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

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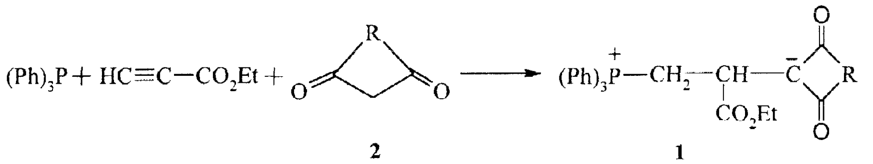
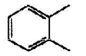
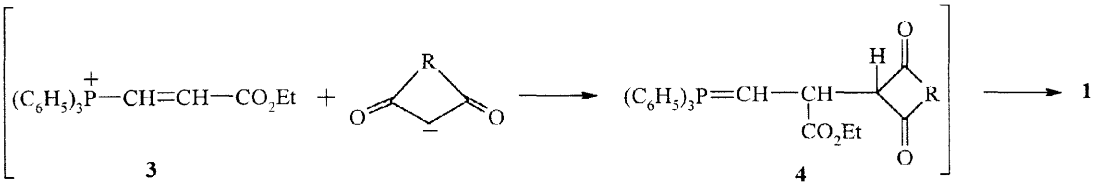
Abstract: Stable crystalline phosphorus betaines are obtained from the 1:1:1 addition reaction between triphenylphosphine and ethyl propiolate in presence of strong CH-acids, such as *N,N′*-dimethylbarbituric acid, Meldrum's acid or indan-1,3-dione. © 1998 Published by Elsevier Science Ltd. All rights reserved.

A number of reactions have been observed which involve the 1,4-diionic phosphorus compounds as elusive transient species.[1] In all of the reactions in which this diionic system is postulated, the betaine cannot be isolated but appears to occur as an intermediate on the pathway to an observed product. To date we know of no published report concerning isolation and characterization of such betaines. We wish to report a facile one-pot synthesis of stable crystalline 1,4-diionic phosphorus compounds **1.** Thus, the reaction of triphenylphosphine and ethyl propiolate in presence of strong CH-acids such as *N,N′*-dimethylbarbituric acid **(2a)**, Meldrum's acid **(2b)** or indandione **(2c)** leads to the corresponding betaines **1**.



1,2	R	%yield of 1
a	$CH_3N-\overset{O}{\overset{\|\|}{C}}-NCH_3$	90
b	$O-C(CH_3)_2-O$	86
c		80

On the basis of the well established chemistry of phosphorus nucleophiles[2] it is reasonable to assume that betaine **1** results[3] from initial addition of triphenylphosphine to ethyl propiolate and concomitant protonation of the reactive 1:1 adduct, followed by attack of carbon atom of the anion of CH-acid to vinyltriphenylphosphonium cation **3** to generate ylide **4** which apparently isomerizes, under the reaction conditions, to produce the 1,4-diionic compound **1**.



Structure **1** was assigned to the isolated products on the basis of their elemental analyses and IR, ^1H NMR, ^{13}C NMR and mass spectral data. NMR spectroscopy was used to distinguish structure **1** from the primary product, the ylide **4**. Thus, the ^1H NMR spectrum of each isolated product showed a methylene and a methine proton signal at about $\delta = 3.8 - 4.6$. Further evidence was obtained from the ^{13}C NMR spectra which

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Table 1 Proton and carbon-13 NMR data for compounds **1a-c**

Compound	$^{1}H/^{13}C$	δ (ppm) ($CDCl_3$ - Me_4Si)
1a	^{1}H	1.18 (3 H, t, *J* 7.2 Hz, CH_3), 3.10 (6 H, s, 2 NMe), 3.8-4.6 (complex m, $CHCH_2P$), 4.10 (2 H, q, *J* 7.2 Hz, OCH_2), 7.4-8.1 (15 H, m, 3 C_6H_5)
	^{13}C	14.17 (CH_3), 23.62 (d, ^{1}J 56.2 Hz, PCH_2), 27.00 (2 NMe), 36.08 (CH), 61.26 (OCH_2), 84.74 [$^{13}C(CO)_2$], 118.73 (d, $^{1}J_{cp}$ 85.3 Hz, C_{ipso}), 129.65 (d $^{3}J_{cp}$ 11.8 Hz, C_{meta}), 133.66 (d, $^{2}J_{cp}$ 10.0 Hz, C_{ortho}) 134.50 (d, $^{4}J_{cp}$ 2.1 Hz, C_{para}), 152.95 ($O{=}CN_2$), 162.35 (2 N-C=O), 176.06 (d $^{3}J_{cp}$ 17.2 Hz, C=O ester).
1b	^{1}H	1.20 (3 H, t *J* 7.2 Hz, CH_3), 161 (6 H, s, 2 CH_3), 3.8-4.4 (3 H, complex m, $CHCH_2P$), 4.14 (2 H, q *J* 7.2 Hz, OCH_2), 7.4-8.1 (15 H, m, 3 C_6H_5).
	^{13}C	13.52 (CH_3), 22.84 (d $^{1}J_{cp}$ 54.4 Hz, PCH_2), 25.24 (2 CH_3), 35.66 (CH), 60.75 (OCH_2), 72.74 [d $^{3}J_{cp}$ 2.7 Hz, $^{13}C(CO)_2$], 100.13 ($^{13}CMe_2$), 118.33 (d $^{1}J_{cp}$ 85.2 Hz, C_{ipso}), 129.32 (d $^{3}J_{cp}$ 12.7Hz, C_{meta}), 133.13 (d $^{2}J_{cp}$ 10.0 Hz, C_{ortho}), 134.02 (d $^{4}J_{cp}$ 2.2 Hz, C_{para}) 165.49 (2 C=O), 173.83 (d $^{3}J_{cp}$ 16.3 Hz, C=O ester).
1c	^{1}H	1.10 (3 H, t *J* 7.2Hz, CH_3), 4.05 (2 H, q *J* 7.2 Hz, OCH_2), 3.7-4.4 (complex m, $CHCH_2P$), 7.2-8.0 (19 H, m, 3 C_6H_5 and C_6H_4).
	^{13}C	13.76 (CH_3), 22.90 (d $^{1}J_{cp}$ 55.3 Hz, PCH_2), 33.23(CH), 61.08 (OCH_2), 100.33 [$^{13}C(CO)_2$], 116.99 (CH), 117.94 (d $^{1}J_{cp}$ 86.1 Hz, C_{ipso}), 128.76 (CH), 129.52 (d $^{3}J_{cp}$ 12.7 Hz, C_{meta}), 133.23 (d $^{2}J_{cp}$ 10.0 Hz, C_{ortho}), 133.97 (d $^{4}J_{cp}$ 2.1 Hz, C_{para}), 139.55 (C), 173.26 (d $^{3}J_{cp}$ 16.3 Hz, C=O ester), 189.55 (2 C=O).

displayed a P-CH_2 doublet at about $\delta = 23$. Structure **1** was further confirmed by the ^{13}C NMR data for the CH-acid residue which exhibits local C_s symmetry (see Table 1).[4]

REFERENCES AND NOTES

1 Bestmann, H.J. and Gross, A. *Tetrahedron Lett.*, **1997**, *38*, 4765; Bestmann, H. J.and Vostrosky, O.*Top. Curr. Chem.*, **1983**, *109*, 85; Bestmann, H. J. and Zimmermann, R. *Top. Curr. Chem.*, **1971**, *20*, 88.

2 Engel, R."Synthesis of Carbon-Phosphorus Bonds", CRC Press, Boca Raton, FL, **1988**; Cadogan, J. I. G. "Organophosphorus Reagent in Organic Synthesis", Academic Press, New York, **1979**.

3 The typical process for the preparation of ethyl 2-(*N,N'*-dimethylbarbituric acid-5-yl-5-ylid)-3-triphenylphosphonio-propionate **1a** is described as an example. To a magnetically stirred solution of *N,N'*-dimethylbarbituric acid (0.156 g, 1 mmol) and triphenylphosphine (0.262 g, 1mmol) in a 1:1 mixture of CH_2Cl_2 and hexane (10 ml) was added, dropwise, a mixture of ethyl propiolate (0.098 g, 1mmol) in CH_2Cl_2 (2 ml) at -5 °C over 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 24 h. The precipitate was filtered and washed with cold diethyl ether (2×5 ml). The product was recrystallized from ethyl acetate-pentane (1:1) to yield **1a** as white crystals (0.47 g, 90%), m.p. 214-215 °C. IR (KBr) (ν_{max} cm^{-1}): 1706 (C=O); 1650 (C=C); 1578 (2 NC=O); 1428 ($N_2C{=}O$); MS (*m/z*,%): 516 (M^+, 18); 262 (Ph_3P, 58); 183 (M^+-$C_{12}H_8P$, 100); 100 (CH_2CHCO_2Et, 58). (Found: C, 65.8; H, 5.75; N, 5.3; $C_{29}H_{29}O_5N_2P$ requires C, 67.44; H, 5.66; N, 5.42%). Selected data for **1b**: yellow crystals m.p. 191-192 °C, yield 0.43, (86%). IR (KBr) (ν_{max}, cm^{-1}): 1699 (C=O); 1656 (C=C); 1592 and 1588 (C=O); MS (*m/z*,%): 505 (M+1, 1); 262 (Ph_3P, 78); 183 (M^+-$C_{12}H_8P$, 100); 108 (PhP, 59). (Found: C, 68.8; H, 5.8; $C_{29}H_{29}O_6P$ requires C, 69.04; H, 5.79%). Selected data for **1c**: yellow crystals, m.p. 110-111 °C), yield 0.40 g, (80%). IR (KBr) (ν_{max}, cm^{-1}): 1708 (C=O); 1645 and 1596 (C=C); 1519 (C=O); MS (*m/z*, %): 446 (M^+-$C_2O_2H_4$, 1); 262 (Ph_3P, 100); 183 (M^+-$C_{12}H_8P$, 35); 108 (PhP, 17). (Found: C, 73.7; H 5.5; $C_{32}H_{27}O_4P$ requires, C, 75.87; H, 5.37%).

4 A cyclic six-membered ring structure for compound **1** is unlikely because it requires several chemical shift coincidences in the ^{1}H and ^{13}C NMR spectra.