The Wittig Rearrangement of Chiral *S*-Methyl Phosphinothioates Promoted by Direct Deprotonation with Lithium Dialkylamides

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Synopsis. Sequential treatment of *S*-methyl (*t*-butyl)phenyl- or (1-naphthyl)phenylphosphinothioates with lithium dialkylamides at −78 °C and then with alkyl halides at 0 °C—r.t. gave the corresponding (alkylthiomethyl)phosphine oxides, the Wittig rearrangement products, in moderate to good yields along with small amount of their overreacted α-alkylated products. The corresponding alkylphosphine oxide was obtained only in the reaction of naphthyl derivative. Optically active Wittig rearrangement products were given in 82 and 78% optical yields, respectively.

Generation of a carbanion at the neighboring position of sulfur atom can be achieved by use of *n*-BuLi in the presence of 1,4-diazabicyclo[2.2.2]octane or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.[1] However, in the case of the present substrate containing electrophilic moiety in the molecule selective deprotonation is difficult, because of the occurrence of competitive nucleophilic substitution reaction, as described previously.[2] We have reported use of the tin–lithium transmetallation in order to avoid such a situation.[3] We have also reported a novel synthetic method for optically active phosphorus compounds via chiral metal phosphinites[4] derived by chemoselective attack of nucleophiles on chalcogen atoms of phosphinodithioates and phosphinoselenoates.[5] Taking an electronic effect of the phosphoryl group into consideration, it is expected that metal dialkylamides can selectively abstract a proton of *S*-methyl group of the phosphinothioates. In this paper we describe the more convenient method for the generation of the carbanion followed by the Wittig rearrangement.

Results and Discussion

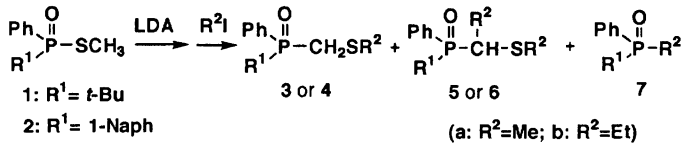
Sequential treatment of racemic *S*-methyl phosphinothioates **1** and **2** with 1.2 molar amount of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C and then with alkyl halides at 0 °C—r.t. gave the corresponding (alkylthiomethyl)phosphine oxides **3** and **4**, the Wittig rearrangement products, along with their overreacted products **5** and **6**, α-alkylated products of **3** and **4**, and alkylphosphine oxide **7**. The results are shown in Table 1. This is the first example for the Wittig rearrangement promoted by direct deprotonation of *S*-methyl phosphinothioate with a metal amide.

In the reaction of **1** the Wittig rearranged species **3a** and **3b** were obtained in 81 and 61% yields along with the overreacted species **5a** (5%) and **5b** (11%) and unreacted **1**, respectively. But in the reaction of **2** the yields of the rearrangement products **4a** and **4b** were low, even those of the overreacted species **6a** and **6b** being added. Compounds **7a** and **7b**, which seem to be formed by alkylation of the phosphinite anion with alkyl halides, were also obtained besides **4** and **6**. As shown in run 5, by use of 0.8 molar amount of LDA, the formation of overreacted compound could be inhibited, although the recovery of **1** increased.

In order to investigate steric effect of amides on the ratio of the rearrangement products **4** to alkylphosphine oxide **7**, the reactions with several amides were carried out and the products ratios were estimated by ^{31}P NMR spectroscopy.[6] The bases used were lithium dicyclohexylamide (LCHA), lithium 2,2,6,6-tetramethylpiperazide (LTMP), and lithium diethylamide (LEA). As shown in Table 2, the ratios of **4a**+**6a** to **7a** were 7:1, 7:2, 8:2, and 5:2 for LCHA, LTMP, LDA, and LEA, respectively, providing a very good similarity except for LEA. These results indicate that the ratio of the products is not influenced by the steric size of the lithium amide. Therefore, it can be concluded that an attack of the nucleophile on the sulfur atom, which selectively occurred in the reactions of phosphinodithioates and phosphinoselenoates with lithium reagents,[4a,4b] plays a very small role if any in the reaction. Generally speaking, nucleophilic substitution is affected by steric bulkiness of the reagent more than deprotonation. Thus, the phosphinite anion can be rationalized to be formed from the carbanion in accompany with elimination of thioformaldehyde. The reason why the phosphinite anion is formed from **2** and not from **1** can be explained from the difference in electronic effects of the substituents on two anions. In other words, the 1-naphthyl and *t*-butyl groups would stabilize and destabilize an anion, respectively, by inductive effect.

The stereochemistry of the present reaction was investigated by using optically active compounds. Optically active *S*-methyl phosphinothioates **1** and **2** were prepared by *S*-methylation of the corresponding optically active phosphinothioic acids with iodomethane, as described previously.[5a] In Table 3 are summarized optical rotation and optical purity of **1**, **2**, **3a**, and **4a** obtained in the present reaction along with those yielded in the reactions induced by tin–lithium transmetallation.[3] The optical rotation of **7a** was zero, indicating that (1-naphthyl)phenylphosphinite racemized completely before the reaction with MeI. The stereochemistry of the products of the LDA route was same as that of the tin containing ester route, showing that the present reaction proceeds with retention of

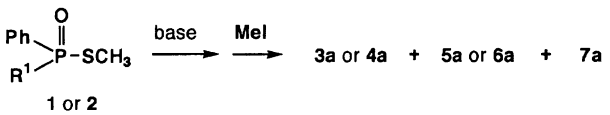
Table 1. Reactions of *S*-Methyl Phosphinothioates **1** and **2** with LDA[a)]



Run	R^1	R^2	Yield[b)]/%			
			3 or **4**	**5** or **6**	**7**	**1** or **2**
1	*t*-Bu	Me	81	5	—	5
2	*t*-Bu	Et	61	11	—	7
3	1-Naph	Me	39	7	12	12
4	1-Naph	Et	40	5	9	10
5[c)]	*t*-Bu	Me	58	—	—	39

a) 1.2 molar amount of LDA was used. b) Isolated yields based on **1** or **2**. c) 0.8 molar amount of LDA was used.

Table 2. The Relative ^{31}P NMR Intensities of Reaction Products of *S*-Methyl Phosphinothioates **1** and **2** with Lithium Dialkylamides[a,b)]



Run	R^1	Base	**3a** or **4a**	**5a** or **6a**	**7a**	**1** or **2**
1	*t*-Bu	LCHA	15	2	—	1
2	*t*-Bu	LTMP	15	2	—	1
3	*t*-Bu	LDA	15	1	—	—
4[c)]	*t*-Bu	LEA	1	—	—	—
5[d)]	1-Naph	LCHA	6	1	2	1
6	1-Naph	LTMP	5	2	2	1
7	1-Naph	LDA	7	1	2	1
8[e)]	1-Naph	LEA	5	—	2	4

a) 1.2 molar amount of bases was used. b) The relative intensity based on the smallest peak. c) Isolated yield of **3a** was 83% d) Isolated yields of **4a**, **6a**, and **7a** were 37, 5, and 10%, respectively. e) Isolated yields of **4a** and **7a** were 26 and 10%, respectively.

configuration. The optical yields of **3a** and **4a** were calculated to be 82 and 78%, respectively, from the optical purity, indicating that a partial racemization occurred in this case. Although there has been no report on configurational stability of lithium (1-naphthyl)phenylphosphinite, lithium (*t*-butyl)phenylphosphinite generated by the reaction of the corresponding phosphinoselenoate with phenyllithium is known not to racemize under the same reaction conditions.[5b)] If the reaction proceeds via an elimination–addition pathway giving a phosphinite anion as an intermediate the bulkiness around a central phosphorus atom would increase through the hydrogen bonding of the phosphinite anion with the amine, so that the ground state maybe become more flat to make inversion barrier lower. An alternative explanation is also possible, namely, if the Wittig rearrangement takes place via three-membered oxide anion the intermediate would be stabilized by hydrogen bonding with the amine to elongate its life time, leading partial racemization by pseudorotation.[7)] Thus, it can be said that the presence or absence of the hydrogen bonding with the amine determines whether racemization occurs or not.

Therefore, plausible mechanism of the present reaction is as follows: First of all proton abstraction occurs to give **A**, which provides **C** with elimination of thioformaldehyde or rearranges to **D** via a three-membered oxidophosphorane **B** (see Scheme 1). The anion **D** could also be formed from **C** by the rapid recombination of the once eliminated thioformaldehyde. Then **D** could lose another proton to give **E** or retain its monoanion form. Thus formed anions **C**, **D**, and **E** could react with various electrophiles to give the corresponding products. Although attempts to trap thioformaldehyde using 1,3-dienes and to detect trithiane, a cyclic trimer of thioformaldehyde, were unsuccessful, presumably because of base-catalyzed polymerization of diene and thioformaldehyde, this mechanism is most likely for the formation of **7**.

Experimental

All melting points and boiling points are not corrected. ^1H NMR spectra were measured with a JEOL EX-270 or Bruker AM-500 spectrometer using tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were taken with a JEOL EX-270 or Bruker AM-500 spectrometer using TMS as internal standard. ^{31}P NMR spectra were measured with a JEOL FX-90Q spectrometer using 85% H_3PO_4 as external standard. Mass spectra were recorded with a JEOL JMX-SX 102 mass spectrometer operating in the electron impact (EI) mode. Optical rotation was measured with a JASCO DIP-181 polarimeter. Dry column chromatography and preparative TLC were carried out with ICN silica DCC 60A and Merck Kieselgel 60 PF_{254}, respectively.

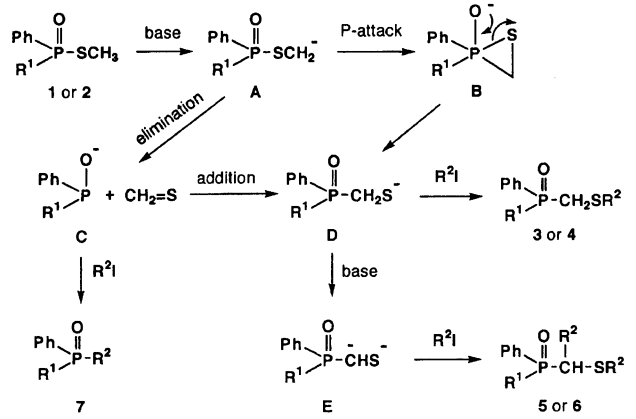
S-Methyl (*t*-butyl)phenylphosphinothioate (**1**) and (1-naphthyl)phenylphosphinothioate (**2**) were prepared from the corresponding phosphinothioic acids.[8)]

1: Bp 110 °C/0.15—0.2 Torr (1 Torr=133.322 Pa). ^1H NMR (270 MHz, $CDCl_3$) δ=1.19 (9H, d, J=16.8 Hz,

Table 3. Optical Rotations and Optical Purity of **1**, **2**, **3a**, and **4a**[a)]

	$[\alpha]_D^T$					$[\alpha]_D^T$			
	α/°	T/°C	c/g dl^{-1}	o.p./%		α/°	T/°C	c/g dl^{-1}	o.p./%
1[b)]	+124	17	1.74	93	**2**[c)]	−43.3	24	0.878	93
3a[d)]	+62.0	16	0.793	76	**4a**[d)]	+6.45	17	0.366	73
3a[e)]	−81.0	17	0.639	99	**4a**[c,f)]	+8.22	20	0.810	93

a) Optical rotations were measured in $CHCl_3$. b) Prepared from 93% optically pure ((+)-(*R*)-*t*-BuPhP(S)OH ($[\alpha]_D^{18}$ +26.1 (*c* 1.29, MeOH)). c) Prepared from 93% optically pure Et_2NH salts of (−)-1-NaphPhP(S)OH ($[\alpha]_D^{25}$ −60.4° (*c* 0.770, $CHCl_3$)). d) This work. e) Ref. 3, (−)-(*S*)-*t*-BuPhP(S)OH ($[\alpha]_D^{22}$ −27.8° (*c* 2.35, MeOH)) (o.p. 99%) was used. f) Ref. 3.



Scheme 1.

$C(CH_3)_3$), 2.14 (3H, d, J=10.5 Hz, SCH_3), 7.36—7.64 (3H, m, *meta*- and *para*-H of Ph), and 7.73—8.06 (2H, m, *ortho*-H of Ph). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$) δ=9.26 (d, ^2J= 3.0 Hz, SCH_3), 24.46 (s, $C(\underline{C}H_3)_3$), 36.8 (d, ^1J=70.6 Hz, $\underline{C}(CH_3)_3$), 128.15 (d, ^3J=11.7 Hz, *meta*-C), 129.83 (d, ^1J= 91.6 Hz, *ipso*-C), 131.80 (d, ^4J=2.8 Hz, *para*-C), and 132.85 (d, $^2J_{CP}$=9.0 Hz, *ortho*-C). ^{31}P NMR (36 MHz, $CDCl_3$) δ=67.78. HRMS (70 eV) Found: m/z 228.0741. Calcd for $C_{11}H_{17}OPS$: M, 228.0738.

2: Mp 183.5—184.5 °C. ^1H NMR (270 MHz, $CDCl_3$) δ=2.32 (3H, d, J=12.2 Hz, $SC\underline{H}_3$), 7.40—7.58 (6H, m), 8.82—7.93 (3H, m), 7.97—8.08 (2H, m), and 8.73—8.82 (1H, m). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ=10.87 (d, $^2J_{CP}$=2.5 Hz, SCH_3), 124.23 (d, ^3J=14.7 Hz), 126.41 (s), 126.80 (d, ^3J=4.9 Hz), 127.18 (s), 128.25 (d, ^1J=103.7 Hz), 128.61 (d, ^3J=13.4 Hz), 128.71 (s), 131.46 (d, ^2J=11.0 Hz), 132.20 (d, ^4J=2.4 Hz), 132.94 (d, ^3J=9.7 Hz), 133.09 (d, ^2J=11.0 Hz), 133.10 (d, ^1J=107.4 Hz), 133.62 (d, ^4J= 3.7 Hz), and 133.82 (d, ^2J=9.7 Hz). ^{31}P NMR (36 MHz, $CDCl_3$) δ=46.44. HRMS (70 eV) Found: m/z 298.0591. Calcd for $C_{17}H_{15}OPS$: M, 298.0581. Found: C, 68.23; H, 4.87%. Calcd for $C_{17}H_{15}OPS$: C, 68.44; H, 5.07%.

Reactions of *S*-Methyl Phosphinothioates with Lithium Amides. The Reaction of 1 with LDA. To a solution of **1** (196 mg, 0.858 mmol) in THF (20 ml) was added freshly prepared LDA (1.2 molar amount) at −78 °C, and the mixture was stirred at 0 °C for 15 min. Then iodomethane (0.25 ml, ca. 4 molar amounts) was added to the solution by a syringe, then the mixture was stirred at room temperature overnight. The reaction mixture was treated with aq NH_4Cl, extracted with CH_2Cl_2, the extracts were dried over anhydrous $MgSO_4$. After removal of the solvent the residue was subjected to dry column chromatography on SiO_2 (ether–ethyl acetate) to give *t*-butyl(methylthiomethyl)phenylphosphine oxide (**3a**) *t*-butyl(1-methylthioethyl)-phenylphosphine oxide (**5a**), in yields of 81 and 5%, respectively, with recovery of **1** (9.8 mg, 5%).

3a: Mp 153—154 °C (hexane–CH_2Cl_2). ^1H NMR (270 MHz, $CDCl_3$) δ=1.17 (9H, d, J=14.5 Hz, $C(C\underline{H}_3)_3$), 2.28 (3H, s, $SC\underline{H}_3$), 3.07 (2H, d, J=6.9 Hz, $PC\underline{H}_2$), 7.44—7.60 (3H, m, *meta*- and *para*-H of PPh), and 7.69—7.80 (2H, m, *ortho*-H of PPh). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$) δ= 17.98 (d, $^3J_{CP}$=2.4 Hz, SCH_3), 24.61 (s, $C(\underline{C}H_3)_3$), 26.38 (d, $^1J_{CP}$=59.8 Hz, PCH_2), 33.49 (d, $^1J_{CP}$=67.1 Hz, $\underline{C}(CH_3)_3$), 128.14 (d, $^3J_{CP}$=11.0 Hz, *meta*-C), 129.50 (d, $^1J_{CP}$=90.4 Hz, *ipso*-C), 131.61 (d, $^4J_{CP}$=2.4 Hz, *para*-C), and 131.88 (d, $^2J_{CP}$=7.3 Hz, *ortho*-C). ^{31}P NMR (36 MHz, $CDCl_3$) δ=47.72. HRMS (70 eV) Found: m/z 242.0900. Calcd for $C_{12}H_{19}OPS$: M, 242.0894. Found: C, 59.20; H, 7.82; S, 13.68%. Calcd for $C_{12}H_{19}OPS$: C, 59.48; H, 7.90; S, 13.23%.

5a: Diastereomeric mixture. ^{31}P NMR (36 MHz, $CDCl_3$) δ=49.4 and 50.41 (45 : 55). HRMS (70 eV) Found: m/z 256.1053. Calcd for $C_{13}H_{21}OPS$: M, 256.1051.

Major diastereomer: ^1H NMR (270 MHz, $CDCl_3$) δ=1.23 (9H, d, $^3J_{HP}$=14.2 Hz, $C(C\underline{H}_3)_3$), 1.68 (3H, dd, J=7.3 Hz, $^3J_{HP}$=13.4 Hz, $CHC\underline{H}_3$), 2.16 (3H, s, $SC\underline{H}_3$), 3.19 (1H, dq, J=7.3 Hz, $^3J_{HP}$=9.2 Hz, $C\underline{H}CH_3$), 7.42—7.59 (3H, m, *meta*- and *para*-H of Ph), and 7.80—7.91 (2H, m, *ortho*-H of PPh).

Minor diastereomer: ^1H NMR (270 MHz, $CDCl_3$) δ=1.29 (9H, d, $^3J_{HP}$=14.5 Hz, $C(C\underline{H}_3)_3$), 1.40 (3H, dd, J=7.3 Hz, $^3J_{HP}$=13.5 Hz, $CHC\underline{H}_3$), 2.36 (3H, s, $SC\underline{H}_3$), 3.12 (1H, dq, J=7.3 Hz, $^3J_{HP}$=5.0 Hz, $C\underline{H}CH_3$), 7.42—7.59 (3H, m, *meta*- and *para*-H of Ph), and 7.69—7.78 (2H, m, *ortho*-H of PPh).

Similar reactions using **1** with EtI instead of MeI as well as those using **2** with MeI or EtI were carried out, the results are summarized in Table 1.

3b: Mp 70—71 °C (hexane–ether). ^1H NMR (270 MHz, $CDCl_3$) δ=1.16 (9H, d, $^3J_{HP}$=14.8 Hz, $C(C\underline{H}_3)_3$), 1.22 (3H, t, ^3J=7.4 Hz, $SCH_2C\underline{H}_3$), 2.59—2.86 (2H, m, $SC\underline{H}_2$), 3.09 (2H, $^2J_{HP}$=6.6 Hz, $PC\underline{H}_2S$), 7.42—7.59 (3H, m, *meta*- and *para*-H of PPh), and 7.67—7.77 (2H, m, *ortho*-H of PPh). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$) δ=14.11 (s, $SCH_2\underline{C}H_3$), 24.10 (d, $^1J_{CP}$=63.5 Hz, PCH_2), 24.57 (s, $C(\underline{C}H_3)_3$), 28.13 (d, $^3J_{CP}$=2.4 Hz, $S\underline{C}H_2CH_3$), 33.40 (d, $^1J_{CP}$=67.1 Hz, $\underline{C}(CH_3)_3$), 128.05 (d, $^3J_{CP}$=11.0 Hz, *meta*-C), 129.45 (d, $^1J_{CP}$=90.3 Hz, *ipso*-C), 131.52 (d, $^4J_{CP}$=2.4 Hz, *para*-C), and 131.79 (d, $^2J_{CP}$=7.31 Hz, *ortho*-C). ^{31}P NMR (36 MHz, $CDCl_3$) δ=47.45. HRMS (70 eV) Found: m/z 256.1044. Calcd for $C_{13}H_{21}OPS$: M, 256.1051. Found: C, 60.91; H, 8.26; S, 12.51%. Calcd for $C_{13}H_{21}OPS$: C, 60.84; H, 7.96; S, 12.62%.

4a: Mp 147—148 °C (decomp) (hexane—ether). ^{1}H NMR (270 MHz, $CDCl_3$) δ=2.21 (3H, s), 3.34—3.50 (2H, m, PC$\underline{H}_2$), and 7.42—7.58 (6H, m), 7.78—7.94 (4H, m), 8.04 (1H, d, J=7.9 Hz), and 8.50—8.58 (1H, m). ^{31}P NMR (36 MHz, $CDCl_3$) δ=32.03. HRMS (70 eV) Found: m/z 312.0734. Calcd for $C_{18}H_{17}OPS$: M, 312.0738. Found: C, 68.95; H, 5.56; S, 10.51%. Calcd for $C_{18}H_{17}OPS$: C, 69.21, H, 5.49; S, 10.26%.

4b: Colorless solid: ^{1}H NMR (270 MHz, $CDCl_3$) δ= 1.19 (3H, t, J=7.4 Hz, $SCH_2C\underline{H}_3$), 2.64 (2H, q, J=7.4 Hz, $SC\underline{H}_2CH_3$), 3.34—3.54 (2H, m, PC$\underline{H}_2$), 7.36—7.58 (6H, m), 7.70—7.92 (4H, m), 7.95—8.08 (1H, m), and 8.46—8.60 (1H, m). ^{31}P NMR (36 MHz, $CDCl_3$), δ=32.11. HRMS (70 eV) Found: m/z 326.0887. Calcd for $C_{19}H_{19}OPS$: M, 326.0894.

5b: Diastereomeric mixture (ca. 1 : 1), which were separated by preparative TLC (SiO_2, ether). Less polar diastereomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.04 (3H, t, J=7.3 Hz, $CHCH_2C\underline{H}_3$), 1.24 (3H, t, J=7.5 Hz, $SCH_2C\underline{H}_3$), 1.28 (9H, d, $^3J_{HP}$=14.4 Hz, $(C\underline{H}_3)_3$), 1.50—1.79 (2H, m, $CHC\underline{H}_2CH_3$), 2.74—2.84 (2H, m, $SC\underline{H}_2CH_3$), 3.01—3.09 (1H, m, $C\underline{H}CH_2CH_3$), and 7.40—7.52 (3H, m, *meta*- and *para*-H of PPh), and 7.68—7.77 (2H, m, *ortho*-H of PPh). ^{31}P NMR (36 MHz, $CDCl_3$), δ=49.47. HRMS (70 eV) Found: m/z 284.1354. Calcd for $C_{15}H_{25}OPS$: M, 284.1364.

Polar diastereomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ= 1.10 (3H, t, J=7.3 Hz, $CHCH_2C\underline{H}_3$), 1.14 (3H, t, J= 7.5 Hz, $SCH_2C\underline{H}_3$), 1.24 (9H, d, $^3J_{HP}$=14.3 Hz, $(C\underline{H}_3)_3$), 1.66—1.76 (1H, m, $CHC\underline{H}H'CH_3$), 2.13—2.23 (1H, m, $CHCH\underline{H}'CH_3$), 2.52—2.66 (2H, m, $SC\underline{H}_2CH_3$), 2.94—3.00 (1H, m, $C\underline{H}CH_2CH_3$), and 7.40—7.47 (3H, m, *meta- para*-H of PPh), and 7.84—7.90 (2H, m, *ortho*-H of PPh). ^{31}P NMR (36 MHz, $CDCl_3$) δ=48.26. HRMS (70 eV) Found: m/z 284.1381. Calcd for $C_{15}H_{25}OPS$, M, 284.1364.

6a: Diastereomeric mixture. HRMS (70 eV) Found: m/z 326.0905. Calcd for $C_{19}H_{19}OPS$: M, 326.0894. ^{31}P NMR (36 MHz, $CDCl_3$) δ=37.36 and 37.89 (43 : 57).

Major diastereomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.61 (3H, dd, J=7.3 Hz, $^3J_{HP}$=15.2 Hz, $CHC\underline{H}_3$), 1.95 (3H, s, SCH_3), 3.99 (1H, dq, J=7.3 Hz, $^2J_{HP}$=10.2 Hz, PCHS), 7.40—7.60 (6H, m), 7.75—8.10 (5H, m), and 8.66—8.76 (1H, m).

Minor diastereomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.63 (3H, dd, J=7.3 Hz, $^3J_{HP}$=15.2 Hz, $CHC\underline{H}_3$), 1.84 (3H, s, SCH_3), 4.07 (1H, dq, J=7.3 Hz, $^2J_{HP}$=10.1 Hz, PCHS), 7.40—7.60 (6H, m), 7.75—8.10 (5H, m), and 8.80—8.90 (1H, m).

6b: Diastereomeric mixture: HRMS (70 eV) Found: m/z 354.1197. Calcd for $C_{21}H_{23}OPS$: M, 354.1207. ^{31}P NMR (36 MHz, $CDCl_3$) δ=36.82 and 37.63 (49 : 51).

Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.93 (3H, t, J=7.4 Hz, $CH_2C\underline{H}_3$), 1.19 (3H, t, J=7.1 Hz, $SCH_2C\underline{H}_3$), 1.62—1.78 (2H, m), 2.15—2.28 (1H, m), 2.49—2.59 (1H, m), 3.22—3.28 (1H, m, PC$\underline{H}$S), 7.40—7.58 (6H, m), 7.65—7.75 (2H, m), 7.98—8.09 (3H, m), and 8.87 (1H, d, J=8.0 Hz).

Minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.03 (3H, t, J=7.4 Hz, $CH_2C\underline{H}_3$), 1.20 (3H, t, J=7.1 Hz, $SCH_2C\underline{H}_3$), 2.02—2.12 (1H, m), 2.15—2.28 (2H, m), 2.36—2.43 (1H, m), 3.10—3.17 (1H, m, PC$\underline{H}$S), 7.40—7.58 (6H, m), 7.65—7.75 (2H, m), 7.98—8.09 (3H, m), and 8.73 (1H, d, J=8.3 Hz).

7a: Mp 152—153 °C (lit,[9] mp 150—153 °C).

7b: Mp 143—144 °C (decomp) (ether). ^{1}H NMR (270 MHz, $CDCl_3$) δ=1.24 (3H, dt, J=7.6 Hz, $^3J_{HP}$=17.4 Hz, $PCH_2C\underline{H}_3$), 2.35—2.46 (1H, m, PC$\underline{H}$H'), 2.48—2.60 (1H, m, PCH$\underline{H}$'), 7.40—7.55 (6H, m), 7.68—7.75 (2H, m), 7.85—7.93 (2H, m), 8.02 (1H, d, J=8.2 Hz), and 8.63 (1H, d, J=8.3 Hz). ^{31}P NMR (36 MHz, $CDCl_3$) δ=36.14. HRMS (70 eV) Found: m/z 280.1024. Calcd for $C_{18}H_{17}OP$: M, 280.1017. Found: 76.90; H, 5.99%. Calcd for $C_{18}H_{17}OP$: C, 77.13; H, 6.11%.

The Reactions of Optically Active 1 and 2. Optically active **1** ($[\alpha]_D^{17}$ +124° (c 1.74, $CHCl_3$)) and **2** ($[\alpha]_D^{24}$ −43.3° (c 0.878, $CHCl_3$)) were prepared from (+)-(*R*)-(*t*-butyl)phenylphosphinothioic acid ($[\alpha]_D^{18}$ +26.1° (c 1.29, MeOH) (optical purity (o.p.) 93%))[8a] and diethylammonium (−)-(1-naphthyl)phenylphosphinothioate ($[\alpha]_D^{25}$ −60.4° (c 0.77, $CHCl_3$) (o.p. 93%)),[8b] respectively.

A similar reaction using optically active **1** and **2** gave (+)-**3a** ($[\alpha]_D^{16}$ +62.0° (c 0.793, $CHCl_3$)) and (+)-**4a** ($[\alpha]_D^{17}$ +6.45° (c 0.366, $CHCl_3$)) in 82 and 78% optical yields, respectively. Spectral data were agreement with those of racemic ones.

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6) Of course the comparison of peak intensity is not suitable for estimation of correct product ratio, because each phosphorus nucleus has different NOE and relaxation time (T1), resulting different relative sensitivity. But, it can be used semiquantitatively as shown from the results after isolation in certain runs.

7) For this racemization Berry pseudorotation mechanism has a large energy barrier, but turnstile rotation mechanism, $(TR)^2$-change pair-$(TR)^3$, can by-pass the barrier. For turnstile rotation, see: P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 91 (1973).

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