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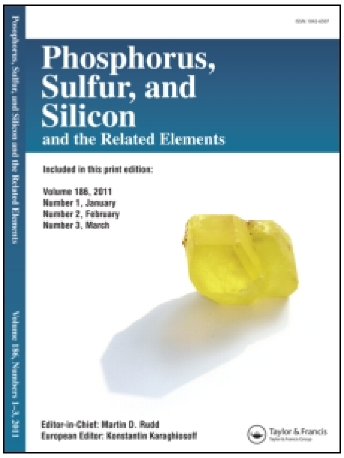

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Stable 1,3-Diionic Organophosphorus Compounds Derived from Ethynyl Phenyl Ketone

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STABLE 1,3-DIIONIC ORGANOPHOSPHORUS COMPOUNDS DERIVED FROM ETHYNYL PHENYL KETONE

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The addition of triphenylphosphine to ethynyl phenyl ketone in the presence of electron-defficient aromatic aldehydes leading to 1,3-diionic organophosphorus compounds is reported.

Keywords: Acetylenic ketone; aromatic aldehydes; phosphorus betaines; triphenylphosphine

INTRODUCTION

In recent years there has been increasing interest in the synthesis of organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom.[1–3] This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial, and chemical synthetic uses. A large number of methods have appeared describing novel synthesis of organophosphorus compounds.

The successful attack by nucleophilic trivalent phosphines on the carbon atom is facilitated when the later is conjugated with a carbonyl group, or when it is part of an unsaturated bond otherwise activated.[1–9] There are many studies on the reactions between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source such as alcohols or CH-acids.[1,9,10] Here we report on a simple one-pot synthesis of stable crystalline 1,3-diionic organophosphorus compounds **2**. Thus, the reaction of triphenylphosphine and ethynyl phenyl ketone in the presence of electron-defficient

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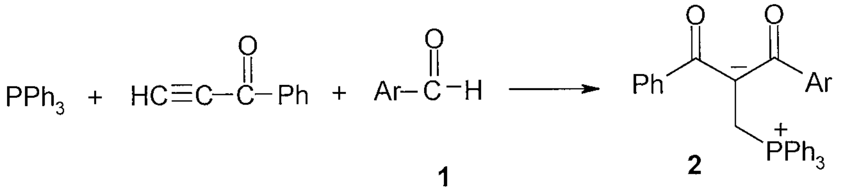


1,2	Ar	%Yiled of **2**
a	Ph	87
b	4-$NO_2C_6H_4$	90
c	3-$NO_2C_6H_4$	85
d	4-$OHCC_6H_4$	85
e	3-Pyridyl	93

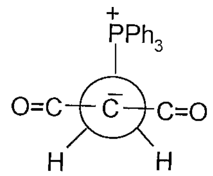
SCHEME 1

aromatic aldehydes **1**, as carbon electrophiles, leads to betaines **2** (Scheme 1).

When ethynyl methyl ketone was employed as acetylenic ketone or when propanal, 4-methoxybenzaldehyde, furfural, cinamaldehyde, or benzophenone were used as carbon electrophile, no product could be isolated.

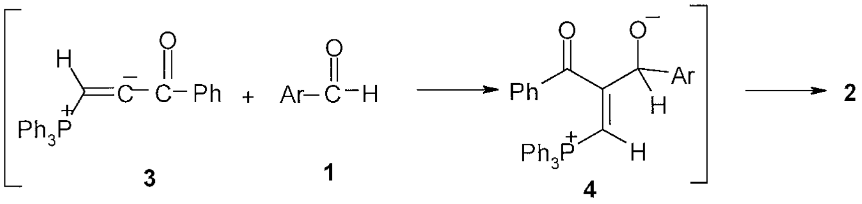
RESULTS AND DISCUSSION

The reaction of ethynyl phenyl ketone with triphenylphosphine in the presence of an aromatic aldehyde proceeded spontaneously at room temperature in ethyl acetate, and was completed within 1 h. ^1H and ^{13}C NMR spectra of the crude product cleanly indicated the formation of fairly stable 1,3-diarylpropane-1,3-dione-2-ylid-triphenylphosphoniumethanes **2**. Any product other than **2** could not be detected by NMR spectroscopy. The structures of **2a–e** were deduced from their elemental analyses and their IR, ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra. The IR spectrum of each isolated product exhibited the absorption bands of carbonyl groups attached to the negatively charged carbon atom at 1464-1451 cm^{-1} and the absorption bands of the triphenylphosphine moiety at about 1395, 1110, and 910 cm^{-1} (see Experimental section). The mass spectra of these compounds displayed molecular ion peaks at appropriate *m*/*z* values. Any initial fragmentation involved the loss of Ph_3P, PhCO, and ArCO moieties. The ^1H NMR spectrum of compounds **2a–e** showed methylene proton signals at about $\delta = 4.5-5.0$, which appear as a doublet with $^2J_{HP}$ value of 8.0–9.5 Hz. The three bond carbon-phosphorus couplings $^3J_{CP}$ depends on configuration. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and pentavalent phosphorus.[13] The $^3J_{CP}$ values of zero for compounds **2a–d** and 1.8–2.0 Hz for **2e**, suggests that in the most stable conformation of the molecule the $CH_2—P$ bond is perpendicular to the line connecting the two carbonyl groups (Scheme 2).



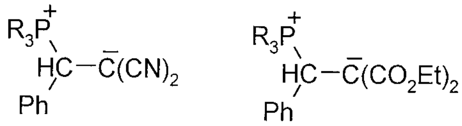
SCHEME 2

We have not established a mechanism for the formation of 1,3-diarylpropane-1,3-dione-2-ylid-triphenylphosphoniumethane **2a–e**, but a reasonable possibility is indicated in Scheme 3. On the basis of the well established chemistry of trivalent phosphorus nucleophiles[1–5] it is reasonable to assume that betaine **2** results from initial addition of triphenylphosphine to ethynyl phenyl ketone and subsequent attack of the resulting anion **3** to the carbonyl carbon of aldehyde **1** to yield betaine **4** which apparently isomerizes, under the reaction conditions employed, to produce the 1,3-diionic compounds **2** (Scheme 3).



SCHEME 3

Closely related to the 1,3-diionic organophosphorus compounds just described are the resonance-stabilized compounds **5** and **6** (see Scheme 4) formed by the addition of trialkylphosphines to benzalmalononitrile and diethyl benzalmalonate, respectively.[11,12] However, the method described by these workers cannot be employed for the synthesis of betaines in which two hydrogen atoms are present on a carbon bound to phosphorus.



5 **6**

SCHEME 4

In summary, the present synthesis of 1,3-diionic organophosphorus compounds complements older methods[11,12] and offers significant advantages for the synthesis of betaines with two hydrogen atoms present on a carbon bound to phosphorus. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also that the substances can be mixed without any activation or modification. The procedure described here may be an acceptable one-pot method for the preparation of betaines with variable functionalities.

EXPERIMENTAL

Melting points were measured on an electrothermal 9100 apparatus. 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. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz respectively. ^{1}H, ^{13}C, and ^{31}P spectra were obtained on solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. Ethynyl phenyl ketone was prepared by addition of ethynylmagnesium bromide to benzaldehyde[14] and oxidation[15] of the propargylic alcohol. Other chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and are used without further purification.

Preparation of 1,3-diphenylpropane-1,3-dione-2-ylid-triphenylphosphoniumethane 2a

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol) and benzaldehyde (0.212 g, 2 mmol) in ethyl acetate (10 mL) was added, dropwise a solution of ethynyl phenyl ketone (0.260 g, 2 mmol) in ethyl acetate (3 mL) at room temperature. After 1 h the solution was cooled in an ice/satl bath and stirred for another 10 min. The precipitate was filtered and washed with cooled ethyl acetate. Yellow powder, 0.86 g, m.p. 118–120°C, yield 87%, IR(KBr) $\nu_{\text{max.}}$ cm^{-1}): 3055 (w), 1731 (w), 1575 (w), 1525 (w), 1505 (w), 1458 (s), 1429 (s), 1399 (m), 1349 (m), 1199 (w), 1106 (m), 910 (m). Analyses: Calc. for $C_{34}H_{27}O_2P$ (498.3): C, 81.93; H, 5.42%. Found: C, 81.8; H, 5.4%. δ_H($CDCl_3$): 4.6 (2 H, d $^2J_{HP}$ 8.6 Hz, CH_2), 6.7–8.0 (25 H, m, $5C_6H_5$). δ_C($CDCl_3$): 27.2 (d, $^1J_{CP}$ 43.1 Hz, CH_2), 101.7 [d, $^2J_{CP}$ 7.5 Hz, $C(CO_2]$, 121.7 (d, $^1J_{CP}$ 83.3 Hz, C_{ipso} of Ph_3P), 125.8, 126.7, 127.8, 128.0 (CH of C_6H_5), 128.5 (d, $^3J_{CP}$ 12.1Hz, C_{meta} of Ph_3P), 132.7 (C_{para} of Ph_3P), 133.5 (d, $^2J_{CP}$ 9.2 Hz, C_{ortho} of Ph_3P), 189.6 (C=O). δ_p($CDCl_3$): 24.7 (Ph_3P^+—CH_2). MS (*m/z,%*): 498 (M^+,1), 262 (99), 183 (75), 105 (100), 77 (61), 51 (55).

Selected data for 1-(4-nitrophenyl)-3-phenylpropane-1,3-dione-2-ylid-triphenylphosphoniomethane ***2b***. Yellow powder, 0.92 g, m.p. 159–161°C, yield 90%, IR (KBr) (ν_{max}, cm^{-1}): 3060 (w), 1549 (w), 1501 (m), 1464 (s), 1433 (s), 1388 (m), 1336 (s), 1184 (w), 1107 (m), 915 (m), 863 (m). Analyses: Calc. for $C_{34}H_{26}NO_4P$ (543.3): C, 75.14; H, 4.79; N, 2.58%. Found: C, 75.2; H, 4.7; N, 2.5%. δ_H($CDCl_3$): 4.6 (2 H, d $^2J_{HP}$ 7.8 Hz, CH_2), 6.7–7.9 (24 H, m, 4 C_6H_5 and $C_6H_4NO_2$). δ_C($CDCl_3$): 27.1 (d, $^1J_{CP}$ 43.7 Hz, CH_2), 103.5 [d, $^2J_{CP}$ 8.0 Hz, $C(CO)_2]$, 121.8 (d, $^1J_{CP}$ 83.3 Hz, C_{ipso} of Ph_3P), 121.8 (CH of $C_6H_4NO_2$), 126.9, 128.5, 128.7, and 128.9 (CH of C_6H_5), 129.3 (d, $^3J_{CP}$ 12 Hz, C_{meta} of Ph_3P), 133.7 (C_{para} of Ph_3P), 134.2 (d, $^2J_{CP}$ 9.3 Hz, C_{ortho} of Ph_3P), 189.6 (C=O), 190.9 (C=O). δ_P($CDCl_3$): 26.1 (Ph_3P^+—CH_2). MS (*m/z,%*): 543 (M^+, 1), 262 (95), 183 (77), 150 (10), 105 (100), 77 (78), 51 (60).

Selected data for 1-(3-nitrophenyl)-3-phenylpropane-1,3-dione-2-ylid-triphenylphosphoniomethane ***2c***. Yellow powder, 0.92 g, m.p. 123–125°C. yield 85%, IR (KBr) (ν_{max}, cm^{-1}): 3050 (w), 1575 (w), 1521 (m), 1460 (s), 1430 (s), 1395 (m), 1339 (s), 1203 (w), 1106 (m), 929 (m). Analyses: Calc. for $C_{34}H_{26}NO_4$ (543.3): C, 75.14; H, 4.79; N, 2.58%. Found: C, 75.2; H, 4.8; N, 2.5%. δ_H($CDCl_3$): 4.7 (2 H, d, $^2J_{HP}$ 9.3 Hz, CH_2), 6.7–7.9 (24 H, m, $4C_6H_5$ and $C_6H_4NO_2$). δ_C($CDCl_3$): 27.2 (d, $^1J_{CP}$ 43.5 Hz, CH_2), 103.4 [d, $^2J_{CP}$ 8.3 Hz, C(C=O)2], 121.8 (d, $^1J_{CP}$ 83.5 Hz, C_{ipso} of Ph_3P), 122.0 and 123.8 (CH of $C_6H_4NO_2$), 126.9, 128.0, 128.4, and 128.7 (CH of C_6H_5), 127.9 (CH of $C_6H_4NO_2$), 129.4 (d, $^3J_{CP}$ 12.2 Hz, C_{meta} of Ph_3P), 133.8, (d,$^4J_{CP}$ 2.5 Hz, C_{para} of Ph_3P), 134.2 (d, $^2J_{CP}$ 9.6 Hz, C_{ortho} of Ph_3P), 142.6, 144.7, and 146.2 (CH of $C_6H_4NO_2$), 186.2 (C=O), 191.1 (C=O). δ_P($CDCl_3$): 26.3 (Ph_3P^+—CH_2). MS (*m/z,%*): 262 (100), 183 (79), 150 (5), 108 (62), 105 (10), 77 (20), 51 (50).

Selected data for 1-(4-formylphenyl)-3-phenylpropane-1,3-dione-2-ylid-triphenylphosphoniomethane ***2d***. Yellow powder, 0.90 g, m.p. 131–133°C. yield 85%, IR (KBr) (ν_{max}, cm^{-1}): 3055 (w), 1684 (s), 1600 (m), 1568 (w), 1532 (m), 1451 (s), 1399 (m), 1340 (m), 1294 (w), 1229 (s), 1162 (m), 1108 (s), 960 (m). Analyses: Calc. for $C_{35}H_{27}NO_3P$ (526.3): C, 79.85; H, 5.13%. Found: C, 79.7; H, 5.2%. δ_H($CDCl_3$): 4.7 (2 H, broad s,

CH_2), 6.7–7.9 (24 H, m, $4C_6H_5$, and C_6H_4), 9.7 (1 H, s, CHO). $\delta_C(CDCl_3)$: 27.3 (d, $^1J_{CP}$ 43.0 Hz, CH_2), 101.8 [d, $^2J_{CP}$ 8.2 Hz, $C(CO)_2$], 122.1 (d, $^1J_{CP}$ 83.3 Hz, C_{ipso} of Ph_3P), 126.7, 128.5, 128.7, and 128.8 (CH of C_6H_5), 128.2 (CH of C_6H_4), 129.3 (d, $^3J_{CP}$ 12.2 Hz, C_{meta} of Ph_3P), 133.6 (C_{para} of Ph_3P), 134.2 (d, $^2J_{CP}$ 9.3 Hz, C_{ortho} of Ph_3P), 134.7, 142.8, and 149.6 (CH of C_6H_4), 188.0 (C=O), 190.8 (C=O), 192.1 (C=O). $\delta_p(CDCl_3)$: 25.9 (Ph_3P^+-CH_2). MS (*m/z,%*): 262 (100), 183 (96), 133 (10), 108 (74), 105 (7), 77 (30), 51 (75).

Selected data for 1-(3-pyridyl)-3-phenylpropane-1,3-dione-2-ylid-triphenylphosphoniomethane ***2e***. Pale yellow powder, 0.92 g, m.p. 121–123°C, yield 93%, IR(KBr) (ν_{max}, cm^{-1}): 3055 (w), 1730 (w), 1578 (w), 1526 (w), 1475 (s), 1430 (s), 1396 (m), 1350 (m), 1202 (w), 1106 (m), 910 (m). Analyses: Calc. for $C_{33}H_{26}NO_2$ (499.3): C, 79.36; H, 5.21; N, 2.81%. Found: C, 79.2; H, 5.2; N, 2.8%. $\delta_H(CDCl_3)$: 4.7 (2 H, d, $^2J_{HP}$ 9.3 Hz, CH_2), 6.7–8.0 (24 H, m, $4C_6H_5$ and C_5H_4N). $\delta_C(CDCl_3)$: 27.3 (d, $^1J_{CP}$ 43.4 Hz, CH_2), 103.5 [d, $^2J_{CP}$ 8.2 Hz, $C(CO)_2$], 121.0 (CH of C_5H_4N), 122.0 (d, $^1J_{CP}$ 83.3 Hz, C_{ipso} of Ph_3P), 127.0, 127.9, 128.5, and 128.7 (CH of C_6H_5), 129.3 (d, $^3J_{CP}$ 12.3 Hz, C_{meta} of Ph_3P), 133.7 (C_{para} of Ph_3P), 134.2 (d, $^2J_{CP}$ 9.2 Hz, C_{ortho} of Ph_3P), 138.9, 142.7, 147.9, and 149.2 (CH of C_5H_4N), 186.6 (d, $^3J_{CP}$ 2.0 Hz, CO), 190.9 (d, $^3J_{CP}$ 1.8 Hz, CO). $\delta_C(CDCl_3)$: 26.0 (Ph_3P^+-CH_2). MS (*m/z,%*): 499(M^+, 1) 262 (100), 183 (69), 106 (35), 108 (30), 105 (98), 77 (55), 51 (53).

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