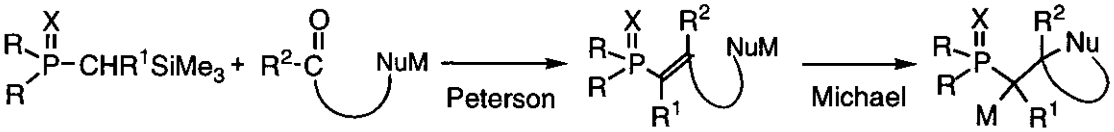
TANDEM PETERSON-MICHAEL REACTION USING α-SILYLALKYLPHOSPHINE CHALCOGENIDES AND HORNER-EMMONS REACTION OF *IN SITU* GENERATED α-CARBANIONS OF ITS PRODUCTS[†]

Takayuki Kawashima,* Mio Nakamura, and Naoki Inamoto
Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Abstract- Title tandem reaction was achieved by using α-(trimethylsilyl)-alkylphosphine chalcogenides and the lithio derivative of 2-hydroxytetrahydropyran. The Horner-Emmons reaction of the tandem products was accomplished to give the corresponding 2-(β-styryl)tetrahydropyran derivatives by *in situ* generation and trapping of α-lithio derivatives, followed by Warren's method of olefination.

INTRODUCTION

Tandem Michael addition and intramolecular Wittig reactions using vinylphosphonium salts or vinylphosphine oxides have been utilized as one of useful methods for synthesis of cyclic or heterocyclic ene compounds.[1] Tandem aza-Wittig reaction/cyclization has been developed for the synthesis of nitrogen-containing heterocycles.[2] The title tandem reaction can be expected in the reaction of α-silyl-α-phosphoryl carbanions[3] with carbonyl compounds having a nucleophilic moiety, giving cyclic compounds functionalized at the side chain. In the previous communication we reported this tandem reaction using 2-lithiooxytetrahydropyran and the Horner-Emmons reaction of the products.[4] In this paper we wish to describe the detailed results.



[†] Dedicated to Professor Emeritus Shigeru Oae of Tsukuba University on the occasion of his 77th birthday.

RESULTS AND DISCUSSION

Tandem Peterson-Michael Reaction Using α-Silylalkylphosphine Chalcogenides.

The sequential reactions of α-trimethylsilylalkylphosphine chalcogenides (**1**) (**a**: R^1=R^2=Ph, R^3=H, X=O; **b**: R^1=R^2=Ph, R^3=H, X=S; **c**: R^1=R^2=Ph, R^3=Me, X=O; **d**: R^1=R^2=Ph, R^3=Me, X=S; **e**: R^1=Ph, R^2=*o*-$MeOC_6H_4$ (*o*-Anisyl), R^3=H, X=O) with *n*-BuLi and then 2-lithiooxytetrahydropyran (**2**), which was prepared by the lithiation of 2-hydroxytetrahydropyran, in tetrahydrofuran (THF) gave the tandem Peterson-Michael products (**3**), the Peterson products (**4**), and their allylic isomers (**5**). The results are summarized in Table 1.

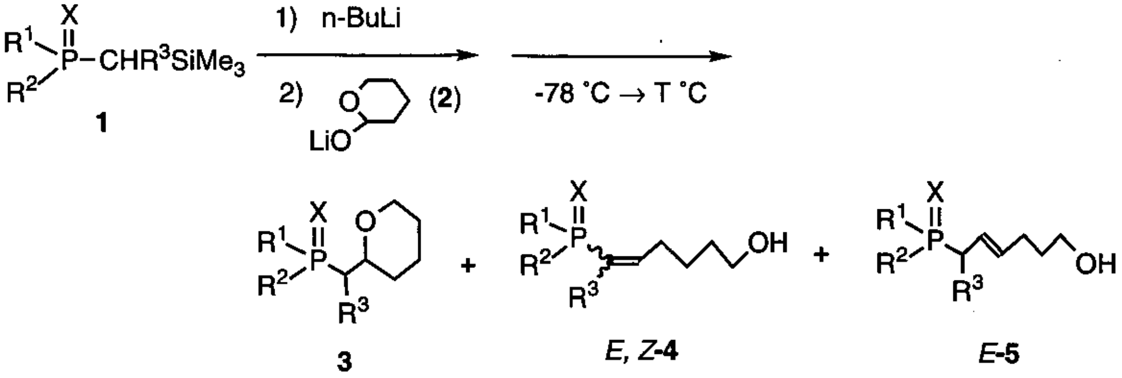


Table 1. Tandem Peterson-Michael Reaction of **1** with **2**[a]

Run	1	R^1	R^2	R^3	X	T/°C	Time/h	Yields[b]/%			
								3	*Z*-**4**	*E*-**4**	*E*-**5**
1	**1a**	Ph	Ph	H	O	0	0.5	-	-	14	72
2	**1a**	Ph	Ph	H	O	r.t.[c]	48	94	-	-	-
3	**1b**	Ph	Ph	H	S	0	3	13	6	44	36
4	**1b**	Ph	Ph	H	S	r.t.	73	36	4	27	32
5	**1b**	Ph	Ph	H	S	reflux	24	70	1	5	22
6	**1c**	Ph	Ph	Me	O	r.t.	24	50[d]	-	50	-
7	**1d**	Ph	Ph	Me	S	r.t.	48	-	-	59	40
8	**1d**	Ph	Ph	Me	S	reflux	16	-	-	50	50
9	**1e**	Ph	*o*-Anisyl	H	O	r.t.	48	56[e]	-	-	20

a) A solution of **1** (*ca.* 1 mmol) in THF (20 ml) was reacted with **2** (1.1 equiv.) at -78 °C and the reaction mixture was kept at T °C with stirring. b) Yields were obtained by glc. c) Room temperature. d) Diastereomeric ratio: 1.5:1. e) Diastereomeric ratio: 1.4:1.

Stereochemistry of the products (**4**) was determined from the magnitude of vicinal coupling constants ($^3J_{HH}$) between olefinic protons, which were obtained by decoupling allylic protons. The values are about 16 Hz and 12 Hz for *E*- and *Z*-isomers, respectively. On the other hand, geometry of **5** was estimated by differential NOE experiments. The NOE between methylene protons or methine proton of C-1 and allylic protons of C-4 was not observed for *E*-isomers. Quenching temperature dependence of the Peterson reaction was investigated using simple reaction of **1a**-**c** with hexanal and the results are summarized in Table 2. The Peterson reaction of **1a** took place at - 78 °C to give *Z*-**6a** predominantly.[3b] The stereochemistry of **6** and **7** was determined by the method similar to that for **4** and **5**. When the quenching temperature raises to room temperature *E*-**6a** and *E*-**7a** were obtained in 29 and 70% yields, respectively. The results indicate that base-catalyzed isomerization of **6a** by $LiOSiMe_3$, which was formed together with **6a** by the Peterson reaction, occurred under the conditions. But, in the cases of the reactions of **1b** and **1c**, the ratio of *Z*-**6**/*E*-**6** was independent on the temperature and the reaction time, indicating that $LiOSiMe_3$ is not strong enough base to catalyze isomerization of **6b** and **6c**.

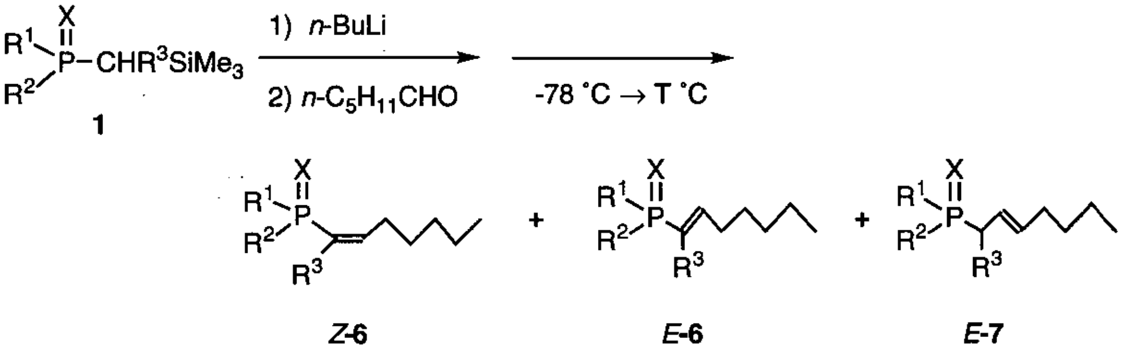


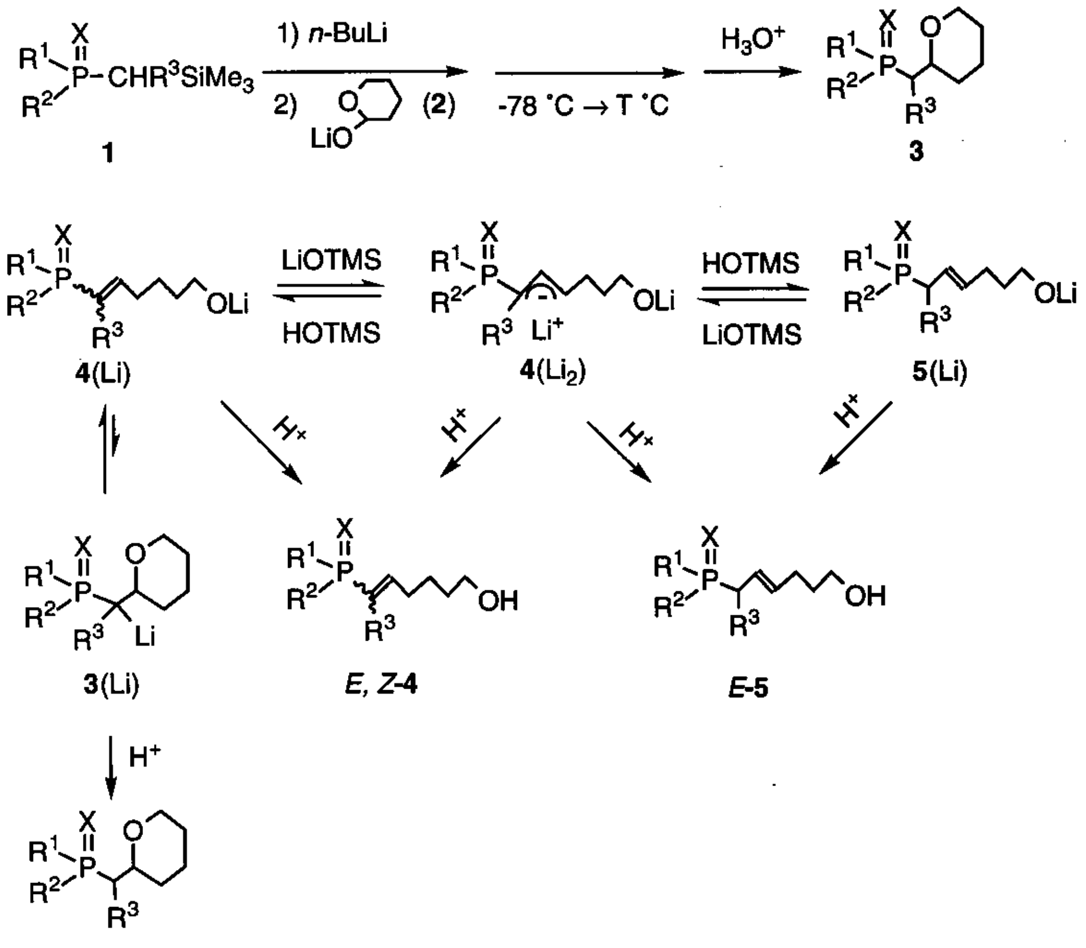
Table 2. The Peterson Reaction of **1** with Hexanal

								Yields[a]/%		
Run	**1**	R^1	R^2	R^3	X	T/°C	Time/h	*Z*-**6**	*E*-**6**	*E*-**7**
1	**1a**	Ph	Ph	H	O	-78	2	69	30	-
2	**1a**	Ph	Ph	H	O	r.t.[b]	12	-	29	70
3	**1b**	Ph	Ph	H	S	-78	2	50	50	-
4	**1b**	Ph	Ph	H	S	r.t.	14	50	50	-
5	**1c**	Ph	Ph	Me	O	r.t.	2	60	39	-

a) Yields were obtained by glc. b) Room temperature.

Taking into consideration the above results, the data in Table 1 strongly suggest that $LiOSiMe_3$ can catalyze the relatively rapid equilibration of **4**(Li) and **5**(Li) (see plausible mechanism). In addition, **4**(Li) is also in equilibrium with **3**(Li). The latter equilibrium lies much toward **4**(Li), as clarified from the results of the deprotonation of **3** (see below). Therefore, an irreversible protonation of **3**(Li) seems to be driving force for the formation of **3**. Stirring at room temperature was enough to produce **3a**, whereas reflux conditions were necessary to obtain **3b** in good yield (Table 1). To our knowledge, this is the first example of a tandem Peterson-Michael reaction.

Plausible mechanism



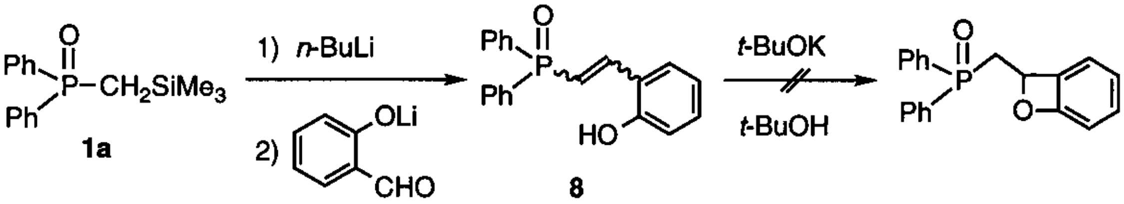
This isomerization seems to take place readily when a stronger base than $LiOSiMe_3$ is used. Thus, the Peterson reaction products (**4a-d**) and (*E*-**5e**) were treated with *t*-BuOK in *t*-BuOH at room temperature to give **3a-e** as shown in Table 3. In the latter three cases diastereomeric mixtures of **3c-e** were obtained in ratios of 1.5:1, 2.6:1 and 1.3:1, respectively.

Table 3. Isomerization of **4** or **5** with *t*-BuOK[a]

Run	4[c] or 5	R^1	R^2	R^3	X	Yields[b]/% 3	4	*E*-5
1	**4a**	Ph	Ph	H	O	100	0	0
2	**4b**	Ph	Ph	H	S	100	0	0
3	**4c**	Ph	Ph	Me	O	66 (1.5:1)[d]	0	34
4	**4d**	Ph	Ph	Me	S	100 (2.6:1)[d]	0	0
5	*E*-**5e**	Ph	*o*-Anisyl	H	O	100 (1.3:1)[d]	0	0

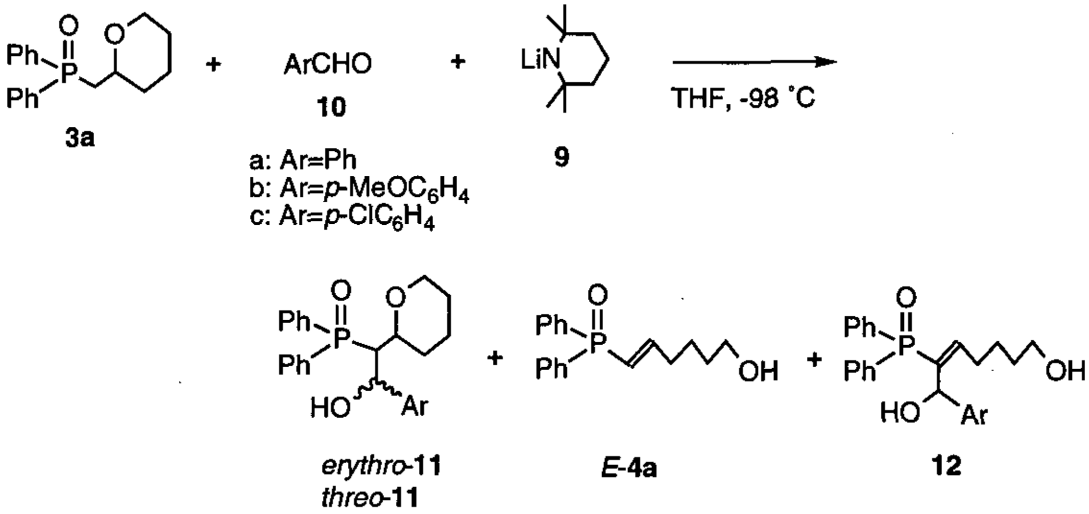
a) The reaction was carried out at room temperature for 2 days. b) Yields were obtained by glc.
c) Diastereomeric ratio. c) *E*/*Z* mixture was used. d) Diastereomeric ratio.

The tandem Peterson-Michael reaction using **1a** and salicylaldehyde was unsuccessful. The reaction products were the Peterson reaction products, 2-hydroxystyrylphosphine oxides(*Z*-**8**)(24%) and(*E*-**8**)(8%), but they did not undergo intramolecular Michael addition even in the presence of *t*-BuOK, because of an increase in strain energy emerging from the formation of four-membered ring.

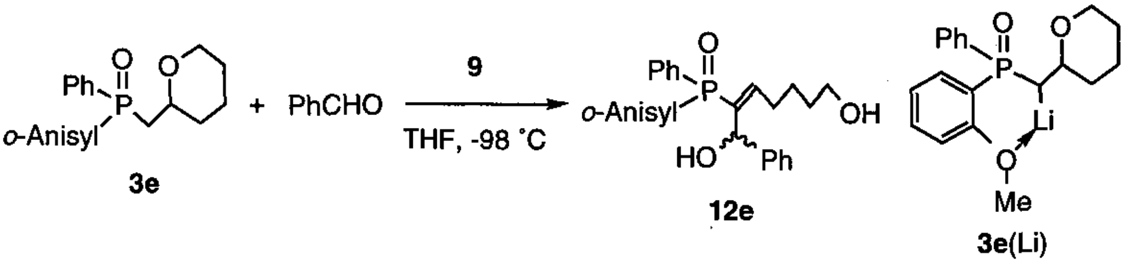


In situ Generation and Trapping of the α-Lithio Derivative of 3 with Carbonyl Compounds.

The deprotonation of **3** with alkyllithium reagents resulted in β-elimination with ring opening (→*E*-**4**) as normally expected for a carbanion bearing a good leaving group at the β-position, though there are a few cases where such elimination does not occur.[5] Even in the case of **3e**, whose α-lithio derivative can be expected to be stabilized by intramolecular chelation (**3e**(Li)) of *o*-methoxyl group, ring opening to **4e**(Li) could not be avoided. Therefore, *in situ* generation and trapping of the α-lithio derivative of **3** seemed to offer the best chance for bringing about the Horner-Emmons reaction. Thus, the reaction of **3a** with lithium 2,2,6,6-tetramethylpiperidide (**9**), a well-known hindered base, in the presence of aromatic aldehydes (**10a-c**) gave mainly a mixture of diastereomers of **11a-c**, together with β-elimination products (**4a**) and (**12a-c**), which were formed by abstraction of a vinyl proton (R^1) of **4a**, followed by the reaction with **10a-c** (Table 4). Structural determination (*erythro* or *threo*) for **11** was carried out from the geometry of the olefin obtained by Warren's method of olefination as described later. *Erythro-* and *threo-***11a-c** were readily separated by chromatography.

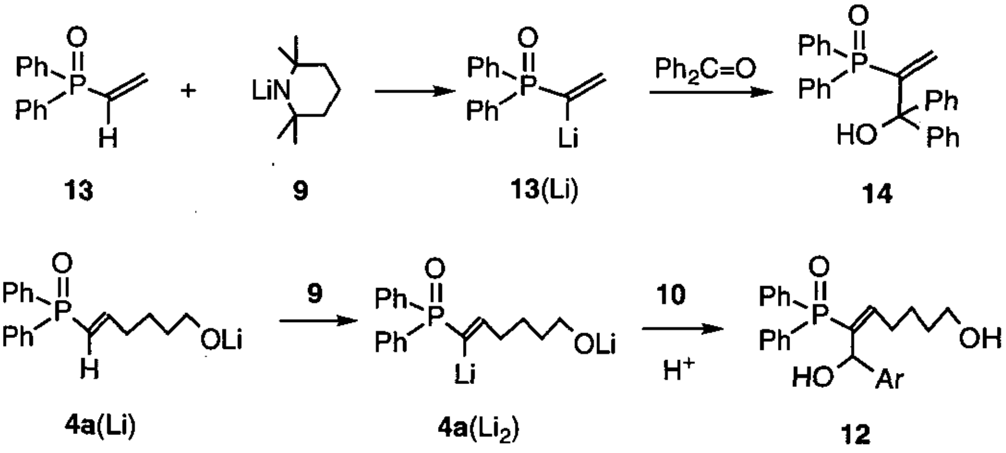


The reactions using **3b**, **3c**, and **3e** under the same reaction conditions as described in the case of **3a** gave **3b** (89% recovery), *E*-**4c** (69%), and **12e** (34%), respectively. The formation of **12e** instead of **11e** can reasonably be understood by steric hindrance of the *o*-methoxyphenyl group.

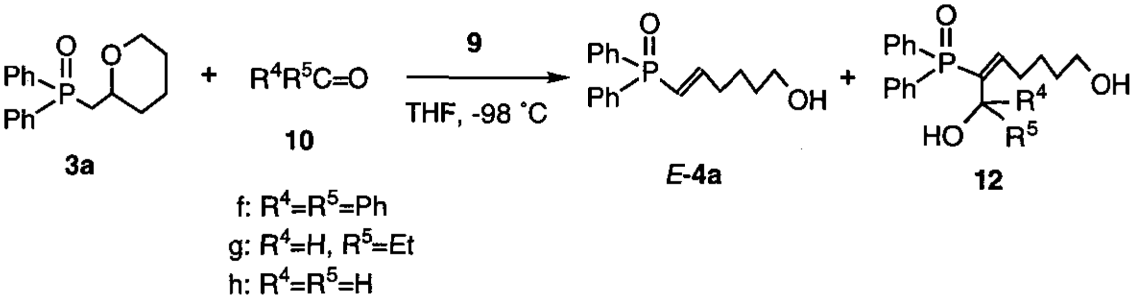


A formation mechanism of **12** *via* **11** was ruled out, because **11** was unchanged under the same reaction conditions. The fact that a similar reaction of diphenylvinylphosphine oxide (**13**) with benzophenone gave

1-(hydroxydiphenylmethyl)ethenyl(diphenyl)phosphine oxide (**14**) suggests the direct deprotonation of vinyl group of **4a**(Li). Therefore, **12a-c** are considered to be formed by abstraction of a vinyl proton of **4a**(Li), which was obtained by retro-Michael addition of **3a**, followed by the reaction with **10a-c** (Table 4).



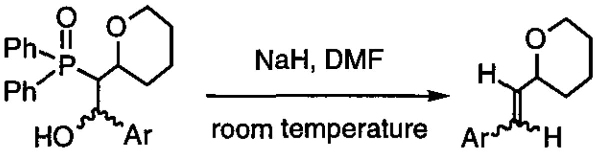
The reactions using benzophenone (**10f**), propanal (**10g**), and paraformaldehyde (**10h**) less reactive than aromatic aldehydes did not give products type of **11**, but **12g-h** in 50-71% yields (See Table 4).



Considering the facts that the reactions of **3b** and **3c** under the same conditions resulted in recovery of **3b** and the formation of a retro-Michael addition product (**4c**), respectively, and that in the cases of the reactions using **3a** and **10f-h** β-elimination occurred in preference to trapping reaction to give **4a** and **12f-h** via **4a**(Li), stability of the first formed α-carbanion and reactivity of carbonyl compounds are concluded to be very important elements for the formation of **11**.

The Olefin Formation from 11 by Warren's Method of Olefination.

The stereospecific olefin formation from β-hydroxyalkyl(diphenyl)phosphine oxides has been reported to proceed *via syn*-elimination of the diphenylphosphinate by Warren and co-workers.[6] According to the Warren's method, less polar and polar diastereomers of **11a-c** were treated with NaH in dimethylformamide (DMF) at room temperature to give strereospecifically the corresponding *Z*- and *E*-olefins (**15a-c**) in fairly good yields, respectively (Table 4). Thus, less polar and polar isomers were identified to be *erythro* and *threo* isomers, respectively. Unfortunately, a similar reaction using benzophenone adduct(**12f**) gave no corresponding allenic compound.



erythro-**11**
threo-**11**

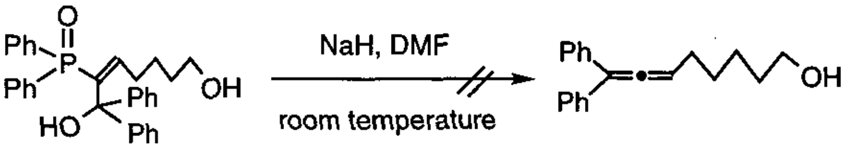
Z-**15**
E-**15**

Table 4. The Horner-Emmons Reaction of **3a**[a]

	Yields[b]/%				Yields[c]/%	
	4a	*erythro*-**11**	*threo*-**11**	**12**	*Z*-**15**	*E*-**15**
PhCHO	0	51	22	14	54	64
p-$MeOC_6H_4CHO$	0	35	22	19	87	67
p-ClC_6H_4CHO	11	25	49	11	65	57
Ph_2CO	18	-	-	71	-	-
$(CH_2O)n$	18	-	-	50	-	-
CH_3CH_2CHO	37	-	-	51	-	-

a) Six equivalents of LiTMP and carbonyl compounds were reacted at -98 °C in THF.

b) Isolated yields based on consumed **3a**. c) Isolated yields based on *erythro*- or *threo* **11**.



12f

In conclusion, tandem Peterson-Michael reaction was demonstrated for the first time by using α-lithio-α-silylphosphine chalcogenides with 2-lithiooxytetrahydropyran. *In situ* generation and trapping of α-lithio derivative of the tandem reaction product, followed by Warren's method of olefination gave 2-(β-styryl)tetrahydropyran derivatives. This *in situ* generation and trapping may provide one useful method for the Horner-Emmons reaction using various phosphoryl compounds having a leaving group at the β-position to the phosphorus atom.

ACKNOWLEDGEMENT

The Authors thank Tosoh Akzo Co. Ltd. and Sin-etsu Kagaku Co. for gifts of alkyllithium and chlorotrimethylsilane, respectively. This work was partially supported by a Grant-in-Aid for General Scientific Research from the Ministry of Education, Science, and Culture, Japan.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H-Nmr spectra were measured with a JOEL FX-90Q (90 MHz) and Bruker AM-500 (500 MHz) spectrometer using tetramethylsilane (TMS) as internal standard. ^{13}C-Nmr spectra were taken with a JEOL FX-90Q (22.5 MHz) or a Bruker AM-500 (125 MHz) spectrometer using TMS as internal standard. ^{31}P-Nmr spectra were recorded with a JEOL FX-90Q (36.3 MHz) spectrometer using 85% H_3PO_4 as external standard. Ir spectra were taken with a Hitachi 260-30 spectrophotometer. Mass spectra were measured at 70 eV with a JEOL 300-D or JEOL JMS-SX102A mass spectrometer. Preparative high-performance liquid chromatography (hplc) was carried out with LC-08 (column: Japan Analytical Industry, JAIGEL 1H+2H, styrene-divinylbenzene copolymer, pore size 25 Å) using chloroform as a solvent. Gas chromatography was performed with a Shimadzu GC-7A gas chromatograph (column: 2% Silicone DC QF-1 80/100 mesh Chromosorb W-AW-DMCS). Dry column chromatography (DCC) and preparative thin-layer chromatography (ptlc) was carried out using ICN silica DCC 60A and Merck Kieselgel 60 PF254 Art. 7747, respectively. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of α-Silylalkylphosphine Chalcogenides (1).

Diphenyl(trimethylsilylmethyl)phosphine oxide (**1a**[7]) and sulfide (**1b**[7]) were prepared by oxidation and sulfurization of diphenyl(trimethylsilylmethyl)phosphine[8] in 94 and 31% yields, respectively. Diphenyl(1-trimethylsilylethyl)phosphine oxide (**1c**[9]) and sulfide (**1d**) were obtained by sequential treatment of **1a** and **1b** with *n*-BuLi and with MeI, in 77% and 57% yields, respectively. *o*-Methoxyphenylphenyl(trimethylsilylmethyl)phosphine oxide (**1e**) was prepared by sequential treatment of ethyl *o*-methoxyphenylphenylphosphinate with thionyl chloride and with trimethylsilylmethylmagnesium chloride[10] in 46% yield.

1d: mp 112.0-113.7 °C (hexane). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= -0.04 (s, 9H, Si(C$\underline{H}_3$)$_3$), 1.23 (dd, $^3J_{HH}$=7.1 Hz, $^3J_{HP}$=20.3 Hz, 3H, CHC$\underline{H}_3$), 2.05-2.45 (m, 1H, PCH), 7.18-7.53 (m, 6H, *m,p*-H of Ph), and 7.77-8.18 (m, 4H, *o*-H of Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 48.3. HRms : *m/z* Found: 320.0947. Calcd for $C_{17}H_{23}PSSi$: 320.0953.

1e: mp 57.5-59.1 °C (hexane). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.03 (s, 9H, Si(C$\underline{H}_3$)$_3$), 1.66-2.14 (m, 2H, PC$\underline{H}_2$), 3.77 (s, 3H, OC$\underline{H}_3$), 6.76-7.24 (m, 2H), 7.30-7.53 (m, 4H), and 7.61-8.28 (m, 3H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 29.4. HRms : *m/z* Found: 318.1188. Calcd for $C_{17}H_{23}O_2PSi$: 318.1205.

Tandem Peterson-Michael Reaction of 1 with 2.

General procedure: Tandem Peterson-Michael reaction of **1**: Compound (**1**) (*ca.* 1 mmol) was allowed to react with 1.1 equiv of *n*-BuLi at -78 °C in tetrahydrofuran (THF) (20 ml) and then with the lithio derivative(**2**) prepared from 2-hydroxytetrahydropyran (1.3 equiv) and *n*-BuLi (1.3 equiv.). After 30 min the reaction mixture was warmed (see Table I), then quenched with saturated aq. NH_4Cl after stirring for the appropriate time. After usual workup the yields of the products (**3**, **4**, and **5**) were obtained by glc. These products were isolated by dry column chromatography (SiO_2, AcOEt), ptlc, or Kugelrohr distillation. The results are summarized in Table 1.

3a: mp 128.0-128.5 °C (Et_2O). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.12-1.79 (m, 6H, OCH$_2$(C$\underline{H}_2$)$_3$), 2.35-2.66 (m, 2H, PC$\underline{H}_2$), 3.06-3.86 (m, 3H, C$\underline{H}$OC$\underline{H}_2$), and 7.26-7.83 (m, 10H, Ph). ^{13}C{^{1}H}-Nmr (125 MHz, $CDCl_3$): δ= 23.3 (s), 25.5 (s), 33.5 (d, $^3J_{CP}$=7.1 Hz), 37.3 (d, $^1J_{CP}$=71.0 Hz), 68.3 (s), 72.6 (d, $^2J_{CP}$=3.7 Hz), 128.4 (d, $^3J_{CP}$=12.1 Hz), 128.5 (d, $^3J_{CP}$=11.7 Hz), 130.6 (d, $^2J_{CP}$=9.3 Hz), 130.9 (d, $^2J_{CP}$=9.5 Hz), 131.5 (d, $^4J_{CP}$=2.6 Hz), 131.6 (d, $^4J_{CP}$=2.6 Hz), and 133.0 (d, $^1J_{CP}$=99.7 Hz). One signal was not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 29.5. HRms : *m/z* Found: 300.1273. Calcd for $C_{18}H_{21}O_2P$: 300.1278. Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.75; H, 7.03.

3b: mp 103.0-103.6 °C (hexane). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.19-1.82 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 2.21-2.96 (m, 2H, $PC\underline{H}_2$), 3.29-3.82 (m, 3H, $C\underline{H}OC\underline{H}_2$), and 7.34-7.52 (m, 6H, *m,p*-H of Ph), and 7.68-7.99 (m, 4H, *o*-H of Ph). $^{13}C\{^1H\}$-Nmr (125 MHz, $CDCl_3$): δ= 23.2 (d, $^4J_{CP}$=1.2 Hz), 25.5 (s), 33.3 (d, $^3J_{CP}$=8.5 Hz), 39.9 (d, $^1J_{CP}$=56.1 Hz), 68.2 (s,), 73.1 (s), 128.4 (d, $^3J_{CP}$=12.5 Hz), 128.7 (d, $^3J_{CP}$=12.2 Hz), 130.9 (d, $^2J_{CP}$=9.9 Hz), 131.2 (d, $^2J_{CP}$=10.4 Hz), 131.1 (s), 131.2 (s), and 134.2 (d, $^1J_{CP}$=81.1Hz). One signal was not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 39.7. HRms : *m/z* Found: 316.1056. Calcd for $C_{18}H_{21}OPS$: 316.1051. Anal. Calcd for $C_{18}H_{21}O_2P$: C, 68.33; H, 6.69; S, 10.13. Found: C, 68.28; H, 6.68; S, 10.31.

3c: mp 133.0-134.0 °C (Et_2O). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.89-1.43 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 1.17 (dd, $^3J_{HP}$= 16.3 Hz, $^3J_{HH}$= 7.3 Hz, 3H), 2.41 -3.01 (m, 1H), 3.01-3.91 (m, 3H), 7.31-7.95 (m, 10H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 34.8, 34.9 (2:3). HRms : *m/z* Found: 314.1437. Calcd for $C_{19}H_{23}O_2P$: 314.1436.

3d: semi solid. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.70-2.09 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 1.10 (dd, $^3J_{HP}$= 19.3 Hz, $^3J_{HH}$= 7.0 Hz, 3H), 2.19-2.83 (m, 1H), 2.83-3.83 (m, 3H), and 7.29-7.96 (m, 10H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 50.2, 50.4 (3.6:1). HRms : *m/z* Found: 330.1201. Calcd for $C_{19}H_{23}OPS$: 330.1206.

3e: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.21-1.95 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 2.35-3.18 (m, 3H), 3.74 (s, 3H), 3.18-4.18 (m, 2H), 6.79-7.33 (m, 2H), 7.33-7.56 (m, 4H), and 7.56-8.17 (m, 3H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 28.4, 28.8 (1:1.4). HRms : *m/z* Found: 330.1390. Calcd for $C_{19}H_{23}O_3P$: 330.1385.

E-**4a**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.48-1.70 (m, 2H, $C\underline{H}_2(CH_2)_2OH$), 1.83-1.93 (m, 2H, $C\underline{H}_2CH_2OH$), 2.16-2.51 (m, 2H, $=CHC\underline{H}_2$), 3.50-3.74 (m, 2H, $C\underline{H}_2OH$), 6.14-6.85 (m, 2H, $C\underline{H}=C\underline{H}$), 7.30-7.83 (m, 10H, Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$) δ= 23.6. Ir (KBr disc): ν_{OH} 3200-3500 cm^{-1}, $\nu_{C=C}$ 1630 cm^{-1}. HRms : *m/z* Found: 300.1288. Calcd for $C_{18}H_{21}O_2P$: 300.1280.

E-**5a**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.44-1.72 (m, 2H, $C\underline{H}_2CH_2OH$), 2.03-2.34 (m, 2H, $=CHC\underline{H}_2$), 3.09 (dd, $^3J_{HH}$=7.4 Hz, $^2J_{HP}$= 13.8 Hz, 2H, $PC\underline{H}_2$), 3.53 (t, $^3J_{HH}$=5.9 Hz, 2H, $C\underline{H}_2OH$), 5.08-5.65 (m, 2H, $C\underline{H}=C\underline{H}$), 7.31-7.51 (m, 6H, *m,p*-H of Ph), and 7.51-7.82 (m, 4H, *o*-H of Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 29.8. Ir (KBr disc): ν_{OH} 3200-3500 cm^{-1}, $\nu_{C=C}$ 1640 cm^{-1}. HRms : *m/z* Found: 300.1296. Calcd for $C_{18}H_{21}O_2P$: 300.1280.

E-**4b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.45-1.59 (m, 2H, $C\underline{H}_2(CH_2)_2OH$), 1.83-2.11 (m, 2H, $C\underline{H}_2CH_2OH$), 2.11-2.48 (m, 2H, $=CHC\underline{H}_2$), 3.43 (t, $^3J_{HH}$=6.8 Hz, 2H, $C\underline{H}_2OH$), 6.13-7.08 (m, 2H, $C\underline{H}=C\underline{H}$), 7.25-7.44 (m, 6H, *m,p*-H of Ph), and 7.44-7.91 (m, 4H, *o*-H of Ph). $^{13}C\{^1H\}$-Nmr (125 MHz, $CDCl_3$): δ= 23.9 (s), 32.0 (s), 33.7 (d, $^3J_{CP}$=21.9 Hz), 61.4 (s), 121.3 (d, $^1J_{CP}$=134.9 Hz), 128.4 (d, $^3J_{CP}$=12.8 Hz), 131.2 (d, $^4J_{CP}$=3.0 Hz), 131.3 (d, $^2J_{CP}$=10.3 Hz), and 152.1 (d, $^2J_{CP}$=3.6 Hz). One signal was not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 23.9. Ir (KBr disc): ν_{OH} 3200-3600 cm^{-1}, $\nu_{C=C}$ 1620 cm^{-1}. HRms : *m/z* Found: 316.1063. Calcd for $C_{18}H_{21}OPS$: 316.1051.

E-**5b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.41-1.69 (m, 2H, $C\underline{H}_2CH_2OH$), 2.29-2.48 (m, 2H, $=CHC\underline{H}_2$), 3.35 (dd, $^3J_{HH}$=7.0 Hz, $^2J_{HP}$=14.3 Hz, 2H, $PC\underline{H}_2$), 3.55 (t, $^3J_{HH}$=6.0 Hz, 2H, $C\underline{H}_2OH$), 5.42-5.59 (m, 2H, $C\underline{H}=C\underline{H}$), 7.34-7.58 (m, 6H, *m,p*-H of Ph), and 7.58-7.98 (m, 4H, *o*-H of Ph). $^{13}C\{^1H\}$-Nmr ($CDCl_3$): δ= 24.6 (s), 32.0 (s), 32.9 (d, $^1J_{CP}$=51.8 Hz), 62.1 (s), 119.6 (d, $^2J_{CP}$=42.7 Hz), 128.4 (d, $^3J_{CP}$=12.8 Hz), 131.2 (d, $^2J_{CP}$=9.7 Hz), 131.2 (d, $^4J_{CP}$=3.0 Hz), and 135.0 (d, $^3J_{CP}$=130.4 Hz). One signal was not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 41.9. HRms : *m/z* Found: 316.1051. Calcd for $C_{18}H_{21}OPS$: 316.1051.

E-**4c**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.02-1.64 (m, 4H), 1.97-2.05 (m, 2H), 3.34-3.83 (m, 2H), 3.67 (dd, $^3J_{HP}$=12.8 Hz, $^4J_{HH}$=1.2 Hz, 3H), 5.31-5.60 (m, 1H), and 7.29-7.96 (m, 10H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 32.5. HRms : *m/z* Found: 314.1445. Calcd for $C_{19}H_{23}O_2P$: 314.1435.

E-**4d**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.22-1.72(m, 4H), 2.05-2.39 (m, 2H), 3.22-3.72 (m, 5H), 5.84-6.64 (m, 1H), and 7.32-8.01 (m, 10H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 38.1. HRms : *m/z* Found: 330.1216. Calcd for $C_{19}H_{23}OPS$: 330.1208.

E-**5d**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.10-1.60 (m, 2H), 1.89 (dd, $^3J_{HP}$=14.0 Hz, $^3J_{HH}$=6.0 Hz, 3H), 2.17-2.41 (m, 3H), 3.40-4.19 (m, 2H), 5.46-5.88 (m, 2H), and 7.30-8.23 (m, 10H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 48.5. HRms : *m/z* Found: 330.1208. Calcd for $C_{19}H_{23}OPS$: 330.1207.

E-**4e**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.49-1.70 (m, 4H), 1.81-2.65 (m, 2H), 3.51-4.08 (m, 2H), 3.65 (s, 3H), 6.06-6.56 (m, 2H), and 6.56-8.24 (m, 9H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 21.1. HRms : *m/z* Found: 330.1391. Calcd for $C_{19}H_{23}O_3P$: 330.1385.

E-**5e**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.20-1.89 (m, 2H), 2.04-2.42 (m, 2H), 2.42-3.13

(m, 2H), 3.17-4.10 (m, 2H), 3.78 (s, 3H), 5.12-5.68 (m, 2H), 6.76-7.34 (m, 2H), 7.34-7.53 (m, 4H), and 7.53-8.14 (m, 3H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 31.0. HRms : *m/z* Found: 330.1390. Calcd for $C_{19}H_{23}O_3P$: 330.1385.

The Peterson Reaction of 1a-c with Hexanal.

General procedure: Compound (**1**) (*ca.* 1 mmol) was allowed to react with 1.1 equiv of *n*-BuLi at -78 °C in THF (20 ml) and then with 1 equiv. of hexanal. After 30 min the reaction mixture was warmed to T °C (see Table 2), then quenched with saturated aq. NH_4Cl after stirring for the appropriate time. After usual workup the yields of the products (*E*-**6**, *Z*-**6**, and *E*-**7**) were obtained by glc. These products were isolated by dry column chromatography (SiO_2, AcOEt) or ptlc. The results are summarized in Table 2.

Z-**6a**: mp 58.0-59.9 °C (Et_2O). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.81 (t, $^3J_{HH}$=5.7 Hz, 3H, $C\underline{H}_3$), 1.08-1.50 (m, 6H, $(C\underline{H}_2)_3CH_3$), 2.38-2.71 (m, 2H, $=CHC\underline{H}_2$), 5.97-6.96 (m, 2H, $C\underline{H}=C\underline{H}$), 7.07-7.28 (m, 6H, *m,p*-H of Ph), and 7.36-7.91 (m, 4H, *o*-H of Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 20.6. HRms : *m/z* Found: 298.1502. Calcd for $C_{19}H_{23}OP$: 298.1487.

E-**6a**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.87 (t, $^3J_{HH}$=6.1 Hz, 3H, $C\underline{H}_3$), 1.10-1.50 (m, 6H, $(C\underline{H}_2)_3CH_3$), 2.38-2.71 (m, 2H, $=CHC\underline{H}_2$), 6.60-6.65 (m, 2H, $C\underline{H}=C\underline{H}$), 7.03-7.31 (m, 6H, *m,p*-H of Ph), and 7.31-7.82 (m, 4H, *o*-H of Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 23.2. HRms : *m/z* Found: 298.1497. Calcd for $C_{19}H_{23}OP$: 298.1487.

E-**7a**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.79-0.94 (m, 3H, $C\underline{H}_3$), 1.10-1.35 (m, 2H, $C\underline{H}_2CH_3$), 1.79-2.08 (m, 2H, $C\underline{H}_2CH_2CH_3$), (m, 2H, $=CHC\underline{H}_2$), 2.95 (dd, $^3J_{HH}$= 4.7 Hz, $^2J_{HP}$=14.6 Hz, 2H, $PC\underline{H}_2$), 5.25-5.34 (m, 2H, $C\underline{H}=C\underline{H}$), 7.28-7.39 (m, 6H, *m,p*-H of Ph), and 7.39-7.881 (m, 4H, *o*-H of Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 30.2. HRms : *m/z* Found: 298.1489. Calcd for $C_{19}H_{23}OP$: 298.1487.

Z-**6b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.79-0.88 (m, 3H, $C\underline{H}_3$), 1.04-1.59 (m, 6H, $(C\underline{H}_2)_3CH_3$), 2.17-2.44 (m, 2H, $=CHC\underline{H}_2$), 6.04-7.08 (m, 2H, $C\underline{H}=C\underline{H}$), and 7.34-7.82 (m, 10H, Ph). $^{13}C\{^1H\}$-Nmr (125MHz, $CDCl_3$): δ= 13.5 (s), 21.9 (s), 27.2 (d, $^4J_{CP}$=1.2 Hz), 30.2 (d, $^3J_{CP}$=9.1 Hz), 30.8 (s), 121.8 (d, $^1J_{CP}$=84.2 Hz), 128.0 (d, $^2J_{CP}$=12.2 Hz), 130.7 (d, $^4J_{CP}$=1.8 Hz), 130.8 (d, $^3J_{CP}$=15.8 Hz), 133.5 (d, $^1J_{CP}$=86.0 Hz), and 152.5 (d, $^2J_{CP}$=12.2 Hz). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 28.3. HRms : *m/z* Found: 314.1268. Calcd for $C_{19}H_{23}PS$: 314.1258.

E-**6b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.78-0.88 (m, 3H, $C\underline{H}_3$), 1.09-1.65 (m, 6H, $(C\underline{H}_2)_3CH_3$), 2.16-2.43 (m, 2H, $=CHC\underline{H}_2$), 5.93-6.63 (m, 2H, $C\underline{H}=C\underline{H}$), 7.22-7.54 (m, 6H, *m,p*-H of Ph), and 7.63-7.97 (m, 4H, $\underline{o}$-H of Ph). $^{13}C\{^1H\}$-Nmr (125MHz, $CDCl_3$): δ= 13.4 (s), 21.8 (s), 27.5 (d, $^4J_{CP}$=1.8 Hz), 30.8 (s), 33.6 (d, $^3J_{CP}$=17.7 Hz), 122.6 (d, $^1J_{CP}$=84.2 Hz), 128.0 (d, $^2J_{CP}$=12.2 Hz), 130.7 (d, $^3J_{CP}$=15.8 Hz), 130.8 (d, $^4J_{CP}$=4.8Hz), 134.3 (d, $^1J_{CP}$=83.6 Hz), and 152.5 (d, $^2J_{CP}$=15.2 Hz). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 35.6. HRms : *m/z* Found: 314.1245. Calcd for $C_{19}H_{23}PS$: 314.1258.

E-**7b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.80-0.87 (m, 3H, $C\underline{H}_3$), 1.08-1.43 (m, 4H, $(C\underline{H}_2)_2CH_3$), 2.03-2.54 (m, 2H, $=CHC\underline{H}_2$), 3.22 (dd, $^3J_{HH}$= 5.9 Hz, $^2J_{HP}$=14.2 Hz, 2H, $PC\underline{H}_2$), 5.29-5.56 (m, 2H, $C\underline{H}=C\underline{H}$), 7.32-7.54 (m, 6H, *m,p*-H of Ph), and 7.65-8.09 (m, 4H, *o*-H of Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 40.9. HRms : *m/z* Found: 314.1249. Calcd for $C_{19}H_{23}PS$: 314.1258.

Z-**7c**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.65-0.97 (m, 3H, $C\underline{H}_3$), 0.97-1.41 (m, 6H, $(C\underline{H}_2)_3CH_3$), 1.72 (dd, $^4J_{HH}$= 1.5 Hz, $^3J_{HP}$=12.5 Hz, 3H, $PCC\underline{H}_3$), 2.17-2.63 (m, 2H, $=CHC\underline{H}_2$), 5.99-6.76 (m, 1H, $=C\underline{H}$), and 7.33-7.87 (m, 10H, Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 28.3. HRms : *m/z* Found: 312.1641. Calcd for $C_{20}H_{25}OP$: 312.1643.

E-**6c**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.78-0.96 (m, 3H, $C\underline{H}_3$), 1.23-1.44 (m, 6H, $(C\underline{H}_2)_3CH_3$), 1.83 (d, $^3J_{HP}$=12.7 Hz, 3H, $PCC\underline{H}_3$), 2.08-2.40 (m, 2H, $=CHC\underline{H}_2$), 5.95-6.58 (m, 1H, $=C\underline{H}$), and 7.35-7.84 (m, 10H, Ph). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 32.5. HRms : *m/z* Found: 312.1642. Calcd for $C_{20}H_{25}OP$: 312.1643.

Isomerization of 4 or 5 with *t*-BuOK.

To a solution of 2 equiv. of *t*-BuOK in *t*-BuOH (1 ml) was added a solution of **4** or **5** (*ca*. 0.1 mmol) in THF (1 ml) at room temperature and the mixture was stirred for 2 day. The mixture was analyzed by glc using anthracene as internal standard as shown in Table 3. Then, the products were isolated by DCC or ptlc after usual workup.

Attempted Tandem Peterson-Michael Reaction of 1a with Salicylaldehyde.

To a THF (4 ml) solution of sodium salt (0.27 mmol) of salicylaldehyde prepared from salicylaldehyde and

NaH was added a THF (4 ml) solution of α-lithio derivative (0.25 mmol) of **1a**, which was prepared as described above, at -78 °C. After the reaction mixture was stirred at room temperature for 4 h was added saturated aq. NH_4Cl to the solution. After usual workup the residue was subjected to ptlc to give *Z*-**8** and *E*-**8** in 24% and 8% yields, respectively. The stereochemistry was determined from the value of vicinal coupling constants between olefinic protons and confirmed by differential NOE experiments. The desired product was not obtained under reflux conditions, neither. Also, treatment of *Z*-**8** and *E*-**8** with *t*-BuOK resulted in recovery of the starting **8**.

Z-**8**: viscous oil. ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 6.35 (dd, $^3J_{HH}$=14.2 Hz, $^2J_{HP}$=22.6 Hz, 1H, PC$\underline{H}$=CH), 6.54 (t, $^3J_{HH}$=7.7 Hz, 1H), 6.84 (d, $^3J_{HH}$=7.7 Hz, 1H), 7.01 (dt, $^3J_{HH}$=7.7 Hz, $^4J_{HH}$=1.5 Hz, 1H), 7.20 (dd, $^3J_{HH}$=7.7 Hz, $^4J_{HH}$=1.5 Hz, 1H), 7.39 (dt, $^3J_{HH}$=7.8 Hz, $^4J_{HP}$=3.0 Hz, 4H, *m*-H of PPh), 7.46 (dt, $^3J_{HH}$=7.8 Hz, $^4J_{HH}$=1.4 Hz, 2H, *p*-H of PPh), 7.68 (dd, $^3J_{HH}$=14.2 Hz, $^3J_{HP}$=41.1 Hz, 1H, PCH=C$\underline{H}$), 7.71 (ddd, $^3J_{HH}$=7.8 Hz, $^4J_{HH}$=1.4 Hz, $^3J_{HP}$=12.1 Hz, 4H, *o*-H of PPh), and 9.32 (br s, 1H, OH). ^{13}C{^{1}H}-Nmr (125 MHz, $CDCl_3$): δ= 119.27 (s), 119.95 (s), 120.63 (d, $^1J_{CP}$=99.5 Hz), 124.82 (d, $^3J_{CP}$=7.1 Hz), 128.55 (d, $^3J_{CP}$=12.3 Hz), 130.60 (s), 130.63 (s), 130.96 (d, $^2J_{CP}$=9.9 Hz), 131.81 (d, $^4J_{CP}$=2.4 Hz), 132.71 (d, $^1J_{CP}$=106.8 Hz), 147.52 (s), and 154.56 (s). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 23.2. HRms : *m/z* Found: 320.0964. Calcd for $C_{20}H_{17}O_2P$: 320.0966.

E-**8**: viscous oil. ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 6.71 (t, $^3J_{HH}$=7.7 Hz, 1H), 6.81 (dd, $^3J_{HH}$=17.7 Hz, $^2J_{HP}$=26.0 Hz, 1H, PC$\underline{H}$=CH), 6.98 (d, $^3J_{HH}$=7.7 Hz, 1H), 7.10 (t, $^3J_{HH}$=7.7 Hz, 1H), 7.35 (d, $^3J_{HH}$=7.7 Hz, 1H), 7.39 (dt, $^3J_{HH}$=7.3 Hz, $^2J_{HP}$=2.8 Hz, 4H, *m*-H of PPh), 7.465 (t, $^3J_{HH}$=7.3 Hz, 2H, *p*-H of PPh), 7.69 (dd, $^3J_{HH}$=7.3 Hz, $^2J_{HP}$=12.2 Hz, 4H, *o*-H of PPh), 8.12 (dd, $^3J_{HH}$=17.7 Hz, $^3J_{HP}$=21.3 Hz, 1H, PCH=C$\underline{H}$), and 10.30 (br s, 1H, OH). ^{13}C{^{1}H}-Nmr (125 MHz, $CDCl_3$): δ= 115.68 (d, $^1J_{CP}$=106.0 Hz), 117.08 (s), 118.97 (s), 122.24 (d, $^3J_{CP}$=18.1 Hz), 127.39 (s), 128.62 (d, $^3J_{CP}$=12.1 Hz), 131.37 (s), 131.45 (d, $^2J_{CP}$=10.5 Hz), 131.89 (d, $^4J_{CP}$=2.5 Hz), 132.72 (d, $^1J_{CP}$=106.8 Hz), 144.52 (d, $^2J_{CP}$=4.6 Hz), and 157.15 (s). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 28.5. HRms : *m/z* Found: 320.0963. Calcd for $C_{20}H_{17}O_2P$: 320.0966.

Horner-Emmons Reaction of 3 with Aromatic Aldehydes.

A mixture of **3** (*ca.* 0.1 mmol) and 8 equiv of aromatic aldehyde (**10**) in THF (5 ml) was treated with freshly prepared LiTMP (6 equiv.) at -96 °C. After stirring for an additional 30 min at -96 °C, the reaction was quenched with saturated aq. NH_4Cl. The reaction mixture was chromatographed (ptlc-AcOEt) to afford **4** and *erythro*- and *threo*-**11** and a mixture of starting **3** and **12**, which was separated by hplc. The results are summarized Table 4.

erythro-**11a**: mp 166.0-167.5 °C (Et_2O). ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 0.76-2.02 (m, 6H, $OCHH'(C\underline{H}_2)_3$), 2.80-3.13 (m, 2H, $PC\underline{H}$, $OC\underline{H}H'$), 3.43-3.90 (m, 2H, $C\underline{H}OCH\underline{H}'$), 4.97-5.14 (br s, 1H, $O\underline{H}$), 5.22-5.38 (m, 1H, $C\underline{H}PhOH$), 7.27 (s, 5H, $CC_6\underline{H}_5$), 7.37-7.39 (m, 6H, *m*, *p*-H of PPh), and 7.83-8.11 (m, 4H, *o*-H of PPh). $^{13}C\{^1H\}$-Nmr (125 MHz, $CDCl_3$): δ= 23.6 (s), 25.3 (s), 31.0 (d, $^3J_{CP}$=7.2 Hz), 51.1 (d, $^1J_{CP}$=67.6 Hz), 68.5 (s), 71.1 (s), 75.6 (s), 125.5 (s), 126.9 (s), 128.0 (d, $^3J_{CP}$=12.2 Hz), 128.1 (s), 128.8 (d, $^3J_{CP}$=11.2 Hz), 130.9 (d, $^2J_{CP}$=8.6 Hz), 131.6 (d, $^2J_{CP}$=10.1 Hz), 131.6 (d, $^4J_{CP}$=3.0Hz), 131.7 (d, $^4J_{CP}$=2.8 Hz), 132.6 (d, $^1J_{CP}$=96.7 Hz), 133.0 (d, $^1J_{CP}$=95.9 Hz), and 142.1 (d, $^3J_{CP}$=12.5 Hz). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 36.6. HRms : *m/z* Found: 406.1697. Calcd for $C_{25}H_{27}O_3P$: 406.1697.

threo-**11a**: mp 173.0-174.0 °C (Et_2O). ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 0.91-0.99 (m, 1H, $OCH_2C\underline{H}H'$), 1.16-1.27 (m, 2H, $OCH_2CH\underline{H}'C\underline{H}H'$), 1.44-1.59 (m, 2H, $O(CH_2)_2CH\underline{H}'C\underline{H}H'$), 1.83-2.04 (m, 1H, $O(CH_2)_3CH\underline{H}'$), 2.95-3.01 (m, 2H, $PC\underline{H}$, $OC\underline{H}H'$), 3.58-3.61 (m, 1H, $OCH\underline{H}'$), 3.67-3.73 (m, 1H, $C\underline{H}OCH_2$), 5.33 (dd, $^3J_{HP}$=9.2 Hz, $^3J_{HH}$=8.5 Hz, 1H, $C\underline{H}(OH)Ph$), 7.22-7.29 (m, 5H, CPh), 7.47-7.52 (m, 6H, *m,p*-H of PPh), and 7.91-8.01 (m, 4H, *o*-H of PPh). $^{13}C\{^1H\}$-Nmr (125 MHz, $CDCl_3$): δ= 23.5 (s), 25.1 (s), 29.8 (d, $^3J_{CP}$=8.2 Hz), 51.6 (d, $^1J_{CP}$=66.7 Hz), 68.5 (s), 72.3 (d, $^2J_{CP}$=2.7 Hz), 76.6 (s), 126.6 (s), 127.1 (s), 127.9 (s), 128.1 (d, $^3J_{CP}$=11.4 Hz), 128.3 (d, $^3J_{CP}$=11.9 Hz), 130.9 (d, $^2J_{CP}$=8.6 Hz), 131.2 (d, $^4J_{CP}$=2.9 Hz), 131.4 (d, $^4J_{CP}$=2.8 Hz), 131.6 (d, $^2J_{CP}$=9.5 Hz), 133.3 (d, $^1J_{CP}$=97.2 Hz), 133.5 (d, $^1J_{CP}$=97.3 Hz), and 142.6 (d, $^3J_{CP}$=5.6 Hz). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 35.8. HRms : *m/z* Found: 406.1714. Calcd for $C_{25}H_{27}O_3P$: 406.1697.

erythro-**11b**: mp 165.0-166.0 °C (Et_2O). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.15-1.61 (m, 6H, $OCHH'(C\underline{H}_2)_3$), 2.85-2.88 (m, 1H, $PC\underline{H}$), 2.99-3.04 (m, 1H, $C\underline{H}H'$), 3.59-3.67 (m, 2H, $OCH\underline{H}'$, $O(CH_2)_4C\underline{H}$), 3.78 (s, 3H, $OC\underline{H}_3$), 4.97-5.05 (br s, 1H, $O\underline{H}$), 5.27 (d, $^3J_{HH}$= 8.7 Hz, 2H, $C\underline{H}(OH)$), 6.82 (d, $^3J_{HH}$= 8.7 Hz, 2H, *m*-H of *p*-Anisyl), 7.18 (d, $^3J_{HH}$= 8.7 Hz, 2H, *o*-H of *p*-Anisyl), 7.42-7.50 (m, 6H, *m*, *p*-H of PPh), and 7.92-7.97 (m, 4H, *o*-H of PPh). $^{13}C\{^1H\}$-Nmr (22.5 MHz,

$CDCl_3$): δ= 23.6 (s), 25.4 (s), 31.0 (d, $^3J_{CP}$=7.0 Hz), 51.2 (d, $^1J_{CP}$=67.2 Hz), 55.2 (s), 68.5 (s), 70.7 (s), 75.6 (s), 113.5 (s), 126.7 (s), 127.9 (d, $^3J_{CP}$=12.2 Hz), 128.7 (d, $^3J_{CP}$=11.3 Hz), 130.8 (d, $^2J_{CP}$=9.7 Hz), 131.6 (d, $^2J_{CP}$=8.5 Hz), 134.1 (s), 134.2 (s), and 158.5 (s). Three signals were not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 36.7. HRms : *m/z* Found: 436.1804. Calcd for $C_{26}H_{29}O_4P$: 436.1803.

threo-**11b**: semi solid. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.24-1.75 (m, 6H, $OCHH'(C\underline{H}_2)_3$), 2.37-2.65 (m, 1H, $PC\underline{H}$), 2.88-3.00 (m, 1H, $OC\underline{H}H'$), 3.64-3.88 (m, 1H, $CH_2OC\underline{H}$), 3.84 (s, 3H, $OC\underline{H}_3$), 5.40-5.46 (m, 1H, $C\underline{H}(OH)$), 6.89 (d, $^3J_{HH}$= 7.7 Hz, 2H, *m*-H of *p*-Anisyl), 7.22 (d, $^3J_{HH}$= 7.7 Hz, 2H, *o*-H of *p*-Anisyl), 7.30-7.85 (m, 10H, PPh), and 8.11-8.42 (m, 1H, $O\underline{H}$). $^{13}C\{^1H\}$-Nmr (22.5 MHz, $CDCl_3$): δ= 23.4 (s), 25.4 (s), 33.4 (d, $^3J_{CP}$=7.3 Hz), 37.0 (d, $^1J_{CP}$=76.1 Hz), 55.1 (s), 68.3 (s), 69.5 (s), 72.5 (s), 113.2 (s), 127.7 (s), 128.1 (d, $^3J_{CP}$=11.9 Hz), 128.5 (d, $^3J_{CP}$=11.6 Hz), 130.6 (d, $^2J_{CP}$=9.3 Hz), 130.9 (d, $^2J_{CP}$=9.9 Hz), 131.6 (s), 132.6 (s), and 158.5 (s). Three signals were not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 35.8. HRms : *m/z* Found: 436.1825. Calcd for $C_{26}H_{29}O_4P$: 436.1803.

erythro-**11c**: mp 199.5-201.0 °C (Et_2O). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.93-0.96 (m, 1H, $O(CH_2)_2C\underline{H}H'$), 1.17-1.26 (m, 2H, $CH_2C\underline{H}H'CH\underline{H}'$), 1.56-1.61 (m, 2H, $OCH_2CH\underline{H}'CH_2C\underline{H}H'$), 1.81-1.84 (m, 1H, $O(CH_2)_3CH\underline{H}'$), 2.85-2.86 (m, 1H, $PC\underline{H}$), 2.98-3.03 (m,. 1H, $OC\underline{H}H'$), 3.59-3.63 (m, 2H, $CH\underline{H}'OC\underline{H}$), 5.10 (br s, 1H, $O\underline{H}$), 5.26 (d, $^3J_{HH}$= 8.9 Hz, 1H, $C\underline{H}(OH)$), 7.09-7.22 (m, 4H, $C_6\underline{H}_4Cl$), 7.46-7.52 (m, 6H, *m*, *p*-H of PPh), and 7.92-7.97 (m, 4H, *o*-H of PPh). $^{13}C\{^1H\}$-Nmr (22.5 MHz, $CDCl_3$): δ= 23.5 (s), 25.3 (s), 31.1 (s), 51.0 (d, $^1J_{CP}$=67.5 Hz), 68.5 (s), 70.6 (s), 75.5 (s), 127.0 (s), 128.0, 128.0 (d, $^3J_{CP}$=11.4 Hz), 128.2 (s), 128.8 (s), 128.8 (d, $^3J_{CP}$=11.6 Hz), 130.8 (d, $^2J_{CP}$=8.5 Hz), 131.5 (d, $^2J_{CP}$=9.6 Hz), 131.7 (s), and 131.8 (s). Two signals were not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 23.5. HRms : *m/z* Found: 440.1314. Calcd for $C_{25}H_{26}O_3{}^{35}ClP$: 440.1308.

threo-**11c**: semi solid. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.80-0.91 (m, 1H, $O(CH_2)_2C\underline{H}H'$), 1.10-1.49 (m, 4H, $CH_2C\underline{H}_2C\underline{H}H'C\underline{H}H'$), 1.61-1.71 (m, 1H, $O(CH_2)_3CH\underline{H}'$), 2.71-2.82 (m, 2H, $PC\underline{H}$, $C\underline{H}H'CH$), 3.39-3.71 (m, 2H, $CH\underline{H}'OC\underline{H}$), 5.50-5.71 (m, 1H, $C\underline{H}(OH)$), 6.83 (s, 1H, $O\underline{H}$), 7.14-7.20 (m, 4H, $C_6\underline{H}_4Cl$), 7.33-7.82 (m, 6H, *m*,*p*-H of PPh), and 7.82-7.98 (m, 4H, *o*-H of PPh). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 37.2. HRms : *m/z* Found: 440.1298. Calcd for $C_{25}H_{26}O_3{}^{35}ClP$: 440.1308.

12a: viscous oil. ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 1.40-1.54 (m, 4H, $(C\underline{H}_2)_2CH_2OH$), 2.26-2.44 (m, 2H, $=CHC\underline{H}_2$), 3.58 (t, $^{3}J_{HH}$=6.1 Hz, 2H, $C\underline{H}_2OH$), 5.83 (dt, $^{3}J_{HP}$=22.0 Hz, $^{3}J_{HH}$=7.3 Hz, 1H, $PC=C\underline{H}-CH_2$), 5.91 (m, 1H, $C\underline{H}(OH)Ph$), 7.03-7.10 (m, 2H, *o*-H of CPh), 7.26-7.33 (m, 3H, *m,p*-H of CPh), 7.40-7.53 (m, 6H, *m,p*-H of PPh), and 7.61-7.65 (m, 4H, *o*-H of PPh). $^{13}C\{^{1}H\}$-Nmr (125 MHz, $CDCl_3$): δ= 25.0 (s), 28.9 (d, $^{3}J_{CP}$=14.6 Hz), 32.1 (s), 62.3 (s), 72.7 (d, $^{2}J_{CP}$=6.9 Hz), 126.1 (s), 127.0 (s), 128.0 (s), 128.1 (d, $^{3}J_{CP}$=12.3 Hz), 128.5 (d, $^{3}J_{CP}$=12.3 Hz), 131.5 (d, $^{2}J_{CP}$=10.3 Hz), 131.5 (s), 132.0 (d, $^{2}J_{CP}$=9.9 Hz), 132.1 (s), 135.4 (d, $^{1}J_{CP}$=93.8 Hz), 142.2 (s), and 146.8 (d, $^{2}J_{CP}$=10.3 Hz). Two signals were not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 37.4. HRms: *m/z* Found: 406.1706. Calcd for $C_{25}H_{27}O_3P$: 406.1697.

12e: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 1.36-1.70 (m, 4H, $(C\underline{H}_2)_2CH_2OH$), 1.70-2.91 (m, 2H, $=CHC\underline{H}_2$), 3.62 (s, 1.5H), 3.74 (s, 1.5H), 3.35-4.01 (m, 2H, CH_2OH), 5.71-6.21 (m, 2H, $C\underline{H}(O\underline{H})Ph$), and 6.62-8.15 (m, 14H). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 35.4 and 36.4 (1:1). HRms: *m/z* Found: 436.1789. Calcd for $C_{26}H_{29}O_4P$: 436.1802.

Horner-Emmons Reaction of 3a with Other Carbonyl Compounds.

A mixture of **3a** (*ca.* 0.1 mmol) and 4 equiv of benzophenone (**10f**) in THF (5 ml) was treated with freshly prepared LiTMP (3 equiv.) at -96 °C. After stirring for an additional 30 min at -96 °C, the reaction was quenched with saturated aq. NH_4Cl. After usual workup the residue was chromatographed (hplc) to give **12f** in 71% yield. Similar reaction using propanal (**10g**) instead of benzophenone gave **12g** (51%) and **4a** (15%) after chromatography (ptlc). Similarly, hplc gave **12h** (50%) and **4a** (18%) after the reaction using paraformaldehyde (**10h**). A similar reaction using diphenylvinylphosphine oxide (**13**), benzophenone (3.1 equiv.) and LiTMP (2 equiv.) gave 1-(hydroxydiphenylmethyl)-1-ethenyl(diphenyl)-phosphine oxide (**14**) in 36% yield.

12f: mp 150.0-151.0 °C (Et_2O). ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.93-0.98 (m, 2H, $C\underline{H}_2(CH_2)_2OH$), 1.05-1.09 (m, 2H, $C\underline{H}_2CH_2OH$), 1.45-4.50 (m, 2H, $=CHC\underline{H}_2$), 3.30 (t, $^{3}J_{HH}$= 6.3 Hz, 2H, $C\underline{H}_2OH$), 5.94 (dt, $^{3}J_{HP}$= 25.0 Hz, $^{3}J_{HH}$= 7.4 Hz, 1H, $=C\underline{H}$), 6.52 (s, 1H, OH), 7.24-7.29 (m, 10H, CPh), 7.44-7.54 (m, 6H, *m, p*-H of PPh), and 7.64-7.88 (m, 4H, *o*-H of PPh). $^{13}C\{^{1}H\}$-Nmr (22.5 MHz, $CDCl_3$): δ= 24.5 (s), 30.0 (d, $^{3}J_{CP}$=15.5 Hz), 32.0 (s), 62.0 (s), 82.9 (d, $^{2}J_{CP}$= 6.6 Hz), 127.9 (s), 128.2 (d, $^{3}J_{CP}$= 11.9 Hz), 131.7 (s), 131.7 (d, $^{4}J_{CP}$=2.7 Hz), 131.8 (d, $^{2}J_{CP}$=9.5 Hz), 132.8 (d,

$^1J_{CP}$=102.9 Hz), and 148.1 (d, $^2J_{CP}$=10.8 Hz). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 39.7. Three signals were not observed. HRms: *m/z* Found: 482.2008. Calcd for $C_{31}H_{31}O_3P$: 482.2009.

12g: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ= 0.82 (t, $^3J_{HH}$= 7.2 Hz, 3H, $C\underline{H}_3$), 1.19-1.63 (m, 6H, $(C\underline{H}_2)_2CH_2OH$, $C\underline{H}_2CH_3$), 1.91-2.41 (m, 2H, $=CHC\underline{H}_2$), 3.60 (t, $^3J_{HH}$= 5.9 Hz, 2H, $C\underline{H}_2OH$), 4.40-4.68 (m, 1H, $C\underline{H}OH$), 5.75 (dt, $^3J_{HP}$=23.0 Hz, $^3J_{HH}$=7.6 Hz, 1H, $=C\underline{H}$), and 7.35-7.84 (m, 10H, PPh). ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ=37.1. HRms: *m/z* Found: 340.1595. Calcd for $C_{21}H_{25}O_2P$: 340.1592.

12h: viscous oil. ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 1.45-1.58 (m, 4H, $(C\underline{H}_2)_2CH_2OH$), 2.33-3.38 (m, 2H, $=CHC\underline{H}_2$), 3.61 (t, $^3J_{HH}$= 6.1 Hz, 2H, $C\underline{H}_2OH$), 4.39 (d, $^3J_{HH}$=14.6 Hz, 2H, $PCC\underline{H}_2OH$), 6.01 (dt, $^3J_{HP}$=21.3 Hz, $^3J_{HH}$=7.4 Hz, 1H, $=C\underline{H}$), 7.45-7.56 (m, 6H, *m*, *p*-H of PPh), and 7.64-7.74 (m, 4H, *o*-H of PPh). $^{13}C\{^1H\}$-Nmr (125 MHz, $CDCl_3$): δ= 25.1 (s), 28.5 (d, $^3J_{CP}$=14.5 Hz), 31.9 (s), 57.7 (d, $^2J_{CP}$=10.6 Hz), 62.1 (s), 128.5 (d, $^3J_{CP}$= 12.2 Hz), 131.0 (d, $^1J_{CP}$=92.9Hz), 131.8 (d, $^2J_{CP}$=10.1 Hz), 132.9 (d, $^4J_{CP}$=2.3 Hz), and 149.4 (d, $^2J_{CP}$=9.6 Hz). One signal was not observed. ^{31}P-Nmr (36.3 MHz, $CDCl_3$): δ= 35.8. HRms : *m/z* Found: 330.1400. Calcd for $C_{19}H_{23}O_3P$: 330.1385.

14: viscous oil. ^{1}H-Nmr (500 MHz, $CDCl_3$): δ= 5.35 (d, $^3J_{HP}$=42.5 Hz, 1H, $=C\underline{H}H'$), 5.55 (d, $^3J_{HP}$=20.2 Hz, 1H, $=CH\underline{H'}$), 6.57 (s, 1H, OH), 7.07-7.14 (m, 6H, *m*,*p*-H of CPh), 7.20-7.26 (m, 4H, *o*-H of CPh), 7.35 (dt, $^3J_{HH}$=7.5 Hz, $^4J_{HP}$=2.6 Hz, 4H, *m*-H of PPh), 7.45 (t, $^3J_{HH}$=7.5 Hz, 2H, *p*-H of PPh), and 7.55 (dd, $^3J_{HH}$=7.5 Hz, $^3J_{HP}$=12.0 Hz, 4H, *o*-H of PPh). $^{13}C\{^1H\}$-Nmr (125 MHz, $CDCl_3$): δ = 83.81 (d, $^2J_{CP}$=6.7 Hz), 127.20 (s), 127.60 (s), 127.79 (s), 128.36 (d, $^3J_{CP}$=12.0 Hz), 131.02 (d, $^2J_{CP}$=10.5 Hz), 131.78 (d, $^2J_{CP}$=10.4 Hz), 131.95 (d, $^4J_{CP}$=2.7Hz), 131.99 (d, $^1J_{CP}$=103.0 Hz), 143.63 (d, $^3J_{CP}$=3.7 Hz), and 149.36 (d, $^1J_{CP}$=88.7 Hz). ^{31}P-Nmr (36.3 MHz, $CDCl_3$) δ= 35.9. HRms : *m/z* Found: 410.1437. Calcd for $C_{27}H_{23}O_2P$: 410.1436.

Olefin Formation Reaction from 11 .

To a suspension of NaH (60% dispersion, 3 equiv.) in DMF (2 ml) was added a solution of *erythro*-**11a** (0.07 mmol) in DMF (1 ml) at 0 °C under Ar and the reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aq. NH_4Cl and the organic layer was extracted with hexane. The extracts were washed with water several times and dried over anhydrous $MgSO_4$. After removal of the solvent the residue was subjected to chromatography (ptlc) to give the corresponding olefin *Z*-**15a** (54%). Similarly, the reaction using other **11** than *erythro*-**11a** gave stereospecifically the corresponding **15**. The results are summarized in Table 4.

Z-**15a**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ=1.32-1.95 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 3.31-3.66 (m, 1H, $OC\underline{H}H'$), 3.99-4.34 (m, 2H, $C\underline{H}OCH\underline{H}'$), 5.65 (dd, $^3J_{HH}$=11.4 Hz, $^3J_{HH}$=8.5 Hz, 1H, $PhCH{=}C\underline{H}$), 6.55 (d, $^3J_{HH}$=11.4 Hz, 1H, $PhC\underline{H}{=}CH$), and 7.30-7.31 (m, 5H, Ph). HRms : *m/z* Found: 188.1205. Calcd for $C_{13}H_{16}O$: 188.1201.

E-**15a**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ=1.44-2.03 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 3.40-3.71 (m, 1H, $OC\underline{H}H'$), 3.88-4.20 (m, 2H, $C\underline{H}OCH\underline{H}'$), 6.18 (dd, $^3J_{HH}$=16.0 Hz, $^3J_{HH}$=5.2 Hz, 1H, $PhCH{=}C\underline{H}$), 6.60 (dd, $^3J_{HH}$=16.0 Hz, $^3J_{HH}$=0.9 Hz, 1H, $PhC\underline{H}{=}CH$), and 7.18-7.43 (m, 5H, Ph). HRms : *m/z* Found: 188.1189. Calcd for $C_{13}H_{16}O$: 188.1201.

Z-**15b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ=1.19-2.05 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 3.30-4.52 (m, 3H, $C\underline{H}_2OC\underline{H}$), 3.82 (s, 3H, $OC\underline{H}_3$), 5.56 (dd, $^3J_{HH}$=8.6 Hz, $^3J_{HH}$=11.5 Hz, 1H, *p*-Anisyl$CH{=}C\underline{H}$), 6.48 (d, $^3J_{HH}$=11.5 Hz, *p*-Anisyl$C\underline{H}{=}CH$), 6.87 (d, $^3J_{HH}$=8.7 Hz, 2H, *m*-H of *p*-Anisyl), and 7.25 (d, $^3J_{HH}$=8.7 Hz, 2H, *o*-H of *p*-Anisyl). HRms : *m/z* Found: 218.1294. Calcd for $C_{14}H_{18}O_2$: 218.1307.

E-**15b**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ=1.05-1.99 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 3.19-4.41 (m, 3H, $C\underline{H}_2OC\underline{H}$), 3.72 (s, 3H, $OC\underline{H}_3$), 5.97 (dd, $^3J_{HH}$=5.7 Hz, $^3J_{HH}$=15.2 Hz, 1H, *p*-Anisyl$CH{=}C\underline{H}$), 6.46 (d, $^3J_{HH}$=15.2 Hz, *p*-Anisyl$C\underline{H}{=}CH$), 6.76 (d, $^3J_{HH}$=8.7 Hz, 2H, *m*-H of *p*-Anisyl), and 7.23 (d, $^3J_{HH}$=8.7 Hz, 2H, *o*-H of *p*-Anisyl). HRms : *m/z* Found: 218.1306. Calcd for $C_{14}H_{18}O_2$: 218.1307.

Z-**15c**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ=1.14-1.95 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 3.27-3.55 (m, 1H, $OC\underline{H}H'$), 2.83-4.23 (m, 2H, $CH\underline{H}'OC\underline{H}$), 5.60 (dd, $^3J_{HH}$=8.6 Hz, $^3J_{HH}$=11.6 Hz, 1H, $ClC_6H_4CH{=}C\underline{H}$), 6.42 (d, $^3J_{HH}$=11.6 Hz, $ClC_6H_4C\underline{H}{=}CH$), and 7.21 (s, 4H, $ClC_6\underline{H}_4$). HRms : *m/z* Found: 222.0807. Calcd for $C_{13}H_{15}O^{35}Cl$: 222.0811.

E-**15c**: viscous oil. ^{1}H-Nmr (90 MHz, $CDCl_3$): δ=0.75-2.03 (m, 6H, $OCH_2(C\underline{H}_2)_3$), 3.32-4.21 (m, 3H, $C\underline{H}_2OC\underline{H}$), 6.16 (dd, $^3J_{HH}$=8.6 Hz, $^3J_{HH}$=15.8 Hz, 1H, $ClC_6H_4CH{=}C\underline{H}$), 6.56 (d, $^3J_{HH}$=15.8 Hz, $ClC_6H_4C\underline{H}{=}CH$), and 7.27 (s, 4H, $ClC_6\underline{H}_4$). HRms : *m/z* Found: 222.0800. Calcd for $C_{13}H_{15}O^{35}Cl$: 222.0811.

REFERENCES

1. For heterocyclic ene compounds: E. Zbiral, 'Organophosphorus Reagents in Organic Synthesis,' ed. by J. I. G. Cadogan, Academic Press, London, 1979, pp. 250-255; For cyclic ene compounds: K. B. Becker, *Tetrahedron*, 1980, **36**, 1717; G. H. Posner, J. P. Mallamo, and A. Y. Black, *Tetrahedron*, 1981, **37**, 3921; R. J. Pariza and P. L. Fucks, *J. Org. Chem.*, 1983, **48**, 2304. Recent examples using vinylphosphonates: M. T. Minami and J. Motoyoshiya, *Synthesis*, 1992, 333; A. Tius and A. H. Fauq, *J. Am. Chem. Soc.*, 1986, **108**, 1035, 6391; T. Minami, Y. Kitajima, and T. Chikugo, *Chem. Lett.*, 1986, 1229; T. Minami, K. Watanabe, and K. Hirakawa, *Chem. Lett.*, 1986, 2027; T. Minami, K. Watanabe, and T. Chikugo, *Chem. Lett.*, 1987, 2369.
2. For recent examples: P. Molina, M. Alajarin, and A. Vidal, *Synthesis*, 1992, 293; P. Molina, M. Alajarin, and A. Vidal, *Tetrahedron*, 1990, **46**, 1063; P. Molina, M. Alajarin, and A. Vidal, *J. Org. Chem.*, 1990, **55**, 6140.
3. a) D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780; b) E. E. Aboujaoude, A. Lie'tje', N. Collignon, M. P. Teulade, and P. Savignac, *Synthesis*, 1986, 934.
4. T. Kawashima, M. Nakamura, and N. Inamoto, *Phosphorus, Sulfur and Silicon*, 1992, **69**, 293.
5. For β-alkoxyphosphonates: H. Takahashi, K. Fujiwara, and M. Ohta, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1498. For phosphonium ylides stabilized by a net positive charge: R. K. Bentley, C. A. Higham, J. K. Jenkins, E. R. H. Jones, and V. Thaller, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1987.
6. For examples see: J. Clayden and S. Warren, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 241; A. D. Buss and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2307; A. D. Buss, W. B. Cruse, O. Kennard, and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1984, 243.
7. E. F. Bugerenk, E. A. Chernyshev, and A. D. Petrov, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, 1965, 286.
8. D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780; T. Kawashima, N. Mitsuda, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 708.
9. I. Fleming and C. D. Floyd, *J. Chem. Soc., Perkin Trans. 1*, 1981, 969.
10. F. C. Whitemore and L. H. Sommer, *J. Am. Chem. Soc.*, 1946, **68**, 481.

Received, 1st May, 1996