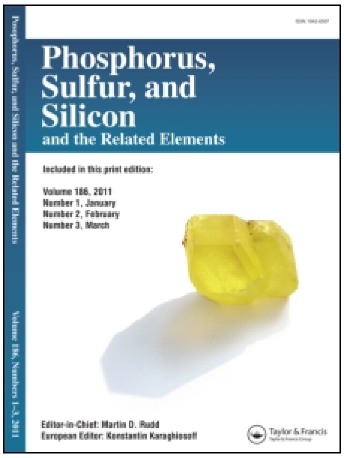

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STEREOSELECTIVE SYNTHESIS OF STABLE 1,4-DIIONIC PHOSPHORUS COMPOUNDS MEDIATED BY A VINYLTRIPHENY LPHOSPHONIUM SALT

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STEREOSELECTIVE SYNTHESIS OF STABLE 1,4-DIIONIC PHOSPHORUS COMPOUNDS MEDIATED BY A VINYLTRIPHENYLPHOSPHONIUM SALT

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The addition reaction of triphenylphosphine to ethyl phenylpropiolate in the presence of strong CH-acids, such as Meldrum's acid, *N,N'*-dimethylbarbituric acid or indane-1,3-dione leading to highly functionalized 1,4-diionic organophosphorus compounds is reported. The stable crystalline phosphorus betaines were characterized by ^{1}H, ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry and elemental analysis.

Keywords: Organophosphorous compounds; CH-acids; Triphenylphosphine; Acetylenic ester; Stereochemistry

The development of new stereoselective reactions has been a major topic in synthetic organic chemistry, resulting now a wide variety of such reactions [1–3]. Controlling the stereochemical aspects of reaction selectivity has always been a prime challenge to synthetic organic chemists. These concerns are especially pressing when the preparations of multifunctional substances of specific biological action are involved. Organophosphorus compounds are synthetic targets of interest, not least because of their value for a variety of industrial and synthetic uses [4–6]. The successful attack by nucleophilic trivalent phosphorus on a carbon atom is facilitated when the latter is conjugated with a carbonyl group, or when it is part of an unsaturated bond otherwise activated [4–13]. There are many studies on

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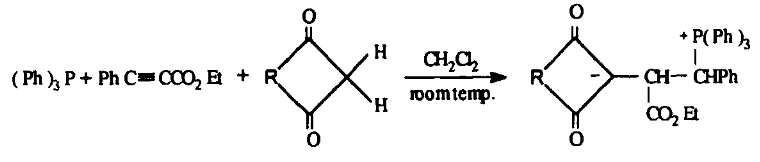
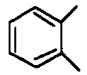
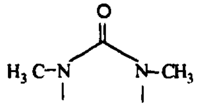
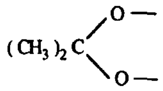
* To receive any correspondence

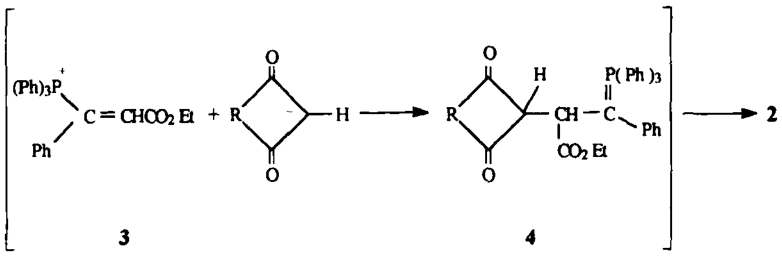
the reaction between trivalent phosphorus nucleophiles and α,β -unsaturated carbonyl compounds in the presence of a proton source such as alcohols or CH-acids[14,15]. We wish to report a facile one-pot stereoselective synthesis of stable I,4-diionic phosphorus compounds **2**. Thus, reaction of triphenylphosphine and ethyl phenylpropiolate in the presence of CH-acids **1** leads to stereoselective synthesis of betaine **2**.



1 **2**

1,2	**R**
a	
b	
c	

Several reactions have been observed which involve the 1,4-diionic phosphorus compounds as transient species [11,12,16]. In all of the reactions in which this diionic system is postulated, the betaine cannot be isolated but appears to occure as an intermediate on the pathway to an observed product. On the basis of the well established chemistry of trivalent phosphorus nucleophiles [4–6] it is reasonable to assume that betaine **2** results from initial addition of triphenylphosphine to ethyl phenylpropiolate and subsequent 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 **2**.



The structures of compounds **2a-c** were deduced from their elemental analyses and their ^{1}H, ^{13}C and ^{31}P 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* = 582, 592 and 580. Initial fragmentations involve loss of the chains [$(Ph_3)P$, CH_3OH, $-CO_2CH_3$] and scission of the heterocyclic ring systems.

A cyclic six-membered ring structure for compound **2** is unlikely because it requires several chemical shift coincidences in the ^{1}H and ^{13}C NMR spectra. If compound **2** had a cyclic structure, then we were to expect a doublet at about $\delta = 160$ for the ^{13}C-O-P moiety in the ^{13}C NMR spectra. Structure **2** was further confirmed by the ^{13}C NMR data for the CH-acid residue which exhibits local *Cs* symmetry (see Table I). Moreover, the ^{31}P NMR spectra of compounds **2a-c** displayed signals at about 25 ppm (downfield from 85% H_3PO_4). These shifts are similar to those observed for alkyl-triphenylphosphonium iodide [17,18]. The ^{31}P chemical shift for a cyclic six-membered ring structure having a P-O bond is expected to be 80–90 ppm more shielded [17–19].

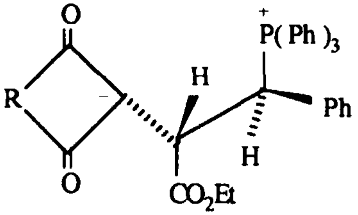
The ^{1}H NMR spectrum of each isolated product showed two vicinal methine proton signals at about $\delta = 4.9$–5.3 and $\delta = 6.0$–6.3, which appear as separate double doublets with $^2J_{HP}$ and $^3J_{HP}$ values of 14 and 9 Hz, respectively. The vicinal proton-proton coupling constant ($^3J_{HH}$) as a function of the torsion angle can be obtained from Karplus equation [20]. Typically J_{gauche} varies between 1.5 and 5 Hz and J_{anti} between 10 and 14 Hz. Observation of $^3J_{HH} = 11.5$ Hz for the vicinal protons in **2a-c** (see Table I) indicates an anti arrangement for these protons. Since compound **2** posses two stereogenic centers, two diastereoisomers with anti HCCH arrangements are possible.

TABLE I Proton and carbon-13 NMR data for compounds ***2a*, *2b*** and ***2c***

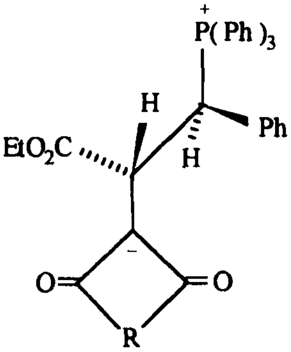
d	$^1H/^{13}C/^{31}P$	$\delta(ppm)\ (CDCl_3 - Me_4Si)$
	^1H	0.9 (3 H, t J 7 Hz, CH_3), 3.8 (2 H, m, ABX_3 system, OCH_2), 4.9 (1H, dd $^3J_{HH}$ 12 Hz $^3J_{HP}$ 9 Hz, CH), 6.0 (1 $^3J_{HH}$12 Hz, $^2J_{HP}$ 14 Hz, CH), 7.0–7.8 (24 H, m, $4C_6H_5$ and C_6H_4)
	^{13}C	13.4 (CH_3), 42.8 (d $^2J_{CP}$ 1 Hz CH-CHP), 42.9 (d $^1J_{CP}$49 Hz, PCH), 59.5(OCH_2), 97.9 [d $^3J_{CP}$ 2 Hz, $C(CO)_2$], 116 of C_6H_4), 116.9^a (d $^1J_{CP}$ 83 Hz C_{ipso}), 128.1 and 128.2 (CH of C_6H_5), 128.4(CH of C_6H_4), 128.9^a (d $^3J_{CP}$ 13 Hz, 130.8 (d $^3J_{CP}$ 5 Hz, CH of C_6H_5), 132.6 (d $^2J_{CP}$ 6 Hz, C_{ipso} of C_6H_5), 133.3^a (d $^4J_{CP}$ 2 Hz, C_{para}), 134.1^a(d $^2J_{C}$ C_{ortho}), 139.4 (C of C_6H_4), 168.6 (d $^3J_{CP}$ 19 Hz, C=O ester), 189.6 (2 C=O)
	^{31}P	24.8
	^1H	0.9 (3 H, t J 7 Hz, CH_3), 3.1 (6 H, s, 2 NCH_3), 3.8 (2 H, m, ABX_3 system, OCH_2), 5.3 (1 H, dd, $^3J_{HH}$ 12 Hz, $^3J_{H}$ CH), 6.3 (1 H, dd $^3J_{HH}$ 12 Hz, $^2J_{HP}$14 Hz, CH), 7.0–7.9 (20 H, m, 4 C_6H_5)
	^{13}C	13.3 (CH_3), 26.6 (2 NCH_3), 42.3 (d $^1J_{CP}$ 48 Hz, P-CH), 43.9 (d $^2J_{CP}$ 1Hz, *C*H-CHP), 59.4 (OCH_2), 82.7 [d $^3J_{C}$ $C(CO)_2$], 117.4^a(d $^1J_{CP}$ 83 Hz, C_{ipso}), 127.8 and 128.3 (CH of C_6H_5), 128.6^a(d $^3J_{CP}$ 13 Hz, C_{meta}), 131.2 (d $^3J_{C}$ CH of C_6H_5), 132.8 (d $^2J_{CP}$ 6 Hz, C_{ipso} of C_6H_5), 133.5^a(d $^4J_{CP}$ 2 Hz, C_{Para}), 134.1^a(d $^2J_{CP}$ 9 Hz C_{ortho}), 52.1 N-C 162.1 (2 N-C=O), 169.2 (d $^3J_{CP}$ 20 Hz, C=O ester)
	^{31}P	25.6
	^1H	0.9 (3 H, t J 7 Hz, CH_3), 1.34 (6 H, s, CMe_2), 3.8 (2 H, m, ABX_3 system, OCH_2), 5.1 (1 H, dd $^3J_{HH}$ 12 Hz, $^3J_{HP}$ CH), 6.1(1 H, dd $^3J_{HH}$ 12 Hz, $^2J_{HP}$14 Hz, CH), 6.9–7.9 (20 H, m, 4 C_6H_5)
	^{13}C	13.8 (CH_3), 25.5 (2 CH_3 of CMe_2), 42.9 (d $^1J_{CP}$ 48 Hz, PCH), 44.5 (d $^2J_{CP}$ 2 Hz, *C*H-CHP), 59.8 (OCH_2), 7 $^3J_{CP}$2 Hz, $C(CO)_2$], 100.2 (CMe_2), 117.8^a(d $^1J_{CP}$ 84 Hz, C_{ipso}), 128.1 and 128.2 (CH of C_6H_5), 129.1^a(d $^3J_{CP}$ C_{meta}), 131.3 (d $^3J_{CP}$ 6 Hz, CH of C_6H_5), 132.6 (d $^2J_{CP}$ 6 Hz, C_{ipso} of C_6H_5), 133.9^a(d $^4J_{CP}$ 2 Hz, C_{para}), 134.5^a(9 Hz, C_{ortho}), 165.7 (2 C=O), 169.7 (d $^3J_{CP}$ 21 Hz, C=O ester)
	^{31}P	25.3

ances of $P(C_6H_5)_3$

The three-bond carbon-phosphorus couplings, $^3J_{CP}$ depends on configuration, as expected, transoid couplings being larger than cisoid ones. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and pentavalent phosphorus[21]. The observation of $^3J_{CP}$ of 19–21 Hz for the ester C=O group (see Table I), is in agreement with the 2*R*, 3*R*-**2** and its mirror image 2*S*, 3*S*-**2**, geometries.



2R, 3R (2S, 3S)-**2**



2S, 3R (2R, 3S)-**2**

In summery, functionalized 1,4-diionic organophosphorus compounds **2a-c** may be considered as potentially useful synthetic intermediates [4–13]. The procedure described here may be an acceptable method for the preparation of betaines with variable functionalities. Further investigations of the present method will be required to establish its utility and scope.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses for the C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were measured with JEOL EX-90A spectrometer at 90 and 22.6 MHz, respectively. The ^{31}P NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 202.4 MHz as solutions in $CDCl_3$ using 85% H_3PO_4 as external standard. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Ethyl phenylpropiolate, *N,N′*-dimethylbarbituric acid, indane-1,3-dione, and Meldrum's acid were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

Preparation of ethyl 2-(indane-1,3-dione-2-yl-2-ylid)-3-phenyl-3-triphenylphosphoniopropiolate 2a. General procedure

To a magnetically stirred solution of triphenylphosphine (0.52 g, 2 mmol) and indane-1,3-dione (0.29 g, 2 mmol) in CH_2Cl_2 (10 ml) was added, dropwise, a mixture of ethyl phenylpropiolate (0.33 ml, 2 mmol) in CH_2Cl_2 (5 ml) at −10°C over 10 min. After 48 hr stirring at room temperature, the product was filtered and recrystallized from dichloromethane:ethyl acetate (1:1), 1.07 g, mp 172–174°C, yield 92%; IR (ν_{max}, cm^{-1}): 1729 (C=O ester), 1607(C=O ketone). MS(*m/z*, %): 582(M^+, 3), 423 (M^+ $C_9H_4O_2$-CH_3, 5), 262.5 ($P\phi_3^+$, 80), 183 ($P\phi_2H_2^+$, 100), 77 (CO_2Et, 30). Analysis: Calc. for $C_{38}H_{31}O_4P$ (582.5): C, 78.3; H, 5.4. Found C, 78.5; H, 5.5.

Selected data for ethyl 2-(N,N′- dimethylbarbituric acid-5-yl-5-ylid)-3-phenyl-3-triphenylphosphonio-propiolate 2b

1.06 g, mp 193–195°C yield 90%; IR(ν_{max}, cm^{-1}): 1733(C=O, ester), 1667(C=O, amide). MS(*m/z*, %): 592 (M^+, 2), 330(M^+-$P\phi_3$, 5), 262.5($P\phi_3^+$, 60), 183($P\phi_2H_2^+$, 100), 77 (CO_2Et^+, 80). Analysis: Calc. for $C_{35}H_{33}N_2O_5P$ (592.6): C, 70.9; H, 5.6. Found C, 69.8; H, 5.5.

Selected data for ethyl 2-(isopropylidenemalonate-5-yl-5-ylid)-3-phenyl-3-triphenylphosphonio-propiolate 2c

1.09 g, mp 185–186°C, yield 94%; IR (ν_{max}, cm^{-1}): 1736 (C=O, ester), 1669 (C=O). MS(*m/z*, %): 580(M^+, 2), 262($P\phi_3^+$, 28), 183 ($P\phi_2H_2^+$, 40), 40(C=C=O^+, 100%). Analysis Calc. for $C_{35}H_{33}O_6P$(580.6): C, 72.4; H, 5.7. Found C, 71.4; H, 5.8.

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