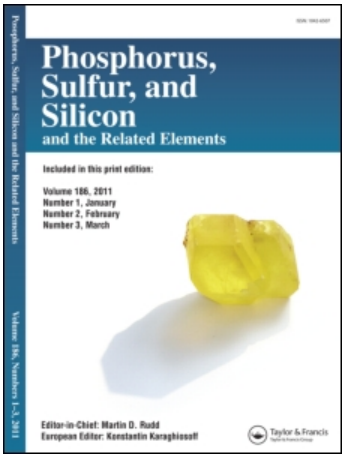

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XLIV. STRUCTURAL EFFECT OF ELECTROPHILES ON THE REGIOSELECTIVITY OF CARBANION DERIVED FROM DIALKYL ALLYLPHOSPHONATES

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS XLIV. STRUCTURAL EFFECT OF ELECTROPHILES ON THE REGIOSELECTIVITY OF CARBANION DERIVED FROM DIALKYL ALLYLPHOSPHONATES

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For the evaluation of the structural effect of electrophiles on the regioselectivity of ambident anions, the reaction of phosphoryl allylic carbanion with p-substituted benzaldehydes was investigated.

Key words: Allylphosphonate carbanion; regioselectivity; structural effect of electrophiles

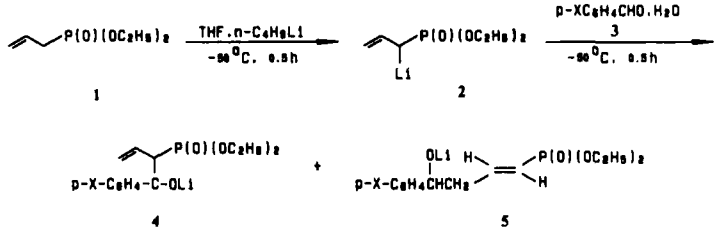
INTRODUCTION

The allylcarbanion stabilized by heteroatom comprises an important class of ambident carbanions with impressive regioselectivity which provides access to potential precursor for a variety of useful synthetic intermediates. The regioselectivity of the allylic carbanion is determined chiefly by the nature and structure of electrophiles. The change in regioselectivity as represented by $\alpha:\gamma$ ratio in the reaction of oxy allylic carbanion with alkyl halide in contrast to carbonyl electrophiles has been well documented.[1-3] It is therefore of interest to examine the regioselectivity of phosphoryl allylic carbanion toward electrophilic addition. As demonstrated by us[4] and others[5] the alkylation of the carbanion of allylphosphonate was shown to be highly α-regioselective. Being a part of systematic studies on the electrophilic addition of allylcarbanion derived from diethyl allylphosphonate and to evaluate the structural factors controlling the regioselectivity of these reaction systems, this paper is concerning with the investigation of the reaction of phosphoryl allylcarbanion with p-substituted benzaldehyde as electrophile. Moreover, the reaction mechanism and the structural effect of electrophile on the regioselectivity were examined by ^{31}P-NMR and MINDO/3 calculation.

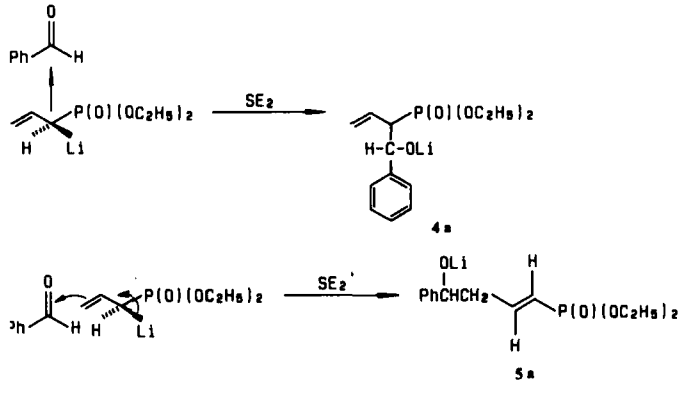
RESULTS AND DISCUSSIONS

1. Reaction mechanism of diethyl allylphosphonate anion with benzaldehyde

Reaction of diethyl allylphosphonate (**1**) with *n*-butyllithium in tetrahydrofuran (THF) at −50°C leads to the corresponding carbanion, α-lithium diethyl allylphosphonate (**2**). On subsequent reaction with benzaldehyde (**3a**), it was found that together with α-substituted product (**4**) formation of the γ-adduct (**5**) was also observed based on ^{31}P-NMR investigation. As shown by us, the ^{31}P-NMR chemical shift of α-substituted product is very close to that of its parent compound (27.8 ppm) while the δ^{31}P value of the γ-adduct exhibits an obvious up field trend (17.9 ppm).[6,7]



Our experimental data demonstrate that formation of **4** and **5** from **2** and **3a** proceeds probably through SE_2 and SE_2, mechanism, respectively.



If this is the case, the possibility of the equilibrium between reaction products **4a** and **5a** should be excluded. In the meantime, the reaction of ambident anion with electrophiles has been shown to proceed either by a thermodynamic controlled[8] or by a kinetic controlled[9,10] pathway. It is well established that the regioselectivity of a thermodynamic controlled reaction is determined by energy difference between two reaction products, while for a kinetically controlled reaction, the degree of nucleophilicity of two reaction centers plays a decisive role in regioselectivity of the ambident species. Upon alkyline hydrolysis of **4a** or **5a** in THF at −70°C for 0.5 hr, no equilibrium between these two isomeric products can be detected by ^{31}P—NMR technique. It seems that the raction of **2** with **3a** proceeds in a kinetic controlled manner under our experimental conditions.

TABLE I

Regioselectivity of the reaction of **2** with **3**

Item	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
X	H	CH_3	CH_3O	$(CH_3)_2N$	Cl	F	NO_2
$\alpha/\alpha+\gamma$(%)	92.4	93.0	93.4	90.7	89.5	83.6	23.1
$\gamma/\alpha+\gamma$(%)	7.6	7.0	6.6	9.3	10.5	16.4	76.9
α/γ(%)	12.1	13.3	14.1	9.7	8.5	5.1	0.30
$\log(\alpha/\gamma)$	1.08	1.12	1.15	0.99	0.93	0.17	0.52
Yield (%)	96	93	96	77	82	47	62

2. *Reaction of carbanion of diethyl allylphosphonates with p-substituted benzaldehydes*

The ambident carbanion, obtained by reaction of *n*-butyl lithium on diethyl allylphosphonate in THF at −70°C for 0.5 hr, was treated with *p*-substituted benzaldehyde (**3**) and followed by subsequent hydrolysis. After suitable treatment, the ratio of α-substituted product (4) and γ-substituted adduct (**5**) was estimated by ^{31}P NMR measurement.

For the purpose of investigating the structural effect of the electrophiles on the regioselectivity, a series of benzaldehydes with substituents of various electronic effects was used in which the interference of a steric effect was excluded. The data are summarized on Table I.

Data in Table I show that the regioselectivity of the addition reaction involving **2** and **3**, as represented by α/γ value, is markedly influenced by the nature of substituents of electropiles. As can be seen, these electrophilic additions exhibite α-regioselectivity except *p*-nitrobenzaldehyde which shows characteristic regioselectivity on γ-position.

The regioselectivity of ambident anion with electrophile can be rationalized by molecular orbital perturbation theory.[11] Upon comparison of the energy contribution from the charge or orbital interactions of the two reaction centers of the ambident anion toward electrophiles, the reaction center with higher stabilization (perturbation) energy usually provides higher reactivity or vice versa.

The MINDO/3 calculation of *p*-substituted benzaldehyde was performed on a primary structure which is optimized by molecular mechanics calculation using MM2 programme. (Table II).

Where q_c is the charge density of the carbonyl carbon atom, E and C represent the energy and orbital coefficient of the lowest unoccupied orbital, respectively.

TABLE II

MINDO/3 Calculation of **3**

Item	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
q_c	0.5923	0.5928	0.6030	0.6037	0.5958	0.6007	0.5819
E_{LUMO}	0.1822	0.1087	0.3849	0.5520	−0.0535	0.0281	−1.0445
C_{LUMO}	0.3887	0.3771	0.4091	0.4074	0.3822	0.3902	0.2667
δ^{12}	0	−0.17	−0.27	−0.83	0.23	0.06	0.78

Due to the limitation of the capacity of the MINDO/3 programme, NH_2 was used instead of $N(CH_3)_2$ in compound **3d**.

Since there is no parameter available for Li—C bond in MINDO/3 programme, an ab initio Gaussian 80 (STO-3G basic set) was used for the evaluation of the structural parameters of **2**. The primary configuration of **2** for this calculation was optimized by molecular mechanics using MM2 programme.[13] In order to simplify the estimation, the two ester ethyl groups in the carbanion molecule were replaced by two hydrogen atoms in ab initio calculation. The results are listed in Table III.

Where q_α and q_γ denote the charge density of the carbon atom located on α and γ position, respectively, E_{HOMO} is the energy of the highest occupied molecular orbital, E is the total energy. As shown in Table II and III, the magnitude of the charge density of the carbonyl carbon (q_c) as well as the orbital coefficient of the lowest unoccupied molecular orbital (C_{LUMO}) of various substituted benzaldehydes are very close, except for 3g. However, the energy of the lowest unoccupied molecular orbital (E_{LUMO}) of **3** changes significantly with the variation of the structure of substituents. The charge density of the α-carbon atom is substantially greater than that of the γ-carbon atom.

The kinetic-controlled reaction involving carbanion **2** with **3** is actually a set of two competition reactions. The regioselectivity of these reactions, as represented by $\log \alpha/\gamma$, is equal to the activation energy difference between these two competition reactions.

As demonstrated by regression analysis involving $\log \alpha/\gamma$ and some structural parameters of Table II, only E_{LUMO} provides a fair correlation coefficient, while the δ value of the substituents gives a less satisfactory result. However, there is no relationship between $\log \alpha/\gamma$ and q_c.

If these two competitive reactions were charge-controlled or orbital-controlled, according to the "Reactivity-Selectivity Principle"[14] the regioselectivity should be in the same direction, which is in contradiction to experimental results.

Since the ambident anion and electrophiles studied were treated by two different quantum chemical calculation methods, the difference of energy in $E_{LUMO} - E_{HOMO}$ in each pair of competition reaction is therefore not comparable. Further investigation is necessary for the quantitative evaluation of the effect of mutual interaction among orbitals.

As shown by data in Table I, II and III, the higher E_{LUMO} value of the electrophile is not favorable for the mutual effect of the orbitals and the reaction

TABLE III

An ab initio (Gaussian 80) calculation of **2**

Item	1s	2s	2Px	2Py	2Pz
C_α	0.02485	−0.06026	−0.26403	−0.48031	0.22114
C_γ	−0.00520	0.02809	0.15774	0.21164	−0.38453
	q_α			−0.31843	
	q_γ			−0.18213	
	E_{HOMO}			−0.21339	
	E (ev)			−681.2720	

was thus highly α-regioselective. Moreover, higher charge density of the α-carbon of the ambident anions is preferable to mutual effects between charges. Therefore, the reactivity on α-position should be considered as the charge controlled reaction. On the other hand, decrease of the E_{LUMO} value of the electrophile will bring significant variation in reaction regioselectivity, and $\log \alpha/\gamma$ correlates linearly with E_{LUMO}. Where the difference of charge density of the carbonyl carbon atom has little influence on the reaction regioselectivity. These facts show that reaction in γ-position is orbital controlled.

On the basis of our experimental results, the following conclusion can be drawn. The localized carbanion derived from diethyl allylphosphonate behaves as ambident anion, which undergoes a kinetic controlled reaction with benzaldehyde via SE_2 or $SE_{2'}$ mechanism. Due to the fact that the reaction on the α-carbon atom is charge controlled, whereas that on the γ-carbon atom is orbital controlled, a high charge density on the carbonyl carbon atom of the ambident is favourable to α-regioselective reaction and a low E_{LUMO} value of substituted benzaldehyde is preferable to regioselective reaction on the γ-position of the ambident carbanion.

EXPERIMENTAL

The ratio of the α-product over γ-adduct in 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 μsec, 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 on a Varian XL-200 Spectrometer. IR spectra were recorded on a IR-440 Spectrophotometer. MS were taken on a Finnigan 4021 Spectrometer. Melting points were determined on a Kofler Hotplate, uncorrected.

The MINDO/3 and ab initio calculations as well as molecular mechanics calculation using MM2 programme were performed on a VAX-780 computer at Shanghai Institute of Organic Chemistry.

MINDO/3 calculation of **3**—The primary structure of **3** was optimized by molecular mechanics calculation using MM2 programme. Only substituted groups were optimized by MINDO/3 method.

ab initio calculation of **2**—The initial structure was established by MM2 calculation. Ab initio calculation was carried out by using Gaussian 80 (STO-3G basis set) programme. The structure was optimized by the bond length of Li—C, C—C and C=C as well as by the bond angle of Li—C—C.

Reaction of **2** with **3a** or **3b** was carried out as described.[15]

Reaction of **2** *with* **3c** To a stirred mixture of **1** (1.78g, 10 mmole) in THF (30 mL) chilled to −70°C, n-C_4H_9Li (10 mmole) was introduced and stirred for 0.5 hr., a solution of p-methoxy benzaldehyde (1.36 g, 10 mmole) in THF (10 mL) was then added. After reaction for an additional 0.5 hr., the mixture was hydrolyzed immediately followed by addition of 50 mL dichloromethane. The organic solution was washed with water and dried over anhydrous sodium sulfate. Upon removal of the solvent under reduced pressure, the residue was examined by ^{31}P NMR and purified by column chromatography on silica gel. Diethyl α-(α'-hydroxy-p-methoxybenzyl)-allylphosphonate (4c) δ^{31}P: 27.89, 27.51(2.1:1) ppm.[15] Diethyl (E)-γ-(α'-hydroxy-p-methoxybenzyl)-propenyl phosphonate (**5c**) δ^{31}P: 17.91 ppm. **4c**/**5c** = 14.1. Thus 2.81 g 6c, b.p. 138–139°C/0.02 Torr. Anal. $C_{15}H_{23}O_5P$. Calc. C, 57.32; H, 7.37; P, 9.85; Found C, 57.40; H, 7.48; P, 9.63. IR 3320 (s, OH), 1640 (m,—CH=CH_2), 1240 (s, P=O) cm^{-1}. ^{1}H NMR 7.04 (q, 4H, —$C_6H_4OCH_3$-p), 4.70–6.00 (m, 4H), 4.04–4.28 (m, 4H), 3.79 (s, 3H, —$C_6H_4OCH_3$-p), 2.63–3.00 (m, H), 1.74 (br, H), 1.22–1.40 (m, 6H) ppm. MS (m/z) 315 ($m^+ + 1$, 1%), 297 ($m^+ - 17$, 97%), 178 ($m^+ - 136$, 100%). **7c** b.p. 146– 148°C/0.01 Torr. Anal. $C_{15}H_{23}O_5P$ Calc. C, 57.32; H, 7.37; Found C, 57.26; H, 7.26. IR 3340 (s, OH), 1630 (m,—CH=CH—), 1240 (s, P=O) cm^{-1}. ^{1}H NMR 7.07(q, 4H, —$C_6H_4OCH_3$-p), 6.61–6.93 (m, H), 5.70 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.81 (t, J_{HH} = 7 Hz, H), 3.90–4.10 (m, 4H), 3.80 (s, 3H, —$C_6H_4OCH_3$-p), 2.60–2.80 (m, 2H), 2.20 (br, H), 1.29 (t, t, $^4J_{PH}$ = 4 Hz, J_{HH} = 7 Hz, 6H) ppm. MS (m/z) 315 ($m^+ + 1$, 19%), 297 ($M^+ - 17$, 100%), 178 ($M^+ - 136$, 65%).

Reaction of **2** *with* **3d** The experimental condition was similar to that of above, diethyl α-(α′-hydroxy-*p*-dimethylamino benzyl)-allylphosphonate (**4d**) δ^{31}P: 28.19, 27.73 (1:1) ppm. diethyl (*E*)-γ-(α′-hydroxy-*p*-dimethylaminobenzyl)-propenyl phosphonate (**5d**) δ^{31}P: 18.21 ppm. **4d/5d** = 9.7, obtained 2.51 g **4d** and **5d**, with yield 77%. **4d** m.p. 123–124°C (recrystallized from ethyl acetate and pentane), Anal. $C_{16}H_{26}NO_4P$, Calc. C, 58.70, H, 8.01, N, 4.28. Found C, 58.92, H, 8.20, N, 4.31. IR 3310 (s, OH), 1640 (m, —CH=CH_2), 1225 (s, P=O) cm^{-1}. ^{1}H NMR 6.93 (q, 4H, —$C_4H_6N(CH_3)_2$-*p*), 4.87–6.10 (m, 4H), 4.04–4.22 (m, 4H), 3.70 (br, H) 2.56–3.10 (m, H), 2.91 (s, 6H, —$C_6H_4N(CH_3)_2$-*p*), 1.24–1.38 (m, 6H) ppm. MS (*m/z*) 327 (m^+, 11%), 310 ($m^+ - 17$, 52%), 178 ($m^+ - 149$, 62%), **7d**, b.p. 150–152°C/0.005 Torr. Anal. $C_{16}H_{26}NO_4P$, Calc. C, 58.70, H, 8.01, N, 4.28; Found C, 59.21, H, 8.04, N, 4.57. IR 3340 (s, OH), 1632 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. ^{1}H NMR 6.92 (q, 4H, —$C_6H_4N(CH_3)_2$-*p*), 6.40–6.80 (m, H), 5.61 (d, d, J_{HH} = 14 Hz, J_{PH} = 21 Hz, H), 4.72 (t, J_{HH} = 7 Hz, H), 3.80–4.10 (m, 4H), 2.92 (s, 3H, —$C_6H_4N(CH_3)_2$-*p*), 2.90 (s, 3H, —$C_6H_4N(CH_3)_2$-*p*), ~2.90 (br, H), 2.50–2.90 (m, 2H), 1.05–135 (m, 6H) ppm. MS (*m/z*) 327 (m^+, 5%), 310 ($m^+ - 17$, 20%), 309 ($m^+ - 18$, 51%), 178 ($m^+ - 149$, 15%).

Reaction of **2** *with* **3e** Analogously, a mixture of diethyl α-(α′-hydroxy-*p*-chloro-benzyl) allylphosphonate (**4e**) δ^{31}P: 27.39, 27.24 (1.6:1) ppm. diethyl (E)-γ-(α′-hydroxy-*p*-chloro-benzyl)-propenyl phosphonate (**5e**) δ^{31}P: 17.75 ppm. was obtained with **4e/5e** ratio, 8.5. Thus 2.33 g **4e** and 0.27 g **5e** obtained. Yield, 82%. **4e**, 122–124°C/0.01 Torr. Anal. $C_{14}H_{20}ClO_4P$ Calc. C, 52.76, H, 6.32, P. 9.72; Found C, 52.94, H, 6.76, P, 9.44. IR 3300 (s, OH), 1638 (m, —CH=CH_2), 1230 (s, P=O) cm^{-1}. ^{1}H NMR 7.10–7.36 (m, 4H, —C_6H_4Cl-p), 4.82–6.00 (m, 3H), 5.24 (d, d, J_{HH} = 8 Hz, J_{PH} = 12 Hz, H), 4.00–4.30 (m, 4H0, 2.70–3.00 (m, H), 1.58 (br, H), 1.20–1.42 (m, 6H) ppm. MS (*m/z*) 319 ($m^+ + 1$, 45%), 301 ($m^+ - 17$, 14%), 178 ($m^+ - 140$, 100%). **5e**, b.p. 140–142°C/0.01 Torr. Anal. $C_{14}H_{20}ClO_4P$ Calc. C, 52.76, H, 6.32, P, 9.72, Found C, 53.04, H6.37, P, 9.91. IR 3320 (s, OH), 1632 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. ^{1}H NMR 7.10–7.35 (m, 4H), 6.65–6.85 (m, H), 5.67 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.82 (t, J_{HH} = 7 Hz, H), 3.90–4.12 (m, 4H), 2.56–2.68 (m, 2H), ~2.60 (br, H), 1.27 (t, t, $^4J_{PH}$ = 1 Hz, J_{HH} = 7 Hz, 6H) ppm. MS (*m/z*) 319 ($m^+ + 1$, 1%), 301 ($m^+ - 17$, 1%), 178 ($m^+ - 140$, 100%).

Reaction of **2** *with* **3f** The experimental condition was similar as described above, but the amount of reagent was deduced to **2** mmole, diethyl α-(α′-hydroxy-*p*-fluoro-benzyl)-allylphosphonate (**4f**) δ^{31}P: 27.42, 27.23 (2.1:1) ppm. dithyl (*E*)-γ-(α′-hydroxy-*p*-fluoro-benzyl)-propenyl phosphonate (**5f**) δ^{31}P: 17.90 ppm. **4f/5f** = 5.1, 0.24 g **4f** and 0.04 g **5f** was obtained, yield, 47%. **4f** b.p. 118–120°C/0.05 Torr. IR 3320 (s, OH), 1640 (m, —CH=CH_2), 1220 (s, P=O) cm^{-1}. ^{1}H NMR 6.92–7.34 (m, 4H), 4.80–6.00 (m, 4H), 3.95–4.16 (m, 4H), 2.60–3.00 (m, H), ~2.00 (br, H), 1.23–1.33 (m, 6H) ppm. MS (*m/z*) 303 ($m^+ + 1$, 23%), 285 ($m^+ - 17$, 81%), 178 ($m^+ - 124$, 84%). **5f**, IR 3330 (s, OH), 1632 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. ^{1}H NMR 6.92–7.35 (m, 4H), 6.60–6.90 (m, H), 5.70 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.82 (t, J_{HH} = 7 Hz, H), 3.90–4.10 (m, 4H), 3.40 (br, H), 2.50–2.78 (m, 2H), 1.27 (t, t, $^4J_{PH}$ = 1.5 Hz, J_{HH} = 7 Hz, 6H) ppm. MS (*m/z*) 303 ($m^+ + 1$, 6%), 285 ($m^+ - 17$, 1%), 178 ($m^+ - 124$, 100%).

Reaction of **2** *with* **3g** Analogously, diethyl α-(α′-hydroxy-*p*-nitro-benzyl)-allylphosphonate (**4g**) δ^{31}P: 27.68, 27.24 (1.5:1) ppm. Diethyl (*E*)-γ-(α′-hydroxy-*p*-nitro-benzyl)-propenyl phosphonate (**5g**) δ^{31}P: 17.69 ppm. with **4g/5g** ratio of 0.3, was obtained 2.04 g **4g** and **5g**, yield 62%. **4g**, m.p. 112–113°C (recrystallized from ethyl ether). Anal. $Cl_4H_{20}NO_6P$, Calc. C, 51.07, H, 6.12, N, 4.25; Found C, 51.23, H, 6.26, N, 4.28. IR 3290 (s, OH), 1640 (m, —CH=CH_2), 1225 (s, P=O) cm^{-1}. ^{1}H NMR: 7.84 (q, 4H, —$C_6H_4NO_2$-*p*), 4.84–6.00 (m, 4H), 4.07–4.29 (m, 4H), 2.74–2.86 (m, H), 1.70 (br, H), 1.34 (t, J_{HH} = 7 Hz, 6H) ppm. MS (m/z) 330 ($M^+ + 1$, 30%), 312 ($m^+ - 17$, 15%), 178 ($m^+ - 151$, 100%). **5g**, b.p. 176–177°C/0.006 Torr. Anal. $C_{14}H_{20}NO_6P$, Calc. C, 51.07, H, 6.12, N, 4.25; Found C, 51.06, H, 6.32, N, 4.52. IR: 3300 (s, OH), 1632 (m, —CH=CH—), 1220 (s, P=O) cm^{-1}. ^{1}H NMR: 7.84 (q, 4H, —$C_6H_4NO_2$-*p*), 6.66–6.98 (m, H), 5.69 (d, d, J_{HH} = 17 Hz, J_{PH} = 21 Hz, H), 4.96 (t, J_{HH} = 7 Hz, H), 3.90–4.06 (m, 4H), 2.65 (d, d, J_{HH} = 6 Hz, 2H), ~1.60 (br, H), 1.26 (t, t, $^4J_{PH}$ = 2.4 Hz, J_{HH} = 7 Hz, 6H) ppm. MS (*m/z*): 330 ($m^+ + 1$, 100), 312 ($m^+ - 17$, 8%), 178 ($m^+ - 151$, 97%).

Experimental condition for the kinetic controlled reaction of **2** with **3a** 0.28 g (1 mmole) **a** in 3 mL THF, −70°C, 1 mmole n-C_4H_9Li was added, and reacted for 0.5 hr, followed by hydrolysis. δ^{31}P: 27.84, 27.58 ppm. 0.28 g (1 mmole) **5a** in 3 mL THF, −70°C, 1 mmole *n*-C_4H_9Li was added, reacted for 0.5 hr, followed by hydrolysis. δ^{31}P: 17.97 ppm.

Experimental condition for the mechanism of the reaction of **2** *with* **3a** **2** in 5 mm NMR tube, its concentration was 0.75 mole dm^{-3}, −50°C, δ^{31}P: 26.38 ppm; **3a** was added, **4**, δ^{31}P: 32.16 ppm, and **5**, δ^{31}P: 19.02 ppm, were resulted in the meantime, hydrolysis, the ratio of **4a/5a** was about 4.0.

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