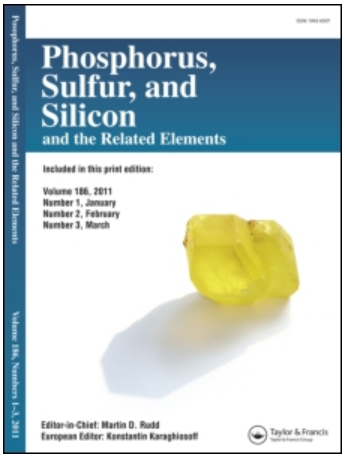

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THE 1,3-DIASTEREOSELECTIVE SYNTHESIS OF 2-HYDROXYALKYLPHOSPHINE OXIDES BASED ON A CHIRAL PHOSPHORUS CENTER

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THE 1,3-DIASTEREOSELECTIVE SYNTHESIS OF 2-HYDROXYALKYLPHOSPHINE OXIDES BASED ON A CHIRAL PHOSPHORUS CENTER

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The title reaction was investigated from the following two approaches; direct addition reaction of α-metallo derivatives of methyl-1-naphthylphenylphosphine oxide with benzaldehyde and reduction of the corresponding 2-oxoalkylphosphine oxide. The diastereomer ratio was determined by ^{31}P NMR spectroscopy. The major diastereomer was (R,S)- or (S,R)-**3**, however, the reverse result was obtained only when diisobutylaluminum hydride was used as a reducing reagent. Transition state models were proposed in order to explain the stereochemistry.

Key words: 1,3-Diastereoselective synthesis; β-hydroxyalkylphosphine oxide; methylnaphthylphenylphosphine oxide; β-oxoalkylphosphine oxide; 1,3-asymmetric induction; transition state model.

INTRODUCTION

Carbonyl condensations of nucleophilic reagents containing a chiral sulfoxide group have been investigated in a view point of synthesis of optically active compounds.[1] As an alternative approach Solladié has reported on the 1,3-asymmetric induction using a chiral 2-oxoalkyl sulfoxide and the application to the synthesis of optically active epoxides.[2] Some improvements and applications were disclosed.[3,4]

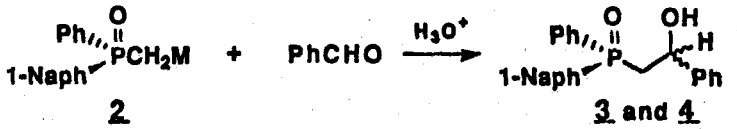
On the other hand, 1,2-diastereoselective synthesis of 2-hydroxyalkylphosphoryl compounds has been widely investigated with a view to synthesize the olefin highly stereoselectively.[5] However, there is no report on 1,3-diastereoselective synthesis of 2-hydroxyalkylphosphine oxides based on a chiral phosphorus center. Now we wish to report on a possibility of such a 1,3-asymmetric induction using a racemic methyl-1-naphthylphenylphosphine oxide (**1**).

RESULTS AND DISCUSSION

Reaction of α-Metallated Derivatives (2) of 1 with Benzaldehyde

α-Lithio derivative (**2a**:M=Li) of methyl-1-naphthylphenylphosphine oxide (**1**) was allowed to react with benzaldehyde in various reaction conditions to give a mixture of diastereomers of 2-hydroxy-2-phenylethyl(1-naphthyl)phenylphosphine oxides (less polar isomer (**3**) and polar one (**4**)) in more than 90% yield. The diastereomers were observed independently by ^{31}P-NMR spectroscopy, so that the diastereomer ratios of **3** and **4** were determined from the ratios of their peak heights in the

proton-noise decoupled ^{31}P-NMR spectrum.[6] The results are shown in Table I. The



2 3 and 4

lower temperature gave better diastereomer ratios as expected. The solvent gave no drastic change as to the ratio. The Grignard reagents prepared by the transmetallation of **2a** with magnesium chloride and the deprotonation of **1** with ethylmagnesium bromide added to benzaldehyde with higher diastereoselectivity, but in lower chemical yields, presumably because of the lower reactivity. The transmetallation using $MgBr_2$, MgI_2, $ZnCl_2$, and $SnCl_2$ gave no product.

1,3-Diastereoselective Reduction of Benzoylmethyl(1-naphthyl)phenylphosphine Oxide (5) with Various Hydride Reagents

Benzoylmethyl(1-naphthyl)phenylphosphine oxide (**5**) was prepared by the reaction of **2a** with benzonitrile, followed by acidic hydrolysis in 88% yield. **5** was reduced

TABLE I

Reaction of lithiomethyl(1-naphthyl)phenylphosphine oxide (**2**) with benzaldehyde

M	Solvent	Temp/°C	4/3[a)]	Yield[b)]/%
Li	THF	-98	0.60	100
Li	THF	-78	0.70	100
Li	Toluene	-98	0.59	98
Li	Toluene (33%THF)	-78	0.73	100
Li	Toluene[c)]	-98	0.72	100
Li	Methylcyclohexane[c)]	-98	0.70	83
Li	Dimethoxymethane[c)]	-98	0.62	94
Li	Dimethoxyethane[c)]	-78	0.66	97
Li	Ether	-98	0.84	99
Li	Ether[c)]	-98	0.62	87
MgCl	THF	-98	0.51	48
MgCl	THF	-78	0.65	57
MgBr	Benzene	reflux	0.65	80

a) Relative ratio of peak height of **4** (δ_P 35.9) to **3** (δ_P 36.9).

b) Isolated yield of a mixture of **3** and **4** based on **1**.

c) It contains 10-20% of THF.

TABLE II

Reduction of benzoylmethyl(1-naphthyl)phenylphosphine oxide (**5**) with various hydrides

Hydride	Equiv[a]	Solvent	Temp/°C	4/3[b]	Yield[c]/%
$NaBH_4$	8	EtOH	-78	0.52	91
$NaBH_4$	1	THF-Et_2O	-78 → -55	0.59	100
n-Bu_4NBH_4	2	THF	-78	0.64	89
$LiBH_4$	7	THF	-78 → r.t.	0.83	88
$Zn(BH_4)_2$	1	THF-EtO_2	-78 → r.t.	0.70	30
DIBAL-$ZnCl_2$	2	THF	-78	0.43	91
DIBAL	2	THF	-78	3.01	99

a) Based on H^- mol/mol.

b) Relative ratio of peak height of **4** (δ_P 35.9) to **3** (δ_P 36.9).

c) Isolated yield of a mixture of **3** and **4** based on **1**.

with various hydrides to give a diastereomeric mixture of **3** and **4**. The results are shown in Table II. The major diastereomer was the same as major one prepared by the reaction of **2a** and Grignard reagents with benzaldehyde. These ratios were much less than reported in the reduction of 2-oxoalkyl sulfoxide.[2-4] The reverse ratio was obtained only when diisobutylaluminum hydride was used as a reducing reagent.

The Structure Determination of 2-Hydroxy-2-phenylethyl(1-naphthyl)phenylphosphine Oxides (3 and 4)

Warren and his coworkers have reported on the X-ray crystal structure of erythro-3-hydroxy-3-phenyl-2-propyl(diphenyl)phosphine oxide (**6**).[7] An interesting feature of the structure is the P=O · · · H—O intramolecular hydrogen bonding, by which the molecule forms a six-membered ring. In the chair conformation α-methine and β-phenyl groups orient to pseudoaxial and pseudoequatorial, respectively, so that hydrogen atoms at α- and β-positions occupy pseudoequatorial and pseudoaxial positions (see Figure 1). The structure in solution seems to be similar to that in solid state, judging from the fact that the coupling constant between the two methine protons is ca. 1 Hz in the ^1H NMR spectrum, as expected from the dihedral angle in the crystal structure.[8] On the other hand, the coupling constant of threo-isomer is 9 Hz, indicating that both hydrogen atoms of α- and β-methine groups occupy the pseudoaxial positions in the same conformation of erythro-**6**. As to the chemical

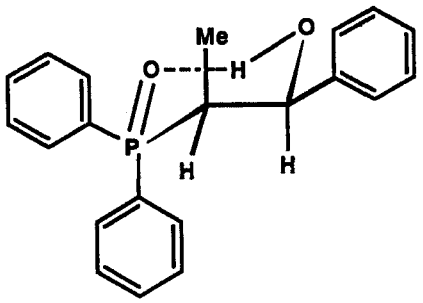


FIGURE 1 The schematic drawing of structure of erythro-**6**.

TABLE III

^{1}H NMR spectral data of aliphatic protrons of diastereomers **3** and **4**

Diastereomer	δ (J/Hz)	Assignment
3	2.63 ($^3J_{H,H}$=1.5, $^2J_{H,H}$=14.8, $^2J_{H,P}$=6.7)	PC<u>H</u>H'
	3.02 ($^3J_{H,H}$=10.6, $^2J_{H,H}$=14.8, $^2J_{H,P}$=10.6)	PCH<u>H'</u>
	5.21 ($^3J_{H,H}$=10.6, $^3J_{H,H}$=1.5, $^3J_{H,P}$=10.6)	C<u>H</u>OH
4	2.84 ($^3J_{H,H}$=2.2, $^2J_{H,H}$=15.3, $^2J_{H,P}$=7.0)	PC<u>H</u>H'
	2.93 ($^3J_{H,H}$=10.1, $^2J_{H,H}$=15.3, $^2J_{H,P}$=10.1)	PCH<u>H'</u>
	5.27 ($^3J_{H,H}$=10.1, $^3J_{H,H}$=2.2, $^3J_{H,P}$=10.1)	C<u>H</u>OH

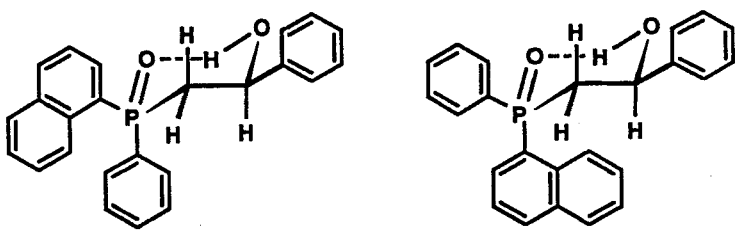
shift of α-protons those of the erythro isomer (pseudoequatorial) and the threo isomer (pseudoaxial) are δ 2.55 and 2.90, respectively. In the IR spectra taken in solution OH stretching (ν_{OH}) was observed at 3375 and 3370 cm^{-1} for **3** and **4**, respectively, and their frequencies did not change when measured at low concentration, indicating the existence of the intramolecular hydrogen bonding in solution. These compounds can be expected to have the similar conformation to that of **6**. The signals due to the protons on the main carbon skelton in ^{1}H NMR spectra of two diastereomers are shown in Table III. The coupling pattern is similar to each other, but the chemical shifts are very different, especially higher field one (δ 2.63 for **3** and 2.84 for **4**) due to one of methylene protons. In comparison with the chemical shifts of α-methine protons of erythro- and threo-**6** it is reasonably concluded that the signal at lower field (δ 3.02 for **3** and 2.93 for **4**) can be assigned to the pseudoaxial proton and that the pseudoequatorial proton of the polar isomer (**4**) resonates at lower field (δ 2.84) than that of erythro-**6** (δ 2.55). These facts can be explained as follows: The coupling constants between β-proton and one of the α-protons are 10.6 Hz for **3** and 10.1 Hz for **4**, suggesting that the β-proton is pseudoaxial, so that the β-phenyl group must occupy pseudoequatorial position in both diastereomers (**3** and **4**). In a chair form an equatorial substituent locates at the equal distant from neighboring axial and equatorial substituents. Since the ring

current of naphthalene seems to affect the neighboring proton more than that of benzene, the pseudoequatorial proton of the methylene group can be expected to be more deshielded when the 1-naphthyl group occupies pseudoaxial position. Therefore, a diastereomer whose signal due to pseudoequatorial proton of methylene resonates at lower field, that is, **4** must have the conformation in which 1-naphthyl and β-phenyl groups occupy pseudoaxial and pseudoequatorial positions, respectively. Thus, the chiral centers at the phosphorus and carbon atoms are S,S, or R,R, for **4**, and S,R or R,S for **3** (see Figure 2).

Transition State Model

The stereochemistry of the addition reaction of metallomethyl(1-naphthyl)-phenylphosphine oxide to benzaldehyde can be explained by the following transition state model: In a chair form of the six-membered ring larger 1-naphthyl group occupies pseudoequatorial position. Two transition states A and B can be considered (see Figure 3). Transition state A where there are no 1,3-interaction between two phenyl groups seems to be favored over the other to give (S,R)- or (R,S)-**3**.

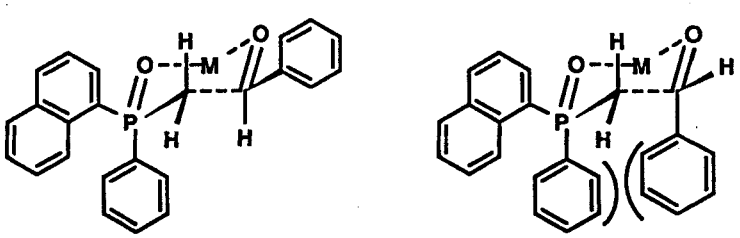
On the other hand the stereochemistry of the reduction of benzoylmethyl(1-naphthyl)phenylphosphine oxide (**5**) can be interpreted by Felkin's model (see Figure 4).[9] In Transition states C and D the largest ligand (the phosphoryl group) is aligned perpendicular to the carbonyl plane and the largest substituent (1-naph-



(*R*,*S*)- or (*S*,*R*)-3 **(*S*,*S*)- or (*R*,*R*)-4**

(Less polar isomer) **(Polar one)**

FIGURE 2 The structures of diastereomers **3** and **4**.



Transition state A **Transition state B**

FIGURE 3 Transition state model in the addition reaction to **2** to benzaldehyde.

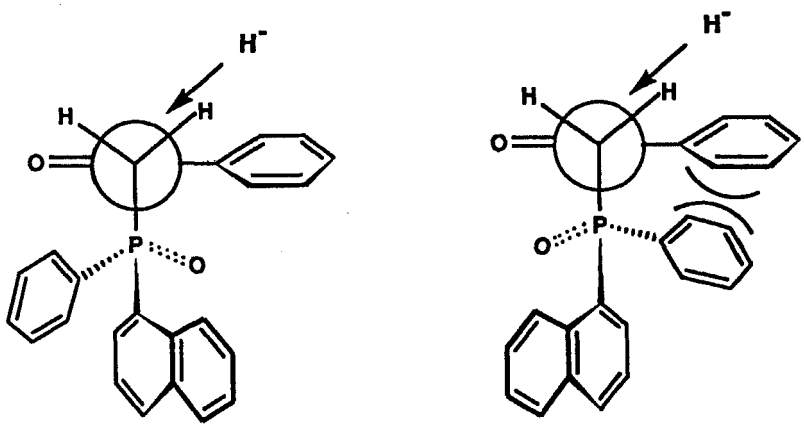


FIGURE 4 Transition state model in the reduction of **5**.

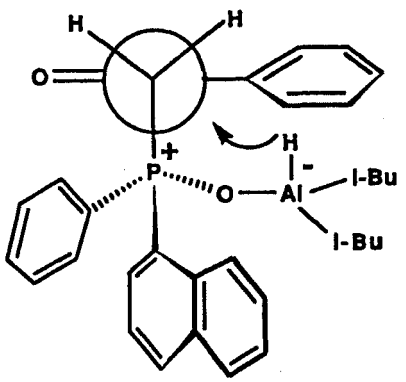


FIGURE 5 Transition state model in the reduction of **5** with DIBAL.

thyl group) of the rest of substituents of the phosphorus atom is aligned anti to C—C(O)Ph bond. Transition state C is favored over D, because of the absence of interaction between two phenyl groups. From Transition state C, **3** is formed predominantly. The present stereoselectivity cannot be explained by the chelation model which was proposed by Kosugi in the reduction of β-oxoalkyl sulfoxides.[4]

The reverse stereoselectivity on using DIBAL can be explained as follows: In Transition state C the oxygen atom of P=O bond coordinates to DIBAL with Lewis acidity to form "ate" complex, in which a hydride may attack to the carbonyl group from the back side (see Figure 5).

EXPERIMENTAL

Melting points and boiling points are uncorrected. ^{1}H NMR spectra were measured with a JEOL FX-90Q (90 MHz) spectrometer or a Bruker AM-500 (500.13 MHz) spectrometer using tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were taken with a Bruker AM-500 (125.77 MHz) spec-

trometer using TMS as internal standard. ^{31}P NMR spectra were recorded with a JEOL FX-90Q (36.28 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 mass spectrometer.

Preparation of methyl-1-naphthylphenylphosphine oxide (**1**). To an ethereal solution of 1-naphthylmagnesium bromide (1.5 M, 18 ml) was added a solution of ethyl methylphenylphosphinate[10] (1.00 g, 5.40 mmol) in benzene (22 ml) at room temperature under Ar. After ether was distilled off the reaction mixture was refluxed for 4 days. The reaction mixture was treated with dil HCl, extracted with dichloromethane, and dried over anhydrous $MgSO_4$. After evaporating the solvent the residue was subjected to chromatography on Al_2O_3 to give crude methyl-1-naphthylphenylphosphine oxide (**1**), which was purified by recrystallization from AcOEt to afford 0.819 g (51% yield) of pure **1**. Mp 150–153°C (lit,[11] mp 150–152°C). ^1H NMR ($CDCl_3$) δ = 2.14 (3H, d, $^2J_{H,P}$ = 12.9 Hz, PC$\underline{H}_3$), 7.38–8.04 (11H, m, Ph + Naph except peri-proton), and 8.37–8.52 (1 H, m, peri-proton of Naph). ^{31}P NMR ($CDCl_3$) δ_P = 31.9.

Preparation of benzoylmethyl(1-naphthyl)phenylphosphine oxide (**5**). To a solution of **1** (0.100 g, 0.38 mmol) in tetrahydrofuran (THF) (20 ml) was added n-BuLi (1.64 M hexane solution) (0.28 ml, 0.46 mmol) at −78°C under Ar. After stirring for 10 min benzonitrile (0.047 ml, 0.46 mmol) was syringed to the solution, then the reaction mixture was allowed to warm to 0°C. The usual workup gave 0.123 g (88%) of **5** as a pasty tar. ^1H NMR ($CDCl_3$) (500 MHz)[12] δ = 4.23 (1H, dd, $^2J_{H,H}$ = 13.8 Hz, $^2J_{H,P}$ = 15.0 Hz, PC$\underline{H}$H′), 4.39 (1H, dd, $^2J_{H,H}$ = 13.8 Hz, $^2J_{H,P}$ = 15.4 Hz, PCH$\underline{H}$′), 7.35 (2H, t, $^3J_{H,H}$ = 8.0 Hz, meta protons of CPh), 7.38–7.43 (2H, m, meta protons of PPh), 7.43–7.54 (5H, m, para protons of CPh and PPh, H-3, H-6, and H-7 of Naph), 7.77 (2H, ddd, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 12.4 Hz, $^4J_{H,H}$ = 1.4 Hz, ortho protons of PPh), 7.85 (1H, d, $^3J_{H,H}$ = 7.7 Hz, Hz, H-5 of Naph), 7.93 (2H, dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.0 Hz, ortho protons of CPh), 7.98–8.06 (2H, m, H-2 and H-4 of Naph), and 8.56 (1H, d, $^3J_{H,H}$ = 8.0 Hz, H-8 of Naph). ^{13}C NMR ($CDCl_3$)[12] δ_C = 43.69 (d,[13] $^1J_{C,P}$ = 59 Hz, P$\underline{C}H_2$), 124.32 (d, $^3J_{C,P}$ = 14 Hz, C-3 of Naph), 126.39 (s, C-6 of Naph), 126.43 (d, $^3J_{C,P}$ = 5.0 Hz, C-8 of Naph), 127.37 (s, C-7 of Naph), 128.32 (s, meta-C of CPh), 128.56 (d, $^3J_{C,P}$ = 12.4 Hz, meta-C of PPh), 128.63 (d, $^1J_{C,P}$ = 113 Hz, ipso-C of PPh), 128.95 (s, C-5 of Naph), 129.07 (s, ortho-C of CPh), 131.09 (d, $^2J_{C,P}$ = 10.5 Hz, ortho-C of PPh), 132.04 (d, $^4J_{C,P}$ = 2.8 Hz, para-C of PPh), 132.46 (d, $^2J_{C,P}$ = 10.5 Hz, C-2 of Naph), 132.57 (d, $^1J_{C,P}$ = 118 Hz, C-1 of Naph), 133.01 (d, $^3J_{C,P}$ = 13.8 Hz, C-4a, of Naph), 133.38 (s, para-C of CPh), 133.50 (d, $^4J_{C,P}$ = 2.8 Hz, C-4 of Naph), 133.74 (d, $^2J_{C,P}$ = 9.1 Hz, C-8a of Naph), 137.00 (s, ipso-C of CPh), and 192.96 (d, $^2J_{C,P}$ = 5.8 Hz, $\underline{C}$=O). ^{31}P NMR ($CDCl_3$) δ_P = 29.8. High resolution mass spectrum (HRMS) (70 eV): m/z Found: 370.1111. Calcd for $C_{24}H_{19}O_2P$: 370.1121.

Reaction of metallomethyl-1-naphthylphenylphosphine oxides with benzaldehyde

Lithio derivative. To a solution of **1** (0.344 g, 1.29 mmol) in THF (15 ml) was added dropwise n-BuLi (1.66 M) (0.93 ml, 1.54 mmol) at −78°C. After stirring for 0.5 to 1 h, benzaldehyde (0.164 g, 1.55 mmol) was added to the solution at −78°C. The reaction mixture was stirred for an additional 30 min, then aq. NH_4Cl was added to the solution. The organic layer was extracted with dichloromethane and dried over anhydrous $MgSO_4$. After removal of the solvent the residue was subjected to dry column chromatography on SiO_2 (Et_2O) to give quantitatively diastereomers **3** and **4** of 2-hydroxy-2-phenylethyl(1-naphthyl)phenylphosphine oxide in a ratio of 1:0.6. Less polar diastereomer (**3**): Mp 144–146°C (AcOEt). ^1H NMR ($CDCl_3$) (500 MHz)[12] δ = 2.63 (1H, ddd, $^3J_{H,H}$ = 1.5 Hz, $^2J_{H,H}$ = 14.8 Hz, $^2J_{H,P}$ = 6.7 Hz, PC$\underline{H}$H′), 3.02 (1H, dt, $^3J_{H,H}$ = $^2J_{H,P}$ = 10.6 Hz, $^2J_{H,H}$ = 14.8 Hz, PCH$\underline{H}$′), 5.21 (1H, dt, $^3J_{H,H}$ = $^3J_{H,P}$ = 10.6 Hz, $^3J_{H,H}$ = 1.5 Hz, C$\underline{H}$OH—), 5.45 (1H, s, O$\underline{H}$), 7.20–7.25 (1$\underline{H}$, m, para proton of CPh), 7.29 (2H, t, $^3J_{H,H}$ = 8.0 Hz, meta protons of CPh), 7.33 (2$\underline{H}$, d, $^3J_{H,H}$ = 7.0 Hz, ortho protons of CPh), 7.42–7.52 (5H, m, H-3, H-6 and H-8 of Naph and meta protons of PPh), 7.52–7.58 (1H, m, para proton of PPh), 7.76 (1H, dd, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 15.0 Hz, H-2 of Naph), 7.82 (2H, dd, $^3H_{H,H}$ = 8.0 Hz, $^3J_{H,P}$ = 12.0 Hz, ortho protons of PPh), 7.85–7.88 (1H, m, H-5 of Naph), 8.00 (1H, d, $^3J_{H,H}$ = 8.0 Hz, H-5 of Naph), and 8.58–8.62 (1H, m, H-8 of Naph). ^{13}C NMR ($CDCl_3$)[12] δ_C = 39.11 (d, $^1J_{C,P}$ = 69 Hz, P$\underline{C}H_2$), 69.16 (s, $\underline{C}$HOH—), 124.2 (d, $^3J_{C,P}$ = 14 Hz, C-3 of Naph), 125.41 (s, ortho-C of CPh), 126.24 (d, $^3J_{C,P}$ = 6 Hz, C-8 of Naph), 126.54 (s, C-6 of Naph), 127.50 (s, para-C of CPh), 127.54 (s, C-7 of Naph), 128.36 (s, meta-C of CPh), 128.43 (d, $^1J_{C,P}$ = 96 Hz, ipso-C of PPh), 128.84 (d, $^3J_{C,P}$ = 12 Hz, meta-C of PPh), 128.95 (s, C-5 of Naph), 130.98 (d, $^2J_{C,P}$ = 10 Hz, ortho-C of PPh), 131.22 (d, $^2J_{C,P}$ = 11 Hz, C-2 of Naph), 132.06 (d, $^1J_{C,P}$ = 98 Hz, C-1 of Naph), 132.08 (s, para-C of PPh), 132.85 (d, $^2J_{C,P}$ = 8 Hz, C-8a of Naph), 133.50 (d, $^4J_{C,P}$ = 3 Hz, C-4 of Naph), 133.75 (d, $^3J_{C,P}$ = 9 Hz, C-4a of Naph), and 143.80 (d, $^3J_{C,P}$ = 14 Hz, ipso-C of CPh). ^{31}P NMR ($CDCl_3$) δ_P = 36.9. HRMS (70 eV): m/z Found: 372.1296. Calcd for $C_{24}H_{21}O_2P$: 372.1280. IR ($CHCl_3$) ν_{OH} 3375 cm^{-1}. Polar diastereomer (**4**): Mp 151–153°C (AcOEt). ^1H NMR ($CDCl_3$) δ = 2.84 (1H, ddd, $^3J_{H,H}$ = 2.2 Hz, $^2J_{H,H}$ = 15.3 Hz, $^2J_{H,P}$ = 7.0 Hz, PC$\underline{H}$H′), 2.93 (1H, dt, $^3J_{H,H}$ = $^2J_{H,P}$ =

10.1 Hz, $^2J_{H,H}$ = 15.3 Hz, PCHH'), 5.20 (1H, s, OH), 5.27 (1H, dt, $^3J_{H,H}$ = $^3J_{H,P}$ = 10.1 Hz, $^3J_{H,H}$ = 2.2 Hz, CHOH—), 7.16–7.21 (1H, m, para proton of CPh), 7.24 (2H, t, $^3J_{H,H}$ = 7.0 Hz, meta protons of CPh), 7.31 (2H, d, $^3J_{H,H}$ = 7.0 Hz, ortho protons of CPh), 7.36 (2H, dt, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,P}$ = 2.8 Hz, meta protons of PPh), 7.40–7.50 (3H, m, H-6 and H-7 of Naph and para proton of PPh), 7.59 (1H, dt, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,P}$ = 2.0 Hz, H-3 of Naph), 7.67 (2H, dd, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,P}$ = 12 Hz, ortho protons of PPh), 7.89 (1H, d, $^3J_{H,H}$ = 8.1 Hz, H-5 of Naph), 8.06 (1H, d, $^3J_{H,H}$ = 8.2 Hz, H-4 of Naph), 8.15 (1H, dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 14.8 Hz, H-2 of Naph), and 8.22 (1H, $^3J_{H,H}$ = 8.0 Hz, H-8 of Naph). ^{13}C NMR ($CDCl_3$) δ_C = 39.02 (d, $^1J_{C,P}$ = 69 Hz, PCH$_2$), 69.40 (s, CHOH—), 124.54 (d, $^3J_{C,P}$ = 13 Hz, C-3 of Naph), 125.37 (s, ortho-C of CPh), 125.96 (d, $^3J_{C,P}$ = 5 Hz, C-8 of Naph), 126.35 (s, C-6 of Naph), 127.00 (d, $^1J_{C,P}$ = 96 Hz, ipso-C of PPh), 127.31 (s, para-C of CPh), 127.39 (s, C-7 of Naph), 128.29 (s, meta-C of CPh), 128.65 (d, $^3J_{C,P}$ = 12 Hz, meta-C of PPh), 129.14 (s, C-5 of Naph), 130.44 (d, $^2J_{C,P}$ = 10 Hz, ortho-C of PPh), 131.91 (s, para-C of PPh), 132.75 (d, $^2J_{C,P}$ = 9 Hz, C-8a of Naph), 132.98 (d, $^2J_{C,P}$ = 9 Hz, C-2 of Naph), 133.52 (d, $^4J_{C,P}$ = 3 Hz, C-4 of Naph), 133.70 (d, $^1J_{C,P}$ = 100 Hz, C-1 of Naph), 133.81 (d, $^3J_{C,P}$ = 9 Hz, C-4a of Naph), and 143.83 (d, $^3J_{C,P}$ = 13 Hz, ipso-C of CPh). ^{31}P NMR ($CDCl_3$) δ_P = 35.9. HRMS (70 eV): m/z Found: 372.1291. Calcd for $C_{24}H_{21}O_2P$: 372.1280. IR ($CHCl_3$) ν_{OH} 3370 cm^{-1}. The results obtained under various conditions are shown in Table I.

Reaction via transmetallation. To the solution of lithiomethyl-1-naphthylphenylphosphine oxide (**2a**) prepared from **1** (0.101 g, 0.379 mmol) as described above was added $MgCl_2$ (0.046 g, 0.483 mmol) (dried over P_4O_{10} under vacuum) at −78°C. The reaction mixture was stirred for 2 h at −50– −30°C. After cooling to −98°C, benzaldehyde (0.046 ml, 0.45 mmol) was added to the solution. It was kept for 1.5 h, was added aq. NH_4Cl to the solution. The usual workup gave a mixture of **1**, **3**, and **4** in a ratio of 1.65:1.0:0.51, respectively. When using $MgBr_2$, MgI_2, $ZnCl_2$, and $SnCl_2$, no product was obtained.

Reaction of Grignard derivative of **1** *prepared by deprotonation.* To the solution of **1** (0.102 g, 0.38 mmol) in THF (15 ml) was added ethylmagnesium bromide (0.954 M, 1.41 ml) and the mixture was refluxed for 4 h. After adding benzaldehyde (0.047 ml, 0.46 mmol), it was refluxed for 1 h. The usual workup gave a mixture (80% yield) of **3** and **4** in a ratio of 1.0:0.65.

Reduction of benzoylmethyl(1-naphthyl)phenylphosphine oxide (**5**) *with hydride reagents.* To a solution of **5** (0.0428 g, 0.116 mmol) in EtOH (5 ml) was added dropwise a solution of sodium borohydride (0.0089 g, 0.235 mmol) in EtOH (3 ml) at −78°C. After stirring for 2.5 h water was added to the solution. The usual workup gave a mixture (91% yield) of **3** and **4** in a ratio of 1.0:0.52. The results are shown in Table II.

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13. Abbreviation shows coupling mode with phosphorus nucleus.