Synthesis and Utility of α-Methoxy Phosphonates with a 1,3,2-Dioxaphosphorinane Ring

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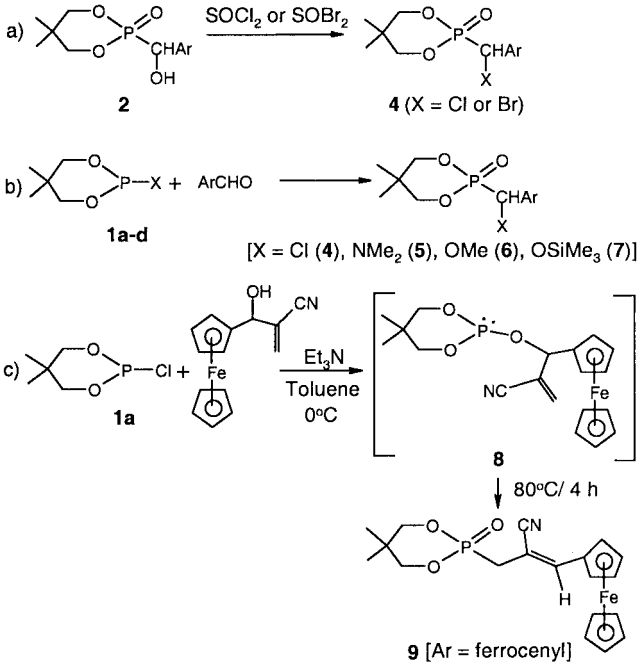
Abstract: Synthesis of several α-methoxy phosphonates with the phosphorus as a part of 1,3,2-dioxaphosphorinane ring by the simple reaction of $(OCH_2CMe_2CH_2O)PCl$ with acetals is described. Analogous methoxy phosphonates using (±) $(C_{20}H_{12}O_2)PCl$ were also synthesized using the same route. Utility of these phosphonates in the synthesis of vinyl ethers via the Horner–Wadsworth–Emmons [HWE] reaction is demonstrated.

Key words: acetals, vinyl ethers, phosphorus, phosphonates, Horner–Wadsworth–Emmons reaction

Phosphonates of the type $(RO)_2P(O)CHR$ are valuable precursors for C–C bond formation using the Horner–Wadsworth–Emmons [HWE] reaction and hence considerable efforts are directed towards the synthesis of new derivatives or improving the existing methodology for the known compounds.[1] In our previous studies, we have shown that the readily prepared, cheap and stable (towards oxidation in air) chlorophosphite $(OCH_2CMe_2CH_2O)PCl$ (**1a**) that features a saturated 1,3,2-dioxaphosphorinane is a convenient starting material for a variety of phosphonates, with or without α-substitution.[2] Thus, while the Pudovik products $(OCH_2CMe_2CH_2O)P(O)CH(Ar)(OH)$ (**2**), obtained from $(OCH_2CMe_2CH_2O)P(O)H$ (**3**, which itself is readily formed by addition of water to **1a**) lead to the α-chloro/bromo phosphonates $(OCH_2CMe_2CH_2O)P(O)CH(Ar)(X)$ [**4**, X = Cl, Br] in high yields, the reaction of the P(III) derivatives $(OCH_2CMe_2CH_2O)PX$ [**1**: X = Cl (**a**), NMe_2 (**b**), OMe (**c**), $OSiMe_3$ (**d**)] with various aldehydes afforded the phosphonates $(OCH_2CMe_2CH_2O)P(O)CH(Ar)(X)$ [X = Cl (**4**), NMe_2 (**5**), OMe (**6**), $OSiMe_3$ (**7**)] in variable yields. In a different approach, we have utilized the facile Arbuzov rearrangement of $(OCH_2CMe_2CH_2O)P[OCH(Ar)C(CN)=CH_2)]$ (**8**; Ar = Ph, C_6H_4-4-Me, ferrocenyl) formed in situ, using a Baylis–Hillman methodology to obtain phosphonates of the type $[(OCH_2CMe_2CH_2O)P(O)CH_2C(CN)=CH(Ar)]$ (**9**). These routes are shown in Scheme 1. In this paper, we report a simple and convenient route to α-methoxy phosphonates of type **6** using the reaction of **1a** and the acetals derived from aromatic aldehydes.[3] Analogous phosphonates based on 1,1′-bi-2-naphthol are also synthesized.



Scheme 1

Utility of these compounds in the synthesis of vinyl ethers by HWE reaction will also be presented.

Treatment of **1a** with the acetals $ArCH(OMe)_2$ in anhydrous toluene affords the α-methoxyphosphonates **6a–i** in good yields by the elimination of CH_3Cl (Scheme 2). In terms of reaction pathway, we believe that species of types **I–III** (Figure 2) are involved; these have some components similar to that reported in the reaction of acetals with a mixture of PCl_3 and $P(OMe)_3$.[4] The formation of the methoxy derivative **1c** [^{31}P (C_6D_6): δ = 122.9 ppm; Lit.[5] ($CDCl_3$): δ = 122.0 ppm] is readily seen by ^{31}P NMR when equimolar quantities of **1a** and the dimethylacetal of benzaldehyde are mixed together in C_6D_6 in a NMR tube. Species **II** could not be clearly identified in the ^1H NMR, probably because the signals overlap with those due to other protons or due to the instability of these species. After 24 hours, only the peak due to the product **6a** was seen (Figure 1). Thus it is clear that this phosphonate is formed quantitatively even at room temperature within a day.

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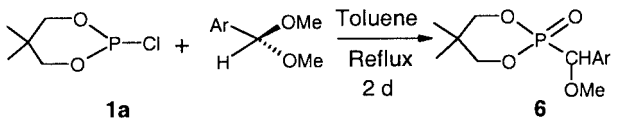


Ar = Ph (**a**) 91%
= C_6H_4-4-Me (**b**) 88%
= C_6H_4-3-Me (**c**) 98%
= C_6H_4-4-OMe (**d**) 80%
= C_6H_4-4-Cl (**e**) 90%
= C_6H_3-3,4-Cl_2 (**f**) 72%
= C_6H_5-3-Br (**g**) 90%
= 1-$C_{10}H_7$ (**h**) 89%
= CH=CHPh (**i**) 90%

Scheme 2

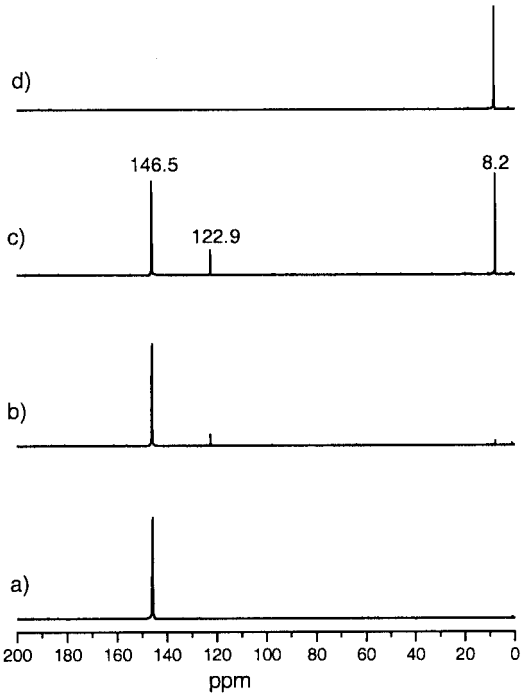


Figure 1 ^{31}P NMR spectra (in C_6D_6) of: (a) pure $(OCH_2CMe_2CH_2O)PCl$ (**1a**), (b) immediately after the addition of acetal $PhCH(OMe)_2$, c) 0.5 h after addition and (d) 24 h after addition.

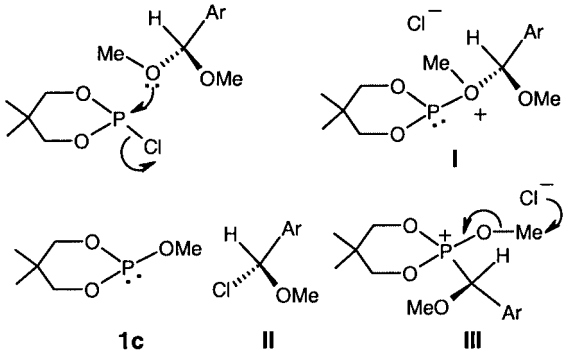
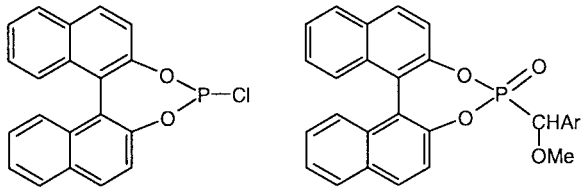


Figure 2

Reaction of the 1,1′-bi-2-naphthoxy compound $(C_{20}H_{12}O_2)PCl$ (**10**) with acetals has also been performed in an effort to see whether diastereomeric phosphonate products can be distinguished (by NMR) or not. Of the four phosphonates **11a–d** (Figure 3) thus prepared by using the racemic binaphthol precursor (±) $(C_{20}H_{12}O_2)PCl$ (**10**), **11c** and **11d** showed two resonances in the ^{31}P NMR spectrum and even when the chiral phosphite (–)-**10** was used, the same two peaks were observed.

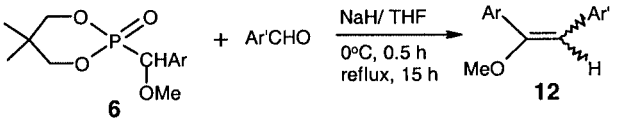


(±) **10**

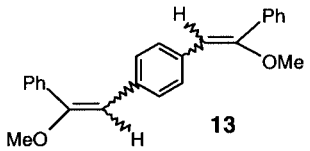
Ar = Ph (**11a**)
= 4-Me-C_6H_4 (**11b**)
= 3-Br-C_6H_4 (**11c**)
= 4-NO_2-C_6H_4 (**11d**)

Figure 3

The methoxy phosphonates **6a–i** are air-stable solids that can be handled conveniently. They undergo HWE reaction with aldehydes very readily in the presence of the cheap base NaH (Scheme 3) to lead to the vinyl ethers **12a–f** and **13**. Earlier, for analogous reactions, the more expensive lithium diisopropylamide was used.[4]



Ar = Ph, Ar' = 4-MeO-C_6H_4 (**a**)
= Ph, Ar' = 4-NO_2-C_6H_4 (**b**)
= CH=CHPh, Ar' = 4-MeO-C_6H_4 (**c**)
= CH=CHPh, Ar' = 4-NO_2-C_6H_4 (**d**)
= 3-Me-C_6H_4, Ar' = C_5H_4-Fe-C_5H_5 (**e**)
= 3,4-$Cl_2C_6H_3$, Ar' = 9-anthryl (**f**)



Scheme 3

To summarize, since (i) the precursor **1a** is cheap and very readily prepared, and (ii) the α-methoxy phosphonates **6a–i** are formed in nearly quantitative yields (Figure 1) under mild conditions, we believe that for the synthesis of various vinyl ethers these phosphonates offer an elegant choice as precursors, since the byproduct phosphate is water-soluble.

Chemicals were procured from Aldrich or local manufacturers and they were purified when required. Solvents were purified according to standard procedures.[6] The acetals except that of benzaldehyde

were prepared by using a literature method.[7] ^{1}H, ^{13}C and ^{31}P NMR spectra (operating at 200 MHz, 50 MHz, and 80.9 MHz respectively) were recorded on a Bruker 200 MHz spectrometer with chemical shifts ($CDCl_3$) measured against TMS (^{1}H, ^{13}C) or 85% H_3PO_4. Elemental analyses were carried out on a Perkin–Elmer 240C CHN analyzer.

2-[Methoxy(3′-methyl-phenyl)methyl]-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (6c); Typical Procedure

Freshly distilled chlorophosphite ($OCH_2CMe_2CH_2O$)PCl (**1a**) (3.03 g, 18.0 mmol)[2b] was added to freshly distilled [3-Me-$C_6H_4CH(OMe)_2$] (3.07 g, 18.5 mmol) in anhyd toluene under a anhyd N_2 atmosphere. The reaction mixture was refluxed for two days. Progress of the reaction was monitored by TLC and the product **6c** was isolated by column chromatography (EtOAc–hexane). Yield: 5.00 g (98%).

All the other compounds **6a–b**, **6d–i** and **11a–d** were prepared analogously using similar molar quantities.

6a

Yield: 91%; mp 115–117 °C (lit.[2c] 120–122 °C).

^{31}P NMR: δ = 9.7 (lit.[2c] 9.8).

6b

Yield: 88%; mp 107–108 °C.

IR: 978, 1008, 1059, 1092, 1273, 1476, 1813, 2942 cm^{-1}.

^{1}H NMR: δ = 0.88, 1.18 (2 s, 6 H, 2 × CH_3), 2.33 (s, 3 H, $ArCH_3$), 3.37 (s, 3 H, OCH_3), 3.90–4.30 (m, 4 H, 2 × OCH_2), 4.68 (d, $^2J_{P–H}$ = 16.6 Hz, 1 H, PCH), 7.15–7.33 (m, 4 H, ArH).

^{13}C NMR: δ = 20.8, 21.2, 21.9, 32.4 (d, $^3J_{P–C}$ = 7.8 Hz, CMe_2), 58.5 (d, $^3J_{P–C}$ = 15.3 Hz, PCO*C*H_3), 77.5, 78.1 (2 d, $^2J_{P–C}$ = 6.9 Hz, 7.0 Hz 2-OCH_2), 82.1 (d, $^1J_{P–C}$ = 163.0 Hz, CH), 127.6, 127.7, 129.3, 131.0, 138.3.

^{31}P NMR: δ = 10.2.

Anal. Calcd for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.39. Found: C, 59.13, H, 7.27.

6c

Yield: 98%; mp 102–104 °C.

IR: 980, 1005, 1053, 1082, 1269, 1368, 1480, 2967 cm^{-1}.

^{1}H NMR: δ = 0.90, 1.21 (2 s, 6 H, 2 × CH_3), 2.37 (s, 3 H, $ArCH_3$), 3.40 (s, 3 H, $PCOCH_3$), 3.99–4.30 (m, 4 H, OCH_2), 4.64 (d, $^2J_{P–H}$ = 15.6 Hz, 1 H, PCH), 7.22–7.24 (2 br s, 4 H, ArH).

^{13}C NMR: δ = 20.7, 21.3, 21.9, 32.3 (d, $^3J_{P–C}$ = 7.3 Hz, *C*Me_2), 58.6 (d, $^3J_{P–C}$ = 17.0 Hz, $POCH_3$), 77.6, 78.2 (2 d, $^2J_{P–C}$ = 7.2 Hz, 7.3 Hz, 2-OCH_2), 82.3 (d, $^1J_{P–C}$ = 162.5 Hz, PCH), 124.7, 124.8, 128.3, 129.2, 133.9, 138.0.

^{31}P NMR: δ = 10.1.

Anal. Calcd for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.39. Found: C, 59.22 H, 7.42.

6d

Yield: 80%; mp 104–106 °C.

IR: 837, 1006, 1057, 1094, 1253, 1472, 1512, 1610, 2940 cm^{-1}.

^{1}H NMR: δ = 0.89, 1.19 (2 s, 6 H, 2 × CH_3), 3.36 (s, 3 H, OCH_3), 3.80 (s, 3 H, $ArOCH_3$), 3.98–4.27 (m, 4 H, 2 × OCH_2), 4.65 (d, $^2J_{P–H}$ = 15.6 Hz, 1 H, PCH), 6.92 and 7.37 (2 d, $^3J_{H–H}$ = 6.8 Hz, 4 H, ArH).

^{13}C NMR: δ = 20.7, 21.8, 32.3 (d, $^3J_{P–C}$ = 7.4 Hz, CMe_2), 55.2, 58.3 (d, $^3J_{P–C}$ = 15.1 Hz, $POCH_3$), 77.4, 77.9 (2 d, $^2J_{P–C}$ = 7.1 Hz, 7.3 Hz 2 OCH_2), 81.6 (d, $^1J_{P–C}$ = 163.9 Hz, PCH), 114.0, 125.9, 129.1, 159.8.

^{31}P NMR: δ = 10.3.

Anal. Calcd for $C_{14}H_{21}O_5P$: C, 56.00; H, 7.06. Found: C, 55.95; H, 7.12.

6e

Yield: 90%; mp 112–113 °C.

IR: 876, 1008, 1059, 1269, 1489, 2932 cm^{-1}.

^{1}H NMR: δ = 0.89, 1.20 (2 s, 6 H, 2 × CH_3), 3.38 (s, 3 H, $COCH_3$), 4.04–4.30 (m, 4 H, 2 × OCH_2), 4.69 (d, $^2J_{P–H}$ = 15.8 Hz, 1 H, PCH), 7.35–7.56 (m, 4 H, ArH).

^{13}C NMR: δ = 20.7, 21.9, 32.4 (d, $^3J_{P–C}$ = 8.3 Hz, CMe_2), 58.7 (d, $^3J_{P-C}$ = 14.7 Hz, $PCOCH_3$), 77.8, 78.4 (2 d, $^2J_{P–C}$ = 6.9 Hz, 7.0 Hz, 2-OCH_2), 81.8 (d, $^1J_{P–C}$ = 162.4 Hz, PCH), 128.6, 129.0, 134.2.

^{31}P NMR: δ = 9.2.

Anal. Calcd for $C_{13}H_{18}ClO_4P$: C, 51.24; H, 5.91. Found: C, 51.10; H, 5.86.

6f

Yield: 72%; mp 104–106 °C.

IR: 982, 1007, 1061, 1094, 1263, 1464, 1587, 2967 cm^{-1}.

^{1}H NMR: δ = 0.93, 1.22 (2 s, 6 H, 2 × CH_3), 3.42 (s, 3 H, OCH_3), 3.90–4.38 (m, 4 H, 2 × OCH_2), 4.67 (d, $^2J_{P–H}$ = 16.6 Hz, 1 H, PCH), 7.30–7.60 (m, 3 H, ArH).

^{13}C NMR: δ = 20.7, 21.9, 32.6 (d, $^3J_{P–C}$ = 7.4 Hz, CMe_2), 59.1 (d, $^3J_{P–C}$ = 14.4 Hz, $POCH_3$), 77.8, 78.6 (2 d, $^2J_{P–C}$ = 7.5, 7.0 Hz, 2-OCH_2), 83.0 (d, $^1J_{P–C}$ = 162.3 Hz, P-CH), 127.1, 129.4, 130.5, 132.5, 132.8, 134.6.

^{31}P NMR: δ = 8.4.

Anal. Calcd for $C_{13}H_{17}O_4Cl_2P$: C, 46.04; H, 5.02. Found C, 46.15, H, 5.08.

6g

Yield: 90%; mp 118–119 °C.

IR: 978, 1005, 1053, 1080, 1192, 1267, 1350, 1476, 2966 cm^{-1}.

^{1}H NMR: δ = 0.90, 1.21 (2 s, 6 H, 2 × CH_3), 3.40 (s, 3 H, OCH_3), 4.05–4.40 (m, 4 H, 2 × OCH_2), 4.67 (d, $^2J_{P–H}$ = 16.6 Hz, 1 H, PCH), 7.20–7.60 (m, 4 H, ArH).

^{13}C NMR: δ = 20.8, 21.9, 32.5 (d, $^3J_{P–C}$ = 7.5 Hz, CMe_2), 59.0 (d, $^3J_{P–C}$ = 14.5 Hz, PCO*C*H_3), 77.8, 78.4 (2 d, $^2J_{P–C}$ = 9.7 Hz, 7.2 Hz, 2-OCH_2), 81.7 (d, $^1J_{P–C}$ = 162.3 Hz, PCH), 122.7, 126.5, 130.3, 131.6.

^{31}P NMR: δ = 9.0.

Anal. Calcd for $C_{13}H_{18}BrO_4P$: C, 44.70; H, 5.16. Found: C, 44.52; H, 5.05.

6h

Yield: 89%; mp 134–136 °C.

IR: 1015, 1061, 1097, 1279, 1472, 2967 cm^{-1}.

^{1}H NMR: δ = 0.83, 1.16 (2 s, 6 H, 2 × CH_3), 3.43 (s, 3 H, OCH_3), 4.01–4.20 (m, 4 H, 2 × OCH_2), 5.50 (d, $^2J_{P–H}$ = 16.0 Hz, 1 H, PCH), 7.51–8.21 (m, 7 H, ArH).

^{13}C NMR: δ = 20.8, 21.9, 32.4 (d, $^3J_{P–C}$ = 7.2 Hz, CMe_2), 58.7 (d, $^3J_{P–C}$ = 14.5 Hz, PCO*C*H_3), 77.5, 77.9 (2 d, $^2J_{P–C}$ = 7.3, 7.3 Hz, 2-OCH_2), 78.8 (d, $^1J_{P–C}$ = 135.8 Hz, PCH), 123.8, 125.2, 126.3, 130.2.

^{31}P NMR: δ = 9.7.

6i

Yield: 90%; mp 82–84 °C.

IR: 945, 979, 1008, 1055, 1086, 1265, 1477, 1579, 1647, 2970 cm^{-1}.

^{1}H NMR: δ = 0.96, 1.21 (2 s, 6 H, 2 CH_3), 3.47 (s, 3 H, OCH_3), 3.97–4.43 (m, 5 H, 2 × OCH_2, PCH), 6.25–6.31 [m, 1 H, PCH(OMe)C*H*], 6.65 (dd, $^3J_{P–H}$ = 4.6, 16.3 Hz, 1 H, CH=C*H*Ph), 7.25–7.44 (m, 5 H, Ar-H).

^{13}C NMR: δ = 20.8, 21.9, 32.5 (d, $^3J_{P–C}$ = 7.5 Hz, CMe_2), 59.0 (d, $^3J_{P–C}$ = 14.5 Hz, PCO*C*H_3), 77.8, 78.4 (2 d, $^2J_{P–C}$ = 9.7, 7.2 Hz, 2-OCH_2), 81.7 (d, $^1J_{P–C}$ = 162.3 Hz, PCH), 122.7, 126.5, 130.3, 131.6.

^{31}P NMR: δ = 10.7.

Anal. Calcd for $C_{15}H_{21}O_4P$: C, 60.81; H, 7.09. Found C, 60.64, H, 7.21.

Methoxy Phosphonates (±) ($C_{20}H_{12}O_2$)P(O) CH(OMe)(Ar) 11a–d; General Procedure

PCl_3 (3.0 mL, 34.0 mmol) was added to binapthol (2.00 g, 7.0 mmol) and the mixture refluxed for 2 d at 90 °C. Excess PCl_3 was removed under vacuum and the solid (±)($C_{20}H_{12}O_2$)PCl [**10**; ^{31}P (C_6D_6): δ = 177.9; lit.[8] 176.4] obtained was directly used for further reactions.

Freshly distilled acetal, $PhCH(OMe)_2$ (0.43 g, 2.8 mmol) was added to (±)(**10**) (1.00 g, 2.8 mmol) in anhyd toluene. This mixture was refluxed at 120 °C for 2 d to give the α-methoxyphosphonates. They were obtained in a pure state by column chromatography (EtOAc–hexane, 1:1).

11a

Yield: 1.1 g (85%); mp > 240 °C (dec.).

IR: 964, 1223, 1271, 1462, 1507, 1589, 1620 (w) cm^{-1}.

^{1}H NMR: δ = 3.28 and 3.36 [5:1 ratio, 2 s, 3 H, CH(OC*H*$_3$)], 4.61 and 4.88 (ratio 1:5, d each, $^2J_{P–H}$ = 13.1 and 15.8 Hz, 1 H, PCH), 7.19–8.20 (m, 17 H, ArH).

^{13}C NMR: δ = 58.3 (d, $^3J_{P–C}$ = 15.2 Hz, PCO*C*H_3), 80.5 (d, $^1J_{P–C}$ = 159.7 Hz, PCH), 120.4, 121.4, 125.6, 125.7, 126.6, 127.2, 128.3, 128.6, 129.2, 130.9, 131.2, 131.5, 132.0, 132.8, 145.6, 148.9, 149.1, 151.8.

^{31}P NMR: δ = 27.6.

Anal. Calcd for $C_{28}H_{21}O_4P$: C, 74.33; H, 4.67. Found C, 74.28; H, 4.62.

11b

Yield: 65%; mp > 240 °C (dec.)

IR: 961, 1225, 1292, 1460, 1508, 1588, 1620 (w) cm^{-1}.

^{1}H NMR: δ = 2.28 (s, 3 H, $ArCH_3$), 3.34 [s, 3 H, CH(OC*H*$_3$)], 4.56 (d, $^2J_{P–H}$ = 13.2 Hz, 1 H, PCH), 7.12–8.18 (m, 16 H, ArH).

^{13}C NMR: δ = 21.3, 57.9 (d, $^3J_{P–C}$ = 16.8 Hz, PCO*C*H_3), 77.8 (d, $^1J_{P–C}$ = 162.9 Hz, PCH), 120.6, 121.3, 125.7, 126.7, 127.3, 128.5,128.7, 128.8, 129.4, 130.9, 131.2, 131.6, 131.9, 132.5, 139.1, 145.6, 148.9, 149.1.

^{31}P NMR: δ = 27.7.

Anal. Calcd for $C_{29}H_{23}O_4P$: C, 74.67; H, 4.97. Found C, 74.70; H, 4.90.

11c

Yield: 85%; mp > 240 °C.

IR: 962, 1225, 1273, 1292, 1325, 1359, 1462, 1506, 1589, 1618 cm^{-1}.

^{1}H NMR: δ = 3.29 and 3.41 [9:1, 2 s, 3 H, CH(OC*H*$_3$)], 4.58, 4.95 (1:9, d each, $^2J_{P–H}$ = 12.6, 14.7 Hz, 1 H, PCH), 7.23–8.06 (m, 16 H, ArH).

The compound was not very soluble to get a good ^{13}C NMR.

^{31}P NMR: δ = 27.8 and 27.6.

Anal. Calcd. for $C_{28}H_{20}BrO_4P$: C, 63.29; H, 3.79. Found C, 63.35; H, 3.81.

11d

Yield: 90%; mp > 240 °C.

IR: 966, 1223, 1271, 1327, 1348, 1464, 1520 (vs), 1591, 1610 cm^{-1}.

^{1}H NMR: δ = 3.33 and 3.38 [1:3, 2 s, 3 H, CH(OC*H*$_3$)], 4.71, 5.04 (2 d, $^2J_{P–H}$ = 14.4, 17.9 Hz, 1 H, PCH), 7.23–8.47 (m, 16 H, ArH).

^{13}C NMR: δ = 58.9 (d, $^3J_{P-C}$ = 15.0 Hz, PCO*C*H_3), 77.5 (d, $^1J_{P-C}$ = 160 3 Hz, PCH), 120.3, 120.9, 123.9, 125.9, 126.0, 126.9, 127.3, 128.9, 129.2, 129.3, 131.2, 131.5, 131.7, 131.9, 132.5, 140.2. The signals of the other isomer are probably merged with those of the major isomer.

^{31}P NMR: δ = 25.2, 24.7.

Anal. Calcd. for $C_{28}H_{20}NO_6P$: C, 67.60; H, 4.05; N, 2.82. Found C, 67.51; H, 4.09; N, 2.86.

MS (FAB): *m*/*z* = 497 $[M]^+$, 498 $[M + 1]^+$.

Vinyl Ethers 12a–f and 13; Typical Procedure

The phosphonate **6a** (0.6 g, 2.21 mmol) was dissolved in THF (10 mL) and slowly added to a suspension of NaH (0.12 g of 80% dispersion, 5.00 mmol) in THF (20 mL) at 0 °C (5 min); the mixture was stirred at this temperature for 0.5 h. Then, 4-methoxybenzaldehyde (0.3 g, 2.20 mmol) in THF (10 mL) was added (5 min) and the mixture heated under reflux for 15 h. Water (20 mL) was added and the aq layer was extracted with Et_2O (3 × 20 mL). The organic layer was collected, dried (Na_2SO_4), filtered and solvent was removed from the filtrate to give a residue that was purified by column chromatography (hexane) to obtain **12a** (0.42 g, 80%) as a mixture of *E* and *Z* isomers.

In the preparation of **13**, 2:1 molar ratio of the phosphonate to terephthalaldehyde was used.

12a

Yield: 80%, oil. Use of K_2CO_3/xylene in place of NaH/THF also gave 1:1 mixture of isomers.

IR: 1510, 1606, 1635 cm^{-1}.

^{1}H NMR: δ = 3.68, 3.78, 3.84, 3.87 (4 s, 6 H, C=COCH_3 and ArOC*H*$_3$, *E*/*Z*, 1:1), 5.85, 6.16 (2 s, 1 H, CH=C), 6.72 (d, $^3J_{H–H}$ = 8.7 Hz, one isomer), 6.96 (d, $^3J_{H–H}$ = 8.7 Hz, 2 H, ArH), 7.31–7.76 (m, 7 H, ArH).

^{13}C NMR: δ = 55.2, 55.3, 55.5, 57.8 (CO*C*H_3, ArO*C*H_3), 101.3, 112.6, 113.6, 126.4, 128.1, 128.3, 128.5, 128.8, 129.4, 130.0, 155.0, 156.5, 157.5, 159.4.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 80.05; H, 6.75.

12b

Yield: 75% (mixture of two isomers); mp 70–72 °C.

IR: 1516, 1610, 1640 cm^{-1}.

^{1}H NMR: δ = 3.65, 3.85 (2 s, 3 H, $COCH_3$, *E*/*Z*, 1:1), 5.85, 6.04 [2 s, 1 H, CH=C(OMe)], 6.95 (d, $^3J_{H–H}$ = 8.6 Hz, 2 H, ArH), 7.30–8.20 (m, 7 H, ArH).

^{13}C NMR: δ = 55.6, 59.2 (CO*C*H_3), 103.0, 113.2, 123.5, 124.5, 127.0–131.5 (many lines), 157.2, 159.6.

Anal. Calcd for $C_{15}H_{13}O_3N$: C, 70.56; H, 5.14; N, 5.48. Found: C, 70.60; H, 5.30; N, 5.50.

12c

Yield: 90%; mp 64–66 °C (lit.[4] mp 62–63 °C).

IR: 1425, 1450, 1512, 1601, 1703 cm^{-1}.

^{1}H NMR: δ = 3.72 (s, 3 H, $COCH_3$), 3.82 (s, 3 H, $ArOCH_3$), 5.94 [s, 1 H, CH=C(COMe)], 6.64 (d, $^3J_{H-H}$ = 16.1 Hz, 1 H, CH=C*H*Ph), 6.84 (d, $^3J_{H-H}$ = 15.5 Hz, 1 H, C*H*=CHPh), 6.86–7.65 (m, 9 H, ArH).

^{13}C NMR: δ = 47.6 ($COCH_3$), 55.3 ($ArOCH_3$), 114.3, 128.3, 128.9, 130.5, 142.5, 157.5, 161.4.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77. Found: C, 81.02; H, 6.52.

12d

Yield: 88% (mixture of two isomers); mp 66–70 °C.

IR: 1338, 1446, 1502, 1579 cm^{-1}.

^{1}H NMR: δ = 3.78 (s, 3 H, $COCH_3$), 3.86 (s, 3 H, $COCH_3$), 5.89, 6.02 [2 s, 1 H, (Ar)CH=C(COMe)], 6.70 (d, $^3J_{H-H}$ = 15.8 Hz, 1 H, CH=C*H*Ph), 6.92 (d, $^3J_{H-H}$ = 15.8 Hz, 1 H, C*H*=CHPh), 6.97–8.22 (m, 9 H, ArH).

^{13}C NMR: δ = 55.3, 59.0 ($COCH_3$), 102.5, 114.3, 119.9, 123.7, 123.8, 124.0, 127.0–132.4 (many lines), 133.2, 136.4, 144.5, 157.0, 159.5.

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.57; H, 5.38; N, 4.97. Found: C, 72.67; H, 5.40; N, 5.00.

12e

Yield: 50%; mp 62–64 °C.

IR: 1001, 1067, 1240, 1273, 1314, 1599 cm^{-1}.

^{1}H NMR: δ = 2.42 (s, 3 H, Ar-CH_3.), 3.64 [s, 3 H, C=C(OCH_3)], 4.16 (s, 5 H, ferrocenyl-H, unsubstituted ring), 4.28, 4.67 (2 s, 4 H, ferrocenyl-H, substituted ring), 5.99 [s, 1 H, C(OMe)=CH], 7.33–7.40 (m, 4 H, ArH).

^{13}C NMR: δ = 21.5 (Ar-CH_3), 57.8 [C=C(OCH_3)], 68.7, 69.0, 69.3, (ferrocenyl-C), 80.8 [*C*(ferrocenyl)CH=C(OMe)-], 111.0, 122.9, 126.4, 128.4, 136.3, 138.0, 153.9 [CH=*C*(OMe)].

Anal. Calcd for $C_{20}H_{20}FeO$: C, 72.30; H, 6.07. Found: C, 72.18; H, 6.06.

12f

Yield: 80% (mixture of isomers); mp 130–132 °C.

IR: 887, 1024, 1103, 1238, 1339, 1381, 1468, 1622 cm^{-1}.

^{1}H NMR: δ = 3.15, 4.12 [2 s, 3 H, C=C(OCH_3), mixture of two isomers, ratio 1:2], 6.39–8.23 [m, 13 H, C(OMe)=CH, anthracenyl-H merged together).

^{13}C NMR: δ = 56.0, 59.1, ($COCH_3$), 97.6, 104.8 [*C*H=C(OMe)], 125.2, 125.3, 125.5, 125.6, 125.8, 125.9, 126.3, 126.5, 126.8, 127.0, 128.2, 128.8, 129.4, 129.5, 129.6, 130.1, 130.2, 130.4, 131.4, 132.9, 137.1, 155.3, 155.7.

Anal. Calcd for $C_{23}H_{16}Cl_2O$: C, 72.83; H, 4.25. Found: C, 72.75; H, 4.22.

13

Yield: 63%; mp 120–122 °C.

IR: 694, 766, 1066, 1448, 1632, 1682, 2932 cm^{-1}.

^{1}H NMR: δ = 3.66, 3.72,3.81, 3.86 [4 s, 6 H, C=C(OCH_3)], 5.81, 5.90, 6.08, 6.20 (4 s, 2 H, CH=C), 6.79–7.79 (m, 14 H, ArH).

^{13}C NMR: δ = 55.5, 55.6, 57.9, 58.0 ($COCH_3$), 101.6, 101.8, 112.9, 126.6 (CH=C), 128.2, 128.3, 128.5, 128.6, 128.7, 128.9, 129.4, 129.0, 129.4, 133.0, 133.9, 134.3, 135.3, 136.6, 155.8, 156.2, 156.9, 157.4 (COMe).

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 84.22; H, 6.42.

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References

(1) Selected references: (a) Shen, Y.; Ni, J.; Li, P.; Sun, J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 509. (b) Iorga, B.; Eymery, F.; Savignac, P. *Synthesis* **2000**, 576. (c) Tago, K.; Kogen, H. *Org. Lett.* **2000**, *2*, 1975. (d) Sun, S.; Turchi, I. J.; Xu, D.; Murray, W. V. *J. Org. Chem.* **2000**, *65*, 2555. (e) Vaes, L.; Rein, T. *Org. Lett.* **2000**, *2*, 2611. (f) Reiser, U.; Jauch, J. *Synlett* **2001**, 90. (g) Crist, R. M.; Reddy, P. V.; Borhan, B. *Tetrahedron Lett.* **2001**, *42*, 619. (h) Kawasaki, T.; Nonaka, Y.; Watanabe, K.; Ogawa, A.; Higuchi, K.; Terashima, R.; Masuda, K.; Sakamoto, M. *J. Org. Chem.* **2001**, *66*, 1200. (i) Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2315. (j) Pamies, O.; Backyall, J.-E. *J. Org. Chem.* **2003**, *68*, 4815.

(2) (a) Kumaraswamy, S.; Selvi, R. S.; Kumara Swamy, K. C. *Synthesis* **1997**, 207. (b) Muthiah, C.; Praveen Kumar, K.; Aruna Mani, C.; Kumara Swamy, K. C. *J. Org. Chem.* **2000**, *65*, 3733. (c) Praveen Kumar, K.; Muthiah, C.; Kumarswamy, S.; Kumara Swamy, K. C. *Tetrahedron Lett.* **2001**, *42*, 3215. (d) Senthil Kumar, K.; Kumara Swamy, K. C. *J. Organomet. Chem.* **2001**, *637-639*, 616. (e) Muthiah, C.; Senthil Kumar, K.; Vittal, J. J.; Kumara Swamy, K. C. *Synlett* **2002**, 1787.

(3) Maleki, M.; Miller, A.; Lever, O. W. Jr. *Tetrahedron Lett.* **1981**, *22*, 365.

(4) Fettes, K.; McQuire, L.; Murray, A. W. *J. Chem. Soc., Perkin 1* **1995**, 2123.

(5) Denney, D. Z.; Denney, D. B. *J. Am. Chem. Soc.* **1966**, *88*, 1830.

(6) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford UK, **1986**.

(7) Meskens, F. A. *Synthesis* **1981**, 501.

(8) Scherer, J.; Huttner, G.; Büchner, M.; Bakos, J. *J. Oganomet. Chem.* **1996**, *520*, 45.