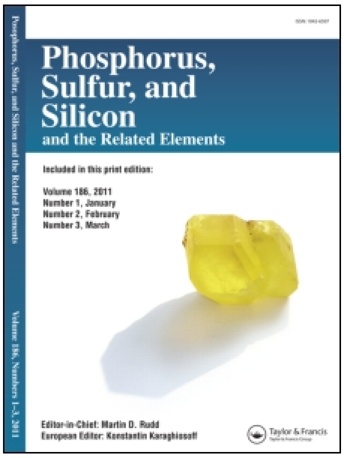

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XLV STRUCTURAL EFFECTS OF ESTER ALKYL GROUP OF DIALKYL ALLYLPHOSPHONATE CARBANION ON THE REGIOSELECTIVITY OF ELECTROPHILIC ADDITION

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XLV STRUCTURAL EFFECTS OF ESTER ALKYL GROUP OF DIALKYL ALLYLPHOSPHONATE CARBANION ON THE REGIOSELECTIVITY OF ELECTROPHILIC ADDITION

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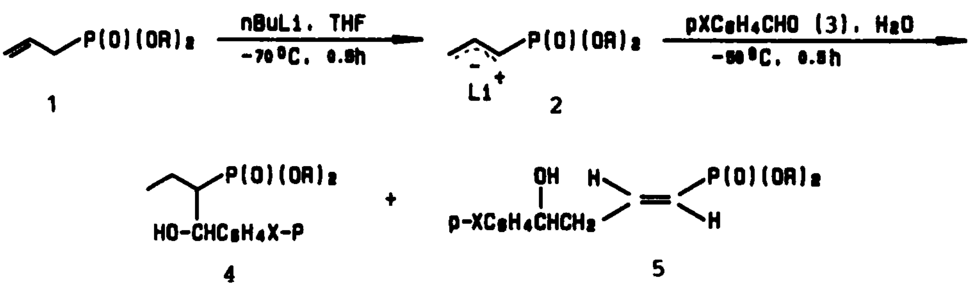
The steric effect of the ester alkyl group of dialkyl allylphosphonate carbanion on the regioselectivity of the reaction with benzaldehyde was investigated. The steric contribution was evaluated by substituent parameter and molecular mechanics calculation.

Key words: Allylphosphonate carbanion; regioselectivity; steric effects.

The ambident nature of carbanion derived from allylphosphonate was evidenced by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and MINDO/3 calculation.[1] As shown by us[2] and others[3] the alkylation of this allylic carbanion was found to be α-regioselective. The regioselectivity of the electrophilic addition reaction with p-substituted benzaldehyde in this system is markedly influenced by the structure of the nuclear substituents. As reported by us, this electrophilic addition exhibits α-regioselectivity except p-nitrobenzaldehyde, which shows characteristic regioselectivity on γ-position.[4] Beside these, the nature of solvent plays an important role in controlling regioselectivity of these reactions.[5] We wish to report in this paper the structural effects of ester alkyl group of phosphoryl allylcarbanion on the regioselectivity of its reaction with benzaldehydes. Benzaldehydes with different performance in such reaction, namely benzaldehyde and p-nitrobenzaldehyde were chosen as electrophilic reagents. The steric effect was investigated by substituent parameters and molecular mechanics calculation.

RESULTS AND DISCUSSIONS

The steric environment of carbanion stabilized by heteroatom shows significant effect on the regioselectivity in the electrophilic addition of this reactive species. The regioselectivity of the reaction involving allylphosphoramide carbanion and acetone was shown to be controlled by the steric effect of the phosphoramide group.[6] For the investigation of the steric effect of the phosphoryl moiety of allylphosphonate carbanion on the regioselectivity of the reaction with benzaldehydes, dialkyl allylphosphonate (**1**) is converted to the corresponding delocalized allylic carbanion (**2**) by reaction with n-butyllithium in THF at −70°C. The resulting carbanion **2** is then directly treated with benzaldehyde (**3f**) or p-nitrobenzaldehyde



$R = CH_3(a), C_2H_5(b), nC_3H_7(c), iC_3H_7(d), tC_4H_9(e), X = H(f), NO_2(g).$

TABLE I

Influence of ester alkyl group on the regioselectivity of the reaction of **2** with **3**

	ν	**4f**(%)	**5f**(%)	**4f/5f**	Yield	**4g**(%)	**5g**(%)	**4g/5g**	Yield
2a	0.36	93.7	6.3	14.9	74%	47.6	52.4	0.91	71%
2b	0.48	92.4	7.6	12.1	96%	23.1	76.9	0.30	62%
2c	0.56	91.4	8.6	10.6	75%	19.2	80.8	0.24	65%
2d	0.75	86.3	13.7	6.3	68%	12.8	87.2	0.15	62%
2e	1.22	75.6	24.4	3.1	68%	5.0	95.0	0.05	57%

(**3g**). Upon suitable work-up the amount of α- and γ-substituted products was estimated by ^{31}P NMR spectroscopy.

Data in Table I reveal that reaction of **2** with **3f** provides high selectivity in the α-position. Increase of steric bulkiness of the ester alkyl group of **2** effects only a slight decrease of the α-selectivity. On the other hand, the specific γ-selectivity of **3g** with **2** is increased markedly with the increase of the steric hindrance of the phosphoryl group. The allylic carbanion with O,O-di-tert-butyl phosphoryl group gives 95% γ-substituted product in reaction with p-nitrobenzaldehyde.

Plot of the ratio of α-substituted product over γ-substituted product as represented by log (**4f/5f**) versus Charton's ν constants of the ester alkyl group gave a straight line (Figure 1). Multiple regression analyses involving log (**4f/5f**) and ν constants gave excellent correlation coefficient:

$$\log(\mathbf{4f/5f}) = 1.458 - 0.808\,\nu$$

$$r = 0.994,\ n = 5$$

Similar situation with log(**4g/5g**):

$$\log(\mathbf{4g/5g}) = 0.202 - 1.274\,\nu$$

$$r = 0.949,\ n = 5$$

However, less satisfactory results were obtained using Taft's E_s constants as substituents parameters for the ester alkyl groups.[7] The correlation coefficient is decreased to 0.963 and 0.907, respectively.

In recent years, molecular mechanics has been successfully used to calculate the steric effect in organic molecules. In the reaction of carbanion with carbonyl group, the electron configuration of the former will be changed from C-sp^2 to C-sp.[3] If

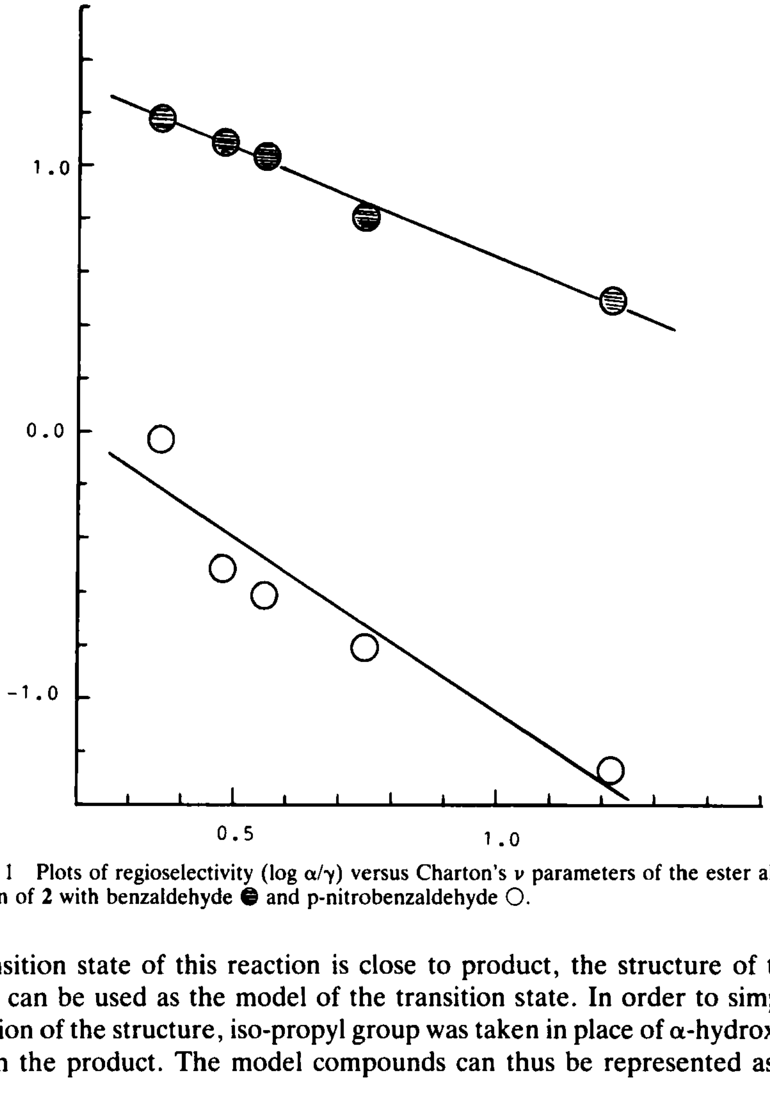
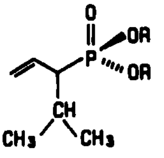
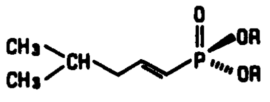


FIGURE 1 Plots of regioselectivity (log α/γ) versus Charton's ν parameters of the ester alkyl group in reaction of 2 with benzaldehyde ● and p-nitrobenzaldehyde ○.

the transition state of this reaction is close to product, the structure of the final product can be used as the model of the transition state. In order to simplify the calculation of the structure, iso-propyl group was taken in place of α-hydroxybenzyl group in the product. The model compounds can thus be represented as **6a** and **6b**:



6a



6b

The calculated steric energies of compounds **6a**, **6b** and **2** are listed in Table II.

Generally, the ΔE between the steric energy of **6a** and **6b** can be used to measure the steric effect, which is due to the alkoxyl group of the phosphoryl moiety. However, the data in Table II demonstrate that the ΔE does not reflect the steric effect of the phosphoryl alkoxyl group. It means that the model compounds **6** can not represent the transition state of the reaction properly. It is reasonable to

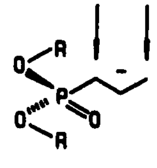
TABLE II

Steric energy of **2**, **6a** and **6b** calculated by molecular mechanics

	E_2	**6a**	E_{6a}	**6b**	E_{6b}	ΔE*
2a	8.107	a	12.972	a	12.051	0.921
2b	8.719	b	13.285	b	12.631	0.645
2c	9.817	c	14.054	c	13.628	0.462
2d	10.470	d	14.388	d	13.878	0.510
2e	13.344	e	17.336	e	17.119	0.617

* $\Delta E = E_{6a} - E_{6b}$; energy in Kcal·Mol^{-1}.

postulate that this reaction has an early transition state. In such case the attack of benzaldehyde on the carbanion takes place from the axial direction of the plane of the allylic carbanion either on α- or on γ-position as shown in structure 7.



7

The electrophilic addition of benzaldehyde to the α-position of the carbanion of allylphosphonate should be hindered by the alkoxyl group of the latter. The results of such treatment will be published elsewhere.

As demonstrated by the experimental data shown in this paper, the regioselectivity of the reaction involving electrophilic addition of substituted benzaldehyde to allylphosphonate carbanion is determined by the nature of the nuclear substituents of benzaldehyde; also structural variations of the ester alkyl group of the phosphonate moiety can have a dramatic influence, which has been studied quantitatively. The regioselectivity as represented by log(α/γ) is correlated linearly with the steric substituent parameters of the ester alkyl group.

EXPERIMENTAL

The regioselectivity as represented by the ratio of α-substituted over γ-substituted products of the reaction of **2** with **3** was estimated from the integral value of ^{31}P-NMR which were recorded on a FX-90Q Spectrometer using $CDCl_3$ as solvent, 80% H_3PO_4 as external standard. Offset observation, 82.90 kHz; pulse width, 7 sec, pulse interval 3.0 sec., data points 8192; spectral width 1810 Hz; decoupling, no NOE; lock, $CHCl_3$, 20°C. ^{1}H-NMR were taken from a Varian XL-200 Spectrometer. IR spectra were recorded on a IR-400 Spectrophotometer. MS were taken on a Finnigan 4021 Spectrometer. Melting points were determined on a Kofler hotplate, uncorrected.

Reaction of **1a** *and* **3f**. **1a** (1.50 g, 10 mmole) was dissolved in THF (30 ml) and then cooled to −70°C, a n-pentane solution of n-BuLi (10 mmole) was introduced and stirred for 0.5 hr followed by addition of **3f** (10 mmole) and then stirred for an additional 0.5 hr at −70°C. After hydrolysis of the reaction mixture, dichloromethane (30 ml) was added and finally washed successively with water and dried (Na_2SO_4). Separation of isomers was achieved by column chromatography with 200–300 mesh silica-gel using petroleum ether-ethyl acetate-anhydrous methanol (14:7:1). Dimethyl α(α′-hydroxybenzyl) allylphosphonate (**4a**, **f**) δ ^{31}P 29.97, 29.92 (1.2:1) ppm. E-Dimethyl γ(α′-hydroxybenzyl)propenyl phosphonate (**5a**, **f**) δ ^{31}P 20.95 ppm. α/γ = 1.49. Thus 1.89 g **4a**, **f** mp. 79–80°C (recrystallized from ethylacetate and n-pentane) was obtained in 74% yield. Anal. $C_{12}H_{17}O_4P$ Calc. C, 56.25; H, 6.69; P, 12.09; Found C, 56.55; H, 7.06; P, 12.00. IR 3320 (s, OH), 1635 (m, —CH═CH$_2$), 1230 (s, P═O)

cm^{-1}. δ ^1H 7.23–7.36 (m, 5H, C_6H_5), 4.87–6.04 (m, 3H, $CH_2{=}CH$—), 5.27 [m, H, CH(OH)] 3.70–3.88 [m, 6H, $2X(OCH_3)$], 4.50 (b, H), 2.54–3.10 [m, H, CHCH(OH)]ppm. m/z 257 ($[m + 1]^+$, 4%), 241 ($[m - 15]^+$, 10%), 239 ($[m - 17]^+$, 21%), 150 ($[m - 106]^+$, 61%); **5a**, **f** bp. 130–132°C/0.05 Torr. Anal. $C_{12}H_{17}O_4P$ Calc. C, 56.25; H, 6.69; Found C, 55.89; H, 6.77. IR 3340 (s, OH), 1625 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. δ ^1H 7.23–7.36 (m, 5H, C_6H_5) 6.52, 6.89 (m, H, CH=CH—P), 5.70 (d, d, J_{PH} = 21 Hz, J_{HH} = 17 Hz, CH—CH—P), 4.84 [t, J_{HH} = 7 Hz, H, $CH_2CH(OH)$], 3.32–3.90 [m, 6H, $2X(OCH_3)$], 2.50–2.90 (m, 2H, —CH=CH—CH_2—CH—), 1.40 (b, H, —OH)ppm. m/z 257 ($[m + 1]^+$, 52%), 239 ($[m - 17]^+$, 100%), 151 ($[m - 105]^+$, 100%).

Reaction of **1b** and **3f** was carried on in the similar manner. Diethyl α(α′-hydroxybenzyl)allylphosphonate (**4b**, **f**, 2.52 g) and E-diethyl-γ-(α′-hydroxybenzyl)propenyl phosphonate (**5b**, **f**, 0.21 g) was obtained, yield 96%. **4b**, **f** bp. 115–116°C/0.01 Torr. Anal. $C_{14}H_{21}O_4P$, Calc. C, 59.15; H, 7.45; P, 10.90; Found C, 58.70; H, 7.96; P, 10.95. IR 1640 (m, $CH{=}CH_2$), 1230 (s, P=O) cm^{-1}. δ ^1H 7.23–7.35 (5H, m, C_6H_5), 4.85–6.02 (3H, m, $CH_2{=}CH$, 5.26 [1H, d, d, J_{HH} = 9 Hz, J_{HP} = 22 Hz, —CH(OH)], 4.00–4.25 [4H, m, $2X(OCH_2CH_3)$], 2.52–3.08 (1H, m, CHP=O), 1.76 (1H, s, OH), 1.20–1.42 [6H, m, $2X(OCH_2CH_3)$] ppm. δ ^{31}P 27.96, 27.47 (2.5/1) ppm. m/z: 285 ($[M + 1]^+$, 29%), 267 ($[M - 17]^+$, 100%), 178 ($[M = 106]^+$, 57%). **5b**, **f** b.p. 148–150°C/0.02 Torr, Anal. $C_{14}H_{21}O_4P$, Calc. C, 59.15; H, 7.45; Found C, 58.89; H, 7.62 IR: 1632 (m, CH=CH), 1230 (s, P=O) cm^{-1}. δ^1 H 7.25–7.36 (5H, m, C_6H_5), 6.62–6.90 (1H, m, CH=CHPO), 5.72 (1H, d, d, J_{HH} = 17 Hz, J_{HP} = 21 Hz, CH=CHPO), 4.86 [1H, t, J_{HH} = 7 Hz, CH(OH)], 3.88–4.20 [4H, m, $2X(OCH_2CH_3)$], 2.52–2.82 (2H, m, $CHCH_2CH{=}CH$), 2.06 (1H, s, OH), 1.20–1.40 [6H, m, $2X(OCH_2CH_3)$] ppm. δ ^{31}P: 17.96 ppm. m/z: 285 ($[M + 1]^+$, 53%), 267 ($[M - 17]^+$, 39%), 178 ($[M - 106]^+$, 100%).

Reaction of **1c** and **3f** was carried on analogously. Di(n-propyl)-α (α′-hydroxybenzyl)allylphosphonate (**4c**, **f**) δ ^{31}P: 27.38, 27.25 (0.63/1 ppm. E-Di(n-propyl)-γ-(α′-hydroxybenzyl)propenyl phosphonate (**5c**, **f**) δ ^{31}P: 18.11 ppm, α/γ = 10.6. Yield of **4c**, **f** and **5c**, **f** was 2.34 g or 75%. **4c**, **f** b.p. 146–148°C/0.01 Torr. Anal. $C_{16}H_{25}O_4P$, Calc. C, 61.53; H, 8.07; P, 9.92; Found C, 60.62; H, 8.64: P, 10.09 IR 3320 (s, OH), 1630 (m, —$CH{=}CH_2$), 1220 (s, P=O) cm^{-1}. δ ^1H 7.14–7.37 (m, 5H), 4.80–6.04 (m, 3H), 5.27 (m, H), 3.86–4.25 (m, 4H), 2.70–3.06 (m, H), 1.60 (s, H), 1.50–1.90 (m, 4H), 0.74–1.10 (m, 6H) ppm. m/z: 313 ($[M + 1]^+$, 50%), 294 ($[M - 18]^+$, 20%), 206 ($[M - 106]^+$, 79%), 164 ($[M - 158]^+$, 58%), 122 ($[M - 190]^+$, 100%). **5c**, **f** b.p. 160–162°C/0.05 Torr. Anal. $C_{16}H_{25}O_4P$, Calc. C, 61.53; H, 8.07; Found C, 60.96; H, 8.15. IR: 3350 (s, OH), 1625 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. δ ^1H 7.14–7.37 (m, 5H), 6.42–6.92 (m, H), 5.72 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.84 (t, J_{HH} = 7 Hz, H), 3.80–4.02 (m, 4H), 2.60–2.92 (m, 2H), 2.10 (b, H), 1.50–1.90 (m, 4H), 0.82–1.00 (m, 6H) ppm. m/z: 313 ($[M + 1]^+$, 14%), 295 ($[m - 17]^+$, 34%), 208 ($[M - 106]^+$, 62%), 164 ($[M - 158]^+$, 41%), 149 ($[M - 173]^+$, 5%), 122 ($[M - 190]^+$, 100%).

Reaction of **1d** and **3f** was carried on analogously. Di(iso-propyl)-α(α′-hydroxybenzyl)allylphosphonate **4d**, **f**) δ ^{31}P: 26.01, 25.96 (1:1) ppm. E-Di(iso-propyl)-γ-(α′-hydroxybenzyl)propenyl phosphonate (**5d**, **f**) δ ^{31}P: 15.97 ppm. **4d**, **f/5d**, **f** = 6.3 Yield 2.12 g or 68%. **4d**, **f** b.p. 140–142°C/0.01 Torr. $C_{16}H_{25}O_4P$, Calc. C, 61.53; H, 8.07; P, 9.92; Found C, 61.59; H, 8.38; P, 9.95. IR: 3320 (s, OH), 1640 (m, —$CH{=}CH_2$), 1230 (s, P=O) cm^{-1}. δ ^1H: 7.18–7.34 (m, 5H), 4.60–6.00 [m, 6H, $CH_2{=}CH$—, CH(OH), $2X(OCH(CH_3)_2]$, 2.58–2.94 (m, H), 1.80 (s, H), 1.22–1.46 [m, 12H, $2X(OCH(CH_3)_2]$ ppm. m/z: 313 ($[m + 1]^+$, 48%), 295 ($[m - 17]^+$, 29%), 253 ($[m - 59]^+$, 11%), 211 ($[m - 101]^+$, 13%), 206 ($[m - 106]^+$, 42%), 122 ($[m - 190]^+$, 100%), **5d**, **f** b.p. 152–154°C/0.05 Torr. IR: 3350 (s, OH), 1630 (m, —CH=CH—), 1230 (s, P=O) cm^{-1}; δ ^1H: 7.12–7.38 (m, 5H), 6.60–6.90 (m, H), 5.72 (d, d, J_{HH} = 17 Hz, H), 4.84 (t, J_{HH} = 7 Hz, H), 4.48–4.70 (m, 2H), 2.52–2.80 (m, 2H), 1.90 (b, H), 1.18–1.32 (m, 12H) ppm. m/z: 313 ($[m + 1]^+$, 100%), 295 ($[m - 17]^+$, 19%), 253 ($[m - 59]^+$, 50%), 211 ($[m - 101]^+$, 52%) 206 ($[m - 106]^+$, 61%), 122 ($[m - 190]^+$, 82%).

Reaction of **1e** and **3f** was carried on analogously. Di(tert-butyl)-α(α′-hydroxybenzyl)allylphosphonate (**4e**, **f**) δ ^{31}P: 20.90 ppm. E-Di(tert-butyl)-γ-(α′-hydroxybenzyl)propenyl phosphonate (**5e**, **f**) δ ^{31}P: 12.70 ppm. **4e**, **f/5e**, **f** = 3.1, Yield 2.31 g or 68%. **4e**, **f** m.p. 102–103°C (recrystallized from ethylacetate and n-hexane) $C_{18}H_{29}O_4P$ Calc., C, 65.31; H, 8.59; Found C, 62.56; H, 8.83. IR: 3320 (s, OH), 1640 (m, —$CH{=}CH_2$), 1395, 1375 [s, —$C(CH_3)_3$], 1240 (s, P=O) cm^{-1}. δ ^1H: 7.24–7.36 (m, 5H), 4.65–6.00 (m, 4H), 2.56–2.80 (m, H), 1.80 (b, H), 1.56 (d, J_{HH} = 7 Hz, 18 H) ppm. m/z: 341 ($[m + 1]^+$, 11%) 285 ($[m - 58]^+$, 16%), 234 ($[m - 106]^+$, 6%), 229 ($[m - 111]^+$, 50%), 122 ($[m - 218]^+$, 100%). **5e**, **f**, crystalline solid decomposed on heating. IR: 3320 (s, OH), 1630 (m, —CH=CH—), 1395, 1370 [s, —$C(CH_3)_3$], 1230 (s, P=O) cm^{-1}. δ ^1H: 7.24–7.40 (m, 5H), 6.48–6.84 (m, H), 5.71 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.80 (t, J_{HH} = 6 Hz, H), 2.56–2.74 (m, 2H), 2.03 (s, H), 1.42 (d, J_{HH} = 3 Hz, 18 H) ppm. m/z: 341 ($[m + 1]^+$, 16%), 285 ($[m - 58]^+$, 32%), 234 ($[m - 106]^+$, 10%), 229 ($[m - 111]^+$, 64%), 122 ($[m - 218]^+$, 99%).

Reaction of **1a** and **3g** was carried on as described for reaction with benzaldehyde. Dimethyl α − (α′-hydroxy-p-nitrobenzyl)allylphosphonate (**4a**, **g**) δ ^{31}P: 29.10, 29.00 (1:1) ppm., E-Dimethyl-γ-(α′-hydroxy-p-nitrobenzyl)propenylphosphonate (**5a**, **g**) δ ^{31}P: 20.52 ppm, **4a**, **g/5a**, **g** = 0.91. Yield 2.14 g or 71%. **4a**, **g** m.p. 104–106°C (solidified and remelted at 124–126°C) (recrystallized from ethylacetate and n-pentane). Anal. $C_{12}H_{16}NO_6P$ Calc. C, 47.85; H, 5.35; N, 4.65; Found C, 48.08; H, 5.48; N, 4.68. IR: 3300 (s, OH), 1640 (m, —CH=CH$_2$), 1220 (s, P=O) cm^{-1}. δ ^{1}H: 7.84 (d, d, AB type, 4H), 4.86–6.04 (m, 4H), 3.70–3.90 (m, 6H), 2.80–3.06 (m, H), 1.84 (b. H) ppm. m/z: 302 ($[m + 1]^+$, 52%), 284 ($[m - 17]^+$, 29%), 150 ($[m - 151]^+$, 100%). **5a**, **g** b.p. 170–172°C/0.01 Torr. Anal. $C_{12}H_{16}NO_6P$ Calc. C, 47.85%; H, 5.35%; N, 4.65%; Found C, 47.72; H, 5.58; N, 4.54. IR: 3320 (s, OH), 1630 (m, —CH=CH—), 1230 (s, P=O) cm^{-1}. δ ^{1}H: 7.87 (d, d, AB type, 4H), 6.75–7.06 (m, H), 5.71 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.97 (t, J_{HH} = 6 Hz, H), 3.65 (d, d, J_{PH} = 9 Hz, J_{HH} = 2 Hz, 6H), 2.60–2.72 (m, 2H), 2.40 (b, H) ppm. m/z: 302 ($[m + 1]^+$, 59%), 284 ($[m - 17]^+$, 8%), 150 ($[m - 151]^+$, 100%).

Reaction of **1b** and **3g** leading to Diethyl α-(α′-hydroxy-p-nitrobenzyl)allylphosphonate (**4b**, **g**) and E-Diethyl-γ-(α′-hydroxy-p-nitrobenzyl)propenylphosphonate (**5b**, **g**) was reported.[4]

Reaction of **1c** and **3g** was being carried out as described above. Di(n-propyl) α-(α′-hydroxy-p-nitrobenzyl)allylphosphonate (**4c**, **g**) δ ^{31}P: 27.01, 26.55 (0.31:1) ppm. E-Di(n-propyl)-γ-(α′-hydroxy-p-nitrobenzyl)propenyl phosphonate (**5c**, **g**) δ ^{31}P: 17.69 ppm. **4c**, **g/5c**, **g** = 0.24, Yield of **4c**, **g** and **5c**, **g** is 2.32 g or 65%. **4c**, **g** m.p. 109–110°C (recrystallized from ethylacetate and n-pentane), Anal. $C_{16}H_{24}NO_6P$ Calc. C, 53.78; H, 6.77; N, 3.92; Found C, 54.20; H, 6.77; N, 4.09. IR: 3310 (s, OH), 1640 (m, —CH=CH$_2$), 1230 (s, P=O) cm^{-1}. δ ^{1}H: 7.83 (d, d, AB type, 4H), 4.46 (b, H), 4.80–6.00 (m, 4H), 3.90–4.02 (m, 4H), 2.75–2.95 (m, H), 1.62–1.85 (m, 4H), 0.86–1.05 (m, 6H) ppm. m/z: 350 ($[m + 1]^+$, 37%), 339 ($[m - 18]^+$, 18%), 206 ($[m - 151]^+$, 67%), 164 ($[m - 193]^+$, 36%), 122 ($[m - 235]^+$, 87%). **5c**, **g** b.p. 168–170°C/0.004 Torr. Anal. $C_{16}H_{24}NO_6P$ Calc. C, 53.78; H, 6.77; N, 3.92; Found C, 54.13; H, 6.93; N, 4.27. IR: 3310 (s, OH), 1625 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. δ ^{1}H: 7.87 (d, d, AB type, 4H), 6.75–7.02 (m, H), 5.71 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.98 (t, J_{HH} = 6 Hz, H), 3.80–4.02 (m, 4H), 2.60–2.74 (m, 2H), 1.94 (b, H), 1.58–1.76 (m, 4H), 1.83 (t, t, J_{HH} = 7 Hz, $^5J_{Ph}$ = 1 Hz, 6 H) ppm. m/z: 358 ($[m + 1]^+$, 20%), 340 ($[m - 17]^+$, 1%), 206 ($[m - 151]^+$, 74%), 164 ($[m - 193]^+$, 32%), 122 ($[m - 235]^+$, 100%).

Reaction of **1d** and **3g** was being carried out as described above. Di(iso-propyl)α-(α′-hydroxy-p-nitrobenzyl)allylphosphonate (**4d**, **g**) δ ^{31}P: 25.38, 25.26 (1:1) ppm., E-Di(iso-propyl)γ-(α′-hydroxy-p-nitrobenzyl)propenylphosphonate (**5d**, **g**) δ ^{31}P: 15.38 ppm., **4d**, **g/5d**, **g** = 0.15. Yield of **4d**, **g** and **5d**, **g** is 2.13 g or 62%. **4d**, **g** m.p. 103–104°C (recrystallized from ethylacetate and n-pentane). Molecular weight calculated from $C_{16}H_{24}NO_6P$, 357.134; Found from high resolution mass spectrometry, 357.1328. IR: 3300 (s, OH), 1640 (m, —CH=CH$_2$), 1220 (s, P=O) cm^{-1}. δ ^{1}H: 7.84 (d, d, AB type, 4H), 4.60–6.00 (m, 6H), 4.46 (b, H), 2.60–3.00 (m, H), 1.22–1.44 (m, 12 H) ppm. m/z: 358 ($[m + 1]^+$, 38%), 340 ($[m - 17]^+$, 4%), 316 ($[m - 41]^+$, 10%), 206 ($[m - 151]^+$, 100%), 165 ($[m - 192]^+$, 74%), 122 ($[m - 235]^+$, 95%). **5d**, **g** b.p. 138–140°C/0.004 Torr. Anal. $C_{16}H_{24}NO_6P$ Calc. C, 53.78; H, 6.77; N, 3.92; Found C, 53.78; H, 6.78; N, 3.83. IR: 3300 (s, OH), 1625 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. δ ^{1}H: 7.88 (d, d, AB type, 4H), 6.68–7.00 (m, H), 5.72 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.97 (t, J_{HH} = 6 Hz, H), 4.54–4.68 (m, 2H), 2.64–2.74 (m, 2H). 1.80 (b, H), 1.22–1.44 (m, 12H) ppm. m/z: 358 ($[m + 1]^+$, 100%), 340 ($[m - 17]^+$, 4%), 316 ($[m - 41]^+$, 11%), 206 ($[m - 151]^+$, 47%), 164 ($[m - 193]^+$, 34%), 122 ($[m - 235]^+$, 96%).

Reaction of **1e** and **3g** was being carried out as described above. Di(tert-butyl)α-(α′-hydroxy-p-nitrobenzyl)allylphosphonate (**4e**, **g**) δ ^{31}P: 19.84, 18.69 (2:1) ppm. E-Di(tert-butyl)γ-(α′-hydroxy-p-nitrobenzyl)propenylphosphonate (**5e**, **g**) δ ^{31}P: 8.54 ppm. **4e**, **g/5e**, **g** = 0.05, **4e**, **g** m/z: 386 ($[m + 1]^+$, 28%), 368 ($[m - 17]^+$, 6%), 330 ($[m - 55]^+$, 42%), 274 ($[m - 101]^+$, 76%), 235 ($[m - 150]^+$, 21%), 122 ($[m - 253]^+$, 100%). Yield of **4e**, **g** is 2.09 g or 57%. **5e**, **g** decomposes during distillation under reduced pressure. IR: 3300 (s, OH), 1630 (m, —CH=CH—), 1395, 1370 [s, —C(CH$_3$)$_3$], 1220 (s, P=O) cm^{-1}. δ ^{1}H: 7.87 (d, d, AB type, 4H), 6.60–7.00 (m, H), 5.75 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.97 (t, J_{HH} = 6 Hz, H), 2.60–2.72 (m, 2H), 1.80 (b, H), 1.43 (d, J_{PH} = 2 Hz, 18 H) ppm. m/z: 386 ($[m + 1]^+$, 1%), 274 ($[m - 101]^+$, 3%), 122 ($[m - 253]^+$, 100%).

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