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Optically Active Trivalent Phosphorus Compounds. 2. Reactivity of Alkylthio- and Alkylselenophosphonium Salts. The First Stereospecific Synthesis of a Chiral Phosphinite

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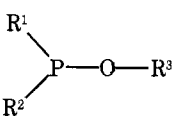
Abstract: It was shown that alkylthio- and alkylselenophosphonium salts react with alkylmercaptide anions to give trivalent phosphorus compounds and disulfides. Reaction of (−)-(*S*)-methylthiomethyl-*n*-propylphenylphosphonium triflate (**6**) with ethylmercaptide anion gave completely racemic methyl-*n*-propylphenylphosphine (**7**). However, when *tert*-butylmercaptide anion was used, optically active phosphine **7** was formed with 59% of initial optical activity and with retention of configuration. Reaction between (−)-(*S*)-methylthioethyl-*tert*-butylphenylphosphonium triflate (**8**) and sodium ethylmercaptide was found to occur with full stereospecificity to give (+)-(*R*)-ethyl-*tert*-butylphenylphosphine (**10**). (−)-(*S*)-*O*-Methyl-*Se*-methyl-*tert*-butylphenylphosphonium triflate (**11**) obtained from (−)-(*S*)-*tert*-butylphenylphosphinoselenoic acid (**12**) was converted stereospecifically to (+)-(*R*)-*O*-methyl *tert*-butylphenylphosphinite (**2**). The latter reaction represents the first stereospecific synthesis of a chiral trivalent phosphorus acid ester.

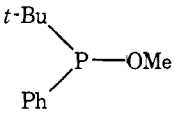
Chiral tertiary phosphines, first prepared by Horner in 1961,[1,2] occupy a central position in the study of dynamic phosphorus stereochemistry.[3] Recently, chiral phosphines have found very important application as ligands for catalysts employed in asymmetric hydrogenation in soluble systems.[4] The efficiency of this process was found to be strongly dependent on the structure of chiral phosphorus ligands. In this connection the synthesis of other classes of chiral trivalent phosphorus compounds is of great interest.

Especially interesting are optically active trivalent phosphorus acids esters (**1**) because the great majority of organophosphorus reactions is based on their conversion into P^{IV}, P^{V}, and P^{VI} compounds. Till now, however, the synthetic approaches to chiral trivalent phosphorus acids esters (**1**) with phosphorus as a sole chirality center are few in number and for the most part of limited applicability.[5,6] Thus, the trimethylsilyl ester **1a** obtained by Benschop et al.[5] by silylation of *O*-isopropyl methylphosphonate was found to be very sensitive to moisture. On the other hand, asymmetric reaction of racemic chlorophosphines with alcohols in the presence of chiral tertiary amines,[6] though very simple and general, leads to chiral esters **1b–d** with low optical purities.



1a, R^1 = Me; R^2 = O-Pr-*i*; R^3 = $SiMe_3$
b, R^1 = Ph; R^2 = Me; R^3 = Me or Pr-*n*
c, R^1 = Ph; R^2 = Et; R^3 = Me or Pr-*n*
d, R^1 = Et; R^2 = SEt; R^3 = Et

We report here the first stereospecific synthesis of chiral *O*-methyl *tert*-butylphenylphosphinite (**2**) as well as the results of a relevant study on the reactivity of alkylthio- and alkylselenophosphonium salts which, as it was found, are useful precursors of chiral trivalent phosphorus compounds.



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Results and Discussion

Generally, phosphonium salts bearing the alkylthio group may react with a nucleophile in three different ways shown schematically below. Nucleophilic attack at phosphorus and carbon [directions (a) and (b)] is well known.[7,8] On the contrary, the attack at sulfur [direction (c)] leading to P^{III} com-

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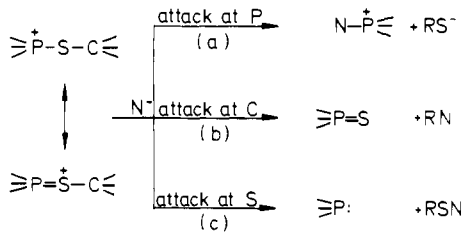


pound has not been, to our knowledge, clearly demonstrated[9] and has received no attention.

We found that reaction of methylthiotriphenylphosphonium triflate (**3**) with ethylmercapto anion, which is known to possess a high "thiophilicity",[10] gave exclusively triphenylphosphine (^{31}P NMR assay) and a mixture of dimethyl, diethyl, and methyl ethyl disulfides.

$$\underset{\mathbf{3}}{Ph_3\overset{+}{P}\text{-}SMe\ CF_3SO_3^-} \xrightarrow[Et_2O\text{-}CH_2Cl_2]{EtSNa} Ph_3P + Me_2S_2 + Et_2S_2 + MeS_2Et \quad (1)$$

Similarly, treatment of methylselenotriphenylphosphonium triflate (**4**) and methylthiotri-*n*-butylphosphonium triflate (**5**) with sodium ethylmercaptide afforded triphenylphosphine and tri-*n*-butylphosphine, respectively.

It should be noted, however, that triphenylphosphine obtained in the reaction shown above (eq 1) does not result from a simple attack of ethylmercaptide anion on the sulfur atom in **3**. The formation of three possible disulfides strongly suggests that the initial reaction stage involves a fast exchange of the alkylthio groups at phosphorus leading to the dynamic equilibrium shown in eq 2.[11] Then, nucleophilic attack of ethylmercaptide and methylmercaptide anions on sulfur in both phosphonium cations results in the formation of triphenylphosphine and a mixture of disulfides.

$$Ph_3\overset{+}{P}\text{-}SMe + EtS^- \rightleftharpoons Ph_3\overset{+}{P}\text{-}SEt + MeS^- \quad (2)$$

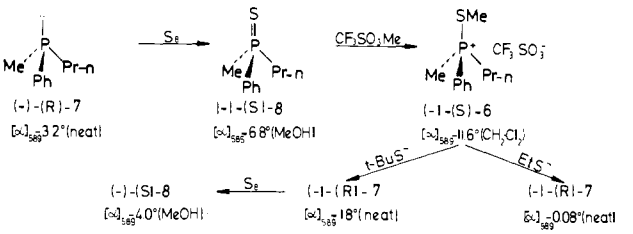
Such a mechanistic picture is supported by the fact that treatment of (−)-(*S*)-methylthiomethyl-*n*-propylphenylphosphonium triflate (**6**) with EtS^- in CH_2Cl_2 at −70 °C leads to an almost racemic methyl-*n*-propylphenylphosphine (**7**) (60% yield after distillation). Racemization is undoubtedly a consequence of a fast alkylthio-alkylthio exchanges at chiral phosphorus in **6** taking place with inversion of configuration.

However, when (−)-**6** was subjected to nucleophilic attack by *t*-BuS^- anion under the same experimental conditions, optically active phosphine **7** (40% yield after distillation) was formed with 59% of initial optical activity. It is evident that nucleophilic attack at tetrahedral phosphorus in **6** by *t*-BuS^- is hindered to a great extent for steric reasons and the better accessible sulfur atom is preferably attacked. As a consequence chiral phosphine **7** is formed from **6** with retention of configuration at phosphorus.

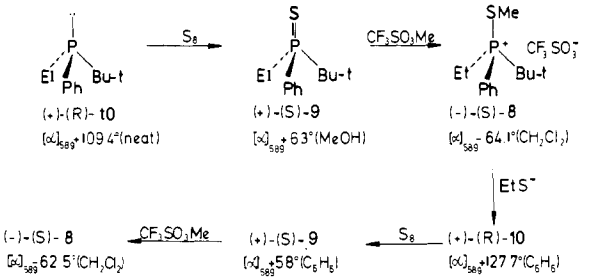
The synthesis and reactions of chiral **6** are shown in Scheme I, which depicts also configurational relationships. In this connection it should be noted that the reactions of chiral phosphines with elemental sulfur proceed with retention of configuration at phosphorus.[12]

Since the *tert*-butyl group directly attached to the phosphorus atom strongly decreases the rate of nucleophilic substitution at phosphorus,[13] in the next step of this study we prepared optically active (−)-(*S*)-methylthioethyl-*tert*-butylphenylphosphonium triflate (**8**) from (+)-(*S*)-ethyl-*tert*-butylphenylphosphine sulfide (**9**) and methyl triflate. As expected, reaction of the salt (−)-(*S*)-**8** with sodium ethylmercaptide under the same experimental conditions as described above resulted in the formation of (+)-(*R*)-ethyl-

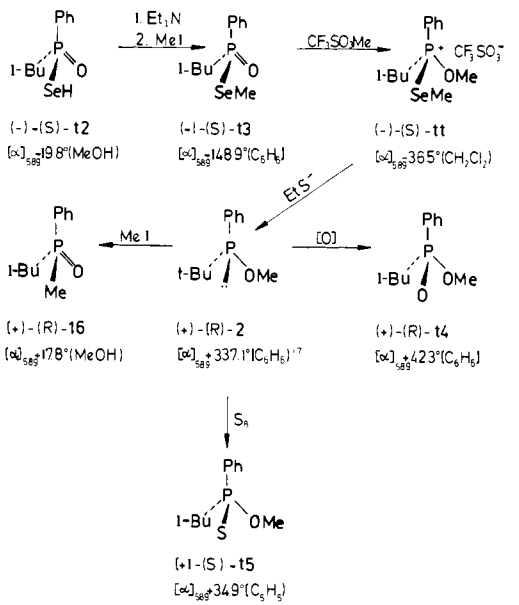
Scheme I



Scheme II



Scheme III



tert-butylphenylphosphine (**10**, yield 52%) with almost full optical activity and retained configuration. This was demonstrated by the conversion of the phosphine **10** obtained into sulfide **9** and phosphonium salt **8**. The experiments discussed above are summarized in Scheme II.

Taking into account the observations presented above on the relationship between the structure of alkylthiophosphonium salts and optical purity of chiral phosphines obtained from them, chiral *O*-methyl-*Se*-methyl-*tert*-butylphenylphosphonium triflate (**11**) was chosen as a starting material for chiral ester **2**. It should be pointed out that in this case the undesired nucleophilic attack at phosphorus by RS^- anion should effectively be prevented by the bulky *tert*-butyl group directly attached to it.

The salt (−)-**11** prepared from the known (−)-(*S*)-*tert*-butylphenylphosphinoselenoic acid (**12**)[14] as outlined in Scheme III was reacted with sodium ethylmercaptide in ether-methylene chloride solution at −70 °C. It is very advantageous to add also tris(dimethylamino)phosphine to the reaction mixture in order to stop the side reaction between **2**

and disulfudes formed. The ester (+)-**2** was purified by distillation. However, the distilled product, $[\alpha]_{589}$ +287.2° (C_6H_6), was contaminated, as evidenced by ^{31}P NMR, with some amounts of *O*-methyl *tert*-butylphenylphosphinate (**14**) formed by oxidation. Therefore, the mixture of (+)-**2** and **14** was oxidized and treated with elemental sulfur and methyl iodide. The corresponding chiral derivatives **14**,[7b] **15**,[15] and **16**[16] obtained from **2** were isolated in the pure state by TLC. Scheme III summarizes their optical rotation and chirality at phosphorus.

The synthesis of chiral ester **2** represents the first stereospecific synthesis of a chiral trivalent phosphorus ester and opens new possibilities for a study of the stereochemistry of $P^{III} \rightarrow P^{IV}$ conversions. Further work in this direction is underway in our laboratory.

Experimental Section

All boiling and melting points are uncorrected. ^1H NMR spectra were measured with a Perkin-Elmer R-12B instrument with HMDSO as external standard. ^{31}P NMR spectra were recorded with a JEOL-JNM FX60 Fourier transform spectrometer at 24.3 MHz with 85% phosphoric acid as external standard. Optical activity measurements were made with a Perkin-Elmer 241 MC photopolarimeter. GLC analysis was carried out with a Varian Aerograph Model 2700 FID gas chromatograph (glass column, silicone OV-101).

Solvents and commercial reagents were distilled and dried by conventional methods. Methyl triflate supplied by Aldrich Co. was used. Optically active *tert*-butylphenylphosphinoselenoic acid was synthesized and resolved into enantiomers according to Michalski et al.[14] Optically active methyl-*n*-propylphenylphosphine was obtained according to the procedure described by Mislow et al.[2]

Methylthiotriphenylphosphonium Triflate (3). A solution of triphenylphosphine sulfide (1.5 g, 0.005 mol) in benzene (20 mL) was treated with methyl triflate (0.84 g, 0.005 mol). The reaction mixture was refluxed for 5 min and then benzene was evaporated under reduced pressure. The residue was treated with ether (15 mL) and cooled to 0 °C. The precipitated salt **3** was filtered off: 2.2 g (94%); mp 88–90 °C; ^1H NMR (CH_2Cl_2) δ 2.26 (d, 3 H, CH_3SP, $^3J_{P-H}$ = 15.2 Hz), 7.49 (m, 15 H, aromatic); ^{31}P NMR (CH_2Cl_2) δ 45.3.

Anal. Calcd for $C_{20}H_{18}PO_3S_2F_3$: C, 52.39; H, 3.96; P, 6.76. Found: C, 52.18; H, 4.05; P, 6.93.

Methylselenotriphenylphosphonium Triflate (4). Triphenylphosphine selenide (2.05 g, 0.006 mol) and methyl triflate (0.98 g, 0.006 mol) gave according to the procedure described above the salt **4**: 2.9 g (96%) mp 103–107 °C; ^1H NMR (CH_2Cl_2) δ 2.61 (d, 3 H, CH_3SeP, $^3J_{P-H}$ = 13.2 Hz), 7.94 (m, 15 H, aromatic); ^{31}P NMR (CH_2Cl_2) δ 36.1 ($^1J_{^{31}P-^{77}Se}$ = 451.2 Hz).

Anal. Calcd for $C_{20}H_{18}PO_3SSeF_3$: C, 47.53; H, 3.59; P, 6.13. Found: C, 47.73; H, 3.73; P, 6.56.

Methylthiotri-*n*-butylphosphonium Triflate (5). According to the procedure described for **3** the salt **5** was obtained from tri-*n*-butylphosphine sulfide (3.0 g, 0.013 mol) and methyl triflate (2.13 g, 0.013 mol); 4.0 g (78%); mp 61–63 °C; ^1H NMR (CH_2Cl_2) δ 1.22 (t_{dis}, 9 H, CH_3C), 1.80 (m, 12 H, CH_2CH_2), 2.64 (m, 6 H, CH_2P), 2.69 (d, 3 H, CH_3S, $^3J_{P-H}$ = 12.6 Hz); ^{31}P NMR (CH_2Cl_2) δ 63.2.

Anal. Calcd for $C_{14}H_{30}PO_3S_2F_3$: C, 42.19; H, 7.59; P, 7.77. Found: C, 42.14; H, 7.60; P, 8.08.

(−)-(*S*)-Methylthiomethyl-*n*-propylphenylphosphonium Triflate (6). To a solution of (−)-(*S*)-methyl-*n*-propylphenylphosphine sulfide (**8**, 4.0 g, 0.02 mol), $[\alpha]_{589}$ −6.8° (*c* 2.87, MeOH), in methylene chloride (30 mL), methyl triflate was added at room temperature. The resulting solution was refluxed for 1 h, cooled, and evaporated. The residue was treated with ether (30 mL). The ethereal solution afforded on cooling the salt **6** as a crystalline compound: 6.8 g (93%); mp 38–45 °C; $[\alpha]_{589}$ −11.6° (*c* 4.30, CH_2Cl_2); ^1H NMR (CH_2Cl_2) δ 1.41 (t, 3 H, CH_3C), 1.96 (m, 2 H, CCH_2C) 2.64 (d, 3 H, CH_3P, $^2J_{P-H}$ = 14.5 Hz), 2.80 (d, 3 H, CH_3S, $^3J_{P-H}$ = 13.2 Hz), 2.94 (m, 2 H, CH_2P), 8.02 (m, 5 H, aromatic); ^{31}P NMR (CH_2Cl_2) δ 52.4.

Anal. Calcd for $C_{12}H_{18}PO_3S_2F_3$: C, 39.77; H, 5.01; P, 8.55. Found: C, 40.23; H, 5.34; P, 9.00.

(−)-(*S*)-Methylthioethyl-*tert*-butylphenylphosphonium triflate (8) was prepared similarly from (+)-(*S*)-ethyl-*tert*-butylphenylphosphine sulfide (**9**,[18] 0.38 g, 0.0017 mol), $[\alpha]_{589}$ +6.3° (*c* 1.43, MeOH), and methyl triflate (0.27 g, 0.0017 mol) in methylene chloride (5 mL). The salt **8** was obtained; 0.59 g (91%); mp 84–87 °C; $[\alpha]_{589}$ −64.1° (*c* 1.28, CH_2Cl_2); ^{31}P NMR (CH_2Cl_2) δ 73.4.

Anal. Calcd for $C_{17}H_{22}PO_3S_2F_3$: C, 43.06; H, 5.68; P, 7.93. Found: C, 43.81; H, 6.10; P, 8.52.

Triphenylphosphine from Methylthiotriphenylphosphonium Triflate (3). To a suspension of sodium ethylmercaptide [prepared from Na (0.25 g, 0.011 mol) and EtSH (2 mL)] in ether (20 mL) a solution of **3** (3.0 g, 0.009 mol) was added dropwise at −30 °C. The reaction mixture was warmed to room temperature. Its ^{31}P NMR spectrum showed only one signal at δ −5.6 ppm characteristic for triphenylphosphine. GLC analysis of the reaction mixture revealed the presence of dimethyl disulfide, methyl ethyl disulfide, and diethyl disulfide. The reaction solution was filtered off and evaporated to afford triphenylphosphine which was recrystallized from benzene: 1.7 g (72%); mp 76–79 °C; mmp 77–79 °C.

Triphenylphosphine from Methylselenotriphenylphosphonium Triflate (4). According to the same procedure as described above from **4** (2.2 g, 0.0043 mol) and EtSNa [prepared from Na (0.12 g, 0.0052 mol) and EtSH (2 mL)] triphenylphosphine was obtained: 0.7 g (62%); mp 78–80 °C; mmp 77–79 °C; ^{31}P NMR (CH_2Cl_2) δ −6.1.

Tri-*n*-butylphosphine from Methylthiotri-*n*-butylphosphonium Triflate (5). The triflate **5** (3.0 g, 0.0075 mol) and EtSNa [prepared from Na (0.18 g, 0.0078 mol) and EtSH (2 mL)] gave under the same experimental conditions as described above tri-*n*-butylphosphine, which was isolated by distillation: 1.1 g (65%); bp 38–40 °C (0.2 mmHg); n^{20}_D 1.4640; ^{31}P NMR (C_6H_6) δ −32.5.

(−)-(*R*)-Methyl-*n*-propylphenylphosphine (7) from Triflate (−)-(*S*)-6 and Sodium Ethylmercaptide. To a suspension of EtSNa [prepared from Na (0.14 g, 0.006 mol) and EtSH (3 mL)] in ether (20 mL) a solution of (−)-(*S*)-**6** (2.2 g, 0.006 mol), $[\alpha]_{589}$ −11.6°, in methylene chloride (15 mL) was added dropwise under N_2 at −70 °C during 15 min. After the reaction mixture was warmed to room temperature the precipitated solid was filtered off and the solvents were evaporated. The residue was distilled to give 0.6 g (60%) of phosphine (−)-**7**: $[\alpha]_{589}$ −0.08° (neat); $[\alpha]_{546}$ −0.12° (neat); n^{20}_D 1.5451; ^{31}P NMR (Et_2O) δ −38.2.

(−)-(*R*)-Methyl-*n*-propylphenylphosphine (7) from Triflate (−)-(*S*)-6 and Lithium *tert*-Butylmercaptide. To a solution of *t*-BuSLi [prepared from *t*-BuSH (1.5 mL) and *n*-BuLi (6.3 mL, 0.0019 mol/mL) in hexane] in ether (30 mL) a solution of (−)-(*S*)-**6** (4.38 g, 0.012 mol), $[\alpha]_{589}$ −11.6°, in methylene chloride (15 mL) was added dropwise under N_2 at −75 °C. The reaction mixture was warmed to room temperature and the solid was filtered off. Removal of the solvents afforded the residue, which was dissolved in benzene (25 mL). The benzene solution was washed with a 5% solution of NaOH (2 × 10 mL) and water (2 × 10 mL) and dried over $MgSO_4$. Removal of benzene afforded the crude phosphine (−)-**7**, which was purified by distillation: 0.8 g (40%); n^{20}_D 1.5465; $[\alpha]_{589}$ −1.8° (neat); ^{31}P NMR (C_6H_6) δ −38.7.

Addition of elemental sulfur to the sample of (−)-(*R*)-**7** obtained in ether gave after the usual workup (−)-(*S*)-methyl *n*-propylphenylphosphine sulfide (**8**): mp 57–60 °C; $[\alpha]_{589}$ −4.0° (*c* 3.07, MeOH); ^{31}P NMR (MeOH) δ −39.4.

(+)-(*R*)-Ethyl-*tert*-butylphenylphosphine (10) from Triflate (−)-(*S*)-8 and Sodium Ethylmercaptide. To a suspension of sodium ethylmercaptide [prepared from Na (0.05 g, 0.0021 mol) and EtSH (1 mL)] in ether (15 mL) a solution of (−)-(*S*)-**8** (0.55 g, 0.0014 mol), $[\alpha]_{589}$ −64.1°, was added dropwise at −68 °C under N_2. The usual workup gave the crude phosphine **10**, which was purified by column chromatography (silica gel, hexane) and then distilled; 0.14 g (52%); $[\alpha]_{589}$ +127.7° (*c* 4.39, C_6H_6); n^{20}_D 1.5372; ^{31}P NMR (C_6H_6) δ 6.9.

To a solution of the phosphine (+)-(*R*)-**10** prepared above in ether elemental sulfur was added. Evaporation of ether gave (+)-(*S*)-ethyl *tert*-butylphenylphosphine sulfide (**9**); mp 65–68 °C; $[\alpha]_{589}$ +5.8° (*c* 1.22; MeOH); ^{31}P NMR (C_6H_6) δ 64.8.

Anal. Calcd for $C_{12}H_{19}PS$: C, 63.68; H, 8.46; P, 13.68. Found: C, 64.19; H, 8.68; P, 13.18.

(+)-(*S*)-Phosphine sulfide (**9**) gave on treatment with methyl triflate (−)-(*S*)-**8**: mp 85–88 °C; $[\alpha]_{589}$ −62.5° (*c* 1.45, CH_2Cl_2); ^{31}P NMR (CH_2Cl_2) δ 73.4.

(−)-(*S*)-*O*-Methyl-*Se*-methyl-*tert*-butylphenylphosphonium Triflate (11). To a solution of (−)-(*S*)-*Se*-methyl *tert*-butylphenylphosphinoselenoate (**13**, 7.31 g, 0.002 65 mol), $[\alpha]_{589}$ −148.9° (*c* 1.55, C_6H_6) [prepared from (−)-(*S*)-*tert*-butylphenylphosphinoselenoic acid (**12**), $[\alpha]_{589}$ −19.8° (*c* 1.70, MeOH), and MeI] in methylene chloride (30

mL), methyl triflate (4.36 g, 0.00265 mol) was added at room temperature. The reaction mixture was refluxed for 1 h. Then the solvent was evaporated and the residue was dissolved in ether (20 mL). The ethereal solution was left to stand for 2 days in a refrigerator. The precipitated triflate **11** was filtered off and dried over P_2O_5: 10.8 g (92.5%); mp 65–77 °C; $[\alpha]_{589}$ −36.5° (*c* 1.92, CH_2Cl_2); ^1H NMR (CH_2Cl_2) δ 1.29 (d, 9 H, *t*-Bu, $^3J_{P-H}$ = 21.1 Hz), 2.35 (d, 3 H, CH_3Se, $^3J_{P-H}$ = 10.9 Hz), 4.13 (d, 3 H, CH_3O, $^3J_{P-H}$ = 12.7 Hz), 7.43–7.93 (m, 5 H, aromatic); ^{31}P NMR (CH_2Cl_2) δ 115.5 ($^1J_{^{31}P-^{77}Se}$ = 546.8 Hz).

Anal. Calcd for $C_{13}H_{20}PO_4SSeF_3$: C, 35.54; H, 4.59. Found: C, 34.64; H, 4.95.

(+)-(*R*)-*O*-Methyl *tert*-Butylphenylphosphinite (2) from (−)-(*S*)-11 and Sodium Ethylmercaptide. To a suspension of sodium ethylmercaptide [prepared from Na (0.3 g, 0.013 mol) and EtSH (4 mL)] in ether (35 mL) a solution of (−)-(*S*)-**11** (4.63 g, 0.0105 mol), $[\alpha]_{589}$ −36.5°, in methylene chloride (15 mL) was added dropwise at −76 °C under N_2. When addition of the salt **11** was complete tris(dimethylamino)phosphine (0.77 g, 0.0097 mol) in ether (15 mL) was added at −76 °C. After 5 min a cooling bath was taken off and the reaction solution was filtered at 10 °C. The solvents were then evaporated and the residue was distilled to give a liquid [0.5 g, n^{20}_D 1.5280, $[\alpha]_{589}$ +287.2° (*c* 2.03, C_6H_6)] which consisted of (+)-*O*-methyl *tert*-butylphenylphosphinite (**2**, 83.1%) [^{31}P NMR (C_6H_6) δ 133.4] and (+)-*O*-methyl *tert*-butylphenylphosphinate (**14**, 16.9%) [^{31}P NMR (C_6H_6) δ 49.0].

To a solution of (+)-**2** (0.1 g) obtained as described above in ether (5 mL), sulfur (0.03 g) was added. Then ether was evaporated, methanol (5 mL) added, and the excess of sulfur filtered off. Preparative TLC (Kieselgel 60 F_{254}; benzene–acetone–1-propanol, 2:1:1) of the crude product gave (+)-(*S*)-*O*-methyl *tert*-butylphenylphosphinothionate (**15**); 0.075 g; $[\alpha]_{589}$ +34.9° (*c* 1.68, C_6H_6); ^{31}P NMR (C_6H_6) δ 105.7.

To boiling methyl iodide (+)-**2** (0.2 g) was added. The reaction mixture was evaporated and the residue chromatographed under the conditions specified above to give (+)-(*R*)-methyl-*tert*-butylphenylphosphine oxide (**16**): 0.12 g; $[\alpha]_{589}$ +17.8° (*c* 1.37, MeOH); ^{31}P NMR (MeOH) δ 52.4.

From the two last experiments (+)-(*R*)-*O*-methyl *tert*-butylphenylphosphinate (**14**) was also isolated: 0.07 g; $[\alpha]_{589}$ +42.3° (*c* 0.6, C_6H_6); ^{31}P NMR (C_6H_6) δ 50.1.

The compounds (+)-**14**, (+)-**15**, and (+)-**16** were shown by GLC to be homogeneous.

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References and Notes

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