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# Stereospecific Synthesis of *P*-Epimeric ($R_P1$, $R_P2$)-Bis-[*O*-l-menthylphenylphosphonothionyl] Diselenide. A New Variant of the Stereoselective Staudinger Reaction

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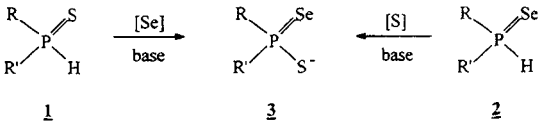
## ABSTRACT

*An efficient procedure is described that leads to pure* ($S_P$)-**O**-l-menthylphenylthiophosphinate. The absolute configuration of this diastereomer was assigned by chemical correlation and confirmed by X-ray crystallography. The reaction of the isomer with phenyl azide, leading to amidate, is a new variant of the stereoselective Staudinger reaction. Addition of elemental selenium to the ($S_P$)-thiophosphinate led to diastereomeric O-l-menthylphenylselenophosphonothioic acid, which was finally oxidized to the diastereomeric ($R_P1$,$R_P2$)-bis-[O-l-menthylphenylphosphonothionyl] diselenide. The diselenide structure was unambiguously confirmed by $^{31}P$ NMR spectroscopy.

## *INTRODUCTION*

The importance of phosphorus, sulfur, and selenium in chemistry and biochemistry is growing, and the special role of structural combinations of these elements has gradually emerged. Such compounds have found an important place in organic and inorganic synthesis, the preparation of new materials, and the modification of biologically important molecules. In contrast to compounds that contain combinations of phosphorus and sulfur or phosphorus and selenium, those in which the three elements together form the backbone of the molecular structure have attracted less attention. Thioselenophosphorus acids are an example. This paper is a part of our extended work on organophosphorus compounds exhibiting properties similar to pseudohalogen species. We now report the first stereospecific synthesis of a *P*-epimeric ($R_P1$, $R_P2$)-bis-(phosphonothionyl) diselenide (**13**) and describe some related new stereochemical correlations.

Thioselenophosphorus acids RR'P(S)SeH, which form stable salts **3**, have been prepared by the addition of elemental selenium to thiophosphonate-type structures **1**. An alternative synthesis of salts **3** involves the addition of elemental sulfur to selenocompounds **2** [1].




The iodine-water oxidation of thioselenoacids, protonated **3**, leads to the formation of bis(thiophosphoryl) diselenides **4**.

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

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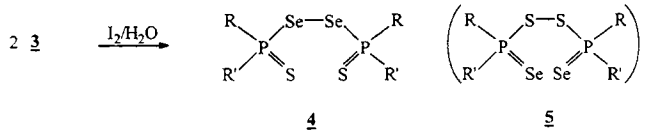


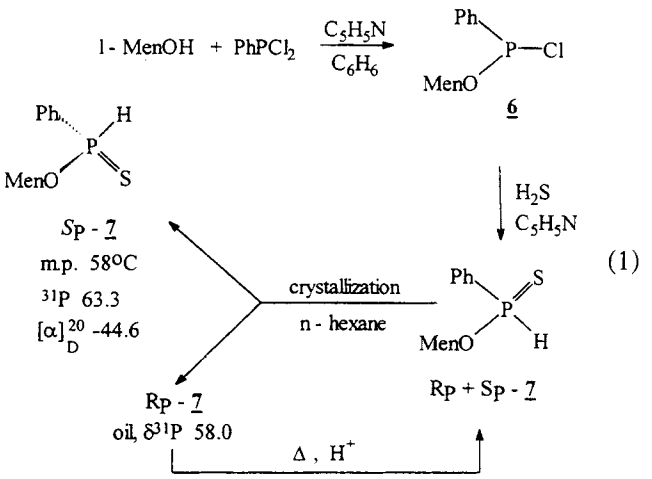
The structure **4** seems to be thermodynamically more stable than the isomeric disulfide structure **5** [2,3]. We have not been able to repeat experiments leading to the structure **5**. Unambiguous assignment of the diselenide structure **4** has been based on $^{31}P$ NMR spectroscopy.

Synthesis of the *P*-chiral thioselenoacids protonated **3** seems likely to be achieved either by resolution of racemic mixtures via the diastereomeric salt with chiral amines or by stereoselective addition of corresponding elements to *P*-chiral hydrogen thiophosphonates **1** or hydrogen-selenophosphonates **2** [4]. In this paper, we describe the use of *P*-chiral hydrogen thiophosphinate **1**. Two optically active compounds of the structure **1** have already been reported. The *O*-isopropylmethylthiophosphinate $Me_2CHO(CH_3)P(S)H$ has been prepared from the corresponding *O*-isopropylmethylphosphinate $Me_2CH(CH_3)P(O)H$ by reaction with $P_4S_{10}$. This conversion proceeded with predominant retention of configuration at the phosphorus atom and gave a product estimated to be 68% optically pure [5]. The highly stereoselective synthesis of the optically active sulfide $Bu^tPhP(S)H$ has been effected by sodium tetrahydroborate reduction of the anhydride $Bu^tPhP(S)\text{-}O\text{-}SO_2CF_3$. Synthesis of both of these compounds involves tedious procedures [4].

## *RESULTS AND DISCUSSION*

Recently, we found out that diastereomeric compounds of type **1** are convenient starting materials in the synthesis of compounds **3**. *O*-l-menthylphenylthiophosphinates $R_P$-**7** and $S_P$-**7** can readily be prepared on a reasonably large scale.

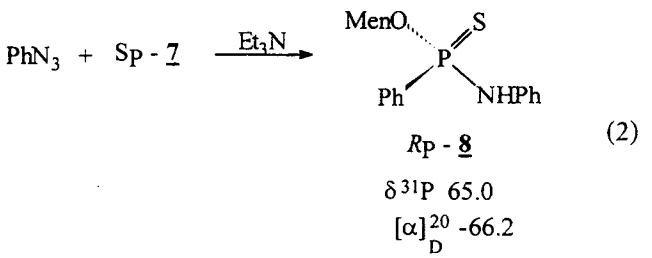
The crude *O*-l-menthylphenylphosphonochloridite **6** was obtained in 80% yield from dichlorophenylphosphine and l-menthol in pyridine-benzene solution, and it was transformed at once in a one-flask procedure by the action of hydrogen sulfide into a 1:1 mixture of diastereoisomers $R_P$-**7** and $S_P$-**7**. This route is more convenient than the alternative one [6], which involves conversion of *O*-l-menthylphenylphosphinate by the action of $P_4S_{10}$ into a 1:1 mixture of diastereoisomeric thiophosphinates $R_P$-**7** and $S_P$-**7**.



(1)

The mixture $R_P$-**7** and $S_P$-**7** was separated by crystallization from *n*-hexane into the crystalline $S_P$-**7** (mp 58–60°C) and an oily residue in which $R_P$-**7** was the main component. The $R_P$-**7** diastereomer seems to be thermodynamically less stable and readily rearranges thermally, or under the influence of protic acids, into a 1:1 mixture of both isomers. The absolute configuration of diastereomers **7** at the phosphorus center was deduced by stereochemical correlations.

($R_P$)-*O* -l -Menthylphenylphosphonophenylamidothioate (**8**) was formed in almost quantitative yield when the isomer $R_P$-**7** was allowed to react with phenyl azide in triethylamine solution. The amine acts both as a solvent and as an indispensable activator.



(2)

Reaction (2) can be considered as a new variant of the Staudinger reaction between azides and tricoordinate phosphorus compounds [7]. To our knowledge, nothing has been published about a similar reaction with oxygen analogues of compounds **1**. The mechanism of Reaction (2) may involve specific solvation by the tertiary amine, which would allow the phosphonate-phosphinate equilibrium to be shifted toward the more reactive tautomer. The anilidate $R_P$-**8** was produced in high purity, but our attempts to obtain it in a crystalline form failed. It is highly probable that the reaction leading to anilidate $R_P$-**8** proceeds with retention of configuration at the phosphorus center. Fortunately, the crystalline anilidate $S_P$-**8** of op-

posite configuration at the phosphorus center can be prepared by two routes.

The hydrogenthiophosphinate $S_P$-**7** was converted by the Todd–Atherton reaction [8] with carbon tetrahalides into the corresponding *O*-l-menthyl-phenylphosphonochloridothioate $R_P$-**9** and bromidothioate $R_P$-**10**. The Todd–Atherton reaction is known to proceed with retention of configuration at the chiral phosphorus center [9]. We anticipated that the reaction of halidates $R_P$-**9** and $R_P$-**10** with aniline should proceed with inversion of configuration. Our assumptions concerning the stereochemistry of reactions (2) and (3) were confirmed by X-ray crystallography of the crystalline anilidate $S_P$-**8** [10].

The configuration of both anilidates $R_P$-**8** and $S_P$-**8** was additionally confirmed by the Wadsworth–Emmons–Stec reaction [11]. They were converted into potassium salts, which in turn were allowed to react with carbon dioxide, followed by methyl iodide, to give $R_P$- and $S_P$-*O*-l-menthyl S-methylphenyl phosphonothiolates (**11**) [12].

The reaction of the thiophosphinate $S_P$-**7** with elemental selenium in the presence of triethylamine led to the salt $R_P$-**12** in almost quantitative yield. It is well established that addition of elemental sulfur to oxygen analogues RR'P(O)H of **7** takes place with retention of configuration. Therefore, one can safely assume that the addition of elemental selenium to the compound $S_P$-**7** proceeds in the same manner. The triethylammonium salt $R_P$-**12** was readily oxidized by elemental iodine in chloroform-water solution to bis-(*O*-l-menthylphenylphosphonothionyl) diselenide $R_P$1, $R_P$2-**13**. The diselenide structure $R_P$1, $R_P$2-**13** was confirmed by $^{31}$P NMR spectroscopy [3,13]. The coupling constant $^1J$ ($^{31}$P-$^{77}$Se) 445 Hz was clearly indicative of the proposed structure and excluded the alternative disulfide structure.

Oxidation of $R_P$-**12** proceeds without bond breaking at the *P*-chiral center and therefore gave the diselenide **13** with the configuration $R_P$1, $R_P$2.

## *CONCLUSION*

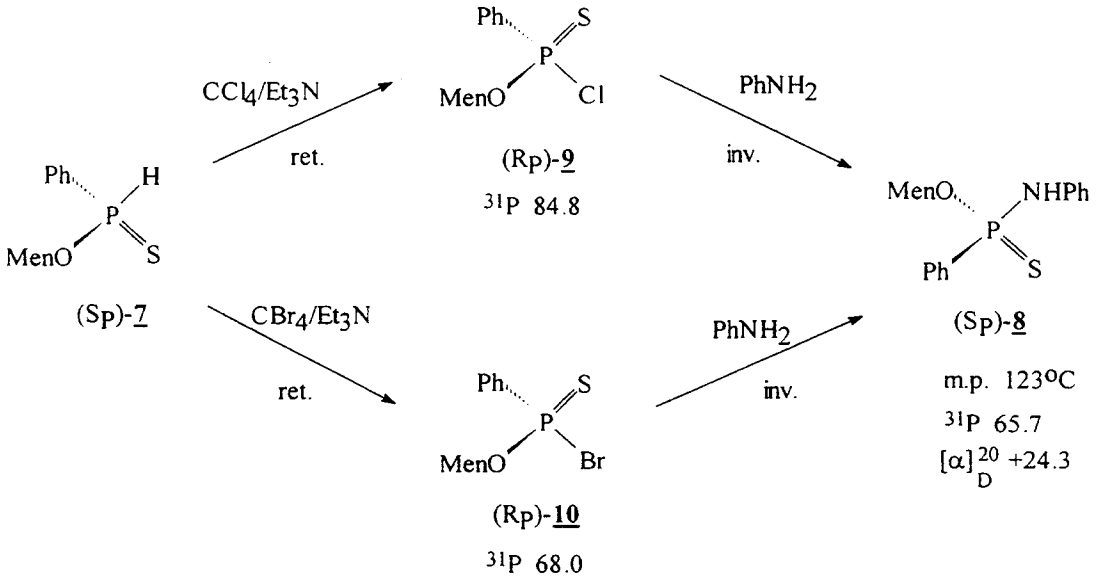
In conclusion, *P*-chiral hydrogen phosphinothionate $S_P$-**7** has been shown to be well suited for the stereospecific synthesis of the *P*-epimeric $R_P$1, $R_P$2 diselenide **13**. This is a unique structure belonging to the class of organophosphorus compounds with properties of pseudohalogens, and this compound is presently being used for further studies.

## *EXPERIMENTAL*

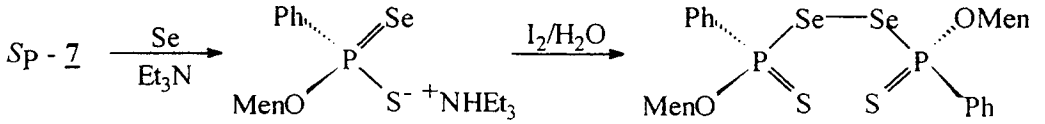
All solvents were reagent grade and were distilled and dried by conventional methods before use. $^1$H NMR spectra were recorded at 300 MHz with Bruker AC-200 (200 MHz) and Bruker MSL-300 (300 MHz) spectrometers for ca. 10% (w/v) solutions at room temperature. The chemical shifts were measured with respect to internal tetramethylsilane (TMS). Positive values are reported for compounds absorbing at lower field than that of TMS. $^{31}$P NMR spectra were obtained on the same instrument operating at 81.1 MHz and 121.4 MHz, respectively, frequency being observed for saturated solutions with external 85% $H_3PO_4$. Melting points were determined on a Boetius PHMK apparatus and are uncorrected. Phenyl azide [14] and dichlorophenylphosphine [15] were synthesized according to described methods.

### *$S_P$(-)-O-l-Menthylphenylthiophosphinate* (**7**)

To a stirred solution of 89.5 g (0.5 mole) of dichlorophenylphosphine in 750 mL of dry benzene




(3)



$S_P$-7 → (Se, $Et_3N$) → $R_P$-12 → ($I_2/H_2O$) → $R_P^1, R_P^2$-13 (4)

$R_P$-12: m.p. 92°C; $^{31}P$ 88.9; $[\alpha]_D^{20}$ -69.3

$R_P^1, R_P^2$-13: m.p. 104°C; $^{31}P$ 76.0; $[\alpha]_D^{20}$ -694.4

was added dropwise at a temperature of 0–5°C 78.0 g (0.5 mol) of l-menthol and 79.0 g (1 mol) of dry pyridine dissolved in 100 mL of benzene. After the addition was complete, the reaction mixture was stirred for a further 60 minutes at a temperature of 0–5°C. The cooling bath was removed and the temperature of the reaction solution was raised slowly to 20–22°C. Stirring was continued for the next 40–60 minutes, and dry hydrogen sulfide was passed through the reaction solution at a temperature of 0–5°C. Pyridine hydrochloride was filtered off, the solvent removed in vacuo, and the residual yellow oily liquid distilled. From the fraction collected at 152–170°C/0.05 mm Hg that contained two isomeric thiophosphinates **7**, after refrigeration, the compound $S_P$-**7** separated as colorless prisms. By recrystallization of the crude product from *n*-hexane, an analytical sample of $S_P$-**7** was obtained, mp 50–60°C, $[\alpha]_D^{20}$ = −44.68 (c 1.0, benzene), $^{31}P$ NMR; ($CDCl_3$): 63.3, $^1J_{P-H}$ 533 Hz, $^1H$ NMR; ($CDCl_3$): $\delta$ 8.8 (d, $J_{P-H}$ 533 Hz, 1H), 7.9–7.4 (m, Ph, 5H), 4.49–4.38 (m, POCH, 1H), 2.19–2.11 (m, $CH_3(CH_3)C\underline{H}$, 1H), 2.03–1.04 (m, 8H), 0.95 (d, $^3J_{HH}$, 7 Hz, $C\underline{H}_3$, 3H), 0.86 (d, $^3J_{HH}$ 7 Hz, ($C\underline{H}_3$)($CH_3$)CH, 3H), 0.84 (d, $^3J_{HH}$ 7 Hz, ($CH_3$), ($C\underline{H}_3$)CH, 3H). Yield 44.4 g (30%); anal calcd for $C_{18}H_{25}OPS$ (296.36), C, 64.83; H, 8.49; P, 10.44; S, 10.81. Found: C, 63.70; H, 8.51; P, 10.46; S, 10.86.

The mother liquor remaining after isolation of the crystalline isomer $S_P$-**7** was composed of a mixture of thiophosphinate $R_P$-**7** $\delta^{31}P$ 58.5 as the major product, and a minor amount of $S_P$-**7**, $\delta^{31}P$ 63.3. This mixture was allowed to stand overnight in benzene solution containing traces of dry pyridine hydrochloride. The solvent was distilled off. Distillation of the residual oily liquid at a pressure of 0.01 mm Hg and a temperature of 160–170°C gave a 1:1 mixture of $S_P$-**7**, $R_P$-**7**, from which a second crop of the $S_P$-**7** isomer ($\delta^{31}P$ 63.3, mp 58–60°C) was separated by crystallization.

### *Reaction of $S_P$ Thiophosphinate* **7** *with Phenylazide*

To a solution of 2.96 g (0.01 mol) of the thiophosphinate $S_P$-**7** $[\alpha]_D^{20}$ 44.8 in 10 mL of dry triethylamine was added dropwise at a temperature of 15–20°C, with stirring, 1.42 g (0.012 mol) of freshly distilled phenyl azide. The stirring was continued for 48 hours at room temperature. The triethylamine was distilled off in vacuo (20°C/0.01 mm Hg), and the crude $R_P$(−)-*O*-l-menthylphenylphosphonophenylamidothioate (**8**) was obtained as an oily liquid, $[\alpha]_D^{20}$ −66.20 (c 2.2, benzene) $^{31}P$ NMR, ($CDCl_3$) $\delta$ = 65.0. Anal calcd for $C_{22}H_{30}NOPS$ (387.52), C, 68.19; H, 7.80; P, 7.99; S, 8.27; N, 3.61. Found: C, 69.80; H, 7.52; P, 6.80; S, 8.22; N, 2.89. Yield 3.87 g (100%).

### *Reaction of $S_P$-7 with Carbon Tetrachloride*

To a stirred solution of 2.96 g (0.01 mol) of $S_P$-**7**, $[\alpha]_D^{20}$ −44.6, in 10 mL of dry hexane, was added at 15–20°C 5 g of dry carbon tetrachloride and 1.01 g of triethylamine (0.01 mole). Stirring was continued at room temperature for 8 hours. The solvent and excess of $CCl_4$ was distilled off at a temperature of 35°C under a pressure of 0.01 mm Hg, and the residual oily liquid was identified as $R_P$(−)-*O*-l-menthylphenylphosphonochloridothioate (**9**), $[\alpha]_D^{20}$ −134.24 (c 2.0, benzene), $^{31}P$ NMR, ($CDCl_3$) $\delta$ = 84.8. Anal calcd for $C_{16}H_{24}ClOPS$ (330.85), C, 58.09; H, 7.31; P, 9.36; S, 9.69; Cl, 10.72. Found: C, 57.9; H, 7.68; P, 9.26; S, 9.51; Cl, 10.62. Yield 3.3 g (100%).

### *Reaction of $S_P$-7 with Carbon Tetrabromide*

Under identical reaction conditions as described for the synthesis of $R_P$-**9**, the reaction of 2.96 g (0.01 mol) of $S_P$-**7** and 3.31 g carbon tetrabromide (0.01 mole) in the presence of 1.01 g (0.01 mol) of dry triethylamine gave $R_P$(−)-*O*-l-menthylphenylphosphono-bromidothioate (**10**) as an oily liquid. The crude product was purified by column chromatography (silica gel 70–230 mesh), eluent heptane-benzene (5:1), $[\alpha]_D$ −92.38 (c 1.3, benzene) $^{31}P$ NMR, ($CDCl_3$) $\delta$ = 67.7, $^1H$ NMR, ($CDCl_3$), $\delta$ = 8.03–7.45 (m, Ph, 5H), 4.87–4.66 (m, P-OC$\underline{H}$, 1H), 2.37–2.25 (m, ($CH_3$)($CH_3$)C$\underline{H}$ 1H), 1.77–1.08 (m, 8H), 0.98 (d, $^3J_{HH}$ 7 Hz, $C\underline{H}_3$, 3H), 0.92 (d, $^3J_{HH}$ 7 Hz, ($C\underline{H}_3$)($CH_3$)CH-, 3H), 0.88 (d, $^3J_{HH}$ 7 Hz,

$(CH_3)(C\underline{H}_3)CH$-, 3H). Anal calcd for $C_{16}H_{24}BrOPS$ (375.31), C, 51.21; H, 6.44; P, 8.25; S, 8.52. Found: C, 51.72; H, 6.53; P, 8.28; S, 8.03. Yield 2.7 g (72%).

### *Reaction of $R_P$-9 with Aniline*

To a solution of 3.3 g (0.01 mol) of the chloridothioate $R_P$-**9** $[\alpha]_D^{20}$ −134.24 in 25 mL of benzene mixed with 5 mL of chloroform was added 1.86 g (0.02 mol) of freshly distilled aniline. The reaction solution was heated on the oil bath at a temperature of 80°C for 6 hours. Aniline hydrochloride was filtered off. The solvents were evaporated in vacuo, and the solid material that had formed was recrystallized from *n*-hexane to give the product that was identified as $S_P$(+)-*O*-l-menthylphenylphosphonophenylamidothioate (**8**); mp 123°C, $[\alpha]_D^{20}$ +24.37 (c 2.5, chloroform), $^{31}P$ NMR, ($CDCl_3$) $\delta$ = 65.7, $^1H$ NMR, ($CDCl_3$), $\delta$ = 7.85–7.35 (m, P-$C_6H_5$, 5H), 7.13–6.76 (m, NH-$C_6H_5$, 5H), 5.58 (d, $^2J_{PH}$ 9 Hz, NHPh, 1H), 4.82–4.70 (m, POC$\underline{H}$, 1H), 2.31–2.19 (m $(CH_3)(CH_3)C\underline{H}$, 1H), 1.74–1.00 (m, 8H), 0.97 (d, $^3J_{HH}$ 7Hz, $CH_3$, 3H), 0.88 (d, $^3J_{HH}$ 6.5 Hz, $(C\underline{H}_3)(CH_3)CH$, 3H), 0.78 (d, $^3J_{HH}$ 6.5 Hz, $(CH_3)(C\underline{H}_3)CH$, 3H). Anal calcd for $C_{22}H_{30}NOPS$ (387.51), C, 68.19; H, 7.80; P, 7.99; S- 8.27; N, 3.61. Found: C, 67.60; H, 7.80; P, 8.15; S, 8.37; N, 3.85. Yield 3.5 g (90%).

### *Reaction of $R_P$-10 with Aniline*

A solution of 3.75 g (0.01 mol) of the bromidothioate $R_P$-**10** and a solution of 1.86 g (0.02 mol) of aniline in 50 mL of dry benzene was stirred at room temperature for 72 hours. Aniline hydrobromide was filtered off. The filtrate was concentrated in vacuo, and a crude solid residue was recrystallized from hexane. The product obtained was identified as a $S_P$(−)-*O*-l-menthylphenylphosphonophenyl amidothioate (**8**) $[\alpha]_D^{20}$ +24.30 (c 2.1, chloroform) ($^1H$, $^{31}P$ NMR, mp, elemental analysis).

### *Conversion of $R_P$ and $S_P$ Anilidates* **8** *into $R_P$ and $S_P$ Phosphonothioloesters* **11**

To finely divided potassium 3.8 g (0.01 mol) in dry THF 20 mL, was added dropwise at 20°C a solution of the respective anilidate (0.01 mol) in 10 mL of THF. The reaction solution was heated at 50°C with stirring for 2 hours. The stirring was continued at 70°C for 30 minutes dry $CO_2$ was bubbled through the reaction mixture for 8 hours. The solution was cooled to 30°C, and 0.02 mole of methyl iodide was added. The reaction mixture was heated under reflux for 3 hours and filtered. The filtrate was evaporated and esters **11** were isolated by column chromatography on silica-gel 70–230 mesh. Elution was performed by a 2:1 v/v mixture of heptane and benzene. Yield 15–20%.

### *$S_P$(−)-O-l-Menthyl S-Methylphenylphosphonothiolate* (**11**)

The reaction of 3.87 g (0.01 mol) of $S_P$-**8** $[\alpha]_D^{20}$ +24.3 with K, $CO_2$, and methyl iodide was performed as described above. The pure ester $S_P$-**11** was isolated by column chromatography, mp 76°C, $[\alpha]_D^{20}$ −132 (c 1.8, benzene), $^{31}P$ (NMR, $CDCl_3$) 44.55; $^1H$ NMR, ($CDCl_3$) $\delta$ = 7.88–7.25 (m, Ph, 5H), 4.50–4.72 (m, OOCH, 1H), 2.34–2.19 [m, $(CH_3)(CH_3)C\underline{H}$, 1H], 2.15 (d, $^3J_{PSCH3}$ 13.6 Hz, $SCH_3$, 3H), 1.7–1.01 (m, 8H), 0.94 (d, $^3J_{HH}$ 7Hz, $CH_3$, 3H), 0.88 [d, $^3J_{HH}$ 5.1 Hz, $(C\underline{H}_3)(CH_3)CH$, 3H], 0.86 [d, $^3J_{HH}$ 4.6 Hz $(CH_3)(C\underline{H}_3)CH$, 3H] (Lit.[12] $^1H$(NMR) $\delta$ PSC$\underline{H}_3$ 2.16). Anal calcd for $C_{17}H_{27}O_2PS$ (326.4), C, 62.56; H, 8.33; P, 9.48; S, 9.82. Found: C, 62.92; H, 8.42; P, 9.36; S, 9.68. Yield 0.65 g (20%).

### *$R_P$(+)-O-l-Menthyl S-Methylphenylphosphonothiolate* (**11a**)

The reaction of $R_P$-**8**, 3.87 (0.01 mol), $[\alpha]_D^{20}$ −66.2, with the K/$CO_2$/MeI system gave the pure ester $R_P$-**11**, mp 47°C, $[\alpha]_D^{20}$ +25 (c 1.8, benzene), $^{31}P$ NMR, ($CDCl_3$) $\delta$ = 44.1, $^1H$ (NMR, $CDCl_3$) 7.65–7.26 (m, Ph, 5H), 4.72–4.50 (m, POCH, 1H), 2.37–2.30 [m $(CH_3^A)(CH_3^B)C\underline{H}$, 1H], 2.20 (d, $^3J_{PSCH3}$ 13.8 Hz, $SCH_3$, 3H), 1.73–1.01 (m, 8H), 0.96 (d, $^3J_{HH}$ 7Hz, $CH_3$, 3H), 0.90 [d, $^3J_{HH}$ 7 Hz, $(C\underline{H}_3)(CH_3)CH$, 3H], 0.87 [d, $^3J_{HH}$ 7 Hz, $(CH_3)(C\underline{H}_3)CH$, 3H] (lit.[12] $^1H$ (NMR) $\delta$ $PSCH_3$ 2.14). Anal calcd for $C_{17}H_{27}O_2PS$ (326.4), C, 62.56; H, 8.33; P, 9.48; S, 9.82. Found: C, 62.92; H, 8.42; P, 9.36; S, 9.68. Yield 0.58 (17.8%).

### *Reaction of $S_P$-7 with Selenium*

To a solution of 2.96 g (0.01 mole) of $S_P$-**7**, $[\alpha]_D^{20}$ −44.56, and 1.01 g (0.01 mol) of triethylamine in 20 mL of dry toluene was added 0.79 g (0.01 g atom) of gray selenium. The reaction mixture was stirred and heated under reflux for 4 hours. The solvent was evaporated in vacuo, and the residual solid was recrystallized from benzene-hexane giving, the triethylammonium salt of $R_P$(−)-*O*-l-menthylphenylthiophosphonoselenoate (**12**); mp 92–93°C, $[\alpha]_D^{20}$ −69.3, $^{31}P$ NMR ($CHCl_3$) $\delta$ = 88.90 $J_{(31P\text{-}77Se)}$ = 656.9 Hz. Anal calcd for $C_{22}H_{39}NOPSSe$ (475.55). C, 55.6; H, 8.3; P, 6.5; S, 6.7; N, 2.9. Found: C, 55.4; H, 8.4; P, 6.5; S, 8.2; N, 2.9. Yield 4.2 g (88%).

### *Reaction of $R_P$-12 with Iodine*

To a stirred mixture of 4.75 g (0.01 mol) of $R_P$-**9** $[\alpha]_D^{20}$ −69.3, water (20 mL) and chloroform (50 mL) was added portionwise at 5–10°C a solution of 1.38 g (0.0055 mol) of iodine in 10 mL of $CHCl_3$. As the $I_2$ was added, the mixture was stirred for 20 minutes. The mixture was filtered and the filtrate washed with an aqueous solution of sodium thiosulfate (2 × 10 mL, conc. 0.5%), then it was dried

over magnesium sulfate and evaporated. The residual solid was crystallized from *n*-pentane. The $R_P1$, $R_P2$ bis[*O*-l-menthylphenylphosphonothioyl]diselenide (**13**) was obtained as yellow needles mp 104°C, $[\alpha]_D^{20}$ −694.4 (benzene). $^{31}P$ NMR ($CDCl_3$) 76.13, $J_{(^{31}P\text{-}^{77}Se)}$ 445 Hz. Anal calc for $C_{32}H_{48}O_2P_2S_2Se_2$ (748.72): C, 51.33; H, 6.46; P, 8.27; S, 8.56. Found: C, 51.08; H, 6.31; P, 8,44; S, 9.13. Yield 3.04 g (80%).

## *ACKNOWLEDGMENT*

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## *REFERENCES*

[1] C. Krawiecki, J. Michalski, Z. Tulimowski, *Chem. Ind.*, 1965, 34; J. Michalski, W. J. Stec, *Chemiker Zeitung, 96*, 1972, 499; J. Michalski, *Chem. Scripta, 8A*, 1975, 56.

[2] A. R. Katritzky, M. R. Nesbit, J. Michalski, Z. Tulimowski, A. Zwierzak, *J. Chem. Soc. (B)*, 1970, 140.

[3] K. Bruzik, A. R. Katritzky, J. Michalski, W. J. Stec, *Polish J. Chem., 54*, 1980, 141.

[4] Z. Skrzypczyński, J. Michalski, *J. Org. Chem., 5*, 1988, 4549.

[5] L. J. Szafraniec, L. F. Reiff, H. S. Aaron, *J. Am. Chem. Soc., 92*, 1970, 6391.

[6] K. E. Debruin, D. M. Johnson, *Phosphorus, 4*, 1974, 17.

[7] H. Staudinger, J. Meyer, *Helv. Chim. Acta, 2*, 1919, 635.; H. Staudinger, E. Mauser, *Helv. Chim. Acta, 4*, 1921, 861.

[8] F. R. Atherton, H. T. Opeushaw, R. R. Todd, *J. Chem. Soc., 2*, 1945, 660.

[9] W. J. Stec, M. Mikolajczyk, *Tetrahedron, 29*, 1973, 539; W. J. Stec, A. Łopusiński, *Tetrahedron, 29*, 1973, 547; E. I. Nifanteev, A. A. Krutchkov, *Zh. Obshch. Khim., 11*, 1981, 2428.

[10] A. E. Kozioł, K. Suwińska, *Acta Crystallogr.*, 1991, 47.

[11] W. S. Wadsworth, W. D. Emmons, *J. Org. Chem., 29*, 1964, 2816; W. J. Stec, *Acc. Chem. Res., 16*, 1983, 411 and references cited therein.

[12] The assignment of the absolute configuration of $R_P$-**11** and $S_P$-**11** is in agreement with that established by W. B. Farnham, R. K. Murray, K. Mislow, *J. Chem. Soc., Chem. Commun.*, 1971, 605; J. Donohue, N. Mandel, W. B. Farnham, R. K. Murray, K. Mislow, H. P. Benschop, *J. Am. Chem. Soc., 93*, 1971, 3792.

[13] W. J. Stec, A. Okruszek, B. Uznański, J. Michalski, *Phosphorus, 2*, 1972, 97.

[14] M. Gold, Houben-Weyl: *Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, Germany, vol. X/3, p. 807, 1965.

[15] B. Buchner, L. B. Lockhart, *J. Am. Chem. Soc., 73*, 1951, 755.