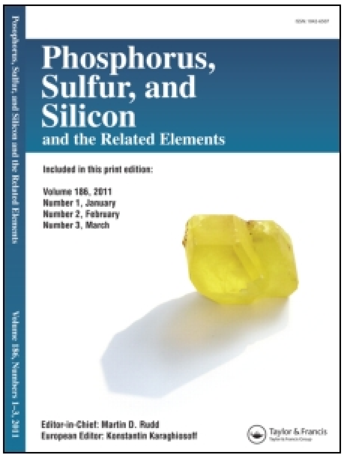

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A Facile Synthesis of Stable 1,4-Diionic Phosphorus Compounds in Aqueous Media

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Stable phosphorus betaines are obtained from the 1:1:1 addition reaction between triphenylphosphine and alkyl propiolates in the presence of CH-acids, such as cyclohexane-1,3-dione or 5,5-dimethylcyclohexane-1,3-dione in THF/H_2O (1:1) in good yields.

Keywords 1,4-Phosphorus betaines; alkyl propiolates, CH-acids; three-component reaction; triphenylphosphine

INTRODUCTION

There are many studies on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presence of OH, NH, or CH acids.[1] In some cases ylide products or diionic phosphorus compounds are stable,[2,3] but in other cases they cannot be isolated and appear to occur as an intermediate on the pathway to an observed product.[4] In many studies these reactions carried out in organic solvents such as dichloromethane, ethyl acetate or diethyl ether.[1–4] The synthesis of stable 1,4-diionic phosphorus compounds such as **1** and **2** from the reaction of acetylenic esters with triphenylphosphine in the presence of strong CH-acids such as *N*, *N*-dimethylbarbituric acid or Meldrum's acid (pK_a 7.3–7.7) have been reported (Scheme 1).[3] In this work we wish to report a facile one-pot synthesis of stable 1,4-diionic phosphorus compounds **5** from the reaction of weaker CH-acids such as cyclohexane-1,3-dione or 5,5-dimethylcyclohexane-1,3-dione (pK_a 11.2)[5] in aqueous media. Thus, reaction of triphenylphosphine and alkyl propiolates **3** in the presence of CH-acids **4** leads to stable betaine **5a–5d** in THF-H_2O (1:1) system in fairly good yields (Scheme 2).

The reaction of triphenylphosphine with alkyl propiolates **3** in the presence of CH-acids **4** proceeded spontaneously at room temperature

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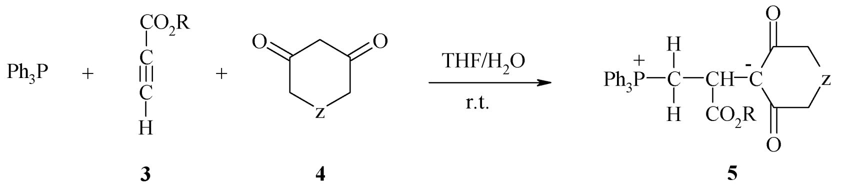
1 **2**

$Z = O\text{-}C(CH_3)_2\text{-}O$ or $CH_3N\text{-}CO\text{-}NCH_3$

SCHEME 1

in THF/H₂O (1:1), and was completed within 2 h. The ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of the stable betaines **5** (Scheme 2). Any product other than **5** could not be detected by NMR spectroscopy.



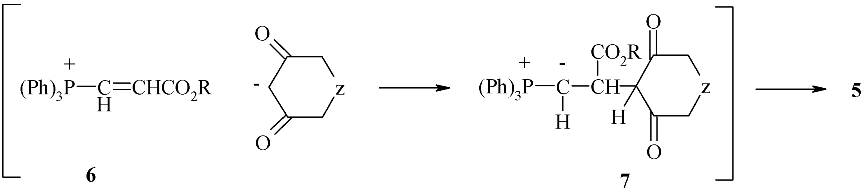
	R
3a	Me
3b	Et

	Z
4a	CH_2
4b	$C(CH_3)_2$

	Z	R	% Yield
5a	CH_2	Me	95
5b	CH_2	Et	96
5c	$C(CH_3)_2$	Me	95
5d	$C(CH_3)_2$	Et	97

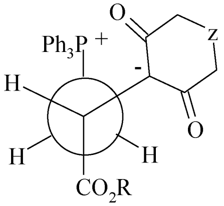
SCHEME 2

On the basis of the well-established chemistry of phosphorus nucleophiles,[6–10] it is reasonable to assume that betaine **5** results from initial addition of triphenylphosphine to alkyl propiolate and subsequent protonation of the reactive 1:1 adduct, followed by attack of carbon atom of the anion of CH-acid to vinyltriphenylphosphonium cation **6** to generate ylide **7** which apparently isomerizes, under the reaction conditions employed, to produce the 1,4-diionic compound **5** (Scheme 3).



SCHEME 3

The structures of compounds **5a-5d** were deduced from their elemental analyses and their IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values. The IR spectrum of each isolated product exhibited the sharp absorption bands of carbonyl groups attached to the negatively charged carbon atom at 1497–1492 cm^{-1}. NMR spectroscopy was used to distinguish structure **5** from the primary product, the ylide **7** (Scheme 3). Thus, the ^{1}H NMR spectrum of each isolated product showed a methylene and a methine proton signal at about δ = 3.8–4.6 ppm. Further evidence was obtained from the ^{13}C NMR spectra which displayed a P-CH$_2$ doublet at about δ = 23 ppm. Structure **5** was further confirmed by the ^{13}C NMR data for the CH-acid residue, which exhibits local C_s symmetry (see experimental section). The three bond carbon-phosphorus coupling $^3J_{\mathrm{CP}}$ depends on configuration. The Karplus relation can be derived from the data for organophosphorus compounds with tetra and pentavalent phosphorus.[11] The observation of $^3J_{\mathrm{CP}}$ of 17–18 Hz for the ester C=O group and $^3J_{\mathrm{pc}}$ of 0-4 Hz for C(CO)$_2$ in **5a–5d**, suggested that in the most stable conformation of the molecule, CH$_2$-P bond is antiperiplanar with the ester group. This conformation is favored, because dipole interaction of the phosphonium ion with the negative charge is possible only when the CH$_2$-P bond is antiperiplanar with the ester group and serves as a stabilizing force for this conformation (Scheme 4).



SCHEME 4

A cyclic six-membered ring structure for compound **5** is unlikely because it requires several chemical shift coincidences in the ^{1}H and ^{13}C NMR spectra. If compound **5** had a cyclic structure, then we were to expect a doublet at about δ 160 for C-O-P moiety in the ^{13}C NMR spectra.

In summary, the three component reaction of triphenylphosphine with alkyl propiolates in the presence of CH-acids in aqueous media provide a simple entry into the synthesis of 1,4-diionic organophosphorus compounds **5a–5d** in excellent yields. The simple experimental and product isolation procedures combined with high yield of products is expected to contribute to the development of a green strategy for synthesis of 1,4-diionic organophosphorus compounds. This methodology is of interest because the water use as solvent, thus minimizing the cost, operational hazards and environmental pollution.

EXPERIMENTAL

Alkyl propiolates, triphenylphosphine, and 1,3-dicarbonyl compounds were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H, ^{13}C, and ^{31}P spectra were measured with a Bruker DRX-250 AVANCE spectrometer at 250.1, 62.9, and 101.2 MHz respectively. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on solution in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. Chemical shifts are given in ppm (δ) relative to internal TMS, and coupling constants (J) are reported in Hertz (Hz). IR spectra were measured on a Shimadzu IR-460 spectrometer.

Preparation of 2-(Cyclohexane-1,3-dione-2-yl-2-ylid)-methyl-3-triphenylphosphonipropanoate (5a)

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.23 g cyclohexane 1,3-dione (2 mmol) in 10 mL THF/H_2O (1:1) was added, dropwise, a mixture of 0.17 g methyl acetylene carboxylate (2 mmol) in 2 mL THF/H_2O (1:1) at 0°C over 5 min. The reaction mixture was then allowed to warm-up to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and crude product washed with cooled n-hexane-ethyl acetate mixture to yield **5a**. White powder; yield: 0.87 g (95%), mp 126-128°C. IR (KBr) (ν_{max}, cm^{-1}): 1716, 1496 (C=O). Anal. Calcd. For $C_{28}H_{27}O_4P$ (458.5): C, 73.35; H, 5.94 Found: C, 73.4; H, 5.9%. MS: m/z (%) = 458 (M^+, 5), 262 (75), 196 (10), 183 (100). ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 1.57–2.13 (6H, m, 3 CH_2), 3.55 (3H, s, OMe), 3.87 (1H, ddd, $^2J_{HH}$ = 16 Hz, $^2J_{HP}$ = 13 Hz, $^3J_{HH(gauche)}$ = 3 Hz, CH of CH_2P), 4.03 (1H, m, CH of CH_2P), 4.53 (1H, ddd, $^3J_{HP}$ = 10 Hz, $^3J_{HH(anti)}$ = 12 Hz, $^3J_{HH(gauche)}$ = 3 Hz, CH), 7.31–7.79 (15H, m, 3 C_6H_5). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.1 (CH_2), 22.9 (d, $^1J_{PC}$ = 55 Hz, CH_2P), 34.1 (CH), 35.5 (2 CH_2), 52.5 (OCH_3), 108.8 ($C(CO)_2$), 119.3 (d, $^1J_{pc}$ = 87 Hz, C_{ipso} of Ph_3P), 129.8 (d, $^3J_{pc}$ = 12 Hz, C_{meta} of Ph_3P), 133.8 (d, $^2J_{PC}$ = 10 Hz, C_{ortho} of Ph_3P), 134.4 (d, $^4J_{pc}$ = 3

Hz, C_{para} of Ph_3P), 175.4 (d, $^3J_{pc} = 17$ Hz, C=O, ester), 190.8 (2 C=O). ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = 23.6$ (Ph_3P^+- CH_2).

2-(Cyclohexane-1,3-dione-2-yl-2-ylid)-ethyl-3-triphenylphosphonipropanoate (5b)

Yellow powder, yield: 0.91 g (96%), m.p. 117–120°C. IR (KBr) (v_{max},cm^{-1}): 1710, 1492 (C=O). Anal Calcd. For $C_{29}H_{29}O_4P$ (472.5): C, 73.72; H, 6.19 Found: C, 73.7; H, 6.2%. MS: *m/z* (%) = 472 (M^+, 4), 262 (75), 183 (100), 77 (45).^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.10$ (3H, t,$^3J_{HH} = 7$ Hz, Me), 1.60–2.12 (6H, m, 3 CH_2), 3.80–4.1 (4H, m, CH_2P and OCH_2), 4.50 (1H, ddd, $^3J_{HH(anti)} = 12$ Hz, $^3J_{HP} = 9$ Hz, $^3J_{HH(gauche)} = 3$ Hz, CH), 7.62–7.81 (15H, m, 3 C_6H_5). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.0$ ($OCH_2\mathit{CH_3}$), 21.3 (CH_2), 22.9 (d, $^1J_{PC} = 54$ Hz, CH_2P), 34.4 (CH), 35.8 (2 CH_2), 61.1 (OCH_2), 108.8 (d, $^3J_{pc} = 4$ Hz, $\mathit{C}(CO)_2$), 119.6 (d, $^1J_{pc} = 87$ Hz, C_{ipso} of Ph_3P), 129.7 (d, $^3J_{pc} = 12$ Hz, C_{meta} of Ph_3P), 133.8 (d, $^2J_{PC} = 10$ Hz, C_{ortho} of Ph_3P), 134.3 (d, $^4J_{pc} = 3$ Hz, C_{para} of Ph_3P), 175.4 (d, $^3J_{pc} = 17$ Hz, C=O, ester), 191.0 (2 C=O). ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = 23.8$ (Ph_3P^+- CH_2).

2-(5,5-Dimethylcyclohexane-1,3-dione-2-yl-2-ylid)-methyl-3-triphenylphosphonipropanoate (5c)

Orange crystals; yield 0.92 g (95%), m.p. 93–95°C. IR (KBr) ($v^{-1}_{max,cm}$): 1721, 1497 (C=O). Anal Calcd. For $C_{30}H_{31}O_4P$ (486.5): C, 74.06; H, 6.42 Found: C, 74.1; H, 6.4%. MS: *m/z* (%) = 486 (M^+, 6), 262 (80), 183 (100). ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 0.96$ (6H, s, 2 Me), 1.72 (2H, d,$^2J_{HH} = 16$ Hz, CH_2), 1.92 (2H, d, $^2J_{HH} = 16$ Hz, CH_2), 3.59 (3H, s, OMe), 3.87 (1H, ddd, $^2J_{HH} = 15$ Hz, $^2J_{HP} = 14$ Hz, $^3J_{HH(gauche)} = 3$ Hz, CH of CH_2P), 4.08 (1H, m, CH of CH_2P), 4.49 (1H, ddd, $^3J_{HP} = 9$ Hz, $^3J_{HH(anti)} = 10$ Hz, $^3J_{HH(gauche)} = 3$ Hz, CH), 7.30-7.84 (15H, m, 3 C_6H_5). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 22.0$ (d, $^1J_{PC} = 55$ Hz, CH_2P), 28.5 (2 Me), 31.7 (2 CH_2), 34.0 (CH), 49.7 ($\mathit{C}(Me)_2$), 52.5 (OMe), 107.1 ($\mathit{C}(CO)_2$), 119.2 (d, $^1J_{pc} = 86$ Hz, C_{ipso} of Ph_3P), 128.5 (d, $^3J_{pc} = 12$ Hz, C_{meta} of Ph_3P), 132.1 (d, $^2J_{PC} = 10$ Hz, C_{ortho} of Ph_3P), 134.3 (d, $^4J_{pc} = 3$ Hz, C_{para} of Ph_3P), 178.5 (d, $^3J_{pc} = 18$ Hz, C=O, ester), 189.9 (2 C=O) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = 23.9$ (Ph_3P^+- CH_2).

2-(5,5-Dimethylcyclohexane-1,3-dione-2-yl-2-ylid)-ethyl-3-triphenylphosphonipropanoate (5d)

White powder; yield: 0.97 g (97%), m.p. 153–155°C. IR (KBr) ($v^{-1}_{max,cm}$): 1713, 1495 (C=O). Anal Calcd. For $C_{31}H_{33}O_4P$ (500.6): C, 74.38; H, 6.64

Found: C, 74.4; H, 6.6%. MS: m/z (%) = 500 (M^+, 4), 262 (60), 183 (100). ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 0.96$ (6H, s, 2 Me), 1.14 (3H, t, $^3J_{HH} =$ 7 Hz, OCH_2*Me*), 1.77 (2H, d, $^2J_{HH} = 16$ Hz, CH_2), 1.94 (2H, d, $^2J_{HH} =$ 16 Hz, CH_2), 3.95-4.13 (4H, m, OCH_2 and CH_2P), 4.46 (1H, m, CH), 7.31–7.78 (15H, m, 3 C_6H_5). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.0$ (OCH_2CH_3), 22.0 (d, $^1J_{PC} = 55$ Hz, CH_2P), 28.4 (2 Me), 31.8 (2 CH_2), 34.0 (CH), 48.9 ($C(Me)_2$), 61.5 (OCH_2), 108.0 (d, $^3J_{pc} = 4$ Hz, $C(CO)_2$), 119.1 (d, $^1J_{pc} = 87$ Hz, C_{ipso} of Ph_3P), 129.9 (d, $^3J_{pc} = 12$ Hz, C_{meta} of Ph_3P), 133.8 (d, $^2J_{PC} = 10$ Hz, C_{ortho} of Ph_3P), 134.5 (C_{para} of Ph_3P), 174.8 (d, $^3J_{pc} = 17$ Hz, C=O, ester), 189.5 (2 C=O) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): $\delta = 23.6$ (Ph_3P^+-CH_2).

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