **2**, respectively) and the corresponding products (ca. 30–31 ppm) allowed easy monitoring of the reaction course by ^{31}P-NMR spectroscopy. To our surprise, in contrast to the reported data concerning the acceleration of the aza-Michael addition for nonphosphorus activated alkenes, the reactions in ILs differing in anion nature were either too sluggish (2–9% yield over 45 min at rt) or do not proceed at all under the above conditions.[8]



Scheme 1

Addition of water to ionic liquid, that is, using the mixture IL/H_2O in a 1:2 ratio (by weight) resulted in a drastic increase of the reaction rate. Under these conditions morpholine was more reactive compared to $^{n}BuNH_2$. The ILs with hydrophobic tetrafluoroborate and hexafluorophosphate anions were less effective for vinylphosphonate **1**, whereas for phosphine oxide **2** the reaction proceeds faster in [bmim]BF_4. Note that the electronic factors for these compounds are close to each other (σ_P is 0.965 and 0.955 for $Ph_2P(O)$ and $(EtO)_2P(O)$ groups, respectively[28]) and steric factors at the remote phosphorus centers should not interfere with the reaction. Therefore, one may assume that the influence of the phosphorus substrate structure on the reaction rate is apparently connected with the specific solvatation of the latter in the mixed solvent in use.

Nevertheless, despite mild reaction conditions (rt, 30 min to 3 h depending on the nature of both components) and excellent yields of β-aminophosphoryl compounds obtained, according to the ^{31}P-NMR data in the IL/water systems, a substantial loss of a product was observed over its extraction with organic solvents.

At the same time, if water was used as the sole medium without any cosolvent or catalyst, the addition of both amines to diethyl vinylphosphonate **1** proceeded with a

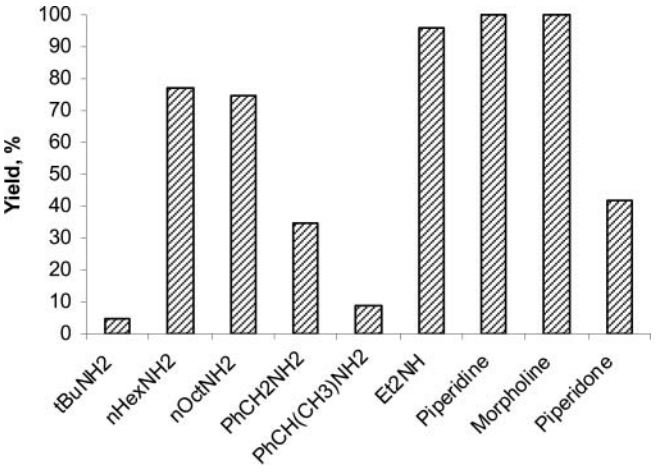
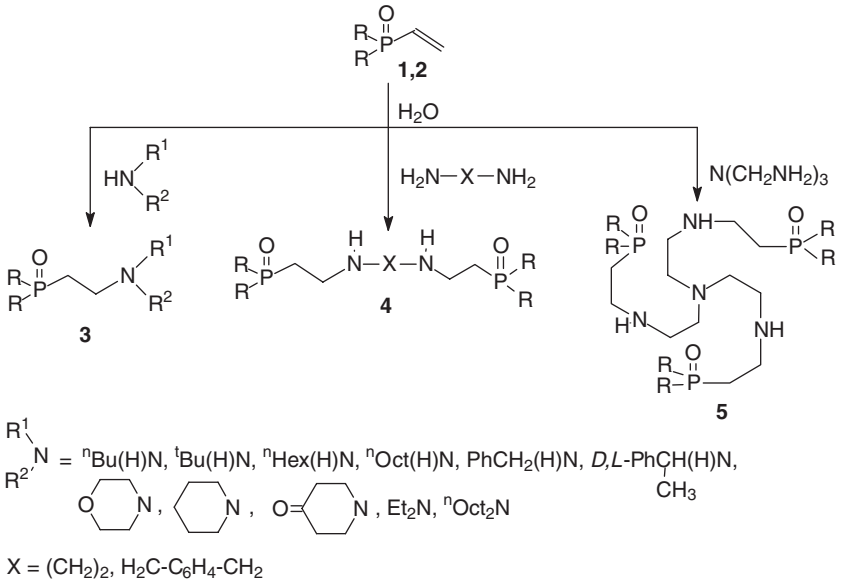


Figure 1 Yields of β-aminophosphonates **3** (indicated above the columns) obtained in reaction of $(EtO)_2P(O)CH{=}CH_2$ **1** with different amines in water (20°C, 45 min).

reaction rate commensurable with that observed in the case of the optimal biphasic system [bmim]Br/H_2O. Even in the case of insoluble in water diphenylvinylphosphine oxide **2**, for which the reaction proceeds in water slower than in the [bmim]BF_4/H_2O system, the prolonged reaction time allowed complete addition at room temperature. Isolation of the final products in quantitative yields after the removal of a solvent (lyophilization) makes the method really green, very simple, and efficient.[7,8]

Detailed investigation of the aza-Michael addition has revealed that the nucleophilicity of amine is the main factor influencing the reaction rate for both phosphorus substrates; that is, it decreased in the series: $Alk_2NH > AlkNH_2 > ArCH_2NH_2$. The steric properties of amine are the second crucial factor. As an illustration, Figure 1 shows the yields of β-aminophosphonates obtained in the reaction of **1** with different amines over 45 min at room temperature. As one can see, the cyclic secondary amines are more active than the linear ones (note that the reaction with piperidine completed after 7 min), excluding less nucleophilic piperid-4-one bearing the carbonyl function. The yield of 2-(*tert*-butylamino)ethylphosphonate is significantly lower comparing to that for its analogue with n-butyl group. Note that aromatic amines did not enter the reaction.

In general, in the case of water-soluble vinylphosphonate **1**, a longer reaction time (up to 48 h in the reaction with ethylenediamine) provided a complete conversion at room temperature, but in the case of phosphine oxide **2**, it took days. However, no side reactions were observed upon performing the reactions at reflux. Hence, the elevated temperatures were used to reduce the reaction time and the quantitative yields of β-aminoethylphosphine oxides were achieved over 30 min for more reactive secondary amines and in a few hours in other cases. Optimized conditions, that is, under ambient conditions for the reactions of vinylphosphonate **1** with more reactive amines and at 100°C in the case of less reactive amines and for addition to diphenylvinylphosphine oxide **2**,[7,8] were used for the synthesis of a wide range of β-aminophosphoryl compounds (Scheme 2) isolated after lyophilization with purity >95% according to multinuclear NMR spectral data. It should be noted that if more than one amine functionality was present in the N-nucleophile, as in ethylenediamine, *meta*-xylylenediamine, and tris(2-aminoethyl)amine, the addition

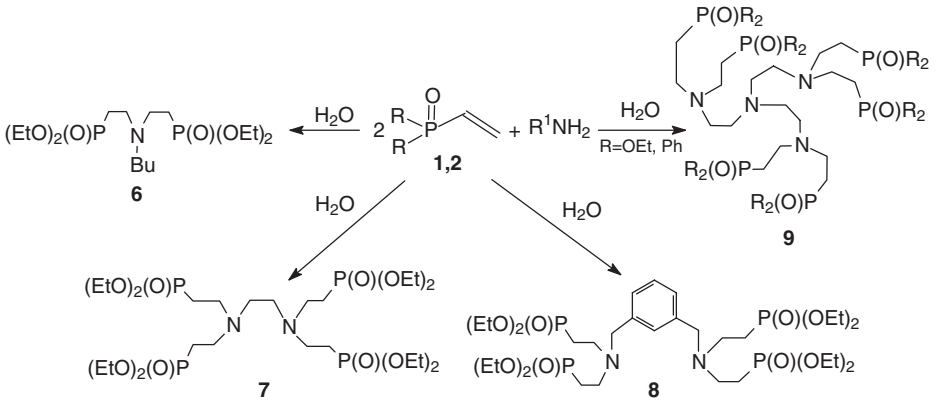


Scheme 2

in water proceeded readily with participation of all of the amine functionalities using an appropriate ratio of the reactants.

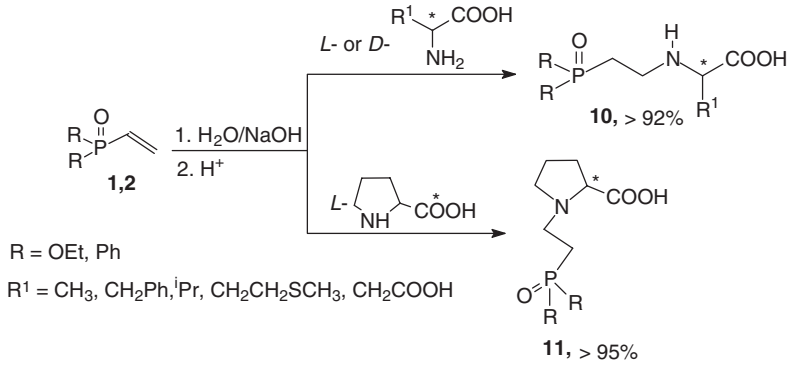
When the starting reactants were used in a 1:1 ratio, only mono adducts were formed in the reactions with primary amines and no traces of the corresponding bis-addition products were observed via the ^{31}P-NMR spectroscopy. However, use of the reactants in the ratio $R_2P(O)CH{=}CH_2$/amine = 2:1 allowed double phosphorylation of primary amines. In other words, β-aminophosphoryl compounds formed may serve as suitable N-nucleophiles for addition to vinylphosphonate and vinylphosphine oxide in water. To the best of our knowledge, no examples of such reactions have been observed previously for diethyl vinylphosphonate **1**, whereas for diphenylvinylphosphine oxide **2** double phosphorylation was performed previously only under severe conditions.[13a,14b,29] It should be emphasized that for nonphosphorylated activated alkenes the double addition to primary amines was not observed in water as a reaction medium.[26] According to ^{31}P-NMR monitoring of the reaction course, the reaction proceeded via a stepwise process, giving firstly the mono adducts followed by the addition to a second molecule of the corresponding vinylphosphoryl compound. Indeed, introduction of the phosphorylethyl moiety to the nitrogen atom of hexylamine reduces the basicity by 3 pK_a units (pK_a is equal to 10.4 and 7.4 for $HexNH_2$ and $HexNH\text{-}CH_2CH_2P(O)(OEt)_2$, respectively, as measured in water/i-PrOH (1:1) mixed solvent).

Therefore, taking into account the difference in reactivity of vinylphosphoryl compounds **1**,**2** in water, we performed the target syntheses of oligo(phosphorylethyl)-substituted amines **6–9**, which are useful as complexing agents for different metals at room temperature for phosphonate **1** and at 100°C for vinylphosphine oxide **2** (Scheme 3). As in the above cases, all compounds bearing two phosphorylethyl moieties at the same nitrogen atom were isolated in quantitative yields with high purity (>95%) after a simple lyophilization procedure.



Scheme 3

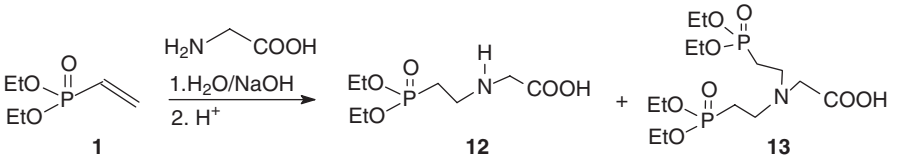
Furthermore, the growing interest in new excitatory amino acid antagonists, in particular selective antagonists of the *N*-methyl-D-aspartate (NMDA) subtype of glutamate receptors combining in the molecular structure the phosphonate moiety and the residue of some amino acids useful for treatment of neurodegenerative disorders,[30] prompted us to involve amino acid derivatives as N-nucleophiles into the aqueous aza-Michael addition. However, neither amino acid esters nor free acids reacted with vinylphosphoryl compounds in the absence of a catalyst, possibly due to a decrease in their nucleophilic properties and formation of zwitterionic species in the case of free acids. Catalytic amounts of tertiary amines (10 mol% Et_3N, $^iPr_2NEt$, or 5 mol% DMAP) accelerated the reaction of vinylphosphonate **1** with *D,L*-alanine used as a representative example; however, the conversion was only ~30% after 3 days at room temperature. Although an increase in the proportion of tertiary amine (Et_3N) up to 1 molar equivalent provided the complete conversion over 24 h in the same reaction and over 6 h in the reaction with *D,L*-proline, we failed to isolate free phosphorylated amino acids **10** by the crystallization or chromatography technique. These drawbacks were avoided in the addition to vinylphosphoryl compounds **1**,**2** of amino acid sodium salts formed in situ, which proceeded readily and provided excellent yields of the desired phosphonates and phosphine oxides **10**,**11** isolated after acidification and removal of water in vacuo, followed by treatment with ethanol to remove the precipitated sodium chloride (Scheme 4). After optimization, optically active *L*- or *D*-amino acids were



Scheme 4

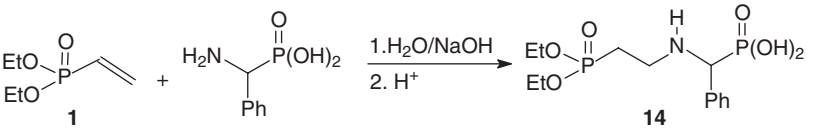
involved in the reaction. Because the chiral carbon atom is not affected over the reaction course, using optically active starting materials, the phosphorylated amino acids **10**,**11** were obtained in optically pure form.

As one may expect, the reactivity of amino acids decreased in the series proline > alanine > phenylalanine; that is, the regularities are similar to those found for nonsubstituted amines where the secondary amine is more reactive than the primary one and steric hindrances decrease the reaction rate. Note that in contrast to other amino acids, the addition of glycine in a 1:1 molar ratio of the reactants afforded a mixture of the corresponding mono- and diphosphorylated products in a 6:4 ratio (**12** and **13**, respectively, Scheme 5). Using a stoichiometric ratio of the reactants resulted in bis(phosphorylethyl)-substituted glycine in a yield close to the quantitative one. We managed to perform the double phosphorylation of *D*-alanine in 85% yield only over 2 days at 70°C.



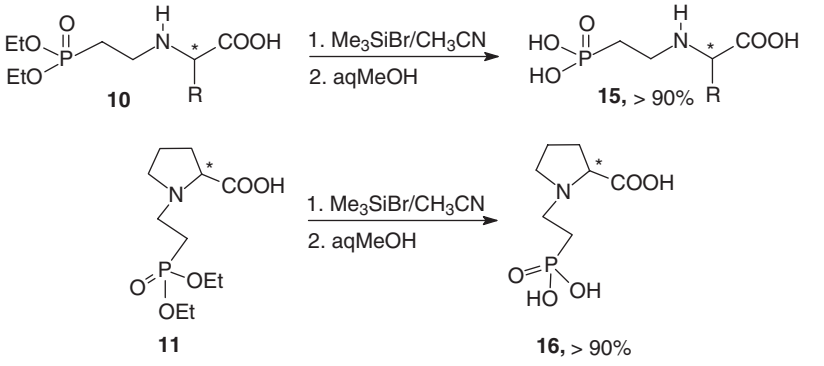
Scheme 5

A similar approach allowed us to carry out the addition of α-aminophosphonic acid to vinylphosphonate **1** to afford the hybrid molecule of α,β-aminophosphonates (Scheme 6).



Scheme 6

Finally, β-aminophosphonates including those bearing the residues of amino acids can be easily converted to the free phosphonic acids via the treatment with Me_3SiBr in acetonitrile followed by methanolysis of the intermediate silyl esters (Scheme 7).



Scheme 7

CONCLUSION

It seems reasonable that acceleration of the aza-Michael addition in ionic liquids in the presence of water or in water alone is promoted by hydrogen bond formation between the H-atom of water with the oxygen atom of the phosphoryl moiety, increasing the electrophilic character of the β-carbon atom, and between the H-atom of the amine with the oxygen atom of water, resulting in increased amine nucleophilic properties. The higher reaction rate in the IL/water biphasic systems in the case of vinylphosphine oxide **2**, which is nonsoluble in water, may be explained by the possibility of IL to serve as a phase transfer agent. Although the rate of the aza-Michael addition in water for vinylphosphoryl compounds is lower than that for more electrophilic α,β-unsaturated carboxylic acid esters, nitriles, or amides, it proceeds much faster compared to the known procedures for the synthesis of β-aminophosphoryl compounds, providing excellent yields of both mono- and diphosphorylated products, including the amino acid derivatives, requiring at the same time a very simple isolation procedure. Such an effective, cheap, and green approach offers wide possibilities to prepare a variety of biologically active substances, complexing agents, or molecular sensors. In general, the wide scope in aqueous synthesis of a variety of β-aminophosphoryl compounds including optically active ones, which provide 100% atom economy using readily available starting materials, proceeds in a natural solvent under mild reaction conditions and results in the desired compounds in high yields without any by-products after a very simple isolation procedure, satisfying all of the stringent criteria for classification as a click reaction.[31]

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