Chlorophosphonates: Inexpensive Precursors for Stereodefined Chloro-Substituted Olefins and Unsymmetrical Disubstituted Acetylenes

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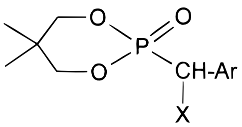
New chlorophosphonates bearing a 1,3,2-dioxaphosphorinane ring which are useful for the stereospecific synthesis of 5-chlorofurfuryl substituted olefins and chloro-substituted dienes have been obtained by an easy, inexpensive route. The utility of some of these in the synthesis of ferrocenyl- and anthracenyl-substituted unsymmetrical acetylenes has been explored. The structures of the phosphonates $(OCH_2CMe_2CH_2O)P(O)CH_2(C_4H_2ClO)$ (**4**) and $(OCH_2CMe_2CH_2O)P(O)(CH{=}CHCH(Cl)Ph$ (**7**) have been determined; in addition, the stereochemistry of (5-chlorofurfuryl)-$CH{=}CH(4\text{-}ClC_6H_4)$ (**13b**) and $2,4\text{-}Cl_2C_6H_3{-}CH{=}CH{-}CH{=}C(Ph)Cl$ (**14a**) is unambiguously proved by the X-ray structure determination.

Introduction

Despite the fact that phosphonates are now well established as having enormous synthetic utility, new reagents that will be useful for specific synthetic goals are still being discovered.[1] We have been interested in developing new phosphonate reagents and have reported the high-yield synthesis of a large number of α-bromo and α-chloro phosphonates **2**[2,3] derived from the readily prepared cyclic phosphite $(OCH_2CMe_2CH_2O)P(O)H$ (**1**). The ease of synthesis and purification coupled with the use of cheap chemicals prompted us to explore their utility and indeed we have been able to achieve an easy access to trisubstituted vinyl chlorides and improved synthesis of chloro and bromostilbenes.[4,5] In the present study we have used the α-hydroxyphosphonates obtained from the Pudovik reaction[6] of **1** with furfuraldehyde and cinnamaldehyde. Chlorination of the α-hydroxyphosphonates occurs in a fashion different from that reported by us before. These results along with the stereospecific synthesis of 5-chlorofurfuryl substituted olefins and trisubstituted dienes are described herein.



2 [**a**: X = Cl; **b**: X = Br]

Another aspect of interest was the inevitable corollary that the phosphonates **2a** can be valuable synthons for unsymmetrical disubstituted acetylenes by the elimination of HCl from the products of the Horner−Wadsworth−Emmons reaction. The present study offers a convenient route to acetylenes bearing ferrocenyl/anthracenyl residues;[7,8] the latter products, we believe, will be interesting electrochemically[9] and photochemically.[10] It is also of interest to note that use of a cyclic phosphonate, in particular one with a six-membered ring, may avoid side reactions, and hence, higher yields of the expected products may be obtained.[11]

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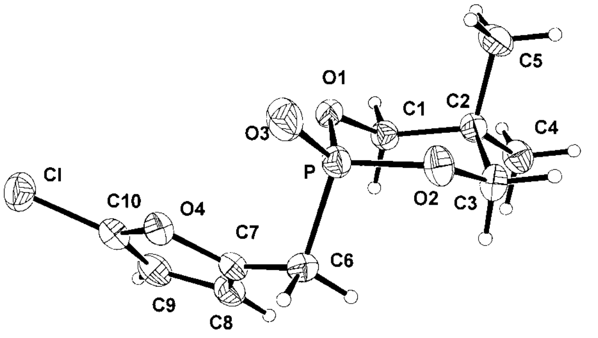
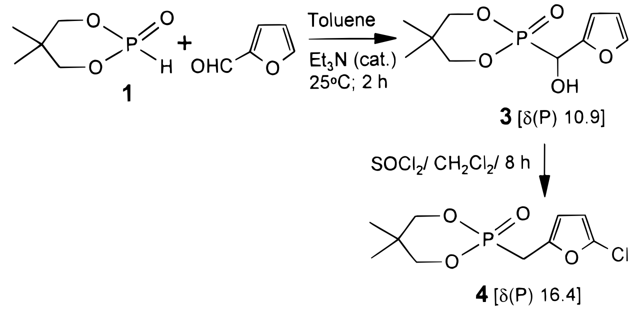
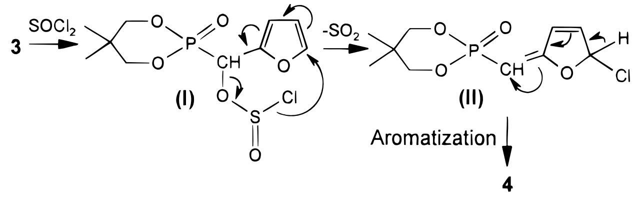


Figure 1. ORTEP drawing of compound **4**·H_2O; the solvent molecule is not shown. Selected distances (Å) and angles (deg): P−O(3) 1.457(4), P−O(1) 1.572(3), P−O(2) 1.577(3), P−C(6) 1.801(4); O(3)−P−O(1) 112.0(2), O(3)−P−O(2) 112.3(2), O(1)−P−O(2) 105.02(16), O(3)−P−C(6) 113.9(2), O(1)−P−C(6) 106.25(18), O(2)−P−C(6) 106.7(2).

Scheme 1



Scheme 2



Results and Discussion

Synthesis of Phosphonates. The α-hydroxy furfuryl phosphonate **3** is readily obtained by reacting the phosphite **1** with furfuraldehyde; treatment of **3** with thionyl chloride afforded the 5-chlorofurfuryl phosphonate **4** (Scheme 1). The identity of **4** was proved by NMR spectroscopy, elemental analysis, as well as X-ray structure determination (Figure 1). Compound **4** contains a PCH_2 moiety instead of the PCH(Cl) moiety present in the normal chlorinated derivatives (cf. **2a**). A possible pathway for the formation of **4** is given in Scheme 2; aromatization appears to be the driving force in the conversion of the intermediate **II** to **4**. We also attempted bromination of **3** with thionyl bromide, but here a large number of products that included (a) those with cleavage of furfuryl ring (^1H NMR), (b) phosphate esters [^{31}P NMR $\delta(P)$ −13.5], and (c) phosphonates [^{31}P NMR: $\delta(P)$ 8.0] were formed.

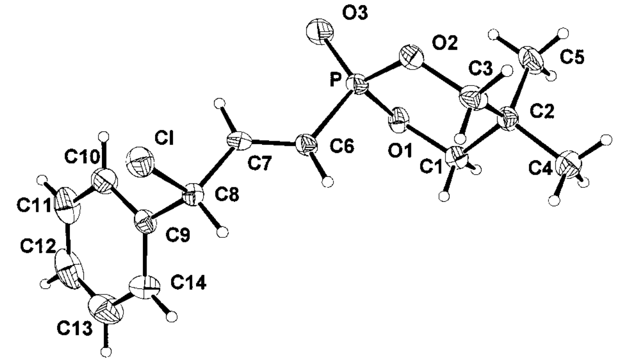
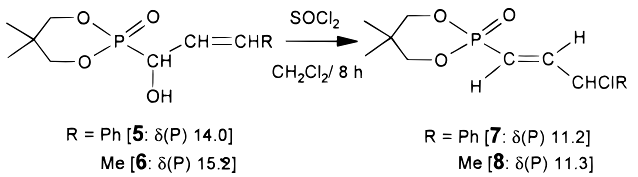
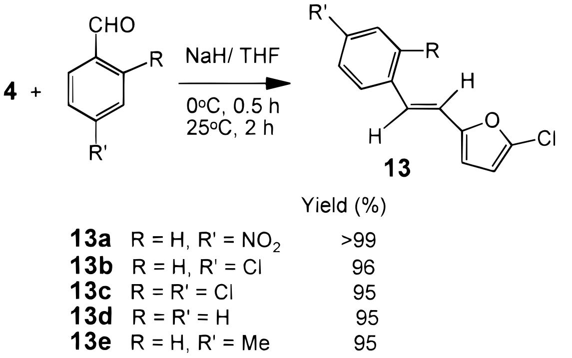


Figure 2. ORTEP drawing of **7**. Selected distances (Å) and angles (deg): P−O(3) 1.445(4), P−O(1) 1.558(4), P−O(2) 1.577(4), P−C(6) 1.774(5), C(8)−C(7) 1.491(7), C(7)−C(6) 1.312(7); O(3)−P−O(1) 111.8(2), O(3)−P−O(2) 112.6(3), O(1)−P−O(2) 104.9(2), O(3)−P−C(6) 114.0(3), O(1)−P−C(6) 106.5(2), O(2)−P−C(6) 106.5(2), C(1)−O(1)−P 121.7(3), C(3)−O(2)−P 120.5(3)°.

Scheme 3

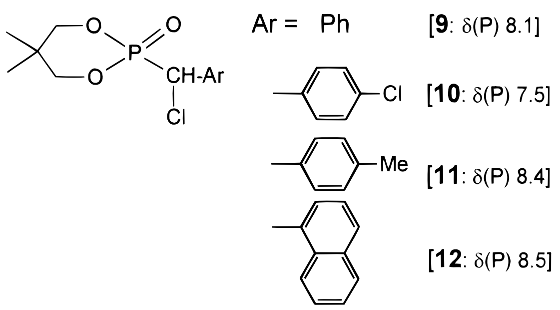


Scheme 4



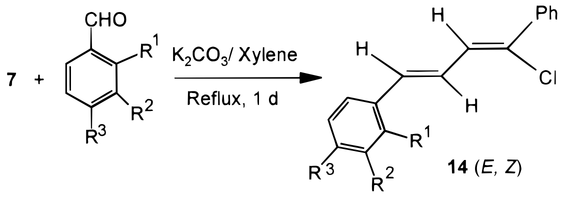
The α-hydroxy phosphonates **5** and **6** derived from the reaction of **1** with cinnamaldehyde or crotonaldehyde undergo allylic chlorination to afford the γ-chloro phosphonates **7** and **8** (Scheme 3). The ^{13}C NMR spectra of **7** and **8** show a characteristic doublet at δ 117.2 [$^1J(P-C)$ 186.0 Hz] and 116.1 [$^1J(P-C)$ 186.5 Hz], respectively. The X-ray structure of **7** (Figure 2) unequivocally established its identity.

The other phosphonates **9**−**12** used in this study are the normal chlorination products of the corresponding α-hydroxy phosphonates.



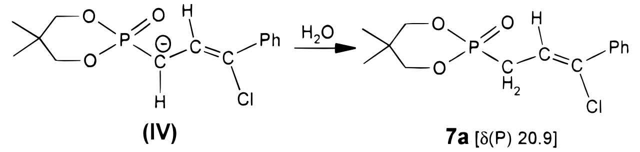
Olefin and Acetylene Synthesis. Reaction of the 5-chlorofurfuryl phosphonate **4** with aromatic aldehydes under mild conditions gives remarkably high (isolated) yields of the *E*-olefin *exclusively* (Scheme 4); the stereochemistry at the double bond was confirmed by deter-

Scheme 5

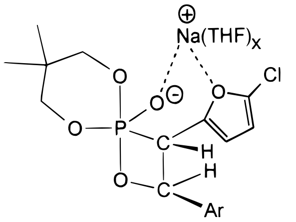


	Yield (%)
14a R^1, R^3 = Cl; R^2 = H	95
14b R^1, R^2 = H; R^3 = NO_2	97
14c R^1, R^2 = H; R^3 = OMe	93
14d R^1, R^2 = C_4H_4 (naphthyl residue); R^3 = H	93
14e R^1, R^2 = H; R^3 = Cl	96
14f R^1, R^2 = H; R^3 = Me	85

Scheme 6



mining the X-ray structure of **13b** (see the Experimental Section). Although phosphonate carbanions are known to furnish a great preponderance of the trans (*E*) olefins,[12] the results obtained here contrast with that obtained using α-chlorophosphonates $(OCH_2CMe_2CH_2O)P(O)(CHCl(Ar))$ [Ar = Ph, 4-MeC_6H_4 etc.] where both *E* and *Z* isomers were obtained in comparable quantities.[4,5] Thus, it is likely that the stereospecificity is imparted by the furfuryl oxygen, which could participate in the transition state as shown in structure **III.**[11-13]



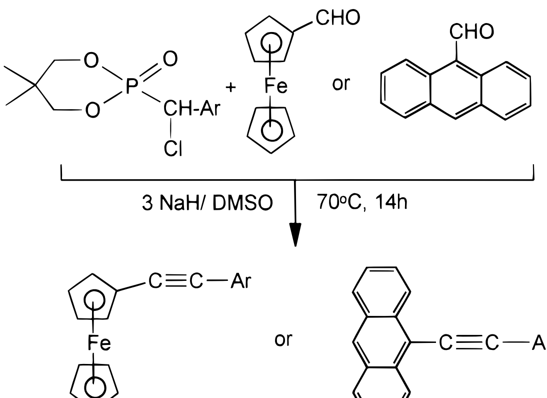
(III)

The reaction of phosphonate **7** with aromatic aldehydes using K_2CO_3/xylene proceeds smoothly (Scheme 5) to give high yields of the chloro-substituted dienes and *only the (E,Z) isomer is obtained*; the stereochemistry was confirmed in the case of **14a** by using X-ray crystallography.

Formation of the (*E*,*Z*) dienes **14** from **7** must have occurred via the carbanion **IV** (Scheme 6) since in a blank reaction of **7** with K_2CO_3/xylene without the aldehyde we were able to isolate the phosphonate **7a**, which has a PCH_2 entity. The stereospecificity observed here may be contrasted with that reported by Murray and co-workers in the reaction of α-methoxy allylphosphonates with aldehydes and ketones using LDA as the base to yield isomeric mixtures of dienes.[14]

Synthesis of acetylenes **15** and **16** is straightforward (Scheme 7). Some other routes to unsymmetrical disubstituted acetylenes are also known.[7-8,15-16] For the synthesis of bis(aryl) acetylenes, the α-chlorophosphonates used in this work are comparable to those used by Zimmer.[7a] Compound **16a** has been previously prepared in good yields from benzyltriphenylphosphonium bromide using a Wittig reaction, bromination, and double-elimination route.[8b] However, starting from the phosphonate reagent, ours is a single-step procedure giving similar yields and is cheaper in our assessment. The transition metal mediated coupling between an aryl halide and a terminal acetylene is also useful, but would require synthesis of the latter in many cases.[7i,k,l,8b]

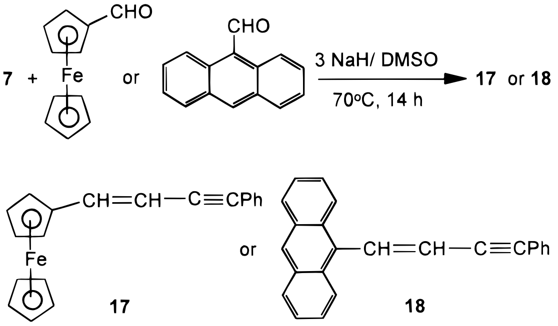
Scheme 7



15 **16**

Ar =	Yield (%)	Ar =	Yield (%)
Ph (**15a**)	67	Ph (**16a**)	50
4-Me-C_6H_4 (**15b**)	68	4-Me-C_6H_4 (**16b**)	51
4-Cl-C_6H_4 (**15c**)	71	4-Cl-C_6H_4 (**16c**)	53
1-naphthyl (**15d**)	35		

Scheme 8



Compound **7** can also be utilized to prepare enynes (Scheme 8); here, isomeric products are possible. Whereas in the case of **17** both *E* and *Z* isomers were obtained (the *Z* isomer is obtained in a pure state), for **18** only the *E* isomer was isolated.

In summary, we have developed new chlorophosphonates that have high potential for use in stereospecific synthesis of chloro-substituted olefins and dienes. Utility of these phosphonates in the synthesis of unsymmetrical acetylenes bearing ferrocenyl and anthracenyl substituents is demonstrated.

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Experimental Section

Compound **1** [δ(P) 2.3] was prepared in 98% yield by adding water dropwise (3.47 g, 0.19 mol) to $(OCH_2CMe_2CH_2O)PCl$ [bp 78−79 °C/20 mm[17]] (32.5 g, 0.19 mol) cooled in ice and stirring the contents for 12 h at room temperature inside an efficient hood; it was dried in a vacuum (0.6 mm) for 2 h (to remove traces of water, if any) and used as such for further reactions. It can also be distilled in a vacuum (bp 93−94 °C/ 0.05 mm[17]). An alternative procedure for **1** is also available.[18] The α-hydroxyphosphonates **3**, **5**, and **6** were prepared by a procedure described by us before.[2]

3: yield 96% (using 2.1 g, 14 mmol of **1**); mp 104−106 °C; IR (cm^{-1}) 3300 (br, ν(OH)); ^{1}H NMR δ 0.92, 1.20 (2 s, 6H), 3.90−4.30 (m, 4H), 5.22 (d, J = 20.0 Hz, 1H), 6.35 (m, 1H), 6.50 (m, 1H), 7.50 (s, 1H); ^{13}C NMR δ 20.8, 21.9, 32.5, 65.6 (d, J = 155.4 Hz), 77.6, 109.5, 109.6, 110.8, 142.9, 149.7; ^{31}P NMR δ 10.9. Anal. Calcd for $C_{10}H_{15}O_5P$: C, 48.77; H, 6.15. Found: C, 48.65; H, 6.06.

5: yield 80% (using 2.1 g, 14 mmol of **1**); mp 141−142 °C; IR (cm^{-1}) 3154 (br, ν(OH)); ^{1}H NMR δ 0.93, 1.14 (2 s, 6H), 3.90−4.10 (m, 2H), 4.20−4.35 (m, 2H), 4.87 (dd, J = 6.0, 16.0 Hz, 1H), 6.35 (ddd, J = 5.0, 6.0, 18.0 Hz, 1H), 6.80 (dd, J = 5.0, 18.0 Hz, 1H), 7.20−7.50 (m, 5H); ^{13}C NMR δ 20.0, 21.8, 32.5 (d, J = 7.5 Hz), 70.6 (d, J = 160.0 Hz) 77.4 ($J \approx$ 5.0 Hz), 123.8, 126.7, 127.9, 128.5, 132.6 (J = 2.5 Hz), 136.3; ^{31}P NMR δ 14.0. Anal. Calcd for $C_{14}H_{19}O_4P$: C, 59.56; H, 6.79. Found: C, 59.45; H, 6.68.

6: yield 20% [using 2.1 g (14 mmol) of **1**; a longer reaction time of 3 d and column chromatographic separation from the starting material was required to get a pure product]; mp 92−94 °C; IR (cm^{-1}) 3412 (br, ν(OH)); ^{1}H NMR δ 0.98, 1.14 (2 s, 6H), 1.74 (m, 3H), 3.90−4.65 (m, 5H), 5.50−6.00 (m, 2H); ^{13}C NMR δ 17.9, 21.0, 21.8, 32.5 (d, J = 7.5 Hz), 70.1 (d, J = 160.0 Hz), 77.2, 125.4, 130.4; ^{31}P NMR δ 15.2. Anal. Calcd for $C_9H_{17}O_4P$: C, 49.08; H, 7.79. Found: C, 49.04; H, 7.68.

Synthesis of compounds **4**, **7**, **8**, and **12** was accomplished in yields ≥90% by treating the respective α-hydroxy phosphonates (10 mmol) with $SOCl_2$ according to the reported procedure.[2]

4: mp 98−100 °C; ^{1}H NMR δ 0.96, 1.03 (2s, 6H), 3.29 (d, J = 22.0 Hz, 2H), 3.80 (dd, $J \approx$ 11.0, 11.0 Hz, 2H), 4.17 (dd, $J \approx$ 11.0, 11.1 Hz, 2H), 6.10 (m, 1H), 6.25 (m, 1H); ^{13}C NMR δ 21.2, 21.4, 25.7 (d, J = 145.0 Hz), 32.4 (d, $J \approx$ 5.0 Hz), 75.7 (d, $J \approx$ 7.0 Hz), 107.4, 111.0, 111.1, 144.6; ^{31}P NMR δ 16.4. Anal. Calcd for $C_{10}H_{14}ClO_4P$: C, 45.37; H, 5.34. Found: C, 45.42; H, 5.38. Crystals of **4** as a hydrate suitable for X-ray crystallography were grown from CH_2Cl_2−hexane mixture in air by slow evaporation of the solvent.

7: mp 120 °C; ^{1}H NMR δ 1.08, 1.10 (2s, 6H), 3.87 (dd, $J \approx$ 11.0 Hz, 12.0 Hz, 2H), 4.20 (dd, $J \approx$ 11.0, 12.0 Hz, 2H), 5.55 (d, $J \approx$ 3.0 Hz, 1H), 6.12 (ddd, $J \approx$ 3.0, 19.1, 19.1 Hz, 1H), 7.00, (ddd, $J \approx$ 8.5, 19.1, 19.1 Hz, 1H), 7.37 (br s, 5H); ^{13}C NMR δ 21.4, 21.6, 32.5 (d, J = 6.0 Hz), 61.7 (d, J = 25.0 Hz), 75.7 (d, J = 4.5 Hz), 117.2 (d, J = 186.0 Hz), 127.0, 127.7, 128.7, 129.0, 137.9, 150.7 (d, J = 5.0 Hz); ^{31}P NMR δ 11.2. Anal. Calcd for $C_{14}H_{18}ClO_3P$: C, 55.91; H, 6.04. Found: C, 55.87; H, 6.15.

8: mp 120 °C; ^{1}H NMR δ 1.08, 1.10 (2 s, 6H), 1.64 (d, $J \approx$ 6.7 Hz, 3H), 3.87 (dd, J = 11.0, 12.0 Hz, 2H), 4.20 (dd, $J \approx$ 11.0, 11.0 Hz, 2H), 4.60 (dqrt, J = 6.7, 6.7 Hz, 1H), 6.00 (dd, J = 19.0, 19.0 Hz, 1H), 6.85 (ddd, $J \approx$ 8.5, 19.0, 19.0 Hz, 1H); ^{13}C NMR δ 21.5, 23.9, 32.5 (d, J = 5.5 Hz), 55.6 (d, J = 25.0 Hz), 75.7, 116.1 (d, J = 186.5 Hz), 152.6; ^{31}P NMR δ 11.3. Anal. Calcd for $C_9H_{16}ClO_3P$: C, 45.29; H, 6.77. Found: C, 45.15; H, 6.64.

12: mp 167−168 °C [starting from $(OCH_2CMe_2CH_2O)P(O)CH(OH)(C_{10}H_7)$, mp 172 °C; ^{31}P NMR δ 13.1; ^{1}H NMR δ 0.64, 1.06 (2s, 6H), 3.63−4.00 (m, 4H), 6.00 (d, J = 11 Hz, 1H), 7.48−8.15 (m, 7H)]; ^{1}H NMR δ 0.89, 1.18 (2s, 6H), 3.99−4.20 (m, 4H), 6.01 (d, J = 14.0 Hz, 1H), 7.44−8.10 (m, 7H); ^{13}C NMR δ 21.0, 21.8, 32.6, 51.0 (d, J = 155.0 Hz), 78.2 122.7, 125.3, 126.0, 127.0, 128.2, 128.3, 129.0, 130.0, 133.8; ^{31}P NMR δ 8.5. Anal. Calcd for $C_{16}H_{18}ClO_3P$: C, 59.18; H, 5.60. Found: C, 59.12; H, 5.49.

(a) Rearrangement of 7 to 7a. Compound **7** (0.6 g, 2.0 mmol) was heated with K_2CO_3 (0.5 g) in xylene (30 mL) at 80 °C for 20 h. To the residue after removal of xylene was added ether, and the contents were washed with water. The ether portion was dried (Na_2SO_4) and the solvent removed. The residue was essentially **7a** (liquid) [NMR, >95%]. Attempted purification by column chromatography (for elemental analysis) was not successful: ^{1}H NMR δ 1.03, 1.06 (2 s, 6H), 3.10 (dd, J = 7.8, 22.5 Hz, 2H), 3.88 (dd, 2H), 4.17 (dd, 2H), 6.19 (td → qrt, 1H), 7.20−7.60 (m, 5H); ^{13}C NMR δ 21.4, 26.7 (d, J = 136.5 Hz), 32.5 (d, J = 4.5 Hz), 75.5, (d, J = 7.0 Hz), 115.9 (d, J = 11.0 Hz), 126.5, 128.4, 129.0, 137.3; ^{31}P NMR δ 20.9; MS 265 $[M - Cl]^+$.

(b) Reaction of 3 with $SOBr_2$. Compound **3** (0.5 g, 2 mmol) in dichloromethane (10 mL) was stirred with an excess of $SOBr_2$ (0.5 mL, 1.3 g, 6.2 mmol) for 1 d at 25 °C. More dichloromethane (10 mL) was added, the solution was washed with water, and the organic layer was dried (Na_2SO_4). The solvent was evaporated to get a solid. It was dissolved in dichloromethane/heptane mixture, when a solid (**A**; 0 05 g) precipitated. **A**: mp 94−96 °C; ^{1}H NMR δ 0.92, 1.39 (2 s, 6H), 4.10 (dd, J = 10.7, 16.7 Hz, 2H), 4.60 (d, J = 10.7 Hz, 2H), 6.64 (d, $J \approx$ 3.8 Hz, 1H), 7.77 (s, 1H), 8.20 (d, $J \approx$ 3.8 Hz, 1H); ^{31}P NMR δ −13.9 [The δ (P) value clearly suggests that the compound is a phosphate ester[19]]; MS 244 [no Br isotopic pattern]. The sample was unstable in $CDCl_3$ solution, and hence, a satisfactory ^{13}C NMR spectrum could not be recorded. The mother liquor showed a large number of peaks in the ^{31}P NMR [−14.2, −13.8, −13.3, (phosphate region); −6.1, −4.5, −4.0, −1.7, 8.0, 12.8]. A small amount of a phosphonate product [^{1}H NMR δ 1.02, 1.10 (2 s, 6H), 3.80−4.10 (m, 4H), 6.32 (d, J = 14.4 Hz, ~1H), 7.30−8.00 (m, ca. 5H); ^{31}P NMR δ 8.0] was also isolated, but was not analyzed further because of the very low yield.

(c) Synthesis of 5-Chlorofurfuryl-Substituted Olefins 13a−e: Typical Procedure for 13a. To a stirred suspension of NaH (0.21 g, 8.75 mmol) in THF (20 mL) was added **4** (0.8 g, 3.02 mmol) in THF (20 mL) at 0 °C. After 30 min, the mixture was brought to 25 °C, and 4-nitrobenzaldehyde (0.48 g, 3.17 mmol) in THF (20 mL) was added dropwise over a period of 15 min. The mixture was stirred for 2 h, quenched with cold water, and then extracted with ether. The ether layer was dried (Na_2SO_4) and the solvent removed to obtain a semisolid that was purified by column chromatography (silica gel, hexane) to obtain **13a** as an yellow solid: yield 0.75 g (≥99%); mp 78 °C; ^{1}H NMR δ 6.25 (d, J = 3.8 Hz, 1H), 6.46 (d, J = 3.8 Hz, 1H), 6.92, 7.04 (AB qrt, J = 16.2 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H); ^{13}C NMR δ 108.9, 112.9, 119.4, 123.7, 124.2, 124.7, 126.6, 143.2, 146.7, 151.9. Anal. Calcd for $C_{12}H_8ClNO_3$: C, 57.72; H, 5.61. Found: C, 57.76; H, 5.65.

The same molar quantities of the reactants were used to prepare **13b−e** (see the Supporting Information for characterization data).

(d) Synthesis of the Dienes 14a−f: Typical Procedure for 14a. A mixture of **7** (0.50 g, 1.66 mmol), 2,4-dichlorobenzaldehyde (0.29 g, 1.66 mmol), and K_2CO_3 (0.68 g, 4.90 mmol) in xylene (10 mL) was heated under reflux for 24 h. After removal of xylene, water was added and the mixture extracted with ether (3 × 25 mL). Water wash, drying (Na_2SO_4), and evaporation of the solvent gave a semisolid that was purified by column chromatography (silica gel, hexane) to obtain **14a**: yield 0.49 g (95%); mp 129−131 °C; ^{1}H NMR δ 6.98 (d, J = 9.3 Hz, 1H), 7.11 (d, J = 17.0 Hz, 1H), 7.20−7.80 (m, 9H); ^{13}C NMR δ 121.2, 125.5, 126.4, 126.5, 127.0, 127.3, 127.7, 128.5, 129.0, 129.9, 131.7. Anal. Calcd for $C_{16}H_{11}Cl_3$: C, 62.06; H, 3.58. Found: C, 62.00; H, 3.60.

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Characterization data for **14b**−**f** is available as Supporting Information.

(e) Synthesis of Disubstituted Acetylenes 15−**18: Typical Procedure for 15b.** To a mixture of the α-chlorophosphonate **11** (0.49 g, 1.73 mmol), ferrocene carboxaldehyde (0.37 g, 1.73 mmol), and DMSO (20 mL) was added sodium hydride (0.12 g, 5.00 mmol). This mixture was then heated at 70 °C for 14 h with stirring. The contents were transferred to a separatory funnel, and ether (50 mL) and water (30 mL) were added. The organic layer was washed with water, dried (Na_2SO_4), and filtered. Removal of the solvent followed by column chromatography (hexane) afforded the acetylene **15b**: yield 0.35 g (68%); mp 170 °C; IR (cm^{-1}) 2206; ^{1}H NMR δ 2.39 (s, 3H, C*H*$_3$), 4.25 (s, 7H, ferrocene-*H*), 4.50 (s, 2H, ferrocene-*H*), 7.15 (d, $J = 12.0$ Hz, 2H, Ar-*H*), 7.40 (d, $J = 12.0$ Hz, 2H, Ar-*H*); ^{13}C NMR δ 65.7, 68.7, 70.0, 71.4 (ferrocenyl-C), 85.0 (*C*≡C), 87.5 (C≡*C*), 121.0, 129.1, 131.3, 137.7. Anal. Calcd for $C_{19}H_{16}Fe$: C, 75.92; H, 5.32. Found: C, 76.02; H, 5.07.

Other compounds were obtained by taking the same molar quantities of the reactants.

15a: yield 67%; mp 120 °C; ^{1}H NMR δ 4.27 (s, 7H), 4.53 (s, 2H), 7.20−7.60 (m, 5H); ^{13}C NMR δ 65.7, 68.8, 70.0, 71.4, 85.0, 87.5, 124.0, 127.7, 128.3, 131.4. Anal. Calcd for $C_{18}H_{14}Fe$: C, 75.47; H, 4.89. Found: C, 75.26; H, 4.81.

15c: yield 71%; mp 146 °C; IR (cm^{-1}) 2211; ^{1}H NMR δ 4.25 (s, 7H), 4.50 (s, 2H), 7.30−7.50 (qrt, 4H); ^{13}C NMR δ 64.9, 69.0, 70.0, 71.5, 84.7, 89.6, 122.6, 128.6, 132.6, 133.6. Anal. Calcd for $C_{18}H_{13}ClFe$: C, 67.40; H, 4.06. Found: C, 67.55; H, 4.05.

15d: yield 35%; mp 160−162 °C; IR (cm^{-1}) 2210; ^{1}H NMR δ 4.32 (s, 7H), 4.64 (s, 2H), 7.35−8.50 (m, 7H); ^{13}C NMR δ 65.1, 69.0, 70.0, 71.6, 84.0, 93.2, 122.5, 125.3, 126.3, 126.6, 128.1, 128.3, 129.9, 133.3. Anal. Calcd for $C_{22}H_{16}Fe$: C, 78.57; H, 4.75. Found: C, 78.50; H, 4.65.

17 (1.2 mmol of phosphonate used): (i) solid, isomer **a**; yield 0.24 g, (64%); mp 88−90 °C; ^{1}H NMR δ 4.22 (s, 5H), 4.35 (s, 2H), 4.92 (s, 2H), 5.76 (d, $J = 11.6$ Hz, 1H), 6.50 (d, $J = 11.6$ Hz, 1H), 7.29−7.50 (m, 5H); ^{13}C NMR δ 69.5, 80.0, 90.0, 93.5, 104.0, 123.4, 128.0, 128.5, 131.2, 138.7. Anal. Calcd for $C_{20}H_{16}Fe$: C, 76.92; H, 4.53. Found: C, 76.25; H, 4.77.

(ii): Liquid ∼0.10 g (27%) [isomer **a** + isomer **b**, ca. 1:2]; NMR data given below only for isomer **b**; ^{1}H NMR δ 4.46 (m, ∼9H), 6.04 (d, $J = 15.8$ Hz, 1H), 6.90 (d, $J = 15.8$ Hz, 1H), 7.30−7.70 (m, 5H); ^{13}C NMR δ 52.7, 67.0, 69.7, 70.3, 81.2, 104.9, 123.0, 127.8, 131.3, 140.7. See above for data on pure isomer **a**.

16a (1.8 mmol of phosphonate used): yield 0.25 g (50%); mp 106−108 °C (lit.[8a] mp 108−109 °C); ^{1}H NMR 7.30−9.00; ^{13}C NMR δ 86.7, 101.0, 117.5, 123.9, 125.8, 126.7, 126.9, 127.9, 128.9, 131.4, 131.8, 132.8. Anal. Calcd for $C_{22}H_{14}$: C, 94.88; H, 5.03. Found: C, 94.48; H, 4.92.

16b (1.8 mmol of phosphonate used): yield 0.27 g (51%); mp 110 °C; ^{1}H NMR 2.41 (s, 3H), 7.25−8.65 (m, 13H); ^{13}C NMR δ 21.6, 85.9, 101.2, 117.7, 120.7, 125.7, 126.6, 126.9, 127.6, 128.8, 129.4, 131.3, 131.6, 132.7, 138.7. Anal. Calcd for $C_{23}H_{16}$: C, 95.52; H, 5.48. Found: C, 95.40; H, 5.38.

16c (3.2 mmol of phosphonate used): yield 0.53 g (53%); mp 147−148 °C; IR (cm^{-1}) 2197 (vw); ^{1}H NMR 7.40−8.60 (m); ^{13}C NMR δ 87.4, 99.6, 116.9, 122.2, 125.7, 126.7, 128.0, 128.8, 128.9, 131.2, 132.7, 132.8, 134.5. Anal. Calcd for $C_{22}H_{13}Cl$: C, 84.49; H, 4.16. Found: C, 84.28; H, 4.02.

18 (1.8 mmol of phosphonate used): yield 0.15 g (27%); mp 120−122 °C; ^{1}H NMR 6.74 (d, $J = 16.2$ Hz, 1H), 7.38−8.65 (m, 15H); ^{13}C NMR δ 87.5, 101.0, 108.5, 117.6, 125.7, 126.5, 126.6, 126.8, 127.7, 128.7, 128.8, 131.3, 132.6, 136.5, 141.3. Anal. Calcd for $C_{24}H_{16}$: C, 94.74; H, 5.26. Found: C, 94.75; H, 5.35.

(f) X-ray Crystallography. A suitable crystal of **4**·H_2O, **7**, **13b**, or **14a** was mounted on a glass fiber, and X-ray data collected at 293 K on an Enraf-Nonius MACH3 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structures were solved and refined by conventional methods.[20]

Crystal data: **4**·H_2O; empirical formula, $C_{10}H_{16}ClO_5P$; formula_weight, 282.65; crystal system, tetragonal; space group, $I\bar{4}$; $a = 20.656(3)$ Å; $b = 20.656(3)$ Å; $c = 6.0420(12)$ Å; $V = 2577.9(7)$ Å^3; $Z = 8$; density (calcd), 1.457 Mg m^{-3}; $\mu = 0.427$ mm^{-1}; $F(000)$ 1184; crystal size, 0.30 × 0.20 × 0.20 mm; θ range, 1.97−27.51°; reflections collected, 5906; independent reflections, 2964 [R(int) = 0.1243]; attempts to solve the structure in other space groups were not successful; refinement method, full-matrix least-squares on F^2; data/restraints/parameters, 2964/0/162; goodness-of-fit on F^2, 1.087; final R indices [$I > 2\sigma(I)$], R1 = 0.0693, wR2 = 0.1759; absolute structure parameter, −0.27(14); largest diff. peak and hole, 0.511 and −0.458 e Å^{-3}.

7: empirical formula, $C_{14}H_{18}ClO_3P$; formula wt, 300.70; crystal system, orthorhombic; space group, *Pbca*; $a = 8.7813(18)$ Å; $b = 10.294(7)$ Å; $c = 33.362(10)$ Å; $V = 3016(2)$ Å^{-3}; $Z = 8$; density (calcd), 1.325 Mg m^{-3}; $\mu = 0.360$ mm^{-1}; $F(000)$, 1264; crystal size, 0.3 × 0.2 × 0.1 mm; θ range, 2.44−24.98°; reflections collected, 2644; independent reflections, 2644 [R(int) = 0.0000]; refinement method, full-matrix least-squares on F^2; data/restraints/parameters, 2644/0/174; goodness-of-fit on F^2, 1.076; final R indices [I > 2$\sigma(I)$], R1 = 0.0680, wR2 = 0.1717; largest diff. peak and hole, 0.592 and −0.373 e A^{-3}.

13b: empirical formula, $C_{12}H_8Cl_2O$; formula wt, 239.08; crystal system, orthorhombic; space group, *Pccn*; $a = 26.895(5)$ Å; $b = 14.810(3)$ Å; $c = 5.579(4)$ Å; $V = 2222.3(17)$ Å^{-3}; $Z = 8$; density (calcd), 1.429 Mg m^{-3}; $\mu = 0.551$ mm^{-1}; $F(000)$, 976; crystal size, 0.3 × 0.2 × 0.2 mm; θ range, 1.51 to 25.46°; reflections collected, 2066; independent reflections, 2066 [R(int) = 0.0000]; refinement method, full-matrix least-squares on F^2; data/restraints/parameters, 2066/0/136; goodness-of-fit on F^2, 1.050; final R indices [$I > 2\sigma(I)$], R1 = 0.0585, wR2 = 0.1253; largest diff. peak and hole, 0.328 and −0.250 e A^{-3}. Further details including an ORTEP drawing are given as Supporting Information.

14a: empirical formula, $C_{16}H_{11}Cl_3$; formula wt, 309.60; crystal system, monoclinic; space group, $P2_1/c$; $a = 7.4728(15)$ Å; $b = 11.6161(16)$ Å; $c = 16.270(3)$ Å; $\beta = 95.947(14)$°; $V = 1404.7(4)$ Å; $Z = 4$; density (calcd), 1.464 Mg m^{-3}; $\mu = 0.634$ mm^{-1}; $F(000)$, 632; crystal size, 0.3 × 0.2 × 0.2 mm; θ range, 2.16−24.96°; reflections collected, 2651; independent reflections, 2459 [R(int) = 0.0320]; refinement method, full-matrix least-squares on F^2; data/restraints/parameters 2459/0/172; goodness-of-fit on F^2, 1.198; final R indices [$I > 2\sigma(I)$], R1 = 0.0312, wR2 = 0.0945; largest diff. peak and hole, 0.200 and −0.306 e Å^{-3}. Further details are available as Supporting Information.

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Supporting Information Available: X-ray structure solution and refinement data for compounds **4**·H_2O, **7**, **13b**, and **14a** and ORTEP drawings of **13b** and **14a**; characterization data for **13b**−**13e** and **14b**−**14f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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