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Phosphonic Systems. Part 15. Addition of Diethyl Prop-2-Enylphosphonate to Aldehydes: Fragmentation vs. Isomerization of Kinetic Products*

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ABSTRACT

Lithiated diethyl prop-2-enylphosphonate adds to an aliphatic or an aromatic aldehyde, yielding a diastereomeric mixture of the kinetically controlled α-adduct. Upon warming, these adducts decompose back to starting materials to give finally the thermodynamically controlled γ-adducts, or undergo fragmentation to diethyl phosphate and (E) dienes. The distribution of the first product between these two pathways is a function of the aldehyde (aromatic vs. aliphatic) and of steric interactions operating within the two diastereomers of the adduct.

INTRODUCTION

The mechanism of the reaction between lithiated diethyl prop-2-enylphosphonate (**1**) and aldehydes has been discussed in our previous article [1]. It has been shown that the addition is reversible, with the α-adduct (**2**) formed as a kinetic and the γ-adduct (**3**), as a thermodynamic product. The kinetic product **2** can, in addition to the retrocondensation step, undergo fragmentation to the diethyl phosphate anion and the corresponding diene (**4**). The reaction is presented in Scheme 1. The synthetic value of the reaction for the preparation of dienes depends on the partitioning of the adduct (**2**) between starting materials (k_{-1}) and the products of the irreversible fragmentation (k_f). The k_{-1}/k_f ratio will, in turn, depend for each adduct on the conformational preferences required for the competitive C_α–P and C_α–C_β bond cleavages. We have demonstrated previously that, for the β-hydroxyalkylphosphonate esters, the most stable conformation about the C_α–C_β bond is determined by the repulsion between the PO_3R_2 group and the β-substituent R and by the attractive interactions between the phosphoryl function and the β-hydroxy group [2]. Since the α-adduct **2** is formed as a pair of diastereomers, the exact steric effects determining the k_{-1}/k_f ratio in **2** should depend strongly on the substituent R, as well as on the relative configurations of both chiral centers. In this work, we report on the addition of lithiated **1** to a series of aldehydes and on subsequent attempts to subject the α-adducts to the base-promoted fragmentation to the corresponding dienes.

RESULTS AND DISCUSSION

Treatment of diethyl prop-2-enylphosphonate (**1**) with BuLi in THF, followed by the addition of an aldehyde, and, finally, quenching the reaction with aq NH_4Cl (all steps at −78°C), resulted in the formation of the kinetic product **2** as a pair of diastereomers. The only exception was the reaction with *p*-nitrobenzaldehyde, in which, even under these conditions, the major product was the ther-

Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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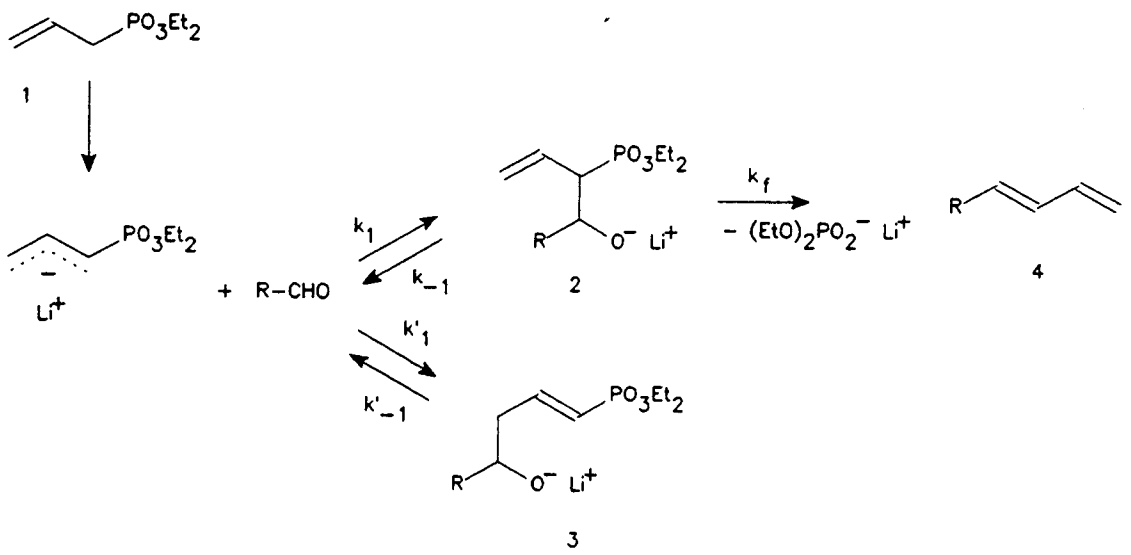
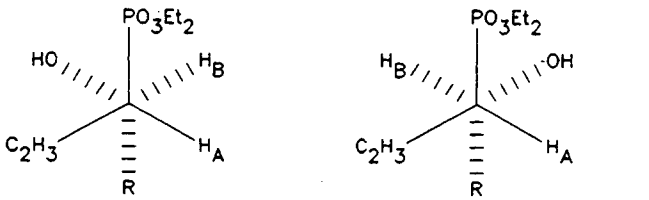


SCHEME 1



Diastereomer A (RR, SS) Diastereomer B (RS, SR)

SCHEME 2

TABLE 1 Addition of Lithiated **1** to Aldehydes under Conditions of Kinetic Control

R in R–CHO	*Yield of* **2** (%, *Isolated*)	*Diastereomer A* (%, $^3J_{AB}$, *Hz*)	*Diastereomer B* (%, $^3J_{AB}$, Hz)
Et	70	25 (2.0)	75 (9.3)
n-C_5H_{11}	85	35 (1.9)	65 (10.4)
cyclo-C_6H_{11}	68	2[a]	98 (9.6)
$PhCH_2$	82	27 (1.7)	73 (7.9)
(E) PhCH=CH	73	28 (2.9)	72 (9.8)
Ph[b]	72	35 (2.7)	65 (9.3)
p-$NO_2C_6H_4$[b]	20[c]	50 (2.0)	50 (9.5)

[a]Not measured.
[b]Taken from Ref. [3].
[c]49% of **3** formed.

modynamically controlled **3** [3]. Following our earlier observations [2], the most stable conformations of both diastereomers of **2** can be presented as shown in Scheme 2. Since the individual diastereomers of the α-adduct **2** for R = *p*-$NO_2C_6H_4$ have been previously isolated and their molecular structure and NMR spectroscopic properties determined [3], it was possible to assign the relative configurations for all pairs of adducts **2** from their ^{1}H NMR spectra. Diastereomer A (RR, SS) should be characterized by a "small" and diastereomer B (RS, SR) by a "large" value of the $^3J_{AB}$ coupling constant in $RC(OH)H_B–CH_A(C_2H_3)PO_3Et_2$. The yields of α-adducts **2**, their diastereomeric composition, and the corresponding $^3J_{AB}$ values are given in Table 1. In all cases (except for R = *p*-$NO_2C_6H_4$), diastereomer B predominates, as it can achieve a conformation with a minimum of nonbonded interactions between the substituents at the $C_\alpha–C_\beta$ bond (or can be formed by the approach of the allylic carbanion to the carbonyl substrate involving lowest possible steric interactions between the substituents at the reacting carbons). If the reaction mixtures, after addition of an aldehyde, were allowed to warm to room temperature and aq. NH_4Cl was added after ca 7 hours, the composition of the product was quite different. ^{31}P NMR spectra of the aqueous solution revealed a phosphorus-containing product of $\delta_P \approx 0$; identified as the diethyl phosphate anion. Column chromatography of the crude product recovered from the organic phase yielded variable amounts of the corresponding dienes **4** (Table 2). Dienes **4** were identified by NMR (^{1}H and ^{13}C) and mass spectrometry, and all were formed as single (E) stereoisomers, as shown by the vicinal coupling constants of the vinylic protons in the ^{1}H NMR spectra.

For the elimination of the phosphate ion and the formation of the olefinic bond to take place, the O^-Li^+ and PO_3Et_2 groups have to attain the eclipsed, or near-eclipsed orientation [4]. For the most populated conformer of the diastereomer A, this can be achieved by a 60° clockwise rotation of

TABLE 2 Preparation of Dienes **4**, R–CH(1)=CH(2)–CH(3)=CH_2(4) from Aldehydes and Lithiated **1**

R in Diene **4**	Yield (%, Isolated)	$\delta_{H(1)}$	$\delta_{H(2)}$	$J_{H(1)H(2)}$ (Hz)	$\delta_{H(3)}$	$\delta_{H,H'(4)}$
Et	41	5.70	5.96	15.5	6.26	4.99
n-C_5H_{11}	38	5.65	5.98	15.7	6.25	4.95
cyclo-C_6H_{11}	63	5.64	6.01	15.3	6.30	5.06
$PhCH_2$	52	5.97	6.25	14.7	6.48	5.20
(E) PhCH=CH	[a]					
Ph	2	6.61	6.48	15.6	6.54	5.27
p-$NO_2C_6H_4$	none					

[a]Not isolated; polymerized in situ, but $(EtO)_2PO_2Li$ was obtained as a major product in the aqueous phase.

the hydroxyl oxygen, and for the diastereomer B, the rotation has to occur in an anticlockwise direction. In the former case, however, the clockwise rotation is also forcing group R in the eclipsed position relative to the vinyl substituent at C_α, whereas for the diastereomer B, groups R and C_2H_3 move away from each other. Upon fragmentation, stereoisomer A should yield the new double bond of configuration Z, whereas B represents a precursor for the E-alkene. Since all dienes prepared had an E configuration of the new double bond; and since the yield of the dienes was always *lower* than the effective yield of diastereomer B of **2** formed in the condensation, we believe that it is only the stereoisomer B of the α-adduct that undergoes fragmentation to the diene product. In stereoisomer A, for steric reasons, $k_{-1} \gg k_f$, and the reversal of the addition predominates, opening the way for the isomerization to the thermodynamically more stable γ-adduct **3**. It is also clear that, for aromatic aldehydes, $k_{-1} > k_f$ for both stereoisomers of **2** (formation of a conjugated carbonyl group in the reverse step), and the fragmentation occurs only to a negligible degree.

Pure, isolated adducts **2** could also be decomposed by adding BuLi to their solution in THF, warming to room temperature, and incubating these solutions for several hours. The products (dienes **4** and isomerized γ-hydroxy-prop-1-enylphosphonates **3**) were formed in approximately the same yields and proportions as those obtained by the direct reactions of **1** with aldehydes. Adducts **2** prepared from propanal, hexanal, and cyclohexylcarboxyaldehyde could also be converted to dienes thermally, by heating the neat compounds at 250°C.

EXPERIMENTAL

Solvents and commercially available substrates were purified by conventional methods immediately before use. All reactions were carried out in an atmosphere of dry nitrogen. For column chromatography, Merck Kieselgel 60 (0.063–0.200 mm) was used. Mass spectra were recorded on a Varian MAT-212 double-focusing direct-inlet spectrometer at an ionization potential of 70 eV. NMR spectra were recorded on a Bruker AC 300 or a Bruker AMX 500 spectrometer. Chemical shifts are given in parts per million relative to $SiMe_4$ (^1H, ^{13}C) as an internal standard and 85% H_3PO_4 (^{31}P) as an external standard. The solvents used for the NMR spectroscopy were $CDCl_3$ (Uvasol, Merck) and methanol-d_4 (Uvasol, Merck), dried over molecular sieves. Diethyl prop-2-enylphosphonate **1** was prepared from triethyl phosphite and 3-bromopropene [5].

Preparation of Diethyl 2-Hydroxyalkenylphosphonates **2**

General Procedure. A solution of **1** (1.50 g, 8.5 mmol) in THF (10 mL) was cooled to −78°C, BuLi (1.6 M solution in hexane, 6.9 mL, 11 mmol) was added, and the solution was kept at that temperature −78°C for 30 minutes. The aldehyde (8.5 mmol) was then added dropwise and the solution was stirred at −78°C for 7 hours. Aqueous NH_4Cl (10%, 15 mL) was added at the same temperature, the mixture was allowed to warm to room temperature and was extracted with chloroform (3 × 15 mL), and the chloroform solution was then dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/chloroform, 3:1) yielding pure **2** as a diastereomeric mixture. Products **2** were identified by NMR (^1H, ^{13}C, ^{31}P) and mass spectrometry. Compounds prepared from benzaldehyde and *p*-nitrobenzaldehyde (**2**, R = Ph, *p*-$NO_2C_6H_4$) were described in a previous article [1]. The NMR and MS data for the remaining products **2** are given below; for the sake of clarity, NMR (^1H and ^{13}C) signals derived from the ethyl groups of the phosphonate function PO_3Et_2 and of group R of an aldehyde used have not been included. For MS, only major fragments, important in structure determination, are given.

Diethyl 1-(1-Hydroxypropyl)-prop-2-enylphosphonate (**2**, *R = Et*)

Diastereomer A. ^1H NMR δ 2.54 (ddd, J = 20.9, 10.1, 2 Hz, 1H), 3.74 (m, 1H), 5.13 (ddd, J = 15.6, 5.3, 1.7 Hz, 1H), 5.22 (ddd, J = 10.2, 3.5, 1.6 Hz, 1H), 5.78 (dddd, J = 15.8, 10.3, 10, 5.2 Hz, 1H); ^{13}C NMR δ 49.0 (d, J = 133.7 Hz), 70.6 (s), 119.7 (d, J = 13.1 Hz), 130.5 (d, J = 10.9 Hz); ^{31}P NMR δ 28.6; MS m/z 235 (M^+-1, 3%), 207 (20), 178 (100), 163 (16), 150 (30), 122 (84), 105 (13), 81 (25), 69 (23).

Diastereomer B. ^1H NMR δ 2.58 (dt, J = 18.6, 9.3 Hz, 1H), 3.72 (dt, J = 9.2, 2.9 Hz, 1H), 5.13 (ddd, J = 15.6, 5.3, 1.7 Hz, 1H), 5.22 (ddd, J = 10.2, 3.5, 1.6 Hz, 1H), 5.48 (dddd, J = 15.8, 10.4, 9.4, 5.2 Hz,

1H); ^{13}C NMR δ 49.1 (d, J = 133.7 Hz), 70.7 (s), 119.7 (d, J = 13.1 Hz), 130.5 (d, J = 10.9 Hz); ^{31}P NMR δ 28.4; MS as for diastereoisomer A.

Diethyl 1-(1-Hydroxyhexyl)-prop-2-enylphosphonate (**2**, *R = n-C_5H_{11}*)

Diastereomer A. ^1H NMR δ 0.68 (t, J = 6.5 Hz, 3H), 1.20 (t, J = 7.1 Hz, 6H), 1.22 (m, 6H), 1.45 (dd, J = 11.3, 7.2 Hz, 2H), 2.51 (ddd, J = 18.6, 10, 1.9 Hz, 1H), 3.52 (br s, 1H), 3.73 (m, 1H), 4.02 (quint, J = 7 Hz, 4H), 5.08 (ddd, J = 16.7, 4.9, 1.7 Hz, 1H), 5.14 (ddd, J = 10.3, 4.6, 1.7 Hz, 1H), 5.80 (dddd, J = 16.9, 10.3, 10.1, 5.7 Hz, 1H); ^{13}C NMR δ 13.5 (s), 15.9 (d, J = 5.3 Hz), 22.1 (s), 24.9 (s), 31.3 (s), 34.4 (s), 49.1 (d, J = 135.9 Hz), 61.7 (d, J = 49.8 Hz), 62.1 (d, J = 49.8 Hz), 69.2 (s), 120.6 (d, J = 13.7 Hz), 128.4 (d, J = 8.2 Hz); ^{31}P NMR δ 28.9; MS m/z 279 (M^+, 100%), 261 (34), 123 (32), 109 (23), 81 (16), 69 (16), 67 (20).

Diastereomer B. ^1H NMR δ 0.68 (t, J = 6.5 Hz, 3H), 1.20 (t, J = 7.1 Hz, 6H), 1.22 (m, 6H), 1.45 (dd, J = 11.3, 7.2 Hz, 2H), 2.54 (dt, J = 18.4, 10.4 Hz, 1H), 3.52 (br s, 1H), 3.77 (m, 1H), 4.02 (quint, J = 7 Hz, 4H), 4.93 (dd, J = 16.7, 4.8 Hz, 1H), 4.97 (ddd, J = 10.5, 4.7, 1.7 Hz, 1H), 5.50 (dddd, J = 16.9, 10.6, 10.3, 5.8 Hz, 1H); ^{13}C NMR δ 13.5 (s), 15.9 (d, J = 5.3 Hz), 22.1 (s), 24.9 (s), 31.3 (s), 34.4 (s), 49.1 (d, J = 135.9 Hz), 61.7 (d, J = 49.8 Hz), 69.2 (s), 120.6 (d, J = 13.7 Hz), 128.4 (d, J = 8.2 Hz); ^{31}P NMR δ 28.7; MS as for diastereomer A.

Diethyl 1-[(Cyclohexyl)(hydroxy)methyl]prop-2-enylphosphonate (**2**, *R = cyclo-C_6H_{11}*)

Diastereomer B. ^1H NMR δ 1.10 (t, J = 7 Hz, 6H), 0.9–1.5 (m, 11H), 2.55 (dt, J = 19.1, 9.6 Hz, 1H), 3.48 (dt, J = 9.7, 1.5 Hz, 1H), 3.90 (quint, J = 7.2 Hz, 4H), 4.90 (ddd, J = 16.5, 5, 1.2 Hz, 1H), 4.96 (dd, J = 10.2, 1.2 Hz, 1H), 5.39 (dddd, J = 16.6, 10.3, 9.8, 5.3 Hz, 1H); ^{13}C NMR δ 15.9 (s), 26.0 (s), 29.9 (s), 40.0 (d, J = 12.6 Hz), 47.1 (d, J = 133.5 Hz), 62.1 (d, J = 25.7 Hz), 72.9 (d, J = 5.8 Hz), 118.8 (d, J = 12.8 Hz), 130.3 (d, J = 11.2 Hz); ^{31}P NMR δ 29.9; MS m/z 291 (M^+, 100%), 273 (50), 151 (13), 135 (55), 122 (26), 83 (6), 67 (11).

Diethyl 1-[(1-Hydroxy-2-phenyl)ethyl]-prop-2-enylphosphonate (**2**, *R = $PhCH_2$*)

Diastereomer A. ^1H NMR δ 1.17 (t, J = 6.7 Hz, 6H), 2.50 (ddd, J = 22.6, 10.1, 1.7 Hz, 2H), 2.87 (dd, J = 13.4, 7.2 Hz, 1H), 3.04 (dd, J = 13.3, 7 Hz, 1H), 3.73 (br s, 1H), 3.97 (quint, J = 4 Hz, 4H), 4.20 (m, 1H), 5.01 (dd, J = 17.5, 5.2 Hz, 1H), 5.13 (ddd, J = 10.3, 5.6, 1.7 Hz, 1H), 6.35 (dddd, J = 17.4, 10.2, 10, 5.5 Hz, 1H), 7.15 (m, 5H); ^{13}C NMR δ 15.7 (s), 40.5 (s), 45.9 (d, J = 130.2 Hz), 61.3 (d, J = 7 Hz), 62.2 (d, J = 7 Hz), 69.9 (s), 121.0 (s), 125.8 (s), 127.2 (s), 128.1 (s), 137.5 (s), 141.5 (d, J = 16.2 Hz); ^{31}P NMR δ 28.7; MS m/z 299 (M^+, 9%), 207 (100), 178 (92), 151 (95), 143 (67), 123 (79), 122 (89), 105 (44), 91 (98), 81 (46), 65 (54).

Diastereomer B. ^1H NMR δ 1.15 (t, J = 7.2 Hz, 6H), 2.57 (dd, J = 13.6, 8.6 Hz, 1H), 2.65 (ddd, J = 19.5, 9.9, 7.9 Hz, 1H), 2.95 (dd, J = 13.5, 3.2 Hz, 1H), 3.73 (br, s, 1H), 3.97 (quint, J = 4 Hz, 4H), 4.26 (m, 1H), 5.17 (ddd, J = 17.5, 5.1, 1.2 Hz, 1H), 5.33 (ddd, J = 10.2, 3.9, 1.2 Hz, 1H); 5.95 (dddd, J = 17.4, 10.2, 9.8, 5.5 Hz, 1H); ^{13}C NMR δ 15.7 (s), 40.5 (s), 47.7 (d, J = 128.6 Hz), 61.3 (d, J = 7 Hz), 62.2 (d, J = 7 Hz), 69.9 (s), 121.0 (s), 125.8 (s), 127.2 (s), 128.1 (s), 137.5 (s), 141.5 (d, J = 16.2 Hz); ^{31}P NMR δ 28.2; MS as for diastereomer A.

(E) Diethyl 1-Vinyl-2-hydroxy-4-phenyl-but-3-enylphosphonate (**2**, *R = (E) PhCH=CH*)

Diastereomer A. ^1H NMR δ 1.16 (t, J = 5.8 Hz, 6H), 2.72 (ddd, J = 18.8, 8.9, 2.9 Hz, 1H), 3.97 (quint, J = 7.1 Hz, 4H), 4.54 (ddd, J = 12.1, 6.5, 3 Hz, 1H), 5.12 (m, 2H), 5.87 (dddd, J = 16.3, 10.3, 8.8, 6 Hz, 1H), 6.16 (dd, J = 15.8, 6 Hz, 1H), 6.55 (d, J = 15.9 Hz, 1H), 7.25 (m, 5H); ^{13}C NMR δ 15.7 (d, J = 5.4 Hz), 49.3 (d, J = 134.2 Hz), 61.6 (d, J = 6.9 Hz), 61.9 (d, J = 6.9 Hz), 70.2 (s), 120.2 (s), 125.9 (s), 126.8 (s), 127.8 (s), 128.8 (s), 129.3 (s), 130.3 (s), 136.1 (s), 141.5 (s); ^{31}P NMR δ 27.3; MS m/z 310 (M^+, 1%), 178 (20), 163 (50), 150 (100), 132 (18), 129 (26), 122 (60), 105 (50), 96 (18), 77 (40).

Diastereomer B. ^1H NMR δ 1.12 (t, J = 5.8 Hz, 6H), 2.77 (dt, J = 18.2, 9.8 Hz, 1H), 3.97 (quint, J = 7.1 Hz, 4H), 4.58 (ddd, J = 12.1, 9.8, 5.9 Hz, 1H), 5.12 (m, 2H), 5.62 (dddd, J = 16.3, 10.2, 9.9, 5.9 Hz, 1H), 6.16 (dd, J = 15.8, 6.1 Hz, 1H), 6.55 (d, J = 15.9 Hz, 1H), 7.25 (m, 5H); ^{13}C NMR δ 15.7 (d, J = 5.4 Hz), 49.8 (d, J = 134.2 Hz), 61.6 (d, J = 6.9 Hz), 61.9 (d, J = 6.9 Hz), 70.2 (s), 119.9 (s), 125.9 (s), 126.9 (s), 127.8 (s), 128.8 (s), 129.3 (s), 130.3 (s), 136.1 (s), 141.5 (s); ^{31}P NMR δ 27.2; MS as for diastereomer A.

Fragmentation of Kinetic Products **2**

General Procedure. The reaction was carried out as described previously, but after the addition of an aldehyde to lithiated **1**, the reaction mixture was allowed to warm to room temperature and was kept at that temperature for 7 hours. After the usual aqueous work-up, extraction, and evaporation of the solvent, the crude product was separated into its components by column chromatography (hexane/chloroform, 1:3) yielding the diene and/or the product **3** as the first and second fractions, respectively.

2: R = Et yielded (E) 1,3-hexadiene (41%); ^1H NMR δ 0.97 (t, J = 7.4 Hz, 3H), 2.06 (dq, J = 7.4,

7.2 Hz, 2H), 4.99 (dd, J = 16.8, 10.5 Hz, 2H), 5.70 (dt, J = 15.4, 6.7 Hz, 1H), 5.96 (dd, J = 15.5, 10.2 Hz, 1H), 6.26 (dt, J = 17.0, 10.3 Hz); ^{13}C (coupled) NMR δ 13.3 (q, J = 124.5 Hz), 18.2 (t, J = 125.2 Hz), 114.5 (t, J = 158.7 Hz), 129.9 (d, J = 147.8 Hz), 136.8 (d, J = 147.7 Hz), 137.3 (d, J = 158.8 Hz); MS m/z 82 (M^+ + 1, 98%), 67 (29), 55 (67), 29 (100).

2: R = n-C_5H_{11} yielded (E) 1,3-nonadiene (38%); ^{1}H NMR δ 0.83 (t, J = 6.8 Hz, 3H), 1.22 (m, 6H), 2.05 (m, 2H), 4.95 (dd, J = 16.5, 10.3 Hz, 2H), 5.65 (dt, J = 15.1, 7.1 Hz, 1H), 5.98 (dd, J = 15.3, 10.2 Hz, 1H), 6.25 (dt, J = 16.8, 10.2 Hz, 1H); ^{13}C (coupled) NMR δ 13.6 (q, J = 124.2 Hz), 22.1 (t, J = 126.7 Hz), 28.5 (t, J = 123.3 Hz), 31 (t, J = 126.2 Hz), 32.1 (t, J = 125.2 Hz), 114.1 (t, J = 156.9 Hz), 130.5 (d, J = 147.1 Hz), 135.1 (d, J = 146.5 Hz), 137 (d, J = 153.4 Hz); MS m/z 125 (M^+ + 1, 14%), 111 (14), 71 (68), 55 (65), 43 (100), 29 (62).

2: R = *cyclo*-C_6H_{11} yielded (E) 1-cyclohexyl-1,3-butadiene (63%); ^{1}H NMR δ 1.03–1.74 (m, 10H), 2 (m, 1H), 5 (dd, J = 17, 10 Hz, 2H), 5.64 (dd, J = 15.3, 6.8 Hz, 1H), 6.01 (dd, J = 15.3, 10.3 Hz, 1H), 6.30 (ddd, J = 17, 10.2, 10 Hz, 1H); ^{13}C (coupled) NMR δ 26.7 (t, J = 127.8 Hz), 33.4 (t, J = 126.6 Hz), 41.3 (d, J = 118.2 Hz), 115.3 (t, J = 154.8 Hz), 129 (d, J = 153 Hz), 138.3 (d, J = 149.1 Hz), 141.8 (d, J = 147.2 Hz); MS m/z 136 (M^+, 59%), 121 (20), 107 (42), 93 (29), 79 (81), 67 (100), 54 (60).

2: R = $PhCH_2$ yielded 5-phenyl-1,3-pentadiene (52%); ^{1}H NMR δ 3.54 (d, J = 6.9 Hz, 2H), 5.20 (dd, J = 16.9, 10.4 Hz, 2H), 5.97 (dt, J = 14.8, 6.5 Hz, 1H), 6.25 (ddd, J = 14.5, 10.2, 1.4 Hz, 1H), 6.48 (dt, J = 17, 10.3 Hz, 1H), 7.41 (m, 5H); ^{13}C (coupled) NMR δ 38.7 (t, J = 126.8 Hz), 115.4 (t, J = 157 Hz), 125.9 (d, J = 153.3 Hz), 128.2 (d, J = 159.5 Hz), 128.3 (d, J = 151 Hz), 131.9 (d, J = 155.2 Hz), 133.2 (d, J = 146.2 Hz), 136.7 (d, J = 156 Hz), 139.8 (s); MS m/z 144 (M^+, 87%), 129 (100), 115 (79), 104 (55), 103 (52), 91 (80), 78 (49), 77 (62), 66 (72), 65 (67), 51 (66).

2: R = Ph yielded 1-phenyl-1,3-butadiene (2%); ^{1}H NMR δ 5.27 (dd, J = 16.9, 9.4 Hz, 2H), 6.54 (dt, J = 16.8, 10.1 Hz, 1H), 6.48 (dd, J = 15.6, 10 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H), 7.26 (t, J = 6.7 Hz, 1H), 7.34 (t, J = 7.2 Hz, 2H), 7.45 (d, J = 7.3 Hz, 2H); ^{13}C (coupled) NMR δ 117.5 (t, J = 157.6 Hz), 126.4 (d, J = 160.9 Hz), 127.6 (d, J = 160.8 Hz), 128.6 (d, J = 167.2 Hz), 129.5 (d, J = 153.2 Hz), 132.8 (d, J = 156.2 Hz), 134.4 (s), 137.1 (d, J = 155.5 Hz); MS m/z 129 (M^+, 100%), 115 (68), 103 (87), 91 (34). Diethyl 4-hydroxy-4-phenyl-but-1-enylphosphonate (**3**, R = Ph) (65%); ^{1}H NMR δ 1.14 (t, J = 7.8 Hz, 3H), 1.17 (t, J = 7.7 Hz, 3H), 2.55 (m, 2H), 3.85 (quint, J = 6.9 Hz, 4H), 4.69 (t, J = 6.4 Hz, 1H), 5.53 (dd, J = 20.2, 17.4 Hz, 1H), 6.63 (ddt, J = 22, 17.3, 7 Hz, 1H), 7.20 (m, 5H); ^{13}C NMR δ 15.8 (d, J = 6.3 Hz), 43.6 (d, J = 22.1 Hz), 61.5 (d, J = 5.2 Hz), 72.1 (s), 118.5 (d, J = 187.1 Hz), 125.4 (s), 127.1 (s), 128 (s), 143.5 (s), 150 (d, J = 4.9 Hz); MS m/z 283 (M^+, 5%), 178 (73), 149 (25), 144 (66), 122 (100), 105 (98), 99 (40), 81 (50), 77 (95), 51 (77).

Decomposition of **2**, R = p-$NO_2C_6H_4$, was described previously [1].

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