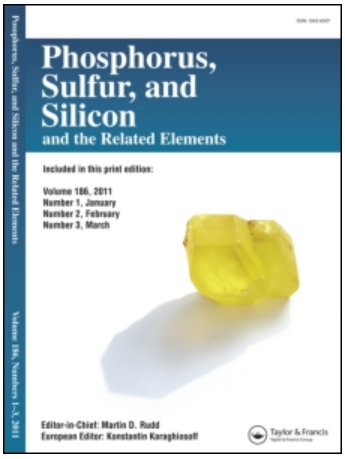

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Stable 1,6-Diionic Phosphorus Betaines Derived from Electron-Deficient Acetylenic Compounds

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STABLE 1,6-DIIONIC PHOSPHORUS BETAINES DERIVED FROM ELECTRON-DEFICIENT ACETYLENIC COMPOUNDS

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*The addition of triphenylphosphine to methyl propiolate, ethyl propiolate, or ethynyl methyl ketone in the presence of a strong NH-acid, such as 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one, leads to stable 1,6-diionic organophosphorus compounds in excellent yields.*

Keywords: Acetylenic ester; acetylenic ketone; NH-acid; 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one; triphenylphosphine

INTRODUCTION

Phosphorus betaines are reactive intermediates, which take part in many valuable reactions in organic synthesis.[1,2] We have recently described[3–7] the synthesis of stable 1,4-diionic organophosphorus compounds from the reaction of triphenylphosphine and electron deficient acetylenic compounds in the presence of strong CH-acids. Here we report on a simple one-pot synthesis of stable crystalline 1,6-diionc organophosphorus compound **3**. Thus, the reaction of triphenylphosphine and 5-nitro-2,4-dihydro-3*H*-1,2,4-triazole-3-one (**2**) in the presence of alkyl propiolates or ethynyl methyl ketone leads to betaines **3** in excellent yields (see Scheme 1).

RESULTS AND DISCUSSION

The reaction of triphenylphosphine and acetylenic compounds **1** in the presence of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazole-3-one (**2**) proceeded spontaneously at room temperature in dichloromethane, and was

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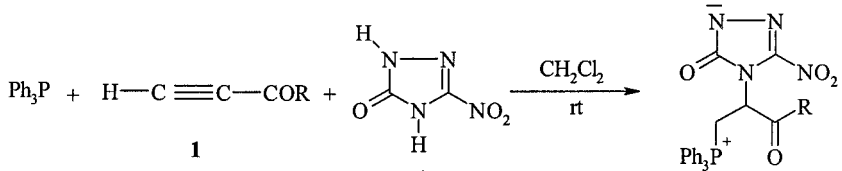
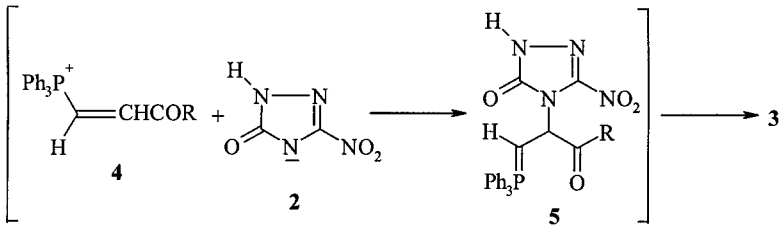


1-3	R	%Yield of 3
a	Me	98
b	OMe	95
c	OEt	95

SCHEME 1

completed within 5 h. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of fairly stable betaine **3**. Any product other than **3** could not be detected by NMR spectroscopy. Compounds **3a–c** are stable solid materials, which are recovered unchanged after refluxing in toluene for 4 h.

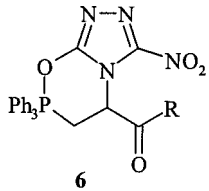
On the basis of the well established chemistry of phosphorus nucleophiles[1,2,8,9] it is reasonable to assume that betaine **3** results from initial addition of triphenylphosphine to the acetylenic compound **1** and subsequent protonation of the reactive 1:1 adduct, followed by attack of the nitrogen atom of the anion of the NH-acid to the vinyltriphenylphosphonium cation **4** to generate ylide **5** which apparently isomerises, under the reaction conditions employed, to produce the 1,6-diionic compound **3** (Scheme 2).



SCHEME 2

NMR spectroscopy was employed to distinguish structure **3** from the primary product, the ylide **5**. Thus, the ^{1}H NMR spectrum of each isolated product showed a methine and two diastereotopic methylene proton signals at about $\delta = 4.15–4.45$. Further evidence was obtained from the ^{13}C NMR spectra which displayed a CH_2—P doublet ($^{1}J_{CP} =$ 55–56 Hz) at about $\delta = 22–25$. A cyclic six-membered ring structure, such as **6**, is unlikely because if compound **3** had a cyclic structure,

then we were to expect a doublet at about $\delta = 160$ for the *C*—O—P moiety in the ^{13}C NMR spectra. Moreover, the ^{31}P NMR spectra of compounds **3a–c** displayed signals at about $\delta = 21.94$–22.65 (downfield from 85% H_3PO_4). These shifts are similar to those observed for alkyltriphenylphosphonium iodide.[10,11] 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.[10–13,16]



6

In summary, the present synthesis of 1,6-diionic organophosphorus compounds 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 in the reaction performed under neutral condition, 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 C, H, and N were performed using a Heraeus CHN—O-Rapid analyzer. IR spectra were recorded as KBr discs on a Shimadzu IR-460 spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 500.1, 125.7, and 202.5 MHz, respectively, on a BRUKER DRX 500-AVANCE FT-NMR instrument with DMSO and $CDCl_3$ as solvents. Compounds **1a** and **2** were prepared according to the published procedures.[14,15] The reagents and solvents used in this work were obtained from Fluka (Buchs, Switzerland) and used without further purification.

Preparation of 2-(5-Nitro-2,4*H*-1,2,4-triazol-4-yl-2-ylid)-1-methyl-3-triphenylphosphoniopropanone 3a

General Procedure

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.26 g 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (2 mmol)

in 10 mL of CH_2Cl_2 was added dropwise to a mixture of 0.136 g 3-butyn-2-one (2 mmol) in 4 mL of dichloromethane at room temperature over 2 min. After 5 h stirring at room temperature, the product was filtered off, and recrystallized from ethyl acetate. Yellow powder, 0.90 g, yield 98%, m.n. 190–192°C (decomp.). Anal. Calcd for $C_{24}H_{21}N_4O_4P$ (460.4): C, 62.60; H, 4.59; N, 12.16%. Found: C, 62.9; H, 4.5; N, 12.2%. IR (KBr) (ν_{max}, cm^{-1}): 1712 (C=O), 1630 (NCON), 1523 (C–NO_2), 1485 (NO_2), 1427 (P–Ph), 1378 (C–NO_2), 1301 (NO_2), 1106 (P–Ph), 991 (P–Ph). ^1H NMR (DMSO, 500.1 MHz): δ_H 1.95 (3 H, s, CH_3), 4.15 (2 H, m, CH_2P), 5.30 (1 H, m, CH), 7.6–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR (DMSO, 125.7 MHz,): δ_C 22.03 (d, $^1J_{CP}$ 55.0 Hz, *C*H_2P), 25.98 (H_3*C*CO), 56.58 (d, $^2J_{CP}$ 3.27 Hz, *C*HCH_2P), 117.82 (d, $^1J_{CP}$ 87 Hz, C_{ipso} of Ph_3P), 129.79 (d, $^3J_{CP}$ 12.8 Hz, C_{meta} of Ph_3P), 133.68 (d, $^2J_{CP}$ 10.5 Hz, C_{ortho} of Ph_3P), 134.60 (d, $^4J_{CP}$ 2.5 Hz, C_{para} of Ph_3P), 159.51 (N*C*ON), 162.0 (*C*–NO_2), 201.55 (d, $^3J_{CP}$ 130.0 Hz, *C*OCH_3). ^{31}P NMR (DMSO, 202.5 MHz): δ_P 22.65 (Ph_3P^+–C). MS (*m/z*, %): 461 (M^++1, 1), 445 (M^+–CH3, 1), 369 ($C_{17}H_{14}N_4O_4P$, 1), 305 (M^+–2PH, 1), 262 (Ph_3P, 100), 183 ($C_{12}H_8P$, 48), 152 ($C_6H_6N_3O$, 10), 108 (C_6H_5P, 50), 77 (Ph, 15), 43 (CH_3–C=O^+, 71).

*Selected data for methyl 2-(5-nitro-2,4*H*-1,2,4-triazol-4-yl-2-ylid)-3-triphenylphosphoniopropionate (**3b**).* Yellow powder, 0.90 g, yield 98%, m.p. 168–170°C (decomp.). Anal. Calcd for $C_{24}H_{21}N_4O_5P$ (476.4): C, 60.50; H, 4.44; N, 11.76%. Found: C, 59.9; H, 4.4; N, 11.9%. IR (KBr) (ν_{max}, cm^{-1}): 1730 (CO_2Me), 1630 (NCON), 1530 (C–NO_2), 1487 (NO_2), 1428 (P–Ph), 1393 (C–NO_2), 1318 (NO_2), 1241 (C–O), 1100 (P–Ph), 1009 (P–Ph). ^1H NMR (DMSO, 500.1 MHz): δ_H 3.60 (3 H, s, CH_3O), 4.27 (1 H, m, CH of CH_2P), 4.45 (1 H, m, CH of CH_2P), 5.35 (1 H, m, CH), 7.6–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR (DMSO, 125.7 MHz): δ_C 23.46 (d, $^1J_{CP}$ 55 Hz, *C*H_2P), 50.60 (d, $^2J_{CP}$ 2.9 Hz, *C*H), 54.87 (O*C*H_3), 117.55 (d,$^1J_{CP}$ 87 Hz, C_{ipso} of Ph_3P), 129.82 (d, $^3J_{CP}$ 12.8 Hz, C_{meta} of Ph_3P), 133.73 (d, $^2J_{CP}$ 10.4 Hz, C_{ortho} of Ph_3P), 134.7 (d, $^4J_{CP}$ 2 Hz, C_{para} of Ph_3P), 159.61 (N*C*ON), 162.0 (*C*–NO_2), 168.35 (d, $^3J_{CP}$ 16.7 Hz, *C*O_2Me). ^{31}P NMR (DMSO, 202.5 MHz): δ_p 21.94 (Ph_3P^+–C). MS (*m/z*, %): 445 (M^+–OCH_3, 1), 262 (Ph_3P, 100), 183 ($C_{12}H_8P$, 67), 139 ($C_5H_5N_4O_4$, 19), 108 (C_6H_5P, 52), 77 (Ph+, 25), 59 (CO_2CH_3, 46).

*Selected data for ethyl 2-(5-nitro-2,4*H*-1,2,4-triazol-4-yl-2-ylid)-3-triphenylphosphoniopropionate (**3c**).* Light yellow powder, 0.98 g, yield 95%, m.p. 158–160°C. Anal. Calcd for $C_{25}H_{23}N_4O_5P$ (490.45): C, 61.22; H, 4.72; N, 11.42%. Found: C, 61.3; H, 4.8; N, 11.5%. IR (KBr) (ν_{max}, cm^{-1}): 1714 (CO_2Et), 1626 (NCON), 1527 (C–NO_2), 1486 (NO_2), 1429 (P–Ph), 1328 (C–NO_2), 1310 (NO_2), 1233 (C–O), 1100 (P–Ph), 1012 (P–Ph). ^1H NMR ($CDCl_3$, 500.1 MHz): δ_H 1.14 (3 H, t, $^3J_{HH}$ 7.0 Hz CH_3), 4.00 (1 H, m, CH of CH_2P), 4.10 (2 H, q, $^3J_{HH}$ 7.0 Hz, OCH_2), 4.25 (1 H,

m, CH of CH_2P), 5.53 (1 H, m, CH), 7.6–7.8 (15 H, m, 3 C_6H_5). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ_C 13.90 (s, CH_3CH_2), 25.00 (d, $^1J_{CP}$ 56 Hz, CH_2P), 51.10 (d, $^2J_{CP}$ 3 Hz, *C*H), 63.10 (OCH_2), 116.66 (d, $^1J_{CP}$ 87 Hz, C_{ipso} of Ph_3P), 130.50 (d, $^3J_{CP}$ 12.4 Hz, C_{meta} of Ph_3P), 133.61 (d, $^2J_{CP}$ 9.3 Hz, C_{ortho} of Ph_3P), 135.50 (d, $^4J_{CP}$ 2 Hz, C_{para} of Ph_3P), 160.31 (N*C*ON), 163.04 (*C*—NO_2), 168.52 (d, $^3J_{CP}$ 16.8 Hz, CO_2Et). ^{31}P NMR ($CDCl_3$, 202.5 MHz): δ_P 21.94 (Ph_3P^+—C). MS (*m*/*z*, %): 461 (M^+—CH_2CH_3, 1), 445 (M^+—OEt, 1), 369 ($C_{17}H_{14}N_4O_4P$, 1), 262 (Ph_3P, 100), 183 ($C_{12}H_8P$, 54), 108 (C_6H_5P, 46), 51 ($C_4H_4^+$, 40).

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