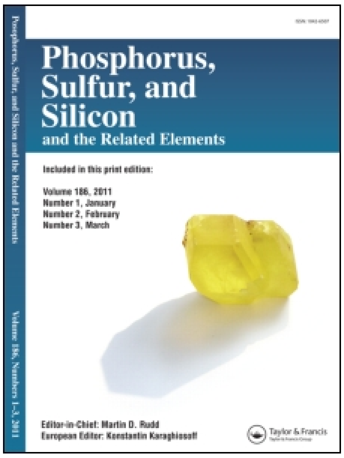

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One-Pot Synthesis of Stable Phosphorus Ylides Using CH-Acid Compounds

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Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and di-tert-butyl acetylendicarboxylate, in the presence of antron, dimedone, indandion, and 3,5-dimethylbarbituric acid. These stable ylides exist in a solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords Acetylenic ester; CH-acids; geometrical isomers; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

The development of simple synthetic routes for widely-used organic compounds from readily available reagents is one of the major tasks in organic chemistry.[1] Phosphorus ylides are reactive systems, which take part in many valuable reactions of organic synthesis.[2–12] These are most often prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from phosphine and an alkyl halide,[3–7] and they are also obtained by the Michael addition of phosphorus nucleophiles to activated olefins.[2,3] Here, we wish to describe an efficient synthetic route for the preparation of stable phosphorus ylides **3** using triphenylphosphine, di-tert-butyl acetylendicarboxylate **1** and CH-acids such as antron, dimedone, indandion, and 3,5-dimethylbarbituric acid **2** (Scheme 1).

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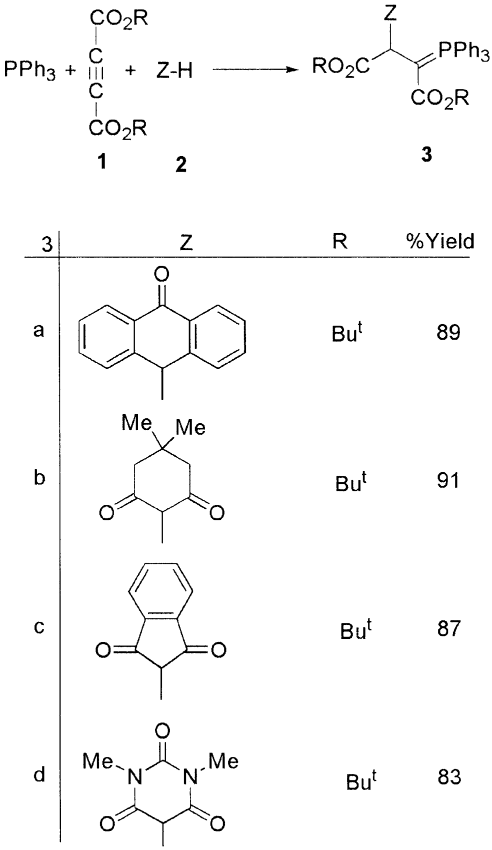


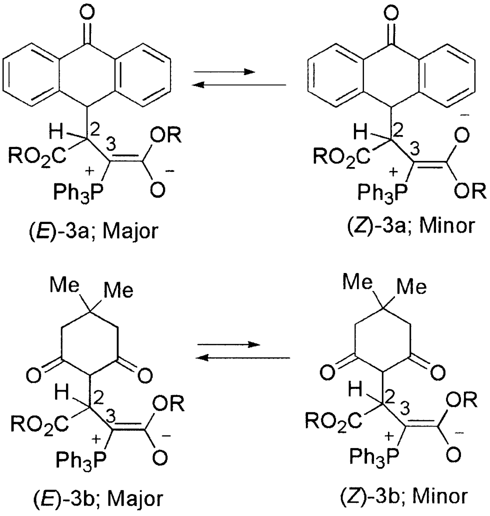
SCHEME 1

RESULTS AND DISCUSSION

Reactions of antron and dimedone with di-tert-butyl acetylendicarboxylate **1** in the presence of triphenylphosphine were carried out in acetone solvent at r.t. and were finished within a few hours. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3a** and **3b.** Any products other than **3a** and **3b** could not be detected by NMR spectroscopy (Scheme 2). Structures of compounds **3a** and **3b** were deduced from their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of them displayed molecular ion peaks at appropriate m/z values. Any initial fragmentations involved missing parts or the complete loss of side chains and a scission of the ring system. ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **3a** and **3b** are consistent

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (*J* in Hz) for OR, CO_2R, C-2, and C-3 in the Major (M) Diastereoisomer of Compounds 3a and 3b

Compound	Isomer (%)	^{1}H NMR spectroscopic data		^{13}C NMR data		^{31}P NMR
		OR	CO_2R	P-C-*C*H ($^{2}J_{pc}$)	*P*-C-CH ($^{1}J_{pc}$)	
3a	M (89)	0.97	1.51	57.19 (13.8)	40.60 (124.5)	24.52
3b	M (91)	1.00	1.50	59.21 (15.6)	41.53 (126.1)	24.75


(*E*)-3a; Major

(*Z*)-3a; Minor

(*E*)-3b; Major

(*Z*)-3b; Minor

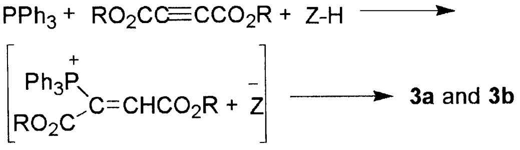
SCHEME 2

with the presence of only one geometrical isomer for the di-tert-butyl derivative because of the bulky tert-butyl group. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants of compounds **3a** and **3b** are shown in Tables I and II.

TABLE II ^{1}H NMR Spectroscopic Data for H2 in Compounds 3a and 3b

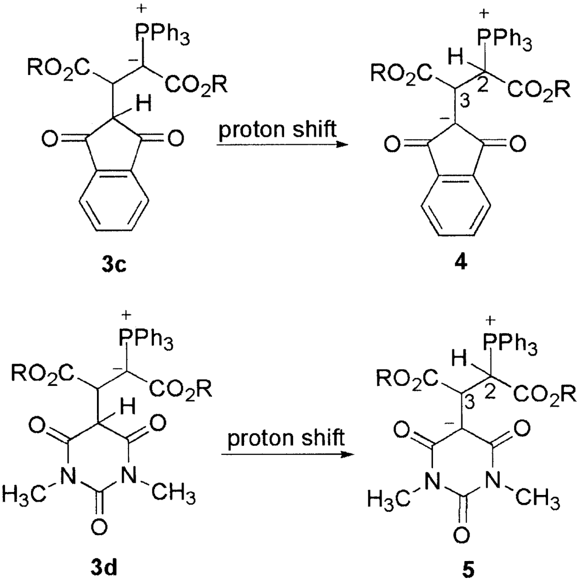
Compound	
3a	4.43 (1H,d, $^{3}J_{HH}$ = 8.9 Hz, P-C-CH-C*H*) 5.54 (1H, dd, $^{3}J_{HH}$ = 8.9 Hz, $^{3}J_{PH}$ = 10.0 Hz, P-C-C*H*-CH)
3b	4.38 (1H, d, $^{3}J_{HH}$ = 9.1 Hz, P-C-CH-C*H*) 5.67 (1H, dd, $^{3}J_{HH}$ = 9.1Hz, $^{3}J_{PH}$ = 10.2 Hz, P-C-C*H*-CH)

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[2–6] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the CH-acid to form phosphoranes **3a** and **3b** (see Scheme 3).



SCHEME 3

The reaction of di-tert-butyl acetylendicarboxylate with indandion and 3,5-dimethyl-barbituric acid in the presence of triphenylphosphine led to stable 1,4-diionic compounds **4** and **5**. These compounds result from the proton transfer reaction in the initial ylides **3c** and **3d** (see Scheme 4). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of 1,4-diionic compounds **4** and **5** are consistent with the presence of one diasteroisomer for the di-tert-butyl derivative.[13] Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants of compounds **4** and **5** are shown in Tables III and IV.



SCHEME 4

TABLE III Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for OR, CO$_2$R, C-2, and C-3 in the Major (M) Diastereoisomer of Compounds 4 and 5

Compound	Isomer (%)	^{1}H NMR spectroscopic data		^{13}C NMR data		^{31}P NMR
		OR	CO$_2$R	P-CH ($^1J_{pc}$)	P-CH-CH ($^2J_{PC}$)	
4	M (87)	0.98	1.52	43.39 (38.7)	43.73 (4.6)	24.15
5	M (83)	1.00	1.51	43.51 (41.4)	44.79 (5.1)	24.73

Briefly, we have prepared novel phosphorus ylides **3a** and **3b** and 1,4-diionic compounds using a one-pot reaction between triphenylphosphine and di-tert-butyl acetylene-dicarboxylate in the presence of antron, dimedone, indandion, and 3,5-dimethyl-barbituric acid. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modifications. Antron and dimedone-containing phosphorus ylides **3a** and **3b** may be considered as potentially useful synthetic intermediates. It seems that the procedure described here may be employed as an acceptable method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and IR spectra of all compounds were measured on an electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Also, the ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a BRUKER DRX-500 AVANCE instrument with CDCl$_3$ as solvent at 500.1, 125.8, and 202.4 MHz, respectively. In addition, the mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Dialkyl

TABLE IV ^{1}H NMR Spectroscopic Data for Two Vicinal Protons in 1,4-Diionic Compounds 4 and 5

Compound	
4	4.63 (1H, dd, $^3J_{HH} = 10.8$ Hz, and $^3J_{PH} = 5.8$ Hz, P-CH-C*H*) 5.76 (1H, dd, $^3J_{HH} = 10.3$ Hz, and $^2J_{PH} = 10.7$ Hz, P-*CH*-CH)
5	5.12 (1H, dd, $^3J_{HH} = 10.5$ Hz, and $^3J_{PH} = 5.6$ Hz, P-CH-C*H*) 5.84 (1H, dd, $^3J_{HH} = 10.5$ Hz, and $^2J_{PH} = 10.7$ Hz, P-C*H*-CH)

acetylenedicarboxylates, triphenlphosphine, antron, dimedone, indandion, and 3,5-dimethylbarbituric acid were purchsed from Fluka, (Buchs, Switzerland) and used without further purifications.

Preparation of Di-tert-butyl 2-(antron-1-yl)-3-(triphenylphosphoranylidene)-butanedioate (3a)

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g or 1 mmol) and antron (0.19 g or 1 mmol) in 10 mL of acetone as solvent, a mixture of di-tert butyl acetylenedicarboxylate (0.23 g or 1 mmol) in 4 mL of acetone was added dropwise at −5°C over 10 min. After approximately 10 h of stirring at r.t., the product was filtered and recrystallized from acetone.

White crystals. m.p. 182–184°C, yield 0.61 g, 89%. IR (KBr) ($\nu_{\max}$, cm^{-1}) 1722 and 1627 (C=O). MS (m/z, %): 580 (M-CO_2CMe_3, 2) 512 (M-$C_{14}H_9$ O, 1), 397 (M-CO_2 CMe_3) and PPh_2, 2), 262 (PPh_3, 100), 183 (PPh_2, 59). Anal. calcd for $C_{44}H_{43}O_5P$(682): C, 77.42; H, 6.30, found: C, 77.21; H, 6.32%.

Di-tert-butyl 2-(dimedon-1-yl)-3-(triphenylphosphoranylidene)-butanedioate (3b)

White crystals, m.p. 135–137°C, yield 0.57 g, 91%. IR (KBr) ($\nu_{\max}$, cm^{-1}): 1712, 1633 and 1615 (C=O). MS (*m/z*, %): 520 (M-PPh, 2), 489 (M-$C_8H_{11}O_2$, 2), 445 (M-PPh2, 8), 262 (PPh_3, 100), 183 (PPh_2, 100), 101 (CO_2CMe_3, 24). Anal. cacld. for $C_{38}H_{45}O_6P$(628): C, 72.61; H, 7.17; found: C, 72.28; H, 7.07%.

Di-tert-Buthyl 2-(Indandion-2-Yl-2-Ylid)-3-Triphenylphosphoniobutane-1,4-Dioate (4)

White crystals, m.p. 139–141°C, yield 0.54 g, 87%. IR (KBr) ($\nu_{\max}$, cm^{-1}) 1735, 1727 and 1706 (C=O). MS (*m/z*, %): 356 (M-PPh_3, 7), 262 (PPh_3, 95), 255 (M-CO_2CMe_3 and PPh_3, 2), 183 (PPh_2, 100). Anal. calcd. for $C_{39}H_{39}O_6P$(634): C, 75.88; H, 5.33% found: C,74.78; H,5.30%.

Di-tert-buthyl 2-(1,3-dimethylbarbituric Acid-5-yl-5-ylid)-3-triphenylphosphoniobutane-1,4-dioate (5)

White crystals, m.p. 162–164°C, yield 0.53 g, 83%. IR (KBr) ($\nu_{\max}$, cm^{-1}): 1716, 1654 and 1579 (C=O). MS (*m/z*, %): 543 (M-CO_2CMe_3, 6), 435 (M-CO_2CMe_3 and PPh, 57), 382 (M-PPh_3, 2), 360 (M-CO_2CMe_3 and

PPh_2, 8), 262 (PPh_3, 100), 183 (PPh_2, 43). Anal. for $C_{36}H_{41}O_7P$(644): C, 67.08; H, 6.37; N, 4.34; found: C, 68.92; H, 6.48; N, 4.38%.

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