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Generation of Metal Phosphinites by the Reaction of *Se*-Alkyl Phosphinoselenoates with Organometallics and Its Application to the Synthesis of Optically Active Organophosphorus Compounds

Takayuki Kawashima,* Hiroki Iwanaga, and Renji Okazaki*

Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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ABSTRACT

Reaction of Se-Alkyl phosphinoselenoates with organometallics resulted in a selective attack on the selenium atom. Sequential treatment of optically active Se-benzyl t-butylphenylphosphinoselenoate with PhLi and then with electrophiles, such as alkyl halides, an α,β-unsaturated ester, and chalcogen atoms, gave optically active phosphorus compounds in 5–91% yields and in high optical yields, with retention of configuration at the phosphorus atom, along with a quantitative yield of benzyl phenyl selenide.

INTRODUCTION

Although nucleophilic substitution reactions at a phosphorus atom have been known as one of the excellent methods for the synthesis of optically active phosphorus compounds, the stereochemistry and stereospecificity are highly dependent on the lifetime of a pentacovalent intermediate [1]. On the other hand, much attention has been paid to optically active secondary phosphine oxides, sulfides, and boranes, because of their easy conversion to optically active phosphorus compounds [2]. In the course of our studies on the reaction of phosphinothioates and phosphinodithioates with nucleophiles [3], we reported the synthesis of optically active phosphine sulfides via the corresponding phosphinothioite [4]. In the previous communication [5], we reported a new synthetic method for optically active phosphorus compounds by chemoselective reaction of optically active phosphinoselenoates with phenyllithium, followed by treatment with electrophiles. In this article, we wish to describe the detailed results as well as the reaction of diphenylphosphinoselenoates.

RESULTS AND DISCUSSION

Reaction of Se-Methyl Diphenylphosphinoselenoate (**1**) *with Organometallics RM* (**2**)*, followed by Benzylation with Benzyl Bromide*

Sequential treatment of **1** with RM (**2**) (1 equiv) and benzyl bromide (1 equiv) gave a mixture of benzyldiphenylphosphine oxide (**3**) and phosphine oxide $Ph_2P(O)R$ (**4**) after dry column chromatography (SiO_2, AcOEt), as shown in Table 1. In the case of the reaction with *n*-BuLi, a complex mixture was obtained, probably because the product formed by an attack on the phosphorus atom has acidic methylene protons attached to the phosphinyl group that can be easily deprotonated with unreacted *n*-BuLi (see run 3). Use of a Grignard reagent gave better selectivity, albeit in lower chem-

Dedicated to Professor Shigeru Oae on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

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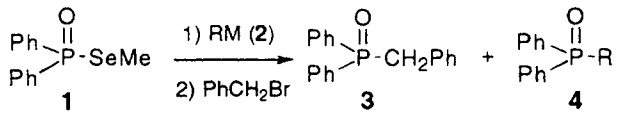
TABLE 1 Reaction of **1** with Organometallics (**2**), followed by Benzylation

Run	*RM*	*Yields*[a]/%	**3**:**4**
1	PhLi	75	60:40
2	PhMgBr	62	80:20
3	*n*-BuLi	16[b]	—
4	*t*-BuLi	—[c]	80:20

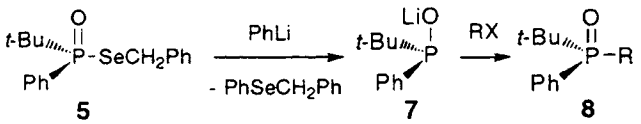
[a]Total isolated yields (**3** and **4**) based on **1**.
[b]A complex mixture was obtained. Only **3** was identified.
[c]Not isolated.

ical yields, than that of the corresponding lithium reagent (see runs 1 and 2).



Reaction of Se-Benzyl t-Butylphenylphosphinoselenoate (**5**) *with PhLi:*

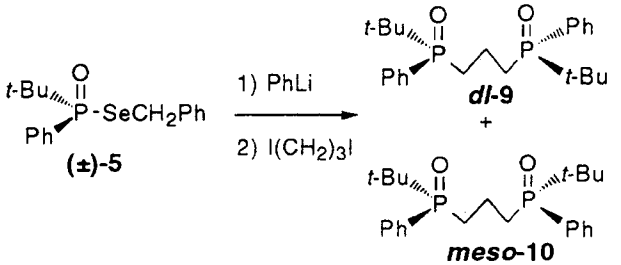
Reaction Using Alkyl Halides as Electrophiles Optically active **5** was prepared by *Se*-benzylation of readily resolved phosphinoselenoic acid **6** [6]. The reaction of racemic or optically active *Se*-benzyl *t*-butylphenylphosphinoselenoate (**5**) (0.29–1.27 mmol) with phenyllithium (1.1–1.2 equiv) was carried out at −78°C in tetrahydrofuran (THF) (8–15 mL) and then an alkyl halide (1.2–1.5 equiv) was added at −78°C. After warming the solution to room temperature for 15 hours, dry column chromatography (dry CC) afforded the corresponding phosphine oxide **8** along with benzyl phenyl selenide. The results of several such sequences of reaction are summarized in Table 2.

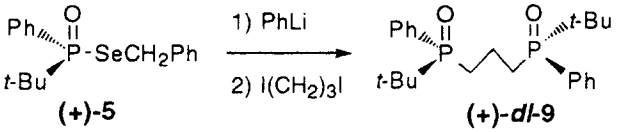


The optical purity (op) of phosphine oxide **8a** was estimated to be 92% from the highest specific rotation [7], where **8a** and **8c** were found to be optically pure by Harger's method [8]. Quantitative formation of benzyl phenyl selenide indicates that phenyl-lithium exclusively attacked the selenium atom to give phosphinite **7** in contrast with the results of reactions of thiol esters of phosphinothioates with nucleophiles [3]. Such a high chemoselectivity is most likely due to faster Li/Se exchange compared with Li/S exchange [9].

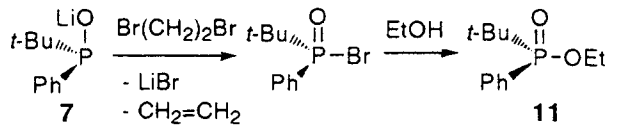
Reaction Using Dihaloalkanes as Electrophiles

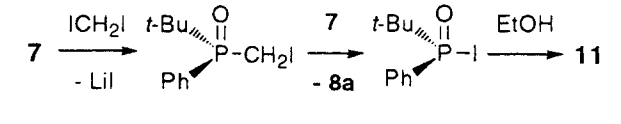
The reaction of racemic phosphinite **7** generated from (±)-**5** with 0.5 equiv of 1,3-diiodopropane gave a 1:1 mixture (93%) of *dl*- (**9**, δ_P 51.5) and *meso*-1,3-bis(*t*-butylphenylphosphinyl)propanes (**10**, δ_P 50.1). Use of (+)-**5** afforded a single diastereomer (+)-*dl*-**9** (76%), showing that no racemization occurred in spite of two opportunities to increase its chance.





The reactions of racemic **7**, generated by reaction of PhLi with racemic **5**, with 1,2-dibromoethane or diiodomethane as electrophile, afforded ethyl *t*-butylphenylphosphinate (**11**) (59%) or a mixture of **11** (39%) and **8a** (35%), respectively, after elution with ethanol in dry CC. These results show that the following halophilic reactions took place, and the resulting phosphinyl halides underwent reaction with ethanol, used as an eluant solvent, to afford **11**.





Reaction Using Methyl Acrylate as an Electrophile

The reaction of chiral phosphinite **7**, generated from (−)-**5**, as described earlier, with methyl acrylate afforded optically active methyl 3-(*t*-butylphenylphosphinyl)propanoate (**12**) (5%). The absolute value of the specific rotation of the product was 1.1°, but it was found by Harger's method that **12** had a high optical purity (>95%), indicating that the value of its specific rotation does not mean that racemization had taken place. The very low yield (5%) of

TABLE 2 Yields and Specific Rotation of *t*-Butylphenylphosphine Oxides **8**

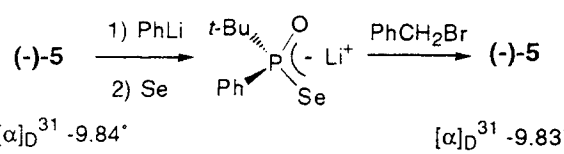
8		R	X	Yields[a] (%)	Specific Rotation
a:	(±)-**5**	Me	I	85	—
	(−)-**5**			91	$[\alpha]_D^{23}$ + 20.9° (c 0.297, MeOH)[b]
b:	(−)-**5**	Et	I	75	$[\alpha]_D^{27}$ − 20.3° (c 0.104, MeOH)
c:	(±)-**5**	$PhCH_2$	Br	89	—
	(−)-**5**			72	$[\alpha]_D^{22}$ − 115.9° (c 0.773, MeOH)
d:	(+)-**5**	*n*-Bu	I	56	$[\alpha]_D^{17}$ + 14.3° (c 0.756, MeOH)

[a] Isolated yields based on **5**.
[b] Optical purity was 92% [7].

12 seems attributable to use of a readily-polymerizable reactant.

Reaction Using Chalcogen Atoms as Electrophiles

The reaction of the chiral lithium phosphinite **7** with elemental sulfur afforded optically active *t*-butylphenylphosphinothioic acid (**13**) (67%). The optical purity of **13** was estimated to be 90% from the highest specific rotation [8]. The ^{31}P NMR spectrum of **13** in the presence of (*S*)-(−)-1-phenylethylamine (op >99%) showed only one singlet, indicating that **13** had a very high optical purity. A similar reaction using (−)-**5**($[\alpha]_D^{31}$ −9.84° (c 0.838, MeOH)), followed by treatment with elemental selenium, and then with benzyl bromide, gave (−)-**5** (61%) with almost the same optical rotation ($[\alpha]_D^{31}$ −9.83° (c 0.290, MeOH)) as that of the starting **5**, indicating also that all steps proceeded with a retention of configuration at the phosphorus atom and without any racemization.



In summary, we have demonstrated that optically active phosphorus compounds can be obtained with a high retention of configuration at the phosphorus atom through chemoselective reaction of phenyllithium on the selenium atom of *Se*-alkyl phosphinoselenoates.

EXPERIMENTAL

All melting points are not corrected. ^1H NMR spectra were measured with a JEOL FX-90 spectrometer using tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were taken with a 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 rotations were measured with a JASCO DIP-181 polarimeter. Dry CC and preparative thin-layer chromatography (PTLC) were carried out with ICN silica DCC 60A and Merck Kieselgel 60 PF_{254}, respectively.

Chemicals

Commercially available optically active (*S*)-(−)-1-phenylethylamine and (*R*)-(+)-1-phenylethylamine were used without further purification. Organolithium compounds were provided from Tosoh Akzo Co. Ltd. (Minato-ku, Tokyo, Japan) as a gift and were used as received.

Preparation of Se-Methyl Diphenylphosphinoselenoate (**1**)

To a reaction mixture of diphenyphosphine oxide [10], which was prepared by hydrolysis of chlorodiphenylphosphine (5.00 g, 22.7 mmol), with selenium (1.80 g, 22.8 mmol) in CH_2Cl_2 (30 mL) was added Et_3N (3.48 mL, 25 mmol), and the mixture was stirred at room temperature for 12 hours. After excess selenium had been removed, the resulting triethylammonium diphenylphosphinoselenoate was treated with iodomethane (2.1 mL, 33.7 mmol) at room temperature. After usual workup, the residue was subjected to dry CC (SiO_2, AcOEt) to give *Se*-methyl diphenylphosphinoselenoate (**1**) (83%).

1: orange viscous oil. ^1H NMR (90 MHz, $CDCl_3$) δ = 2.10 (d, ^3J = 10.5 Hz, $SeCH_3$), 7.29–7.61 (6H, m, *m*- and *p*-H of PPh), and 7.71–8.04 (4H, m, *o*-H of PPh). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 40.5. HRMS (70 eV) *m/z*; found: 295.9874. Calcd for $C_{13}H_{13}OP^{80}Se$: M, 295.9869.

Optical Resolution of t-Butylphenylphosphinoselenoic Acid (**6**) [*6*]

To a solution of *t*-butylphenylphosphinoselenoic acid (**6**) (5.50 g, 21.05 mmol) in ether (30 mL) was added (*R*)-(+)-1-phenylethylamine (2.66 mL, 1 equiv). The resulting precipitates were collected (3.49 g). Their ^{31}P NMR spectrum showed two signals at δ_P 77.6 and 77.9 due to the presence of (−)(*R*)- and (+) (*R*)-1-phenylethylammonium *t*-butylphenylphosphinoselenoates [11], respectively, in a ratio of 9/1. Colorless crystals were recrystallized from CH_2Cl_2-ether to give only (−)(*R*)-salt (δ_P 77.6) in 26% yield. This amine salt was treated with aqueous

NaOH and then with HCl to afford optically active **6**. (−)-**6**: $[\alpha]_D^{20}$ −37.8° (c 0.56, MeOH) ($[\alpha]_D$ 30.35° (MeOH)(91% optical purity) [6]. A similar treatment of the salt obtained from the first filtrate gave 66% optical pure (+)-**6** ($[\alpha]_D^{20}$ +24.4° (c 1.20, MeOH)). Fractional recrystallization of (+)-enantiomer-enriched **6** with (*S*)-(−)-1-phenylethylamine afforded optically pure (+)(*S*)-salt (37%), from which optically pure (+)-**6** was obtained. (+)-**6**: $[\alpha]_D^{20}$ +36.5° (c 0.767, MeOH). (±)-**6**: mp 94–96°C. ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.12 (9H, d, J = 18.0 Hz, $C(CH_3)_3$), 6.28–6.72 (1H, brs, POH), 7.19–7.52 (3H, m, *m*- and *p*-H of Ph), and 7.74–8.09 (2H, m, *o*-H of Ph). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 98.1.

Preparation of Optically Active Se-Benzyl t-Butylphenylphosphinoselenoate (**5**)

To a solution of optically pure (+)(*S*)-salt (0.542 g, 1.42 mmol) in CH_2Cl_2 (27 mL) was added benzyl bromide (0.18 mL, 1.05 equiv) at room temperature under argon, and the mixture was stirred overnight. After usual workup, the residue was subjected to dry CC on SiO_2 (AcOEt) to give optically active *Se*-benzyl *t*-butylphenylphosphinoselenoate (**5**) in 90.4% yield.

(−)-**5**: colorless viscous oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ = 1.17 (9H, d, ^3J = 17.8 Hz, $C(CH_3)_3$), 3.70–4.30 (2H, m, $SeCH_2Ph$), 7.13 (5H, br s, $CH_2C_6H_5$), 7.34–7.59 (3H, m, *m*- and *p*-H of PPh), and 7.68–8.08 (2H, m, *o*-H of PPh). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 24.2 (s, C(CH_3)$_3$), 26.4 (d, $^2J_{CP}$ = 2.1 Hz, PSeCH_2Ph), 37.3 (d, ^1J = 62.0 Hz, $C(CH_3)_3$), 126.5 (s, *p*-C of CPh), 127.6 (d, ^3J = 11.7 Hz, *m*-C of PPh), 127.9 (s, *m*- or *o*-C of CPh), 128.6 (s, *m*- or *o*-C of CPh), 131.4 (d, ^4J = 2.8 Hz, *p*-C of PPh), 131.5 (d, ^1J = 81.2 Hz, *ipso*-C of PPh), 132.1 (d, ^2J = 9.4 Hz, *o*-C of PPh), and 137.6 (d, $^3J_{CP}$ = 3.7 Hz, *ipso*-C of CPh). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 67.6. HRMS (70 eV) *m/z*; found: 352.0487. Calcd for $C_{17}H_{21}OP^{80}Se$: M, 352.0495. $[\alpha]_D^{31}$ −9.84° (c 0.838, MeOH).

REACTION OF Se-METHYL DIPHENYLPHOSPHINOSELENOATE (**1**)

Reaction of **1** *with Phenyllithium and Then with Benzyl Bromide*

To a solution of **1** (125 mg, 0.425 mmol) in THF (5 mL) was added PhLi (1.21 M cyclohexane-ether solution, 0.35 mL, 1.0 equiv) at −78°C under an argon atmosphere. After the solution had been stirred for 1.5 hours, benzyl bromide (51 μL, 0.43 mmol) was added to the solution at the same temperature, and then the reaction mixture was allowed to warm to room temperature during 15 hours. The reaction mixture was treated with aq NH_4Cl, extracted with CH_2Cl_2, and the extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to dry CC on SiO_2 (AcoEt) to give a mixture (75%) of benzyldiphenylphosphine oxide (**3**) [10] and triphenylphosphine oxide (**4a**), whose ratio was estimated to be 60:40 by ^{1}H NMR spectroscopy.

Reaction of **1** *with Phenylmagnesium Bromide*

To a solution of **1** (528 mg, 1.76 mmol) in THF (15 mL) was added PhMgBr (0.88 M THF solution, 2.00 mL, 1.76 mmol) at −78°C. After a period of stirring at 0°C for 3 hours, benzyl bromide (0.21 mL, 1.76 mmol) was added to the mixture at −78°C. A similar treatment to that described earlier gave a mixture (61%) of **3** and **4a**, whose ratio was 80:20.

Reaction of **1** *with n-BuLi and t-BuLi*

A reaction using **1** (197 mg, 0.667 mmol), *n*-BuLi (1.76 M hexane solution, 0.38 mL, 0.669 mmol), and benzyl bromide (79 μL, 0.66 mmol) gave **3** in 16% yield, along with six unidentified products.

Use of **1** (492 mg, 1.67 mmol), *t*-BuLi (1.70 M pentane solution, 0.98 mL, 1.67 mmol), and benzyl bromide (0.20 mL, 1.68 mmol) gave a mixture of **3** and *t*-butyldiphenylphosphine oxide (**4b**) [13] in a ratio of 4:1.

REACTION OF OPTICALLY ACTIVE OR RACEMIC Se-BENZYL t-BUTYLPHENYLPHOSPHINOSELENOATE (**5**) WITH PHENYLLITHIUM

Reaction Using Alkyl Halides as Electrophiles

To a solution of optically active (−)-**5** (181 mg, 0.515 mmol) in THF (8 mL) was added PhLi (1.20 M solution in cyclohexane-ether, 0.47 mL, 1.1 equiv) at −78°C under an argon atmosphere. After a period of stirring for 1 hour, iodomethane (48 μL, 1.5 equiv) was added to the solution, and the reaction mixture was allowed to warm to room temperature during 15 hours. After usual workup, the residue was subjected to dry CC (SiO_2, AcOEt) to afford optically active *t*-butylmethylphenylphosphine oxide (**8a**) in 91% yield ($[\alpha]_D^{23}$ +20.9° (c 0.297, MeOH)) along with quantitative yield of benzyl phenyl selenide.

(+)-**8a**: mp 98–100°C (mp 99–100°C, $[\alpha]_D^{25}$ −22.7° (c 1.0, MeOH) [7]). A similar reaction using iodoethane or benzyl bromide instead of iodomethane gave *t*-butylethylphenylphosphine oxide (**8b**) (75%) or benzyl-*t*-butylphenylphosphine oxide (**8c**) (72%), respectively.

(−)-**8b**: colorless viscous oil. ^{1}H NMR (90 MHz, $CDCl_3$) δ = 1.12 (9H, d, J = 14.5 Hz, $C(CH_3)_3$), 0.89–1.32 (3H, m, CH_3), 1.80–2.33 (2H, m, PCH_2), 7.48–7.84 (5H, m, C_6H_5). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 52.0. HRMS (70 eV) *m/z*; found: 210.1174. Calcd for $C_{12}H_{19}OP$: M, 210.1173. $[\alpha]_D^{27}$ −20.3° (c 1.04, MeOH).

(−)-**8c**: mp 190–191°C (Et_2O) (mp 187–189°C [10]). ^1H NMR (90 MHz, $CDCl_3$) δ = 1.15 (9H, J = 14.7 Hz, $C(CH_3)_3$), 3.35–3.58 (2H, m, PCH_2), 7.05–7.88 (10H, m, 2 × C_6H_5). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 46.8. $[\alpha]_D^{22}$ −115.9° (c 0.773, MeOH). A reaction using (+)-**5** and 1-iodobutane afforded optically active butyl-*t*-butylphenylphosphine oxide (**8d**) (56%).

(+)-**8d**: colorless viscous oil. ^1H NMR (90 MHz, $CDCl_3$) δ = 0.71–1.60 (9H, m, C_4H_9), 1.12 (9H, d, J = 14.5 Hz, $C(CH_3)_3$), 7.29–7.91 (5H, m, C_6H_5). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 13.5 (s), 22.4 (d, J = 64.7 Hz), 23.3 (d, J = 4.2 Hz), 24.2 (d, J = 13.8 Hz), 24.3 (s), 32.5 (d, J = 68.6 Hz), 128.0 (d, J = 10.5 Hz), 129.9 (d, J = 86.0 Hz), 131.2 (d, J = 2.6 Hz), 131.7 (d, J = 7.9 Hz). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 50.3. $[\alpha]_D^{17}$ +14.2° (c 0.756, MeOH). HRMS (70 eV) m/z; found: 238.1495. Calcd for $C_{14}H_{23}OP$: M, 238.1487.

Reaction Using Dihaloalkanes as Electrophiles

1,3-Diiodopropane. To a solution of (±)-**5** (368 mg, 1.05 mmol) in THF (15 mL) was added PhLi (1.1 equiv) at −78°C under argon. After the solution had been stirred for 30 minutes, 1,3-diiodopropane (0.5 equiv) was added to the solution. Usual workup gave a 1:1 diastereomeric mixture (93%) of *dl*- and *meso*-1,3-bis-(*t*-butylphenylphosphinyl)-propanes **9** and **10**. The ^{31}P NMR spectrum of the mixture showed two signals at δ_P 51.6 and 50.1 for **9** and **10**, respectively. A mixture of **9** and **10**: ^1H NMR (90 MHz, $CDCl_3$) δ = 1.02 (d, J = 14.7 Hz, $C(CH_3)_3$), 1.09 (d, J = 14.5 Hz, $C(CH_3)_3$), 1.58–2.68 (m, $(CH_2)_3$), 7.19–7.92 (m, C_6H_5). The reaction using 1,2-dibromoethane and diiodomethane instead of 1,3-diiodopropane afforded ethyl *t*-butylphenylphosphinate (**11**) (59%) and a mixture of **11** (39%) and **8a** (35%), respectively, after elution with ethanol in dry CC.

A similar reaction using optically active (+)-**5** gave a single diastereomer (+)-*dl*-**9** (76%). (+)-*dl*-**9**: mp 173.0–174.0°C. ^1H NMR (500 MHz, $CDCl_3$) δ = 1.09 (18H, J = 14.5 Hz, $C(CH_3)_3$), 1.71–1.84 (2H, m), 2.03–2.18 (2H, m), 2.45–2.52 (2H, m), 7.32–7.38 (4H, m), 7.40–7.45 (2H, m), 7.57–7.61 (4H, m), $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 14.8 (t, J = 4.3 Hz), 22.4 (dd, J = 63.8 Hz, J = 9.4 Hz), 24.3 (s), 32.3 (d, J = 68.7 Hz), 127.8 (d, J = 10.8 Hz), 128.7 (d, J = 86.4 Hz), 131.0 (d, J = 2.5 Hz), 131.6 (d, J = 8.1 Hz). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 51.5. HRMS (70 eV) m/z; found: 404.2036. Calcd for $C_{23}H_{30}O_2P_2$: M, 404.2034. $[\alpha]_D^{22}$ +42.7° (c 0.808, MeOH).

11: colorless viscous oil. ^1H NMR (90 MHz $CDCl_3$) δ = 1.13 (18H, J = 15.8 Hz, $C(CH_3)_3$), 1.34 (3H, t, J = 7.0 Hz, $CH_2\underline{CH_3}$), 3.77–4.32 (2H, m, $\underline{CH_2}CH_3$), 7.34–7.89 (5H, m, $\underline{C_6H_5}$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 16.3 (d, J = 6.1 Hz), 24.0 (s), 32.3 (d, J = 101 Hz), 60.6 (d, J = 7.2 Hz), 128.1 (d, J = 11.5 Hz), 128.5 (d, J = 94.7 Hz), 131.8 (d, J = 2.3 Hz), 133.0 (d, J = 8.7 Hz). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 51.2. HRMS (70 eV) m/z; found: 226.1117. Calcd for $C_{12}H_{19}O_2P$: M, 226.1123.

Reaction of (−)-5 with Methyl Acrylate

To a solution of (−)-**5** (267 mg, 0.759 mmol) in THF (10 mL) was added PhLi (1.2 equiv) at −78°C under Ar. Stirring was continued for 1 hour, and then methyl acrylate (89 μL, 1.3 equiv) was added to the solution. The reaction mixture was allowed to warm to room temperature during 15 hours. The ^{31}P NMR spectrum of the reaction mixture was very complex. After usual workup, the residue was subjected to dry CC (SiO_2, AcOEt), followed by PTLC (SiO_2, AcOEt-EtOH (9:1)) to yield (+)-methyl 3-(*t*-butylphenylphosphinyl)propanoate (**12**) (5%).

(+)-**12**: viscous oil. ^1H NMR (90 MHz, $CDCl_3$) δ = 1.15 (9H, J = 15.0 Hz, $C(CH_3)_3$), 2.22–2.87 (4H, m, $(CH_2)_2$), 3.65 (3H, s, OCH_3), 7.42–7.87 (5H, m, C_6H_5). ^{31}P NMR (36 MHz, $CDCl_3$) δ = 49.2. HRMS (70 eV) m/z; found: 237.1047. Calcd for $C_{13}H_{18}O_2P$: M^+ −MeO, 237.1045. $[\alpha]_D^{26}$ +1.1° (c 0.180, MeOH).

Reaction with Elemental Sulfur, Selenium, and Tellurium

The reaction using (−)-**5** (154 mg, 0.440 mmol) and PhLi (1.1 equiv), followed by addition of sulfur (21 mg, 1.5 equiv), was quenched with water after the mixture had been allowed to warm to room temperature. The solvent was evaporated and washed with ether. The aqueous solution was acidified (pH ca. 2) with dilute HCl, extracted with CH_2Cl_2, and dried over anhydrous $MgSO_4$. Removal of the solvent gave (*R*)-(+)-*t*-butylphenylphosphinothioic acid (**13**) (67%) (mp 104–106°C, $[\alpha]_D^{29}$ +25.2° (c, 0.932, MeOH)(mp 103–106°C, $[\alpha]_D^{20}$ +28.1° (c, 2.4, MeOH) [8]).

A similar reaction using selenium (1.5 equiv) instead of sulfur gave crude *t*-butylphenylphosphinoselenoic acid (**6**) (61%), which was treated with benzyl bromide (48 μL) in the presence of Et_3N (37 μL) in THF (8 mL) to afford (−)-**5** (61%) ($[\alpha]_D^{31}$ −9.84° (c, 0.838, MeOH)).

Although a similar reaction with tellurium was carried out and the signal at δ_P 45.5 due to lithium *t*-butylphenylphosphinotelluroate was observed by ^{31}P NMR, attempted isolation of a compound containing tellurium was unsuccessful.

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