Synthesis, Acetylation and Silylation of (1*E*)-2-Diethoxyphosphonylbuta-1,3-dien-1-ols: A Convenient Route to New, Activated Dienylphosphonates

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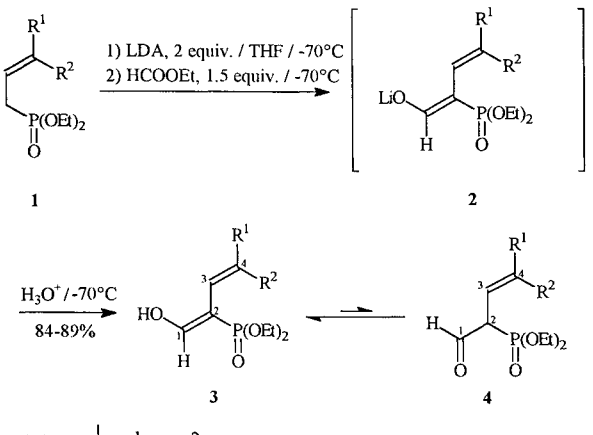
Lithiated carbanions of allylic phosphonates **1** showed strict α-regioselectivity in their reaction with ethyl formate, giving stereoselectively (1*E*)-2-phosphonodienols **3b** and **3d**, or a mixture of **3c** with its tautomeric aldehyde **4c**, or the conjugated aldehyde **5** resulting from the prototropy of the enol **3a**. All these compounds, obtained in high yields, were readily transformed into the corresponding stable *O*-acetylated derivatives **6** or into the *O*-silylated derivatives **7**, whose stability depends on the silicon substituents.

Trialkylsilyloxy- and acyloxy-substituted dienes are interesting forms of protected β,γ-unsaturated carbonyl compounds. For example, 1-trimethylsilylbuta-1,3-dienes proved to be remarkable γ-regioselective carbanion equivalents of their unsaturated carbonyl precursors.[1] On the other hand, variously substituted silyloxy-dienes have been used extensively in the Diels–Alder reaction, especially by Danishefsky and co-workers.[2,3] To the best of our knowledge, apart from 3-methoxy- (or 3-propargyloxy)-2-dialkylphosphonylalka-1,3-dienes used as precursors of 2-dialkylphosphonyl α,β-unsaturated ketones,[4,5] no examples of phosphonic oxygen-substituted 1,3-alkadienes have been reported.

Within the scope of our studies on the reactivity of allylic phosphonate carbanions, we have described an efficient synthesis of 2-diethoxyphosphonylalka-1,3-dienes, based on the high or exclusive α-regioselectivity of hydroxyalkylation reaction of these carbanions with aldehydes.[6] Moreover, we recently proved that sterically hindering the α position of diethyl crotylphosphonate with a trimethylsilyl group resulted in a strict γ-regioselective reactivity of the corresponding anion towards ethyl formate or ethyl chloroformate, leading to attractive γ-functional β,γ-unsaturated phosphonates.[7]

Pursuing this work, we decided to examine the reactivity of carbanions derived from allylic phosphonate **1** towards ethyl formate (Scheme 1), in order to afford new unsaturated phosphonic aldehydes **4**.



1, 2, 3, 4	R1	R2
a	H	H
b	Me	H
c	Me	Me
d	Ph	H

Scheme 1

Thus treating the readily available phosphonates **1**[6] with a two-fold excess of lithium diisopropylamide (LDA) in THF at −70 °C, followed by addition of ethyl formate (1.5 equiv) at the same temperature, led, after about 15 min irrespective of R^1 and R^2, to the complete formation of enolates **2** [^{31}P NMR (THF), ca. $\delta = 30$, as a broad peak]. Subsequent acidic hydrolysis of the mixture at −70 °C,[8] followed by usual workup and purification gave results which depended on the nature of substituents R^1 and R^2 (Table 1). For the crotyl and cinnamyl series, enols **3b** and **3d** were the sole products of the reaction; no trace of the corresponding aldehydes **4b** or **4d** was ever observed. For the prenyl series, a tautomeric mixture of **3c** and **4c** (in a 7:3 ratio) was obtained. Finally, for the allyl series, only the enol **3a** was detected in the organic phase resulting from acidic hydrolysis of **2a** but, after evaporation of the solvent, the crude product was a mixture of enol **3a** and of the more stable conjugated aldehyde **5**. During the subsequent purification process (either distillation or flash chromatography), enol **3a** was quantitatively transformed into **5**, isolated as a mixture of *Z* and *E* stereoisomers in a ratio of 65:35.

In all cases, the isolated products, which resulted from an exclusive α-regioselectivity of the metallated starting phosphonates in their reaction with ethyl formate, were obtained in very good yields. Moreover, ^{1}H NMR spectra unambiguously established the *E* configuration of the enol double bond of **3**, confirming the excellent stereoselectivity of the reaction. Furthermore, the more stable transoid structure depicted in Scheme 1 for **3** might represent the major conformer of these dienols; the relative *Z* stereoselectivity observed in the formation of **5** from **3a**, by a prototropic process, might be explained by the predominant transoid conformation of **3a**.

In the second part of this work, ethereal solutions of **3** (or of the mixture **3c**/**4c**) were treated with acetyl chloride or with a trisubstituted silyl chloride, at 0 °C, in the presence of a small excess (1.1 equiv) of triethylamine (Scheme 2). The reaction was complete after ca. 15 min in most cases, as proved by ^{31}P NMR analysis of samples of the mixture. In the acetylation reaction, subsequent workup and purification led to 1-acetoxy-2-diethoxyphosphonyl-1,3-alkadienes **6** in high yield (Table 2). In the silylation reactions, the stability of isolated products

Table 1. Synthesis and NMR Data of Enols **3** and of Aldehyde **5**

Product	Yield[a] (%)	^{31}P NMR ($CDCl_3$), δ	^{1}H NMR ($CDCl_3$) δ, J (Hz)	$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ, J (Hz)
3a	–[b]	21.8	1.2–1.4 (m, 6H, CH_3CH_2O), 3.9–4.2 (m, 4H, CH_3CH_2O), 5.1 (d, J = 11.0, 1H, HC-4), 5.4 (d, J = 17.3, 1H, HC-4), 6.6 (ddd, J = 29.0, 17.3, 11.0, 1H, HC-3), 7.4 (d, J = 11.7, 1H, HC-1)	16.1 (d, J = 6.8, CH_3CH_2O), 62.0 (d, J = 5.7, CH_3CH_2O), 99.0 (d, J = 193.5, C-2), 121.0 (d, J = 6.9, C-4), 126.1 (d, J = 5.7, C-3), 157.0 (d, J = 25.8, C-1)
3b	84[c]	22.7	1.2–1.4 (m, 6H, CH_3CH_2O), 1.8 (d, J = 6.7, 3H, CH_3C-4), 3.9–4.2 (m, 4H, CH_3CH_2O), 5.9 (dq, J = 16.2, 6.7, 1H, HC-4), 6.3 (dd, J = 16.2, 8.4, 1H, HC-3), 7.35 (d, J = 10.4, 1H, HC-1)	16.2 (d, J = 6.9, CH_3CH_2O), 19.0 (s, CH_3C-4), 61.5 (d, J = 5.7, CH_3CH_2O), 99.0 (d, J = 192.9, C-2), 120.0 (d, J = 6.8, C-4), 125.5 (d, J = 5.6, C-3), 156.2 (d, J = 25.7, C-1)
3c	–[c,d]	22.1	1.6–1.9 [m, 6H, $(CH_3)_2$C=C], 3.9–4.2 (m, 4H, CH_3CH_2O), 5.4 (m, 1H, HC-3), 7.3 (d, J = 11.1, 1H, HC-1)	16.0 (d, J = 6.8, CH_3CH_2O), 20.8 and 25.0 [2s, $(CH_3)_2$–C=C], 61.2 (d, J = 5.0, CH_3CH_2O), 99.0 (d, J = 195.0, C-2), 113.0 (d, J = 4.8, C-3), 138.1 (d, J = 11.8, C-4), 155.0 (d, J = 27.9, C-1)
3d	88[c]	22.1	1.35 and 1.36 (2t, J = 7.0, 6H, CH_3CH_2O), 4.0–4.2 (m, 4H, CH_3CH_2O), 6.8–7.5 (m, 6H, H_{arom}, HC-3), 7.6 (d, J = 9.9, 1H, HC-1)	16.2 (d, J = 6.9, CH_3CH_2O), 62.0 (d, J = 4.6, CH_3CH_2O), 99.5 (d, J = 193.3, C-2), 123.0 (d, J = 6.9, C-4), 125.0–129.0 (o,m,p-C_{arom}), 128.2 (d, J = 5.0, C-3), 138.5 (s, i-C_{arom}), 159.0 (d, J = 25.7, C-1)
5	86[e]	12.5 (E), 9.9 (Z)	1.2–1.4 (m, 6H, CH_3CH_2O), 2.3 [dd, J = 7.4, 3.0, (E)-CH_3C=C], 2.34 [dd, J = 7.3, 3.2, (Z)-CH_3C=C], 4.0–4.3 (m, 4H, CH_3CH_2O), 7.5 [dq, J = 44.6, 7.3, (Z)-HC=C], 7.6 [dq, J = 22.9, 7.4, (E)-HC=C], 9.5 [d, J = 15.5, (Z)-HC=O], 10.3 [d, J = 17.0, (E)-HC=O]	15.8 (m, CH_3C=C), 16.4 and 16.5 (2d, J = 6.1, CH_3CH_2O), 62.2 and 62.3 (2d, J = 6.9 and 6.7, CH_3CH_2O), 131.0 [d, J = 179.5, (E)-C-2], 133.1 [d, J = 179.0, (Z)-C-2], 161.2 [d, J = 7.0, (E)-C-3], 166.0 [d, J = 9.1, (Z)-C-3], 188.4 [d, J = 10.6, (E)-CHO], 191.0 [d, J = 12.6, (Z)-CHO]

[a] Yields of purified products (oils), whose MS data were in accordance with the proposed structures. Satisfactory microanalyses obtained: C ± 0.60, H ± 0.48.
[b] Enol **3a** was obtained as crude product (yield ca. 98%).
[c] Products purified by acid–base double extraction, followed by flash chromatography (silica gel; Et_2O).
[d] Enol **3c** was the major product (ca. 70%) of the tautomeric mixture **3c**/**4c**, which was obtained in 89% yield. In the ^{31}P NMR ($CDCl_3$) spectrum, aldehyde **4c** was observed at δ = 17.3.
[e] Purified by bulb-to-bulb distillation [bp (0.35 Torr) = 95°C]. Isolated as a E/Z mixture in a ratio of 35 : 65.

Table 2. Synthesis and NMR Data of Diethyl 1-Acetoxypenta-1,3-dien-2-ylphosphonates **6**

Product	Yield[a] (%)	^{31}P NMR ($CDCl_3$), δ	^{1}H NMR ($CDCl_3$) δ, J (Hz)	$^{13}C\{^1H\}$ NMR ($CDCl_3$) δ, J (Hz)
6a	85	15.8	1.3 (t, J = 7.1, 6H, CH_3CH_2O), 2.25 (s, 3H, CH_3C=O), 4.0–4.2 (m, 4H, CH_3CH_2O), 5.3 (d, J = 11.4, 1H, HC-4), 5.7 (d, J = 17.9, 1H, HC-4), 6.6 (ddd, J = 28.6, 17.9, 11.4, 1H, HC-3), 7.9 (d, J = 11.8, 1H, HC-1)	17.0 (d, J = 6.6, CH_3CH_2O), 21.0 (s, CH_3C=O), 62.2 (d, J = 5.2, CH_3CH_2O), 111.5 (d, J = 183.9, C-2), 119.8 (d, J = 5.9, C-4), 125.8 (d, J = 5.5, C-3), 145.0 (d, J = 27.8, C-1), 166.2 (s, C=O)
6b	81	16.4	1.3 (t, J = 7.1, 6H, CH_3CH_2O), 1.85 (d, J = 5.1, 3H, H_3CC-4), 2.24 (s, 3H, CH_3C=O), 3.95–4.2 (m, 4H, CH_3CH_2O), 6.2–6.4 (m, 2H, HC-3, HC-4), 7.8 (d, J = 11.9, 1H, HC-1)	16.5 (d, J = 6.5, CH_3CH_2O), 19.0 (s, CH_3C=O), 21.0 (s, CH_3C=), 62.0 (d, J = 5.2, CH_3CH_2O), 111.8 (d, J = 182.5, C-2), 120.0 (d, J = 5.6, C-4), 131.7 (d, J = 5.0, C-3), 143.0 (d, J = 27.8, C-1), 166.2 (s, C=O)
6c	83	16.7[b]	1.3 (t, J = 7.1, 6H, CH_3CH_2O), 1.6–1.9 [m, 6H, $(CH_3)_2$C=], 2.2 (s, 3H, CH_3C=O), 4.0–4.2 (m, 4H, CH_3CH_2O), 5.2–5.3 (m, 1H, HC-3), 7.85 (d, J = 11.6, 1H, HC-1)[b]	16.3 (d, J = 6.4, CH_3CH_2O), 20.5 (s, CH_3C=O), 20.0 and 25.5 [2s, $(CH_3)_2$C=], 61.5 (d, J = 5.5, CH_3CH_2O), 111.6 (d, J = 184.9, C-2), 113.0 (d, J = 3.6, C-3), 140.5 (d, J = 11.6, C-4), 143.0 (d, J = 30.9, C-1), 166.0 (s, C=O)[b]
6d	84	15.5	1.4 (t, J = 7.1, 6H, CH_3CH_2O), 2.35 (s, 3H, CH_3C=O), 4.0–4.3 (m, 4H, CH_3CH_2O), 7.1 (dd, J = 35.5, 16.7, 1H, HC-3), 7.3–7.5 (m, 6H; H_{arom}, HC-4), 7.6 (d, J = 9.9, 1H, HC-1)	16.0 (d, J = 6.5, CH_3CH_2O), 20.3 (s, CH_3C=O), 62.3 (d, J = 5.1, CH_3CH_2O), 111.2 (d, J = 182.4, C-2), 118.0 (d, J = 5.6, C-4), 127.0–129.0 (3s, o,m,p-C_{arom}), 133.8 (d, J = 4.5, C-3), 137.0 (d, J = 0.9, i-C_{arom}), 145.0 (d, J = 27.6, C-1), 166.3 (s, C=O)

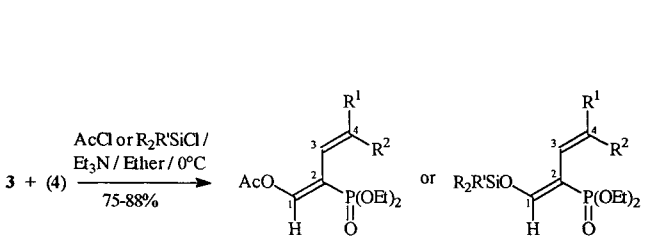
[a] Yields of purified products (oils), whose MS data were in accordance with the proposed structures. Purification by flash chromatography (silica gel; Et_2O). Satisfactory microanalyses obtained: C ± 0.46, H ± 0.35. Products **6** may be distilled without noticeable decomposition: **6a**, bp (0.35 Torr) 105°C; **6b**, bp (0.35 Torr) 117°C; **6c**, bp (0.35 Torr) 125°C; **6d**, bp (0.35 Torr) 165°C.
[b] NMR data for the E isomer only. The purified product was a mixture of E/Z isomers in a ratio of 85 : 15. ^{31}P NMR signal for the Z isomer was observed at δ = 12.2 (in $CDCl_3$).

Table 3. Synthesis and NMR Data of Diethyl 1-(Trisubstituted silyloxy)penta-1,3-dien-2-ylphosphonates **7**

Product	Yield[a] (%)	^{31}P NMR ($CDCl_3$), δ	^{1}H NMR ($CDCl_3$) δ, J (Hz)	^{13}C{^{1}H} NMR ($CDCl_3$) δ, J (Hz)
7a	75	20.8	0.2 [s, 9H, $(CH_3)_3Si$], 1.3 (m, 6H, CH_3CH_2O), 1.5–1.8 [m, 6H, $(CH_3)_2C=$], 3.9–4.2 [m, 4H, CH_3CH_2O], 5.3–5.5 (m, 1H, HC-3), 7.05 (d, J = 9.6, 1H, HC-1)	0.05 [s, $(CH_3)_3Si$], 16.2 (d, J = 6.5, CH_3CH_2O), 19.0 (d, J = 2.1, $CH_3C=$), 27.8 (d, J = 1.2, $CH_3C=$), 61.0 (d, J = 5.0, CH_3CH_2O), 106.5 (d, J = 187.6, C-2), 113.5 (d, J = 4.7, C-3), 138.5 (d, J = 12.1, C-4), 155.0 (d, J = 27.6, C-1)
7b	85	20.9	0.2 [s, 6H, $(CH_3)_2Si$], 0.9 [s, 9H, $(CH_3)_3CSi$], 1.2–1.4 (m, 6H, CH_3CH_2O), 1.5–1.8 [m, 6H, $(CH_3)_2C=$], 3.9–4.1 (m, 1H, HC-3), 7.05 (d, J = 9.8, 1H, HC-1)	−3.0 [s, $(CH_3)_2Si$], 16.0 (d, J = 6.4, CH_3CH_2O), 19.5 (d, J = 2.0, $CH_3C=$), 22.0 [s, $(CH_3)_3CSi$], 25.0 (d, J = 1.1, $CH_3C=$), 25.3 [s, $(CH_3)_3CSi$], 61.3 (d, J = 5.0, CH_3CH_2O), 107.5 (d, J = 188.0, C-2), 113.6 (d, J = 5.1, C-3), 138.8 (d, J = 11.8, C-4), 155.0 (d, J = 27.8, C-1)
7c	83	18.6	1.1 [s, 9H, $(CH_3)_3CSi$], 1.2 (t, J = 7.0, 6H, CH_3CH_2O), 4.0 (qui, J = 7.0, 4H, CH_3CH_2O), 5.3 (d, J = 11.0, 1H, HC-4), 5.7 (d, J = 18.1, 1H, HC-4), 6.9 (ddd, J = 29.0, 18.1, 11.0, 1H, HC-3), 7.15 (d, J = 10.0, 1H, HC-1), 7.3–7.8 (m, 10H, H_{arom})	16.0 (d, J = 6.7, CH_3CH_2O), 19.0 [s, $(CH_3)_3CSi$], 26.0 [s, $(CH_3)_3CSi$], 62.0 (d, J = 4.9, CH_3CH_2O), 109.0 (d, J = 189.6, C-2), 116.0 (d, J = 4.9, C-3), 126.0 (d, J = 6.5, C-4), 127.0–138.0 (m, C_{arom}), 154.0 (d, J = 27.3, C-1)
7d	88	19.5	1.1 [s, 9H, $(CH_3)_3CSi$], 1.3 (t, J = 7.0, 6H, CH_3CH_2O), 1.9 (d, J = 6.1, 3H, $CH_3C=$), 4.0 (qui, J = 7.0, 4H, CH_3CH_2O), 6.2 (dq, J = 17.6, 6.1, 1H, HC-4), 6.6 (dd, J = 28.5, 17.6, 1H, HC-3), 7.0 (d, J = 9.1, 1H, HC-1), 7.3–7.8 (m, 10H, H_{arom})	16.0 (d, J = 6.8, CH_3CH_2O), 19.0 [s, $(CH_3)_3CSi$], 19.3 (s, $CH_3C=$), 26.0 [s, $(CH_3)_3CSi$], 62.0 (d, J = 5.0, CH_3CH_2O), 108.0 (d, J = 186.6, C-2), 121.0 (d, J = 6.7, C-4), 127.0–138.0 (m, C_{arom}), 135.2 (d, J = 4.8, C-3), 152.1 (d, J = 27.3, C-1)
7e	86	19.9	1.1 [s, 9H, $(CH_3)_3CSi$], 1.3 (t, J = 7.0, 6H, CH_3CH_2O), 1.5–1.9 [m, 6H, $(CH_3)_2C=$], 3.9–4.1 (m, 4H, CH_3CH_2O), 5.5 (m, 1H, HC-3), 6.6 (dd, J = 28.5, 17.6, 1H, HC-3), 7.1 (d, J = 9.6, 1H, HC-1), 7.2–7.8 (m, 10H, H_{arom})	16.0 (d, J = 6.8, CH_3CH_2O), 19.0 [s, $(CH_3)_3CSi$], 20.5 (d, J = 1.9, $CH_3C=$), 25.5 (d, J = 1.1, $CH_3C=$), 26.5 [s, $(CH_3)_3CSi$], 61.8 (d, J = 5.2, CH_3CH_2O), 108.0 (d, J = 189.0, C-2), 114.0 (d, J = 4.5, C-3), 127.0–136.0 (m, C_{arom}), 139.0 (d, J = 11.5, C-4), 151.8 (d, J = 30.2, C-1)
7f	88	18.7	1.25 [s, 9H, $(CH_3)_3CSi$], 1.35 (t, J = 7.0, 6H, CH_3CH_2O), 4.0 (qui, J = 7.0, 4H, CH_3CH_2O), 7.15 (dd, J = 28.8, 16.8, 1H, HC-3), 7.2 (d, J = 12.0, 1H, HC-1), 7.3–7.8 (m, 16H, H_{arom}, HC-4)	16.05 (d, J = 6.6, CH_3CH_2O), 19.0 [s, $(CH_3)_3CSi$], 26.0 [s, $(CH_3)_3CSi$], 61.3 (d, J = 4.9, CH_3CH_2O), 109.0 (d, J = 185.9, C-2), 118.4 (d, J = 6.6, C-4), 126.0–138.0 (m, C_{arom}), 131.0 (d, J = 5.7, C-3), 154.0 (d, J = 27.0, C-1)

[a] Yields of purified products (oils), whose MS data were in accordance with the proposed structures. Purification of **7c–f** by flash chromatography (silica gel; Et_2O). Satisfactory microanalyses obtained: C ± 0.49, H ± 0.44.

depended on the nature of the silicon substituents R and R′ (Table 3). With trimethylchlorosilane used as silylating agent, we were unable to isolate any trimethylsilylated derivative of **3a, b** or **d**; rapid desilylation occurred during evaporation of the solvent, to give back the starting enols. However, starting from a mixture of **3c** and **4c**, it was possible to isolate and analyze the corresponding trimethylsilyl dienol ether **7a**, which underwent complete desilylation after only a few hours at room temperature. On the other hand, on using *tert*-butyldimethylsilyl chloride to silylate the same mixture **3c**/**4c**, the *tert*-butyldimethylsilyl dienol ether **7b** was isolated in good yield and could be stored in the cold under an inert atmosphere for many days without noticeable decomposition.[9] Finally, substituting the *tert*-butyldimethylsilyl group by the more sterically demanding *tert*-butyldiphenylsilyl group,[10] resulted in an efficient protection of enols **3**. The corresponding *tert*-butyldiphenylsilyl dienol ethers **7c–f** were obtained in high yield, by an initial filtering off of triethylammonium chloride, then subsequent evaporation of the solvent under reduced pressure at room temperature and final flash chromatography over silica gel. These compounds showed good stability when kept in the refrigerator.



6	R^1	R^2
a	H	H
b	Me	H
c	Me	Me
d	Ph	H

7	R^1	R^2	R	R'
a	Me	Me	Me	Me
b	Me	Me	Me	*t*-Bu
c	H	H	Ph	*t*-Bu
d	Me	H	Ph	*t*-Bu
e	Me	Me	Ph	*t*-Bu
f	Ph	H	Ph	*t*-Bu

Scheme 2

Moreover, acetylation or *tert*-butyldiphenylsilylation of aldehyde **5** under similar conditions to those used for its precursor **3a** gave acetyloxydiene **6a** (86% yield) or *tert*-butyldiphenylsilyloxydiene **7c** (85% yield), respectively.

In conclusion, taking advantage of the α-regioselective reactivity of carbanions of allylic phosphonates towards ethyl formate, this work presents an efficient synthesis of new *O*-acetylated or *O*-silylated (1*E*)-2-diethoxyphosphonylbuta-1,3-dien-1-ols. Studies are in progress in our laboratories to test, in particular, the reactivity of the new dienoxysilanes **7**.

All syntheses were performed under an atmosphere of dry argon. THF was dried over CaH_2 and distilled from solutions of sodium–benzophenone before use. TLC was performed on Merck 60 F-254 silica gel plates, and column chromatography over silica gel (230–400 mesh). Gas chromatography (GC) was performed on a Girdel chromatograph equipped with a 2 m OV17 column. Elemental microanalyses were carried out on a Carlo Erba 1106 analyser. Mass spectra were obtained with a GC-MS Hewlett Packard 5970 spectrometer. NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200 MHz for proton, 50.3 MHz for carbon and 81.01 HMz for phosphorus; chemicals shifts (δ) are expressed in ppm relative to TMS for ^1H and ^{13}C nuclei and to H_3PO_4 for ^{31}P nucleus; coupling multiplicities are reported using conventional abbreviations.[6] IR spectra were recorded on a Perkin-Elmer 1600 series FT IR spectrometer.

(1*E*)-2-Diethoxyphosphonylbuta-1,3-dien-1-ols 3; General Procedure:

To a stirred 1.6 M solution of BuLi in hexane (14 mL, 22 mmol) at −20 °C was added dropwise diisopropylamine (2.23 g, 22 mmol) in THF (30 mL). After 15 min, the mixture was cooled to −70 °C and phosphonate **1** (10 mmol) in THF (15 mL) was added dropwise. Stirring was continued at −70 °C for ca. 30 min (for allyl-, crotyl- and prenylphosphonates) or 10 min (for cinnamylphosphonate) until complete metallation was achieved.[6] Then ethyl formate (1.11 g, 15 mmol) in THF (10 mL) was slowly added and stirring was continued at −70 °C for 30 min. ^{31}P NMR analysis showed a broad signal at ca. $\delta = 30$, corresponding to lithiated enolate **2**. Acidic hydrolysis was then rapidly performed, at −70 °C, with 3 N aq HCl until ca. pH 3, followed by addition of Et_2O (15 mL) and the mixture was allowed to warm to r.t. The aqueous phase was extracted with Et_2O (3 × 15 mL) and the combined organic layers dried ($MgSO_4$). The solvent was removed under reduced pressure to give the crude mixture, which was dissolved in Et_2O (20 mL) and stirred with 10% aq NaOH (20 mL). The separated aqueous layer was extracted with Et_2O (2 × 10 mL), then treated with 2 N aq HCl, in the presence of CH_2Cl_2 (30 mL), until ca. pH 2 and finally extracted once more with CH_2Cl_2 (2 × 15 mL). The combined CH_2Cl_2 layers were dried ($MgSO_4$) and evaporated under reduced pressure, giving a nearly pure product, which was flash chromatographed (silica gel; Et_2O) and analyzed by GC, by ^{31}P, ^1H and ^{13}C NMR spectroscopy and by GC-MS spectrometry. The infrared spectra of enols **3** and aldehyde **5** were in good agreement with the assigned structures.

Diethyl 1-Acetoxypenta-1,3-dien-2-ylphosphonates 6 and Diethyl 1-(Trisubstituted silyloxy)penta-1,3-dien-2-ylphosphonates 7; General Procedure:

To a stirred solution of enol **3** (or of the mixture **3c**/**4c**, or of aldehyde **5**) (10 mmol) in Et_2O (20 mL) was added at 0 °C, under argon, a solution of triethylamine (11 mmol) in Et_2O (10 mL). The mixture turned dark yellow. Then a solution of acetyl chloride or silylating reagent (10 mmol) in Et_2O (10 mL) was slowly added at 0 °C, with continuous stirring for 15 min. Triethylammonium chloride was then filtered off and the filtrate was evaporated under reduced pressure to give the crude product, which was purified by flash chromatography (silica gel; Et_2O) or distilled under reduced pressure giving the dienylphosphonate **6** or **7** whose purity was established by GC, ^{31}P, ^1H and ^{13}C NMR spectroscopy (Tables 2 and 3) and by GC-MS spectrometry.

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(8) Allowing the mixture to warm to room temperature before hydrolysis resulted in the decomposition of enolates **2**.
(9) It is commonly accepted that the *tert*-butyldimethylsilyoxy group is about 10^4 times more stable than the trimethylsilyloxy group towards protonolysis; see for example: Fieser, M.; Fieser, L.F. *Reagents for Organic Synthesis*; Wiley: New York, 1974; Vol. 4, p 176.
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