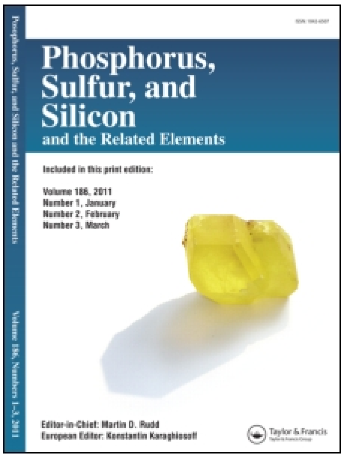

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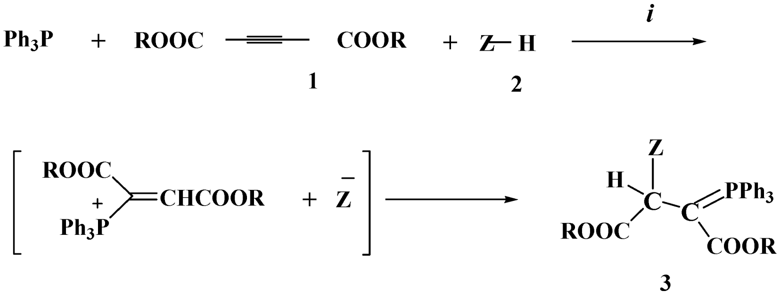

***i*.H_2O,Polyacrylamide**

Stable crystalline phosphorus ylides were obtained in good to excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dialkyl acetylenedicarboxylates and β-dicarbonyl or heterocyclic compounds such as, diethyl malonate, acetyl acetone, 1, 3-dimethylbarbituric acid, meldrum's acid, 2-benzoxazolinone, pyrrole-2-carboxaldehyde, benzotriazole, 5-methyl benzotriazole, and 5-chloro benzotriazole, in the presence of polyacrylamide in water. The green and mild reaction conditions, medium to short reaction time, low cost, ready preparation are the main advantages of this method.

Keywords Acetylenic esters; water; triphenylphosphine; stable phosphorus ylides; polyacrylamide

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INTRODUCTION

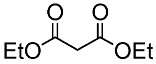
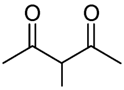
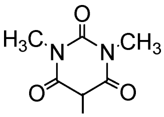
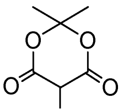
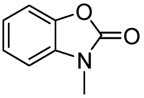
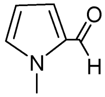
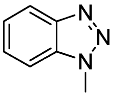
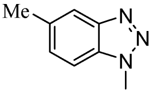
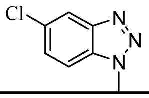
Recently, organic reactions in water have attracted much attention because water as a solvent is not only inexpensive and environmentally benign, but also shows completely different reactivity to organic solvents.[1–5] Various reactions that are traditionally carried out in organic solvents have been equally successful or even more effective in aqueous media.[6–12] If water could also replace organic solvents more often on the industrial scale, it would save money, increase the safety of chemical facilities, and reduce stress on the environment. Another advantage is that after the reaction, the organic and aqueous phases separate, eliminating the need for complex isolation steps to obtain the product. In recent years there has been increasing interest in the synthesis of organophosphorus compounds having a carbon atom bonded directly to the phosphorus atom.[13–15] This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial, and chemical synthetic uses. A large number of methods have appeared describing novel syntheses of organophosphorus compounds. The preparation of phosphorus ylides generally involves the initial addition of a desired phosphine to an alkyl halide to provide a phosphonium salt. Subsequently, addition of a base to the salt affords the required phosphorus ylide.[14,16]

Thus, the preparation of the required phosphorus ylide often needs two steps that involve the formation of phosphonium salts as intermediates and the addition of a base to convert these salts to ylides. Traditionally, these steps often occur in organic solvents, such as diethyl ether, tetrahydrofuran, and toluene. Phosphorus ylides have earlier been prepared in several steps using a basic aqueous solution.[17] The mechanical generation of phosphonium salts and phosphorus ylides in the solid state followed by the Wittig reaction in the absence of a solvent has been described.[18,19] In the course of our investigation devoted to the development of synthetic methods for the preparation of organic compounds using phosphorus compounds, we found that the addition of polyacrylamide to water provided an efficient system for the synthesis of stable phosphorus ylides in aqueous media.

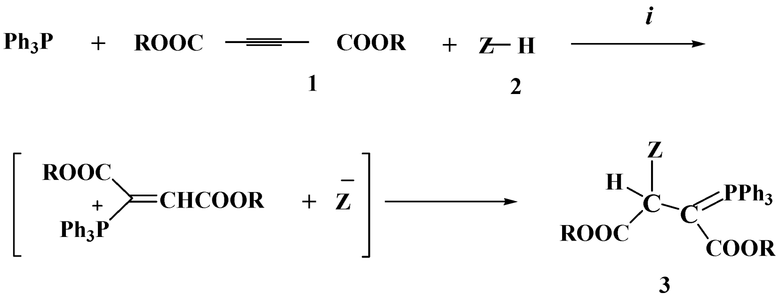
RESULTS AND DISCUSSION

We found that the reaction of triphenylphosphine with acetylenic esters (**1**) and β-dicarbonyl or heterocyclic compounds (**2**), in water (without additives of organic solvents) afforded the corresponding stable phosphorus ylides (**3**) in good to excellent yields (Scheme 1).

TABLE I Synthesis of Stable Phosphorus Ylides in the Presence of Polyacrylamide in Water at Room Temperature

Entry	Z	Product	R		
1		3a	Me	85	192–194
2		3b	Et	75	164–166
3		3c	Me	85	174–175
4		3d	Et	76	165–166
5		3e	t-Bu	85	146–148
6		3f	Me	86	154–156
7		3g	Et	75	153-155
8		3h	t-Bu	90	161–163
9		3i	Me	89	181–183
10		3j	Et	78	163–165
11		3k	t-Bu	90	182–183
12		3l	Me	95	160–162
13		3m	Et	89	185–187
14		3n	t-Bu	92	190–193
15		3o	Me	83	178–180
16		3p	Et	71	154–156
17		3q	t-Bu	85	191–193
18		3r	Me	91	143—145
19		3s	Et	73	147–149
20		3t	t-Bu	83	155–157
21		3u	Me	86	163–165
22		3v	Et	71	147–149
23		3w	t-Bu	82	165–167
24		3x	t-Bu	85	170–172

Based on the well-studied chemistry of trivalent phosphorus nucleophiles,[20,21] it is reasonable to assume that phosphorus ylide (**3**) is formed due to the initial addition of triphenylphosphine to the acetylenic ester (**1**) and concomitant protonation of the 1:1 adduct by the β-dicarbonyl or heterocyclic compounds such as diethyl malonate, acetyl acetone, 1,3-dimethylbarbituric acid Meldrum's acid, 2-benzoxazolinone, pyrrole-2-carboxaldehyde, benzotriazole, 5-methyl



i. H_2O,Polyacrylamide

SCHEME 1

benzotriazole, and 5-chloro benzotriazole, to form phosphoranes (**3**) were obtained in good to excellent yields. The results are summarized in Table I.

The spectral data and physical properties of the phosphoranes **3a–x** were in agreement with those of literature reported.[22–27]

CONCLUSION

In conclusion, we showed that polyacrylamide could be used for a convenient and rapid synthesis of organophosphorus compounds in aqueous media. Although, the yields of corresponding products are not better than those for organic solvents, but the reaction times are shorter and water as a solvent has advantages, including its low cost, low flammability, and most important, that it is non-toxic.

EXPERIMENTAL

Dialkyl acetylenedicarboxylates, triphenylphosphine, diethyl malonate, acetyl acetone, 1,3-dimethylbarbituric acid, Meldrum's acid, 2-benzoxazolinone, pyrrole-2-carboxaldehyde, benzotriazole, 5-methyl benzotriazole, and 5-chloro benzotriazole, were obtained from Fluka or Merck companies. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-460 spectrometer (pellets with KBr). ^1H NMR spectra were measured on a Bruker DRX-500 AVANCE spectrometer instrument with $CDCl_3$ as solvent.

Preparation of Stable Phosphorus Ylides—General Procedures

To a magnetically stirred solution of a C-H or N-H acid (1 mmol) and polyacrylamide (0.0025 g) in water (10 mL), Ph_3P (0.26 g, 1 mmol) was added. Dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) was added dropwise at room temperature over 10 min. After approximately 1–5 h of stirring, the solution was filtered and was washed with dichloromethane. The solvent was evaporated under reduced pressure, and the precipitate was thoroughly washed with cold diethyl ether.

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