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An efficient method for synthesis of organophosphorus compounds in aqueous media

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Abstract

A convenient and facile one-pot synthesis of stable phosphorus ylides and 1,4-diionic organophosphorus compounds is reported by the reaction of triphenylphosphine, dialkylacetylenedicarboxylates and N–H, C–H or S–H acids in the presence of polyethyleneglycol (PEG), β-cyclodextrin (β-CD), glycerine (Gly) or ethyleneglycol (EG) in water. This methodology is of interest due to the use of water as a solvent, thus minimizing the cost operational hazards, and environmental pollution.

Keywords: Water; Triphenylphosphine; Acetylenic esters; Stable phosphorus ylides; Polyethyleneglycol; β-Cyclodextrin; Glycerine; Ethyleneglycol

Recently, organic reactions in water have attracted much attention because water is the most readily available solvent and safe. Hydrophobic effects strongly enhance the rate of several organic reactions previously, the scant solubility of reactants was the main reason preventing the use of water as a solvent [1].

We found that the addition of polyethyleneglycol, β-cyclodextrin, glycerine or ethyleneglycol to the water provided an efficient system for the synthesis of stable phosphorus ylides and 1,4-diionic organophosphorus compounds in aqueous media. However, some catalysts must be added to promote the solubility of reactants in water. Thus, we rationalized that β-cyclodextrin, polyethyleneglycol (200), glycerine or ethyleneglycol might be suitable for increasing the solubility in water of N–H, C–H or S–H acids, acetylenic esters, and triphenylphosphine, whose molecule contains three phenyl rings.

Phosphorus ylides are reactive systems, which take part in many valuable reactions of organic synthesis. Several methods have been developed for preparation of phosphorus ylides. These ylides are usually prepared by the treatment of a phosphonium salt with a base, and phosphonium salts are usually made from the phosphine and an alkyl halide. Phosphonium salts also are obtained by the Micheal addition of phosphorous nucleophiles to activated olefins, among other methods.

We now report a simple and an efficient route for the synthesis of stable phosphorus ylides (**3**) using triphenylphosphine, dialkylacetylenedicarboxylates (**1**) and N–H, C–H or S–H acids (**2**), such as 2-thiazoline-2-thiol, 2-benzoxazolinone, pyrrole-2-carboxaldehyde, benzotriazole, 5-methylbenzotriazole, 5-chlorobenzo-triazole, diethylmalonate, acetyl acetone, without using toxic organic solvents in aqueous media (Scheme 1).

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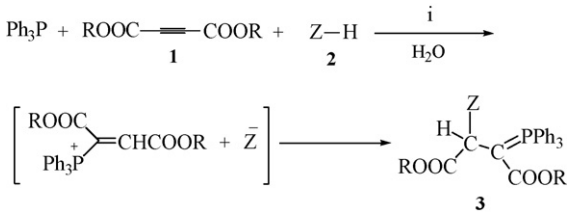
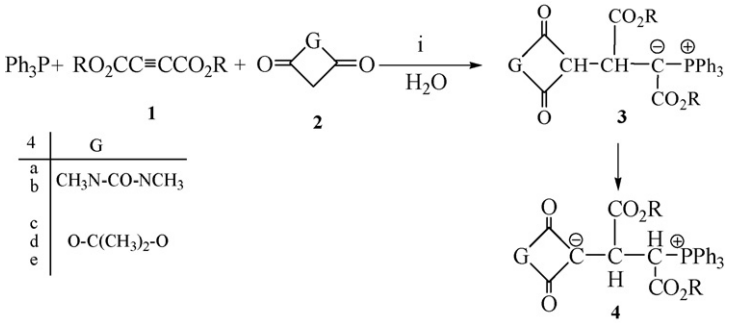


i. polyethyleneglycol, B-cyclodextrin, glycerine or ethyleneglycol

Scheme 1.



i. polyethyleneglycol, B-cyclodextrin, glycerine or ethyleneglycol

Scheme 2.

1,4-Diionic organophosphorus compounds (**4**) were synthesized from the reaction of triphenylphosphine, dialkylacetylenedicarboxylates (**1**), 1,3-dimethylbarbituric acid, and Meldrum's acid, in the presence of polyethyleneglycol (200), β-cyclodextrin, glycerine or ethyleneglycol in aqueous media (Scheme 2).

The spectral data and physical properties of the phosphoranes **3a–r**, **4a–e** were in agreement with those of literature reported [2–8]. The results are summarized in Tables 1 and 2.

In conclusion, we showed that polyethyleneglycol, β-cyclodextrin, glycerine or ethyleneglycol can be used for a convenient and rapid synthesis of organophosphorus compounds in aqueous media. The use of polyethyleneglycol has several advantages, including low cost, easy and clean work-up compared with β-cyclodextrin and higher yields compared with to glycerine and ethyleneglycol. 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 not toxic.

1. Experimental

Dialkyl acetylenedicarboxylates, triphenylphosphine, 2-thiazoline-2-thiol, 2-benzoxazolinone, pyrrole-2-carboxaldehyde, benzotriazole, 5-methylbenzotriazole, 5-chlorobenzo-triazole, diethylmalonate, acetyl acetone, 1,3-dimethylbarbituric acid, and Meldrum's acid, 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). ^{1}H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer instrument with $CDCl_3$ as solvent.

General procedures for synthesis of organophosphorus compounds in the presence of (PEG), (Gly) or (EG) in water: To a magnetically stirred solution of a N–H, C–H or S–H acids (1 mmol) and Ph_3P (0.26 g, 1 mmol) in water (10 mL), (0.5 mL) from (PEG, 200), (Gly) or (EG), was added. Dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) was added dropwise at room temperature over 10 min. After approximately 1–4 h stirring, the solution was filtered. The viscose product dried at room temperature and was thoroughly washed with cold diethyl ether.