

A New and Efficient Synthesis of Highly Functionalized (Triphenylphosphoranylidene)cyclopentadienes with Zwitterionic Resonance Structures

by **Abdolali Alizadeh***

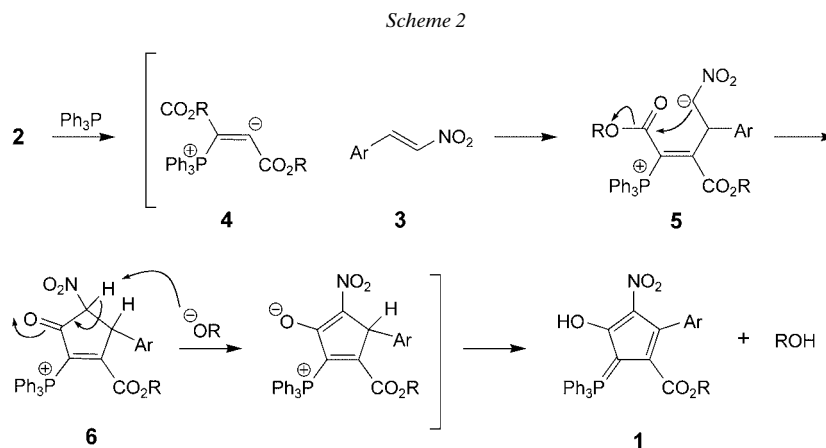
Department of Chemistry, Tarbiat Modares University, P. O. Box 14155–175, Tehran, Iran
(phone: +92-21-8006631; fax: +98-21-8006544; e-mail: abdol_alizad@yahoo.com and aalizadeh@modares.ac.ir)

Different esters of 2-aryl-4-hydroxy-3-nitro-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylates **1** were prepared in excellent yields from the 1 : 1 : 1 reaction between Ph_3P , dialkyl acetylenedicarboxylates **2**, and (substituted) 2-(nitroethenyl)benzenes **3** (*Scheme 1*). The structures of the highly functionalized compounds **1** were corroborated spectroscopically (IR, ^1H -, ^{13}C -, ^{31}P -NMR, EI-MS) and by elemental analyses. A plausible mechanism for this type of cyclization is proposed (*Scheme 2*).

Introduction. – Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities [1]. (Triphenylphosphoranylidene)cyclopentadienes are usually prepared by deprotonation of related phosphonium salts; the latter, in turn, are prepared by the reaction of Ph_3P and a cyclopentadienyl halide [2]. Cyclopentadiene-based ylides are of interest to us, because these compounds may serve as ligands in the synthesis of many inorganic complexes, and since they are usually stable and quite unreactive for ylide species [3].

Zwitterionic species are known to arise from the addition of nucleophiles such as Ph_3P [4], pyridine [5], a wide range of tertiary amines [6], and isocyanide [7] to activated acetylenes [8]. Earlier attempts to trap these species with dipolarophiles to generate cyclic compounds have been essentially unsuccessful [9]. We have recently shown that these species can be efficiently trapped by dipolarophiles such as aryl aldehydes [10], ‘isopropylidene *Meldrum’s* acid’ (=2,2-dimethyl-5-(1-methylethylidene)-1,3-dioxane-4,6-dione) [11], and aryl isocyanates [12], leading to a facile synthesis of 1,3-diionic organophosphorus compounds, 1,5-diionic organophosphorus compounds, and β -lactam derivatives, respectively. Considering the above background and also the importance of conjugate addition of nucleophiles to electron-deficient alkenes for the creation of carbon–carbon or carbon–heteroatom bonds, we surmised that the zwitterions might undergo cycloaddition to activated alkenes, thus constituting a synthesis of highly substituted (triphenylphosphoranylidene)cyclopentadienes. We now report an efficient synthesis of 2-aryl-4-hydroxy-3-nitro-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylates from Ph_3P , dialkyl acetylenedicarboxylates **2**, and substituted (2-nitroethenyl)benzenes **3** (*Scheme 1*).

Although the mechanism of the reaction between **2** and **3** in the presence of Ph_3P has not yet been established experimentally, a possible explanation is proposed in *Scheme 2*. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles [13–20], it is reasonable to assume initial addition of Ph_3P to dialkyl acetylenedicarboxylate, followed by attack of the resulting zwitterion **4** on the *Michael* acceptor **3** to yield betaine **5**, which then cyclizes. Finally, the resulting cation **6** loses ROH to produce compound **1**.



In conclusion, the present method has the advantage that the reaction can be performed under neutral conditions, and that the substances can be mixed without any activation or modification. The simplicity of this procedure makes it an interesting alternative to complex, multistep approaches.

Experimental Part

General. All reagents and solvents were obtained from *Fluka* (Buchs, Switzerland) and used without further purification. Compounds **3a–c** were prepared according to a published procedure [21]. Melting points (m.p.): *Electrothermal 9100* apparatus; uncorrected. IR spectra: *Shimadzu IR-460* spectrometer; in cm^{-1} . ^1H -, ^{13}C -, and ^{31}P -NMR Spectra: recorded at 500.1, 125.7, and 202.4 MHz, resp., on a *Bruker DRX-500-AVANCE* instrument; in CDCl_3 ; δ in ppm rel. to SiMe_4 ($=0$ ppm), J in Hz. EI-MS (70 eV): *Finnigan MAT-8430* mass spectrometer; in m/z (rel. %). Elemental analyses: *Heraeus CHN-O-Rapid* analyzer.

General Procedure for the Preparation of Compounds 1. To a magnetically stirred soln. of **2** (1 mmol) and **3** (1 mmol) in anhyd. Et_2O (5 ml) was added dropwise a soln. of Ph_3P (0.26 g, 1 mmol) in Et_2O (3 ml) at r.t. over 10 min. The mixture was stirred for 1 h, the resulting solid was filtered off, washed with anhyd. Et_2O , and dried *in vacuo* to afford 95–98% of **1**.

Methyl 4-Hydroxy-3-nitro-2-phenyl-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylate (1a). Yield: 98%. Orange powder. M.p. 130–132° (dec.). IR (KBr): 3410 (OH), 1698 (CO_2Me), 1655 ($\text{C}=\text{C}$), 1544 (Ph), 1415 and 1374 (NO_2), 1290 ($\text{C}-\text{O}$ of $\text{C}-\text{OH}$), 1201 ($\text{C}-\text{O}$ of ester), 1105 and 991 (P–Ph). ^1H -NMR (500.1 MHz, CDCl_3): 2.84 (s, 3 H); 7.28 (dd, $J=6.8, 6.8$, 1 H); 7.33–7.38 (m, 4 H); 7.54–7.56 (m, 6 H); 7.65 (dd, $J=7.2, 7.2$, 3 H); 7.73 (dd, $J=13.0, 7.7, 6$ H); 10.95 (s, 1 H). ^{13}C -NMR (125.7 MHz, CDCl_3): 49.41; 68.55; 111.62; 122.94; 124.36; 125.89; 126.43; 128.30; 129.02; 129.26; 132.00; 133.19; 133.65; 159.18; 164.71. ^{31}P -NMR (202.4 MHz, CDCl_3): 12.64 (P $_3$ P=C). EI-MS: 521 (1, M^+), 473 (1), 432 (1), 403 (1), 386 (1), 363 (2), 329 (1), 304 (2), 278 (59), 262 (100), 183 (73), 152 (14), 108 (28), 77 (30), 51 (14). Anal. calc. for $\text{C}_{31}\text{H}_{24}\text{NO}_5\text{P}$ (521.50): C 71.40, H 4.64, N 2.69; found: C 71.3, H 4.5, N 2.6.

Ethyl 4-Hydroxy-3-nitro-2-phenyl-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylate (1b). Yield: 95%. Yellow powder. M.p. 116–118° (dec.). IR (KBr): 3425 (OH), 1708 (CO₂Et), 1630 (C=C), 1528 (Ph), 1429 and 1380 (NO₂), 1263 (C–O of C–OH), 1233 (C–O of ester), 1097 and 995 (P–Ph). ¹H-NMR (500.1 MHz, CDCl₃): 0.48 (*t*, *J* = 6.8, 3 H); 3.35 (*q*, *J* = 6.8, 2 H); 7.30 (*dd*, *J* = 7.2, 7.2, 1 H); 7.35 (*d*, *J* = 7.0, 2 H); 7.45 (*d*, *J* = 6.5, 2 H); 7.52 (*m*, 6 H); 7.62 (*dd*, *J* = 6.7, 6.7, 3 H); 7.71 (*dd*, *J* = 13.0, 7.8, 6 H); 10.94 (*s*, 1 H). ¹³C-NMR (125.7 MHz, CDCl₃): 12.64; 58.70; 68.65; 112.25; 122.95; 124.43; 125.74; 126.36; 128.30; 128.65; 129.32; 132.30; 133.26; 136.03; 159.14; 164.66. ³¹P-NMR (202.4 MHz, CDCl₃): 12.64 (Ph₃P=C). EI-MS: 535 (1, *M*⁺), 447 (1), 369 (1), 320 (1), 262 (100), 245 (17), 217 (10), 199 (10), 183 (79), 152 (17), 125 (107), 108 (79), 77 (17), 47 (68), 31 (100). Anal. calc. for C₃₂H₂₆NO₃P (535.48): C 71.77, H 4.89, N 2.61; found: C 71.6, H 4.8, N 2.6.

Methyl 4-Hydroxy-3-nitro-2-(4-nitrophenyl)-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylate (1c). Yield: 98%. Yellow powder. M.p. 185–187° (dec.). IR (KBr): 3400 (OH), 1695 (CO₂Me), 1687 (C=C), 1541 (Ph), 1504 and 1382 (NO₂), 1292 (C–O of C–OH), 1203 (C–O of ester), 1116 and 963 (P–Ph). ¹H-NMR (500.1 MHz, CDCl₃): 2.83 (*s*, 3 H); 7.52 (*d*, *J* = 8.2, 2 H); 7.57 (*m*, 6 H); 7.68 (*dd*, *J* = 6.7, 6.7, 3 H); 7.72 (*dd*, *J* = 13.1, 7.7, 6 H); 8.19 (*d*, *J* = 8.2, 2 H); 10.69 (*s*, 1 H). ¹³C-NMR (125.7 MHz, CDCl₃): 49.54; 69.80; 112.03; 121.72; 122.62; 123.85; 125.92; 128.36; 130.42; 132.52; 133.16; 143.44; 145.89; 158.93; 164.17. ³¹P-NMR (202.4 MHz, CDCl₃): 12.88 (Ph₃P=C). EI-MS: 566 (1, *M*⁺), 277 (100), 199 (23), 183 (20), 152 (20), 77 (20). Anal. calc. for C₃₁H₂₃N₂O₇P (566.50): C 65.73, H 4.09, N 4.94; found: C 65.6, H 4.0, N 4.8.

Ethyl 4-Hydroxy-3-nitro-2-(4-nitrophenyl)-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylate (1d). Yield: 95%. Yellow powder. M.p. 184–185° (dec.). IR (KBr): 3400 (OH), 1682 (CO₂ Me), 1587 (C=C), 1543 (Ph), 1502 and 1342 (NO₂), 1292 (C–O of C–OH), 1210 (C–O of ester), 1109 and 993 (P–Ph). ¹H-NMR (500.1 MHz, CDCl₃): 0.47 (*t*, *J* = 6.8, 3 H); 3.36 (*q*, *J* = 6.8, 2 H); 7.52 (*d*, *J* = 7.7, 2 H); 7.56 (*m*, 6 H); 7.67 (*dd*, *J* = 6.8, 6.8, 3 H); 7.73 (*dd*, *J* = 12.8, 7.7, 6 H); 8.19 (*d*, *J* = 7.7, 2 H); 10.70 (*s*, 1 H). ¹³C-NMR (125.7 MHz, CDCl₃): 12.64; 59.00; 69.80; 112.47; 121.65; 122.64; 123.99; 125.95; 128.30; 130.50; 132.46; 133.20; 143.90; 145.83; 158.91; 164.01. ³¹P-NMR (202.4 MHz, CDCl₃): 12.88 (Ph₃P=C). EI-MS: 580 (1, *M*⁺), 537 (1), 522 (1), 479 (2), 463 (2), 445 (1), 369 (1), 325 (1), 304 (1), 277 (100), 262 (86), 199 (20), 183 (63), 108 (16), 77 (16), 51 (16). Anal. calc. for C₃₂H₂₅N₂O₇P (580.53): C 66.21, H 4.34, N 4.83; found: C 66.1, H 4.3, N 4.7.

Methyl 2-(4-Chlorophenyl)-4-hydroxy-3-nitro-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylate (1e). Yield: 98%. Orange powder. M.p. 182–183° (dec.). IR (KBr): 3420 (OH), 1702 (CO₂ Me), 1676 (C=C), 1549 (Ph), 1467 and 1373 (NO₂), 1285 (C–O of C–OH), 1209 (C–O of ester), 1100 and 963 (P–Ph). ¹H-NMR (500.1 MHz, CDCl₃): 2.86 (*s*, 3 H); 7.3 (*s*, 4 H); 7.55 (*m*, 6 H); 7.66 (*dd*, *J* = 6.7, 3 H); 7.72 (*dd*, *J* = 13.1, 7.5, 6 H); 10.86 (*s*, 1 H). ¹³C-NMR (125.7 MHz, CDCl₃): 49.45; 69.93; 111.77; 122.82; 124.19; 126.64; 127.44; 128.28; 130.79; 131.71; 132.30; 133.14; 134.16; 159.10; 164.52. ³¹P-NMR (202.4 MHz, CDCl₃): 12.72 (Ph₃P=C). EI-MS: 555 (1, *M*⁺), 510 (1), 479 (1), 461 (1), 445 (1), 423 (2), 370 (1), 324 (2), 278 (100), 262 (100), 199 (23), 183 (100), 152 (20), 108 (34), 77 (10). Anal. calc. for C₃₁H₂₃ClNO₃P (555.95): C 66.97, H 4.17, N 2.52; found: C 66.8, H 4.1, N 2.5.

Ethyl 2-(4-Chlorophenyl)-4-hydroxy-3-nitro-5-(triphenylphosphoranylidene)cyclopenta-1,3-diene-1-carboxylate (1f). Yield: 95%. Yellow powder. M.p. 174–175° (dec.). IR (KBr): 3400 (OH), 1682 (CO₂Et), 1676 (C=C), 1547 (Ph), 1465 and 1379 (NO₂), 1291 (C–O of C–OH), 1207 (C–O of ester), 1107 and 989 (P–Ph). ¹H-NMR (500.1 MHz, CDCl₃): 0.53 (*t*, *J* = 7.0, 3 H); 3.39 (*q*, *J* = 7.0, 2 H); 7.31 (*s*, 4 H); 7.56 (*m*, 6 H); 7.65 (*dd*, *J* = 6.6, 6.6, 3 H); 7.73 (*dd*, *J* = 13.0, 7.8, 6 H); 10.88 (*s*, 1 H). ¹³C-NMR (125.7 MHz, CDCl₃): 13.16; 59.30; 69.40; 112.77; 123.88; 124.76; 126.99; 127.52; 128.67; 131.31; 132.01; 132.73; 133.64; 135.04; 159.50; 164.85. ³¹P-NMR (202.4 MHz, CDCl₃): 12.51 (Ph₃P=C). EI-MS: 569 (1, *M*⁺), 525 (2), 468 (1), 423 (1), 397 (3), 379 (1), 360 (1), 310 (2), 278 (100), 262 (56), 199 (13), 183 (76), 152 (20), 108 (56), 77 (33), 44 (100). Anal. calcd. for C₃₂H₂₅ClNO₃P (569.97): C 67.43, H 4.42, N 2.46; found: C 67.3, H 4.3, N 2.4.

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Received December 7, 2004