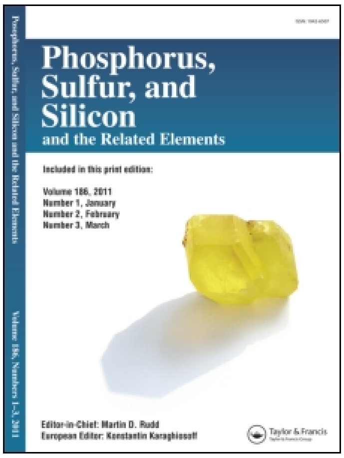

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ONE-POT SYNTHESIS OF STERICALLY CONGESTED PHOSPHORUS YLIDES

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ONE-POT SYNTHESIS OF STERICALLY CONGESTED PHOSPHORUS YLIDES

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Protonation of the reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by 1,3-diphenylpropane-1,3-dione leads to vinylphosphonium salts, which undergo Michael addition with the conjugate base of the CH-acid to produce highly functionalized salt-free phosphorus ylides in excellent yields.

Keywords: Stabilized ylides; triphenylphosphine; acetylenic esters; CH-acids

Phosphorus ylides are reactive systems, which take part in many reactions of value in the synthesis of organic products.[1–10] Several methods have been developed for preparation of phosphorus ylides. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide.[2–3] Phosphonium salts are also prepared by Michael addition of phosphorus to activated olefines and in other ways.[1] The phosphonium salts are most often converted to the ylide by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. We wish to report an efficient synthetic route to sterically congested phosphorus ylides **3** using triphenylphosphine, dialkyl acetylenedicarboxylates (**1**) and a carbon acid, such as 1,3-diphenylpropane-1,3-dione, in excellent yields.

On the basis of the well established chemistry of trivalent phosphorous nucleophiles[1–5] it is reasonable to assume that phosphorous ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and a concomitant protonation of the 1:1 adduct by 1,3-diphenylpropane-1,3-dione. Then the positively charged ion is attacked by the enolate anion of the diketone to form phosphorane **3**.

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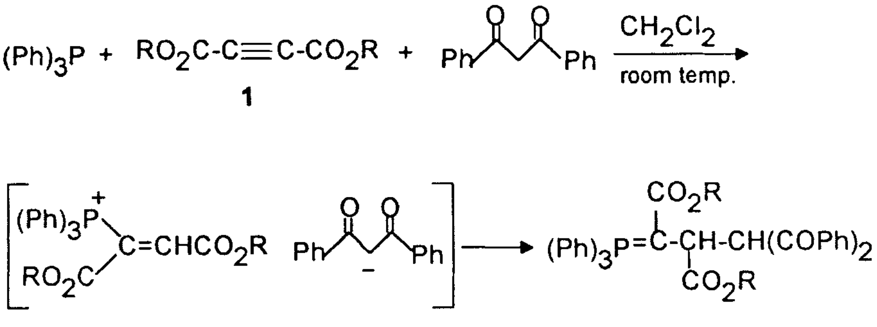

2 **3**

1,2,3	R
a	Me
b	Et
c	t-But

The structures of compounds **3a-c** were deduced from their elemental analyses and their ^1H and ^{13}C NMR and IR spectral data. The nature of these compounds as 1:1:1 adducts was apparent from the mass spectra which displayed molecular ion peaks at m/z = 628, 656, and 712. Initial fragmentations involve loss of the chains [$(Ph)_3P$, ROH, CO_2R, PhCOCHCOPh, PhCO, C_6H_5].

The ^1H NMR spectrum of **3a** exhibited two sharp lines (δ = 3.02 and 3.58 ppm) arising from methoxy protons along with signals for vicinal methine protons at δ = 3.87 and 7.15 ppm, which appear as double doublet ($^3J_{HP}$ = 18.0 Hz and $^3J_{HH}$ = 10.4 Hz) and doublet ($^3J_{HH}$ = 10.4 Hz), respectively. The aromatic protons appear as a multiplet at δ = 7.2–8.25 ppm. The phenyl groups of the propane-1,3-dione moiety, are diastereotopic and exhibite two clear double doublets for the protons in the *ortho*-position relative to the carbonyl group (see Table I). The ^{13}C NMR spectrum of **3a** displayed twenty one distinct resonances in agreement with the phosphorane structure. Although the presence of the ^{31}P nucleus complicates both the ^1H and ^{13}C NMR spectra of **3a**, it helps in assignment of the signals by long-range couplings with ^1H and ^{13}C nuclei (see Table I). The ^1H and ^{13}C NMR spectra of **3b** and **3c** are similar to those of **3a**, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts (see Table I).

The structural assignments made on the basis of the ^1H and ^{13}C NMR spectra of compounds **3a-c** were supported by measurement of their IR spectra. The carbonyl region of the spectrum exhibited four distinct absorption bands for each compound (see Experimental section). Of special interest is the ester absorption

TABLE I Proton and carbon-13 NMR data for compounds 3a-c

Compound	*$^{1}H/^{13}C$*	*δ(ppm) (CDCl$_3$-Me$_4$Si)*
3a	^{1}H	3.02 and 3.58 (6H, 2s, 2 OMe), 3.87 (1H, dd, $^{3}J_{HH}$ 10.4 Hz and $^{3}J_{PH}$ 18.0 Hz, P=C-CH), 7.15 (1H, d, $^{3}J_{HH}$ 10.4 Hz, P=C-CH), 7.2–7.7 (6H, m, PhCO^{a}), 7.95 (2H, dd, $^{3}J_{HH}$ 8.2 Hz and $^{4}J_{HH}$ 1.6 Hz, PhCO^{b}), 8.25 (2H, dd, $^{3}J_{HH}$ 8.2 Hz and $^{4}J_{HH}$ 1.6 Hz, PhCO^{b})
	^{13}C	39.66 (d, $^{1}J_{PC}$ 125.2 Hz, P=C), 45.92 (d, $^{2}J_{PC}$ 13.8 Hz, P=C-^{13}C), 48.62 and 51.43 (2 OMe), 55.19 (d, $^{3}J_{PC}$ 4.6 Hz, P=C-C-^{13}C), 127.98, 128.40, 128.56 and 129.33 (PhCO^{c}), 132.65 and 133.50 (PhCO^{d}), 137.11 and 137.47 (PhCO^{e}), 128.26 (d, $^{3}J_{PC}$ 12.9 Hz, *meta*-C^{f}), 129.98 (d, $^{1}J_{PC}$ 85.0 Hz, *ipso*-C^{f}), 131.70 (d, $^{4}J_{PC}$ 2.2 Hz, *para*-C^{f}), 133.68 (d, $^{2}J_{PC}$ 9.2 Hz, *ortho*-C^{f}), 169.71 (d, $^{2}J_{PC}$ 13.8 Hz, ester C=O), 174.97 d, $^{3}J_{PC}$ 3.7 Hz, ester C=O), 194.03 and 195.34 (2C=O)
3b	^{1}H	0.42 (3H, t, $^{3}J_{HH}$ 7.3 Hz, CH$_3$), 1.07 (3H, t, $^{3}J_{HH}$ 7.3 Hz, CH$_3$), 3.69 (1H, dd, $^{3}J_{HH}$ 10.7 Hz and $^{3}J_{PH}$ 18.0 Hz, P=C-CH), 3.71 (2H, q, $^{3}J_{HH}$ 7.3 Hz, CH$_2$), 4.08 (2H, q, $^{3}J_{HH}$ 7.3 Hz, CH$_2$), 7.17 (1H, d, $^{3}J_{HH}$ 10.7 Hz, P=C-C-CH), 7.2–7.8 (6H, m, PhCO^{a}), 7.97 (2H, dd, $^{3}J_{HH}$ 8.2 Hz and $^{4}J_{HH}$ 1.6 Hz, PhCO^{b}), 8.3 (2H, dd, $^{3}J_{HH}$ 8.2 Hz and $^{4}J_{HH}$ 1.6 Hz, PhCO^{b})
	^{13}C	13.59 and 14.05 (2CH$_3$), 39.95 (d, $^{1}J_{PC}$ 125.2 Hz, P=C), 46.40 (d, $^{2}J_{PC}$ 13.8 Hz, P=C-^{13}CH), 55.22 (d, $^{3}J_{PC}$ 4.5 Hz, P=C-C-^{13}C), 57.25 and 60.59 (2 OCH$_2$), 128.27, 128.52, 128.72 and 129.61 (PhCO^{c}), 132.46 and 133.28 (PhCO^{d}), 137.39 and 137.88 (PhCO^{e}), 128.22 (d, $^{3}J_{PC}$ 12.8 Hz, *meta*-C^{f}), 129.67 (d, $^{1}J_{PC}$ 85.6 Hz, *ipso*-C^{f}), 131.73 (d, $^{4}J_{PC}$ 2.6 Hz, *para*-C^{f}), 133.98 (d, $^{2}J_{PC}$ 10.1 Hz, *meta*-C^{f}) 169.61 (d, $^{2}J_{PC}$ 13.8 Hz, ester C=O), 175.30 (d, $^{3}J_{PC}$ 4.7 Hz, ester C=O), 194.20 and 195.58 (2C=O)
3c	^{1}H	0.86 and 1.38 (18 H, 2s, 2 CMe$_3$), 3.68 (1H, dd, $^{3}J_{HH}$ 10.8 Hz and $^{3}J_{PH}$ 18.0 Hz, P=C-CH), 7.16 (1H, d, $^{3}J_{HH}$ 10.8 Hz, P=C-C-CH), 7.2–7.6 (6H, m, PhCO^{a}), 7.96 (2H, dd, $^{3}J_{HH}$ 8.2 Hz and $^{4}J_{HH}$ 1.6 Hz, PhCO^{b}), 8.32 (2H, dd, $^{3}J_{HH}$ 8.2 Hz and $^{4}J_{HH}$ 1.6 Hz, PhCO^{b})
	^{13}C	28.22 and 28.34 (^{13} CH$_3$ of 2 CMe$_3$), 39.50 (d, $^{1}J_{PC}$ 125.2 Hz, P=C), 46.95 (d, $^{2}J_{PC}$ 14.7 Hz, P=C-^{13}C), 55.54 (d, $^{3}J_{PC}$ 3.7 Hz, P=C-C-^{13}C), 76.76 and 80.10 (2 ^{13}CMe$_3$), 128.19, 128.64, 128.80 and 129.86 (PhCO^{c}), 132.30 and 133.03 (PhCO^{d}), 137.39 and 138.04 (PhCO^{e}), 128.04 (d, $^{3}J_{PC}$ 2.0 Hz, *meta*-C^{f}), 129.67 (d, $^{1}J_{PC}$ 85.6 Hz, *ipso*-C^{f}), 131.57 (d, $^{4}J_{PC}$ 2.8 Hz, *para*-C^{f}), 134.38 (d, $^{2}J_{PC}$ 10.1 Hz, *ortho*-C^{f}), 169.32 (d, $^{2}J_{PC}$ 12.9 Hz, ester C=O), 174.02 (d, $^{3}J_{PC}$ 4.6 Hz, ester C=O), 194.16 and 196.27 (2C=O)

[a] Aromatic protons in the *meta*- and *para*-position relative to the carbonyl group.
[b] Aromatic protons in the *ortho*-position relative to the carbonyl group.
[c] *Ortho*- and *meta*-C of diastereotopic PhCO groups.
[d] *Para*-C of PhCO.
[e] *Ipso*-C of PhCO.
[f] Carbon atoms of the (Ph)$_3$ group.

at 1727–1687 cm^{-1} for these compounds. Conjugation with the carbon-carbon double bond appears to be a plausible factor in the reduction of these absorption frequencies.[11]

Functionalized phosphorus ylides **3a-c** may be considered as potentially useful synthetic intermediates.[1–3] The procedure described here may be an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses for C, H, and N were performed using a Heracus CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with JEOL EX-90A spectrometer at 90 and 22.6 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. 1,3-Diphenylpropane-1,3-dione and dialkyl acetylenedicarboxylates were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

Preparation of dimethyl 2-(1,3-diphenylpropane-1,3-dione-2-yl)-3-(triphenylphosphoranylidene)-butanedioate 3a. General procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and 1,3-diphenylpropane-1,3-dione (0.22 g, 1 mmol) in CH_2Cl_2 (5 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.12 ml, 1 mmol) in CH_2Cl_2 (2 ml) at -10°C over 5 min. After 24 hr stirring at room temperature, the product was filtered and recrystallized from ethanol. (0.59 g, m.p. 205°C, yield 95%); IR (KBr) (ν_{max}, cm^{-1}): 1727 and 1689 (C$=$O, ester), 1660 and 1624 (C$=$O, ketone). MS (*m/z*, %): 628 (M^+, 7); 335 (M^+-2 PhCO-CO_2Me-C_2H_2, 100); 105 (M^+ of PhCO, 75); 262 (M^+ of $(Ph)_3P$ 58). Analysis: Calc. for $C_{39}H_{33}O_6P$ (628.66): C, 74.51, H, 5.29; found: C, 74.6, H, 5.3.

Selected data for diethyl 2-(1,3-diphenylpropane-1,3-dione-2-yl)-3-(triphenylphosphoranylidene)-butanedioate ***3b***: 0.62 g, m.p 206°C, yield 95%, IR (KBr) (ν_{max}, cm^{-1}): 1726 and 1687 (C$=$O, ester), 1652 and 1624 (C$=$O, ketone). MS (*m/z*, %): 657 (MH^+, 24); 584 (M^+-CO_2Et, 27); 433 [M^+-$CH_2(COPh)_2$, 78], 275 (433-CO_2Et, 42), 262 [$(Ph)_3P$, 100), 105 (PhCO, 75). Analysis: Calc. for $C_{41}H_{37}O_6P$ (656.74): C, 74.98, H, 5.68; found: C, 74.8, H, 5.8.

Selected data for di-tert-butyl 2-(1,3-diphenylpropane-1,3-dione-2-yl)-3-(triphenylphosphoranylidene)-butanedioate ***3c***: 0.69 g, m.p 208°C, yield 98%, IR

(KBr) (ν_{max}, cm^{-1}): 1715 and 1693 (C=O, ester), 1615 and 1593 (C=O, ketone). MS (*m/z*, %): 712 (M$^+$, 5); 611 (M$^+$-CO_2CMe_3, 45); 183 [M$^+$-$(Ph)_3P$-$2CO_2CMe_3$-CO-C_3H_1, 90]. Analysis: Calc. for $C_{45}H_{45}O_6P$ (712.82): C, 75.82, H, 6.36; found: C, 73.5, H, 6.1.

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