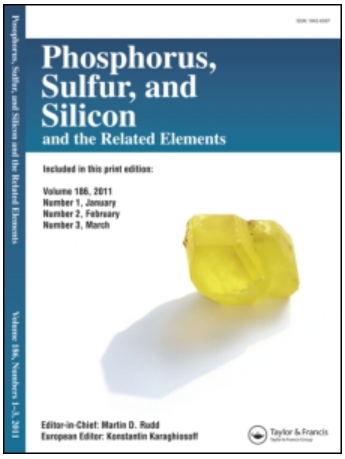

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CHEMO- AND STEREOSELECTIVE ADDITION OF DIORGANYLPHOSPHINE OXIDES TO α,β-ETHYLENIC ALDEHYDES

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CHEMO- AND STEREOSELECTIVE ADDITION OF DIORGANYLPHOSPHINE OXIDES TO α,β-ETHYLENIC ALDEHYDES

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Secondary phosphine oxides $(R^1)_2P(O)H$ ***1–3*** *react with* α,β*-ethylenic aldehydes* $R^2CH{=}CHC(O)H$ ***4–6*** *under mild conditions (THF, 22–42°C) to form chemo- and stereoselectively hydroxyethenylphosphine oxides* $(R^1)_2P(O)CH(OH)CH{=}CHR^2$ *(E)* ***7a–h*** *in high yield.*

Keywords: Addition; α,β-ethylenic aldehydes; secondary phosphine oxides

Nucleophilic addition of PH-acids to the C=O or C=C double bonds activated by electron-withdrawing substituents represents one of the most convenient approaches to the C—P bond formation and continues to attract attention as an efficient method for the atom-economic synthesis of phosphines and phosphine oxides, including asymmetric and functionalized ones. Thus, secondary phosphine oxides react readily with aliphatic,[1a–d] aromatic,[1a,c,2a–d] heteroaromatic,[3] and functionalized[1a,c,2d,4a–c] aldehydes in the presence[1a–c,2b,c] (or in the absence[1c,d,2a,4a,b,e]) of base catalysts to give corresponding hydroxyphosphine oxides. Nucleophilic addition of secondary phosphine oxides to the double bond of electrophilic alkenes can be effected under both noncatalytic (for example, with methacrylates[5] or

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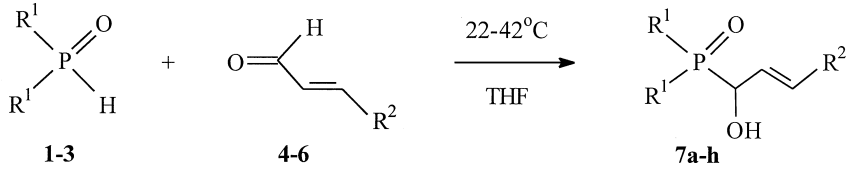
vinyldiphenylphosphine oxide[6]) and base-catalyzed conditions (reactions with acrylonitrile,[7] vinyl sulfoxides,[8a–c]-sulfones,[9]-pyridines,[10] arylalkenes[10,11]).

In the present work, to gain a better understanding of regularities and peculiarities of the addition of PH-acids to the conjugated C=O and C=C double bonds simultaneously present in one molecule, we have for the first time investigated the reaction of α,β-ethylenic aldehydes with secondary phosphine oxides. The latter are now readily accessible from the direct reaction of elemental phosphorus with alkyl halides or styrene.[12a,b] Additionally, the question: "Which of the two interacting electrophilic centers (C=C and C=O) is more complementary to the secondary phosphine oxides?" has to be answered. A new general route to functionalized tertiary phosphine oxides was also expected to be developed.

RESULTS AND DISCUSSION

Secondary phosphine oxides **1–3** have been found to react with 2-propenal **4**, (*E*)-2-butenal **5** and (*E*)-3-phenyl-2-propenal **6** at room temperature or upon slight heating in THF to afford chemoselectively the carbonyl group adducts **7a–h** in high preparative yield (84–88%) (Table I). The resultant phosphine oxides with propenyl and styryl moieties **7d–h** are formed stereoselectively in *E*-configuration (Table II, Scheme 1).



1-3 **4-6** **7a-h**

SCHEME 1

Under identical conditions (26–27°C, THF), the reaction of 2-propenal with dibutylphosphine oxide lasts 24 h, whereas full conversion of dihexyl- and bis(2-phenylethyl)phosphine oxides is reached in 48 and 72 h respectively (Table I, runs 1–3). A similar dependence is also observed when phosphine oxides **1–3** are reacted with aldehyde **5** at 22°C (Table I, runs 4–6). Thus, the reactivity of the phosphine oxides in this process drops in the following order: **1** > **2** > **3**.

On the example of (*E*)-2-butenal **5** it has been shown that increasing the temperature from 22 to 40–42°C allows to reduce the reaction time thrice (Table I, compare runs 6 and 11).

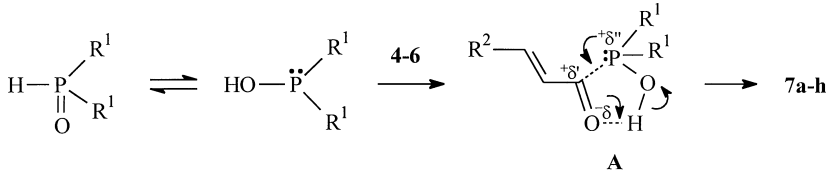
TABLE I Experimental Data and Product Yields

Run	$(R^1)_2P(O)H$	$R^2CH{=}CHC(O)H$	T, °C (Time, h)	Product **7**	Yield, %
1	**1**, $R^1 = n$-Bu	**4**, $R^2 = H$	26–27 (24)	**a**	86[a]
2	**2**, $R^1 = n$-C_6H_{13}	**4**, $R^2 = H$	26–27 (48)	**b**	88[a]
3	**3**, $R^1 = Ph(CH_2)_2$	**4**, $R^2 = H$	26–27 (72)	**c**	84[a]
4	**1**, $R^1 = n$-Bu	**5**, $R^2 = Me$	22 (168)	**d**	84[a]
5	**2**, $R^1 = n$-C_6H_{13}	**5**, $R^2 = Me$	22 (216)	**e**	86[a]
6	**3**, $R^1 = Ph(CH_2)_2$	**5**, $R^2 = Me$	22 (360)	**f**	88[a]
7	**3**, $R^1 = Ph(CH_2)_2$	**4**, $R^2 = H$	26–27 (5)	**c**	48[b]
8	**3**, $R^1 = Ph(CH_2)_2$	**5**, $R^2 = Me$	26–27 (5)	**f**	2[b]
9	**3**, $R^1 = Ph(CH_2)_2$	**6**, $R^2 = Ph$	26–27 (5)	**h**	12[b]
10	**3**, $R^1 = Ph(CH_2)_2$	**5**, $R^2 = Me$	40–42 (48)	**f**	65[b]
11	**3**, $R^1 = Ph(CH_2)_2$	**5**, $R^2 = Me$	40–42 (120)	**f**	97[b]
12	**3**, $R^1 = Ph(CH_2)_2$	**6**, $R^2 = Ph$	26–27 (84)	**h**	87[a]

[a]Isolated yields.
[b]Yields calculated from the ^{31}P NMR spectra of crude products.

Expectedly, the addition rate depends on the structure of the aldehyde employed (Table I, runs 7–9). The most active is 2-propenal **4** (Table I, run 7), whereas the least active turns out to be (*E*)-2-butenal **5** (Table I, run 8).

Higher reactivity of 2-propenal **4** in the reaction is associated with a stronger electron-withdrawing power of the ethenyl group as compared to the phenylethenyl and 1-propenyl groups. This assumption is in accordance with the σ^* Taft constants, which values decrease in the order $CH_2{=}CH > PhCH{=}CH > MeCH{=}CH$.[13] As a result, the stability of the transition state **A** is to decrease in the same order (Scheme 2).



SCHEME 2

The above scheme also allows one to explain the different reactivity of starting secondary phosphine oxides: more reactive dialkylphosphine oxides **1** and **2** as bearing electron-donating substituents should decrease the transition state **A** energy more than bis(2-phenylethyl)phosphine oxide **3**.

IR spectra of the α-hydroxyphosphine oxides **7a–h** (Table II) indicate the presence of the intramolecular hydrogen bond between the

TABLE II Physical, Analytical, and Spectral Data of Products **7a–h**

Product	m.p. (°C)	$M_F/(M_W)$	Found (calcd.) (%) C	H	P	Infrared Spectra (cm^{-1})[a]
7a	[b]	$C_{11}H_{23}O_2P$ (218.27)	60.35 (60.53)	10.59 (10.62)	14.08 (14.19)	3180 ν (OH); 3019 ν (=CH); 2957, 2932, 2872 ν (C—H); 1636 ν (C=C); 1465, 1406, 1379, 1220 δ (CH_2, CH_3); 1147 ν (P=O); 1124 δ (CH_2); 1093 δ (COH); 998, 918 δ (=CH); 813, 719 ν (P—C)
7b	[b]	$C_{15}H_{31}O_2P$ (274.38)	65.49 (65.66)	11.31 (11.39)	10.87 (11.29)	3160 ν (OH); 3018 ν (=CH); 2956, 2928, 2857 ν (C—H); 1636 ν (C=C); 1466, 1406, 1378, 1206 δ (CH_2, CH_3); 1143 ν (P=O); 1122 δ (CH_2); 1063 δ (COH); 998, 920 δ (=CH); 814, 734 ν (P—C)
7c	112–114	$C_{19}H_{23}O_2P$ (314.36)	72.48 (72.59)	7.28 (7.37)	9.79 (9.85)	3160 ν (OH); 3086, 3060, 3027 ν (=CH); 2955, 2926, 2863 ν (C—H); 1636 ν (C=C); 1602, 1586, 1496, 1452 ν (C=C, Ar); 1433, 1401, 1213 δ (CH_2); 1145 ν (P=O); 1110 δ (CH_2); 1068 δ (COH); 996, 924 δ (=CH); 781, 749, 701 δ (CH, Ar), ν (P—C)
7d	[b]	$C_{12}H_{25}O_2P$ (232.29)	61.98 (62.04)	10.72 (10.85)	13.16 (13.33)	3160 ν (OH); 3030 ν (=CH); 2958, 2931, 2872 ν (C—H); 1667 ν (C=C); 1465, 1407, 1378, 1220 δ (CH_2, CH_3); 1144 ν (P=O); 1121 δ (CH_2); 1089 δ (COH); 970, 828 δ (=CH); 898, 719 ν (P—C)

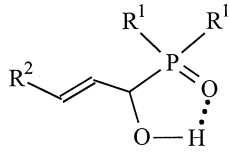
TABLE II *(Continued)*

Product	m.p. (°C)	$M_F/(M_W)$	Found (calcd.) (%) C	H	P	Infrared Spectra (cm^{-1})[a]
7e	[b]	$C_{16}H_{33}O_2P$ (288.41)	66.49 (66.63)	11.42 (11.53)	10.59 (10.74)	3160 ν (OH); 3030 ν (=CH); 2955, 2926, 2857 ν (C—H); 1667 ν (C=C); 1464, 1407, 1378, 1205 δ (CH_2, CH_3); 1142 ν (P=O); 1121 δ (CH_2); 1088 δ (COH); 970, 827 δ (=CH); 801, 715 ν (P—C)
7f	116–118	$C_{20}H_{25}O_2P$ (328.39)	73.09 (73.15)	7.56 (7.67)	8.95 (9.43)	3160 ν (OH); 3085, 3060, 3028 ν (=CH); 2957, 2918, 2853 ν (C—H); 1633 ν (C=C); 1602, 1496, 1452 ν (C=C, Ar); 1213 δ (CH_2); 1144 ν (P=O); 1109 δ (CH_2); 1067 δ (COH); 967 δ (=CH); 784, 767, 747, 701 δ (CH, Ar), ν (P—C)
7h	162–164	$C_{25}H_{27}O_2P$ (390.45)	76.84 (76.90)	7.01 (6.97)	8.03 (7.93)	3438[c] ν (OH); 3085, 3060, 3026 ν (=CH); 2904, 2868, 2832 ν (C—H); 1632 ν (C=C); 1601, 1496, 1452 ν (C=C, Ar); 1216 δ (CH_2); 1143 ν (P=O); 1116 δ (CH_2); 1097 δ (COH); 972 δ (=CH); 786, 751, 700 δ (CH, Ar), ν (P—C)

[a] Spectra of products **7a, b, d, e** were taken in microlayer; spectra of products **7c, f, h** were run in KBr.
[b] A viscous liquid.
[c] The spectrum was taken in vaseline oil.

OH group and the phosphoryl moiety. Thus, IR spectra recorded in the film or in KBr pellets, show a broad band of ν_{OH} stretching vibrations at 3000–3300 cm^{-1}, which is retained in the spectra taken in chloroform solutions of concentrations larger than 0.1 mol/l. Further dilution decreases this band's intensity up to its complete disappearance and results in appearance of a band with absorption maximum at

$\sim$3550 cm^{-1}, whose position and intensity remain unchanged regardless of further decreasing the solute concentration. IR spectra of diluted solutions (<0.01 mol/l) of the compounds **7a–h** show stretching vibrations of the free OH groups (3590 cm^{-1}) and bound OH groups which take part in formation of the five-membered intramolecular hydrogen bond (3545–3550 cm^{-1}).



This corresponds to the literature data[14] for similar α-hydroxyphosphine oxide.

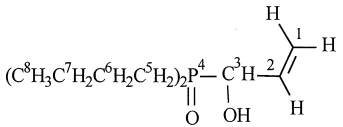
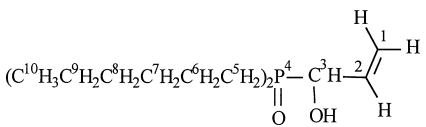
In the ^{1}H and ^{13}C NMR spectra of the compounds **7a–h** (Table III), the most characteristic signals are those of the CH group in the OCHP=O fragment: a peak at 4.40–4.73 ppm with the geminal coupling constant ^{31}P-^{1}H of 6.5–9.9 Hz (^{1}H NMR) and a doublet at 70.03–71.44 ppm, $^{1}J_{PC} \sim 74$–77 Hz (^{13}C NMR). Anisochronism of the chemical shifts of two substituents at the phosphorus atom in ^{1}H and ^{13}C NMR spectra is caused by the asymmetric carbon atom in the CH group. The same non-equivalence was observed in ^{1}H and ^{13}C NMR spectra of 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles[3] and adducts of secondary phosphine oxides and 3-(trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals.[4]

Thus, the reaction of secondary phosphines with α,β-ethylenic aldehydes represents a convenient and efficient method for the synthesis of chiral unsaturated tertiary phosphines, highly reactive building blocks and prospective lipophylic ligands.

EXPERIMENTAL

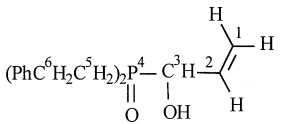
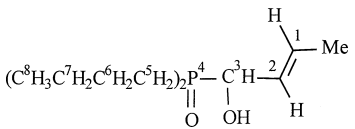
^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Bruker DPX 400 (400, 100, and 161.98 MHz, respectively) spectrometer in $CDCl_3$ solutions and referenced to internal HMDS and external 85% H_3PO_4 respectively. IR spectra were run on a Bruker IFS 25 instrument in KBr pellets, in thin film and in chloroform solutions (d = 0.4 ÷ 2 cm). NMR and IR spectral characteristics, as well as data of elemental analyses of compounds **7a–h**, are presented in Tables II and III.

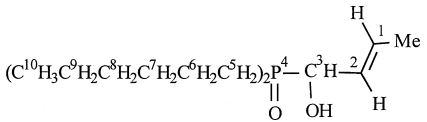
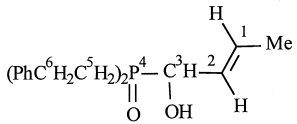
TABLE III NMR Spectral Data of Products **7a–h**

Product	Formula	NMR ($CDCl_3$), δ (ppm), J (Hz)		
		^1H	^{13}C	^{31}P
7a		0.86 (t, 6H, C^8-H, $^3J_{CH_3\text{-}CH_2}$ = 7.3), 1.38 (hex, 4H, C^7-H, $^3J_{HH}$ = 7.3), 1.58 ÷ 1.82 (m, 8H, $C^{5,6}$-H), 4.53 (ddt, 1H, C^3-H, $^2J_{P\text{-}C\text{-}H}$ = 9.9, $^3J_{H\text{-}C\text{-}C\text{-}H}$ = 5.4, $^4J_{H\text{-}C\text{-}C{=}C\text{-}H}$ = 1.7), 5.29 (ddd, 1H, C^1-H, $^3J_{H\text{-}C{=}C\text{-}H}$ = 10.5, $^2J_{H_2\text{-}C=} \approx {}^4J_{H\text{-}C\text{-}C{=}C\text{-}H}$ = 1.7), 5.47 (ddd, 1H, C^1-H, $^3J_{H\text{-}C{=}C\text{-}H}$ = 17.2), 5.67 (s br. 1H, C^3-OH), 6.02 (dddd, 1H, C^2-H, $^3J_{P\text{-}C\text{-}C\text{-}H}$ = 3.2)	13.63 (C^8), 23.34 (C^7, d, $^3J_{PC}$ = 7.7), 23.42 (C^7, d, $^3J_{PC}$ = 7.8), 24.35 (d, C^6, $^2J_{PC}$ = 14.2), 24.45 (d, C^5, $^1J_{PC}$ = 61.6), 24.49 (d, C^5, $^1J_{PC}$ = 63.4), 70.72 (d, C^3, $^1J_{PC}$ = 77.2), 116.89 (d, C^1, $^3J_{PC}$ = 9.5), 133.67 (C^2)	51.70
7b		0.87 (t, 6H, C^{10}-H, $^3J_{H\text{-}H}$ = 6.7), 1.29 (m br, 8H, $C^{9,8}$), 1.38 (m, 4H, C^7-H), 1.51–1.88 (m, 8H, $C^{5,6}$-H), 4.50 (dd, 1H, C^3-H, $^2J_{P\text{-}C\text{-}H}$ = 8.5, $^3J_{H\text{-}C\text{-}C\text{-}H}$ = 5.4), 5.45 (dd br., 1H, C^1-H, $^3J_{H\text{-}C{=}C\text{-}H}$ = 17.2, $^4J_{P\text{-}C\text{-}C{=}C\text{-}H}$ = 3.8), 5.56 (s br., 1H, C^3-OH), 5.99 (dddd, 1H, C^2-H, $^4J_{P\text{-}C\text{-}CH=}$ = 3.3)	14.05 (C^{10}), 21.41 (C^9), 22.50 (C^8), 24.65 (d, C^5, $^1J_{PC}$ = 62.5), 25.00 (d, C^5, $^1J_{PC}$ = 61.6), 30.98 (d, C^6, $^2J_{PC}$ = 13.4), 31.37 (C^7), 71.04 (d, C^3, $^1J_{PC}$ = 75.0), 117.11 (d, C^1, $^3J_{PC}$ = 9.5), 133.51 (C^2)	51.61

(Continued on next page)

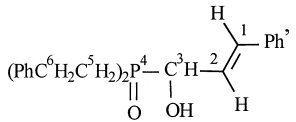
TABLE III NMR Spectral Data of Products **7a–h** *(Continued)*

Product	Formula	NMR ($CDCl_3$), δ (ppm), J (Hz)		
		^1H	^{13}C	^{31}P
7c		2.05 (m, 4H, C^5-H), 2.95 (m, 4H, C^6-H), 4.53 (s br., 1H, OH), 4.55 (t br., 1H, C^3-H), 5.35 (d br., 1H, C^1-H, $^3J_{H\text{-}C=C\text{-}H}$ = 10.5), 5.47 (d br., 1H, C^2-H, $^3J_{H\text{-}C=C\text{-}H}$ = 17.1), 6.04 (ddd, 1H, C^2-H, $^3J_{P\text{-}C\text{-}H=}$ = 4.3), 7.23 (m, 10H, Ph)	26.93 (d, C^5, $^1J_{PC}$ = 59.5), 26.99 (d, C^5, $^1J_{PC}$ = 61.2), 27.40 (C^6, $^2J_{PC}$ = 7.0), 27.42 (C^6, $^2J_{PC}$ = 7.0), 71.12 (d, C^3, $^1J_{PC}$ = 76.3), 117.40 (d, C^1, J_{PC} = 9.1), 126.43 (C-*p*), 128.06 (C-*o*), 128.64 (C-*m*), 133.17 (C^2), 141.06 (d, C-*i*, $^3J_{PC}$ = 14.2), 141.20 (d, C-*i*, $^3J_{PC}$ = 14.2)	49.00
7d		0.91 (t, 6H, C^8-H, $^3J_{CH_3\text{-}CH_2}$ = 7.3), 1.40 (hex, 4H, C^7-H, $^3J_{HH}$ = 7.3), 1.58 (m, 4H, C^6-H), 1.71 (m, 4H, C^5-H), 1.75 (dd, 3H, C^1-Me, $^5J_{P\text{-}C\text{-}C=C\text{-}C\text{-}H}$ = 4.5; $J_{H\text{-}C\text{-}C\text{-}H}$ = 6.2), 4.40 (t, 1H, C^3-H, $^2J_{P\text{-}C\text{-}H} \approx {}^3J_{H\text{-}C\text{-}C\text{-}H}$ = 6.5), 5.34 (s br., 1H, C^3-OH), 5.60 (dddq, 1H, C^2-H, $^3J_{H\text{-}C=C\text{-}H}$ = 15.3, $^3J_{P\text{-}C\text{-}C\text{-}H}$ = 3.7, $^4J_{HC=C\text{-}C\text{-}H}$ = 1.7), 5.85 (dqdd, 1H, C^1-H, $^4J_{P\text{-}C\text{-}C=C\text{-}H}$ = 3.8; $^4J_{H\text{-}C\text{-}C=C\text{-}H}$ = 1.4; $^3J_{H\text{-}C\text{-}C\text{-}H}$ = 6.2)	13.48 (C^8), 17.85 (C^1-Me), 23.20 (C^7, d, $^3J_{PC}$ = 8.0), 23.22 (C^7, d, $^3J_{PC}$ = 8.0), 24.03 (d, C^5, $^1J_{PC}$ = 62.0), 24.22 (C^6 d, $^3J_{PC}$ = 13.6), 24.29 (d, C^5, $^1J_{PC}$ = 62.0), 70.03 (d, C^3, $^1J_{PC}$ = 76.1), 126.25 (C^2), 128.73 (C^1, $^3J_{PC}$ = 10.5)	49.79

7e		0.88 (t, 6H, C^{10}-H, $^{3}J_{CH_3\text{-}CH_2} = 6.8$), 1.21 ÷ 1.47 (m, 12H, $C^{9,8,7}$-H), 1.50 ÷ 1.83 (m, 8H, $C^{6,5}$-H), 1.75 (dddd, 3H, C^{1}-Me, $^{3}J_{H\text{-}C\text{-}C\text{-}H} = 6.6$; $^{5}J_{P\text{-}C\text{-}C{=}C\text{-}C\text{-}H} = 5.4$; $^{4}J_{H\text{-}C\text{-}C{=}C\text{-}H} \approx {}^{5}J_{Me\text{-}C\text{-}C\text{-}H} = 1.6$), 4.40 (tt, 1H, C^{3}-H, $^{2}J_{P\text{-}C\text{-}H} \approx {}^{3}J_{H\text{-}C\text{-}C\text{-}H} = 6.9$; $^{4}J \approx {}^{5}J = 1.4$), 5.52 (s br. 1H, OH), 5.60 (dddq, 1H, C^{2}-H, $^{3}J_{H\text{-}C{=}C\text{-}H} = 15.3$, $^{3}J_{P\text{-}C\text{-}C\text{-}H} = 3.7$), 5.85 (dqdd, 1H, C^{1}-H, $^{4}J_{P\text{-}C\text{-}C{=}C\text{-}H} = 3.8$; $^{4}J_{H\text{-}C\text{-}C{=}C\text{-}H} = 1.3$).	13.92 (C^{10}), 17.91 (C^{1}-Me), 21.16 (d, C^{9}, $^{5}J_{PC} = 3.7$), 21.23 (d, C^{9}, $^{5}J_{PC} = 3.7$), 22.35 (C^{8}), 24.50 (d, C^{5}, $^{1}J_{PC} = 62.0$), 30.87 (C^{6}, $^{2}J_{PC} = 12.7$), 31.22 (C^{7}), 70.30 (d, C^{3}, $^{1}J_{PC} = 74.4$), 126.21 (C^{2}), 129.00 (d, C^{1}, $J_{PC} = 9.9$)	50.36
7f		1.76 (t br., 3H, Me, $^{3}J_{CH_3\text{-}CH} \approx {}^{5}J_{P\text{-}C\text{-}C{=}C\text{-}C\text{-}H} = 5.0$), 2.05 (m, 4H, C^{5}-H), 2.95 (m, 4H, C^{6}-H), 3.75 (s br., 1H, C^{3}-OH), 4.46 (t, 1H, C^{3}-H $^{2}J_{P\text{-}C\text{-}H} \approx {}^{3}J_{H\text{-}C\text{-}C\text{-}H} = 6.5$), 5.63 (d br., 1H, C^{2}-H, $^{3}J_{H\text{-}C\text{-}C\text{-}H} = 15.3$), 5.88 (m, 1H, C^{1}-H), 7.23 (m, 10H, Ph)	18.04 (C^{1}-Me), 27.04 (d, C^{5}, $^{1}J_{PC} = 60.3$), 27.17 (d, C^{5}, $^{1}J_{PC} = 60.3$), 27.43 (d, C^{6}, $^{2}J_{PC} = 7.8$), 27.47 (d, C^{6}, $^{2}J_{PC} = 8.2$), 71.07 (d, C^{3}, $^{1}J_{PC} = 77.2$), 125.59 (C^{2}), 126.30 (C-*p*), 126.37 (C-*p*), 128.06 (C-*o*), 128.64 (C-*m*), 130.34 (d, C^{1}, $J_{PC} = 9.9$), 141.13 (d, C-*i*, $^{3}J_{PC} = 13.4$).	48.80

(Continued on next page)

TABLE III NMR Spectral Data of Products **7a–h** *(Continued)*

Product	Formula	NMR ($CDCl_3$), δ (ppm), J (Hz)		
		^{1}H	^{13}C	^{31}P
7h		2.03 ÷ 2.17 (m br., 4H, C^5-H), 2.94 (m, 4H, C^6-H), 4.26 (s br., 1H, C^3-OH), 4.73 (t, 1H, C^3-H, $^{2}J_{P\text{-}C\text{-}H} \approx {}^{3}J_{H\text{-}C\text{-}C\text{-}H} \approx 7.3$), 6.33 (ddd, 1H, C^2-H, $^{3}J_{H\text{-}C{=}C\text{-}H} = 15.3$, $^{3}J_{P\text{-}C\text{-}C\text{-}H} = 3.8$), 6.76 (dd, 1H, C^1-H, $^{4}J_{P\text{-}C\text{-}C{=}C\text{-}H} = 3.2$), 7.17 (m, 5H, Ph′), 7.23 (m, 10H, Ph)	27.24 (d, C^5, $^{1}J_{PC} = 62.5$), 27.43 (d, C^5, $^{1}J_{PC} = 59.6$), 27.61 (d, C^6, $^{1}J_{PC} = 6.0$), 27.57 (C^6, $^{2}J_{PC} = 6.0$), 71.44 (d, C^3, $^{1}J_{PC} = 75.4$), 123.85 (C-*p*), 126.55, 126.60, (C′-*o*, C′-*m*), 126.72 (C-*o*), 128.21 (C-*o*), 128.77 (C-*m*), 132.70 (C^1, $^{2}J_{PC} = 9.9$), 136.08 (C^2), 140.14 (C′-*i*), 141.03 (d, C-*i*, $^{2}J_{PC} = 10.3$), 141.15 (d, C-*i*, $^{2}J_{PC} = 12.1$)	49.47

[a]Assignment of C^1-H and C^2-H peaks in ^{1}H and ^{13}C NMR spectra was done using the inverse C—H correlation method (HMQC).
[b]The existence of a rather high (~5 Hz) coupling constant between phosphorus atom and methyl protons through five bonds was confirmed by a ^{31}P-^{1}H decoupling experiment, in which this coupling disappeared.

Synthesis of 1-(Diorganylphosphoryl)-2-alken- 1-ols 7a-h

General Procedure

A mixture of aldehyde (**4–6**) (11 mmol) and secondary phosphine oxide (**1–3**) (10 mmol) in THF was stirred under an argon atmosphere at room temperature or upon heating at 26–42°C (see Table I for reaction times). The reaction was monitored using ^{31}P NMR spectra by disappearance of peaks of the initial secondary phosphine oxides **1–3** in the 30–32 (δ) ppm region and appearance of new peaks at 48–52 ppm, corresponding to tertiary phosphine oxides. The solvent was then removed under reduced pressure and the residue was re-precipitated from chloroform into petroleum ether to give products **7a–h** (Table I, runs 1–6, 12 respectively).

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