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Synthesis of Highly Stabilized Phosphorus Ylides from Acetylenic Esters, CH-acids and Triphenylphosphine in Aqueous Media

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Protonation of the highly reactive 1 : 1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by CH-acids (nitromethane, acetylacetone, dibenzoylmethane and diethyl malonate) leads to vinyl triphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce corresponding highly stabilized phosphorus ylides in the mixture of acetone-water (2 : 1).

Key Words: CH-acid, Triphenylphosphine, Highly stabilized phosphorus ylide, Vinyl triphenylphosphonium salt, Water, Environment-friendly.

INTRODUCTION

Phosphorus ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity[1]. Since its development the Wittig reaction has remained one of the primary routes utilized in synthetic organic chemistry for the construction of carbon-carbon double bonds[1]. The Wittig reagent, or ylide, necessary for the reaction, is produced by deprotonation of the corresponding phosphonium salt generated by the quaternization of a phosphine with an organic halide[2]. The phosphonium salts that are used most often are alkyltriphenylphosphonium halides[2]. In recent years, we have established a one-pot method for the synthesis of stabilized ylides[3–13]. In this paper, we wish to describe the environment-friendly[14] preparation of highly stabilized phosphorus ylides from CH-acids (nitromethane, acetylacetone, dibenzoylmethane and diethyl malonate) in the mixture of acetone-water (2 : 1) **(Scheme-1).**

RESULTS AND DISCUSSION

The ylide (**5**) may result from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1 : 1 adduct, followed by attack of the CH-acid anion on the vinyl triphenylphosphonium cation **4** to produce corresponding highly stabilized phosphorus ylides **5** in the mixture of acetone-water (2 : 1). **(Scheme-1)**. In acetone-water[14] system, isolation and purification of

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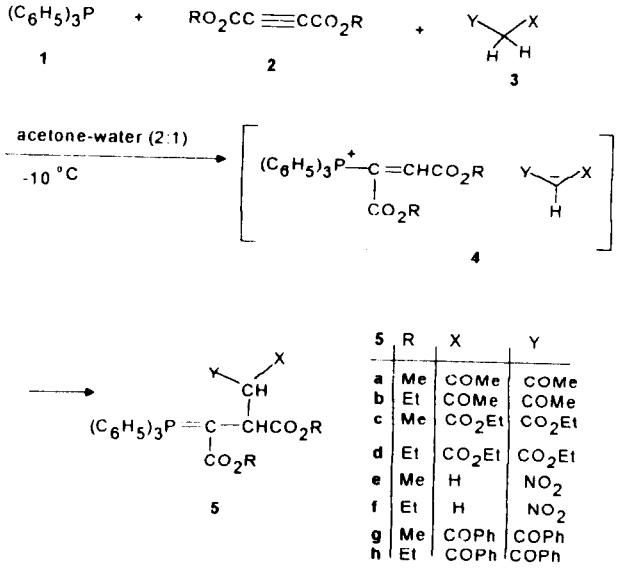
the highly stabilized phosphorus ylides **5** is very simple. In this condition, white crystalline highly stabilized phosphorus ylides **5** participated in the mixture of acetone-water (2 : 1) in the reaction vessel and pure products **5** were isolated *via* simple filtration.



5	R	X	Y
a	Me	COMe	COMe
b	Et	COMe	COMe
c	Me	CO_2Et	CO_2Et
d	Et	CO_2Et	CO_2Et
e	Me	H	NO_2
f	Et	H	NO_2
g	Me	COPh	COPh
h	Et	COPh	COPh

Scheme-1

The structures **5a–h** were deduced from their ^1H NMR and ^{13}C NMR spectra. The full characterization data of the highly stabilized phosphorus ylides are given in our previous report[13]. We have proved the stereochemistry of compounds **5a** and **5h** *via* single crystal X-ray diffraction (Fig. 1 and Fig. 2) method[12].

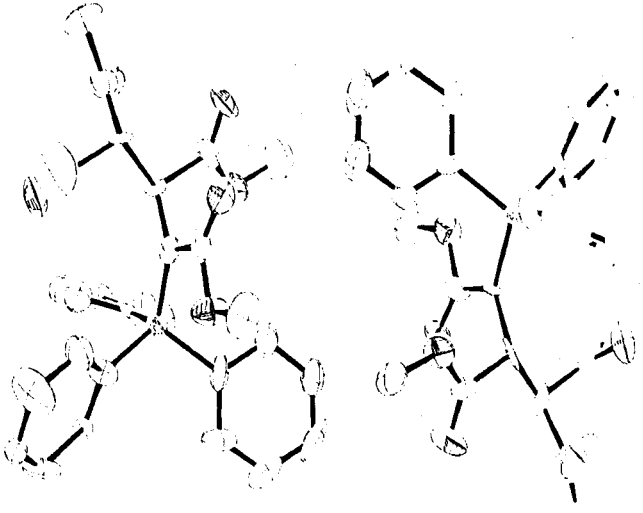


Fig. 1. ORTEP diagram of **5a**

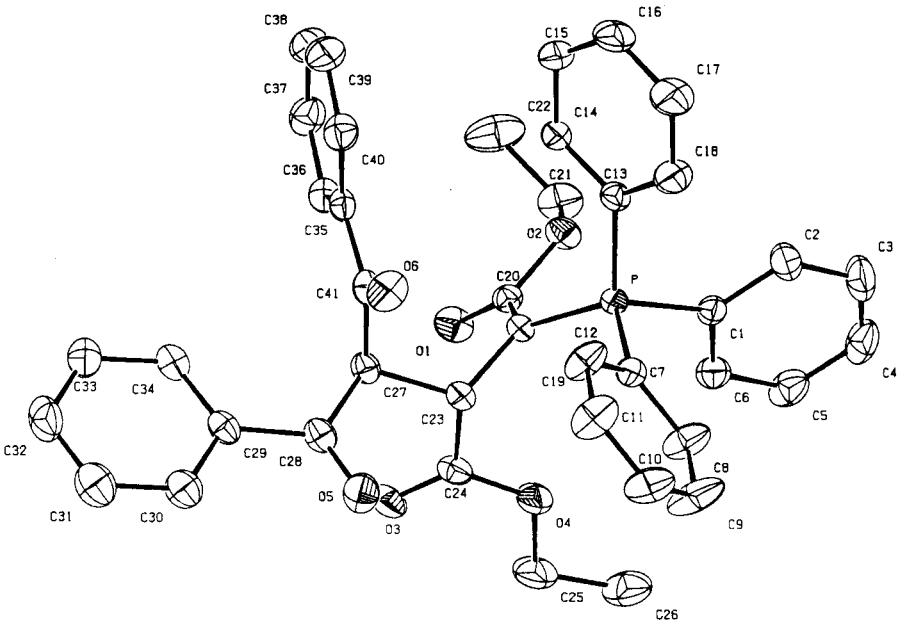


Fig. 2. ORTEP diagram of **5h**

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively. The full characterization data of the highly stabilized phosphorus ylides are given in our previous report[13].

General procedure for preparing highly stabilized phosphorus ylides from CH-acids (5a–h)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and **3** (1 mmol) in acetone-water (2 : 1) (6 mL) was added dropwise a mixture of **2** (1 mmol) in acetone-water (2 : 1) (3 mL) at −10°C over 15 min. The mixture was allowed to warm up to room temperature. White crystalline highly stabilized phosphorus ylides **5** participated in the mixture of acetone-water in the reaction vessel and pure products **5** were isolated *via* simple filtration with filter paper. White crystalline highly stabilized phosphorus ylides **5** were dried (yields: 70–75%) at room temperature.

In conclusion, we have developed an environmentally popular, simple one-pot method for preparing highly stabilized phosphorus ylides (**5a–h**) utilising *in situ* generation of the phosphonium salts **4** in acetone-water[14] (2 : 1). Other aspects of this process are under investigation.

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