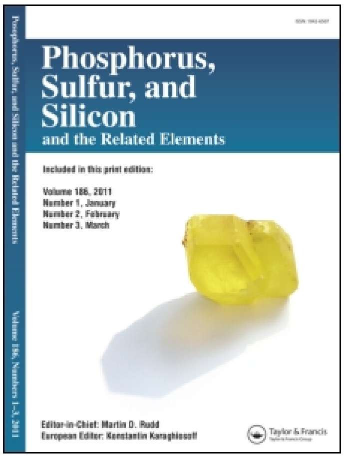

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A Facial Route for the Preparation of Dialkyl 2-(Dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates from Triphenylphosphine, Acetylenic Esters and Malononitrile

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A Facial Route for the Preparation of Dialkyl 2-(Dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates from Triphenylphosphine, Acetylenic Esters and Malononitrile

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*A one-pot synthesis of dialkyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates in fairly high yields by the reaction of malononitrile, dialkyl acetylenedicarboxylates and triphenylphosphine are reported. The formulas of these compounds were confirmed by IR, ^1H,^{31}P, and ^{13}C NMR spectroscopy. The NMR spectra indicated that solutions of the phosphorus ylides ($CDCl_3$ as solvent) contain two rotamers (**E** and **Z**). The relative percentages of rotamers in $CDCl_3$ for each phosphorus ylide were determined from the ^1H NMR spectra.*

Keywords Acetylenic esters; malononitrile; Michael addition; phosphorus ylide; vinyltriphenylphosphonium salt

INTRODUCTION

Phosphorus ylides are important reagents in synthetic organic chemistry,[1–16] especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity.[6] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[18–30] Phosphorus ylides are a class of special type of zwitterions, which bear strongly nucleophilic electron rich carbanions. The electron distribution around the $P^+{-}C^-$ bond and its consequent chemical implications had been probed and assessed through theoretical, spectroscopic, and crystallographic

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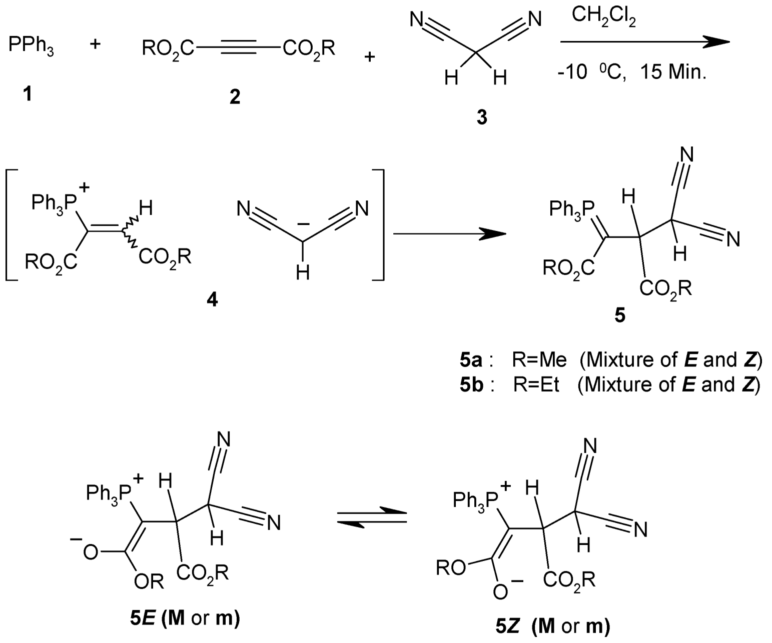

5a : R=Me (Mixture of ***E*** and ***Z***)
5b : R=Et (Mixture of ***E*** and ***Z***)

SCHEME 1 **M** = major rotamer and **m** = minor rotamer.

investigations.[30] Proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[17,30] The nucleophilicity at the ylidic carbon is a factor of essential mechanistic importance in the use of these ylides as Wittig reagents. In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[18–28] In this paper, we wish to describe a simple method for the preparation of dialkyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates from three-component reaction of malononitrile, dialkyl acetylenedicarboxylates and triphenylphosphine in fairly high yields (Scheme 1).

RESULTS AND DISCUSSION

The phosphorus ylide (**5**) may result from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct by malononitrile **3** leads to vinyltriphenylphosphonium salts **4**, which undergo Michael addition reaction with conjugate base to produce sterically congested phosphorus ylide (**5**). TLC indicated formation of ylides **5** in CH_2Cl_2. The reaction was completed at

−10°C in 15 min. The mechanism of the reaction has not been established experimentally. However, a possible explanation is proposed in Scheme 1. The formulas of the products **5** were deduced from their IR, ^{1}H NMR, ^{13}C NMR, and ^{13}P NMR spectra (See Experimental section). The NMR spectra indicated that solutions of compound **5** ($CDCl_3$ as solvent) contain two rotamers (**5***E* and **5***Z*). The relative percentages of rotamers in $CDCl_3$ for each ylide **5** were determined from the ^{1}H NMR spectra. The IR spectrum of **5a** showed strong adsorptions at 1738 (C=O, ester) and 1620 (C=O, ester) cm^{-1} indicating the presence of two the ester carbonyl groups. The ^{1}H NMR spectrum of **5a** compound exhibited eight signals readily recognized as arising from four OMe groups (δ = 3.16, 3.57, 3.75 and 3.76 ppm, 4 s), $CHCO_2$ (δ = 2.85–2.96 ppm,m), $CH(CN)_2$ (δ = 4.90 and 5.45, 2 d, $^{3}J_{HH}$ = 10.5 Hz,) and aromatic moieties (δ = 7.26–7.73 ppm, m). The ^{1}H decoupled ^{13}C NMR spectrum of **5a** showed 20 distinct resonances in agreement with the **5a** formula. Partial assignment of these resonances is given in the spectral analysis section (See experimental section). The ^{31}P NMR spectrum of **5a** exhibited two signals readily recognized as arising from phosphorus atom of P = C groups (δ = 22.89 and 23.58 ppm, *Z* and *E* rotamers). The ^{1}H, ^{31}P NMR, and ^{13}C NMR spectra of compound **5b** are similar to those of **5a**, except for the ester groups (^{1}H and ^{13}C NMR), which exhibit characteristic signals with appropriate chemical shifts (see spectral analysis section).[28,31]

CONCLUSION

In summary, we have found a simple method for the preparation of dialkyl 2-(dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinates (**5**) from the three-component reaction of malononitrile, dialkyl acetylenedicarboxylates, and triphenylphosphine in fairly high yields. We believe the reported method offers a simple and efficient route for the preparation of the stabilized phosphorus ylides **5** (Scheme 1). Its ease of work up and fairly good yields make it a useful addition to modern synthetic methodologies.[28,31] Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a FT-IR Mattson 1000 spectrometer. ^{1}H, ^{31}P, and ^{13}C NMR spectra were measured with a BRUKER DRX-250 AVANCE spectrometer at 250.00, 101.25, and 62.50 MHz respectively.

General Procedure for the Preparation of Ylides 5a–b

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1.00 mmol) and malononitrile (0.066 g, 1.00 mmol) in dichloromethane (5 ml) was added dropwise a mixture of dialkyl acetylenedicarboxylate (0.13 ml, 1.0 mmol) in dichloromethane (2 ml) at −10°C over 15 min. The mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel, hexane-ethyl acetate). (**5a**, white crystals, m.p. 168.0–169.2°C, yield 90.0%; **5b**, white crystals, m.p. 166.0–168.5°C, yield 85.5%). The characterization data of the compounds (**5a–b**) are given below.

Spectral Data for Dimethyl 2-(Dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinate 5a

IR (KBr) (v_{max}, cm^{-1}): 1738; 1620; 1481; 1435. ^{1}H NMR (CDCl$_3$, major rotamer (M) 70.60% and minor rotamer (m) 29.40%), δ_H : 2.85–2.96 (1 H, m, CHCO$_2$Me); 3.16, 3.57, 3.75, and 3.76 (6 H, 4 s, 4 OCH$_3$); 4.90 and 5.45 (1 H, 2 d, ^{3}J$_{HH}$ = 10.5 Hz, CH(CN)$_2$); 7.26–7.73 (15 H, m, arom.).^{13}C NMR (CDCl$_3$)δ_C : 24.92 (d, $^3J_{PC}$ = 3.2 Hz) and 26.32 (d, $^3J_{PC}$ = 4.5 Hz) (2 ^{13}CH(CN)$_2$); 39.62 (d, $^1J_{PC}$ = 125.3 Hz) and 41.03 (d, $^1J_{PC}$ = 127.5 Hz) (2 P=C); 46.23 (d, $^2J_{PC}$ = 15.02 Hz) and 47.05 (d, $^2J_{PC}$ = 16.12 Hz) (2 P=C-^{13}C); 49.33, 50.50, 52.49 and 52.59 (4 OCH$_3$); 113.55 and 113.95 (2 CN); 124.3–134.0 (fairly complex, arom.); 169.32 (d, $^2J_{PC}$ = 13.66 Hz), 171.10 (d, $^3J_{PC}$ = 4.69 Hz), 171.45 (d, $^3J_{PC}$ = 4.39 Hz) and 171.60 (d, $^2J_{PC}$ = 14.03 Hz) (4 CO of esters).^{31}P NMR (CDCl$_3$) δ_P : 22.89 and 23.58.

Selected Data for Diethyl 2-(Dicyanomethyl)-3-(triphenyl-λ^5-phosphoranylidene)succinate 5b

IR (KBr) v_{max}, cm^{-1}): 1735, 1638, 1435. ^{1}H NMR (CDCl$_3$, major rotamer (M) 76.86% and minor rotamer (m) 23.14%), δ_H : 0.45, 1.15, 1.18 and 1.31 (6 H, 4 t,^{3}J$_{HH}$ = 7.25 Hz, 4 CH$_3$); 2.83–2.96 (1 H, m, CHCO$_2$Et); 3.67–3.75, 3.94–4.03 and 4.14–4.30 (4 H, 3 m, 4 OCH$_2$); 4.91 and 5.44 (1 H, 2 d,^{3}J$_{HH}$ = 10.25 Hz) (CH(CN)$_2$); 7.26–7.78 (15 H, m, arom). ^{13}C NMR (CDCl$_3$) δ_C : 13.79, 14.04, 14.11 and 14.91 (4 CH$_3$); 24.85 (d, $^3J_{PC}$ = 4.5 Hz) and 26.42 (d, $^3J_{PC}$ = 3.4 Hz) (2 ^{13}CH(CN)$_2$); 39.72 (d, $^1J_{PC}$ = 124.3 Hz) and 40.96 (d, $^1J_{PC}$ = 128.3 Hz) (2 P=C); 46.49 (d, $^2J_{PC}$ = 16.24 Hz) and 46.21 (d, $^2J_{PC}$ = 17.22 Hz) (2 P=C-^{13}C); 58.01, 58.63, 61.33 and 61.87 (4 OCH$_2$); 113.87 and 114.02 (2 CN); 124.5–134.0 (fairly complex, arom); 168.92 (d, $^2J_{PC}$ = 12.97 Hz), 170.73 (d, $^3J_{PC}$ = 5.01 Hz), 171.32 (d, $^3J_{PC}$ = 4.97 Hz) and 169.43 (d, $^2J_{PC}$ = 13.12 Hz) (4 CO of esters).^{31}P NMR (CDCl$_3$) δ_P : 22.79 and 23.59.

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